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THE RICE INSTITUTE

Part One - The Synthesis of Ethyl 1-Phenyl-2-hydroxyindene-3-carboxylate

Part Two - The Anionic Polymerization of 1,1-Dicyanocyclopropane

by

Eugene L. Mitch

A THESIS

SUBMITTED TO THE FACULTY

IN PARTIAL FULFILLMENT OF THE

REQUIREMENTS FOR THE DEGREE OF

Doctor of Philosophy

Houston, Texas
May, 1959

*Approved,
Martin Ettinger*

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To my wife, Lil

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PART ONE

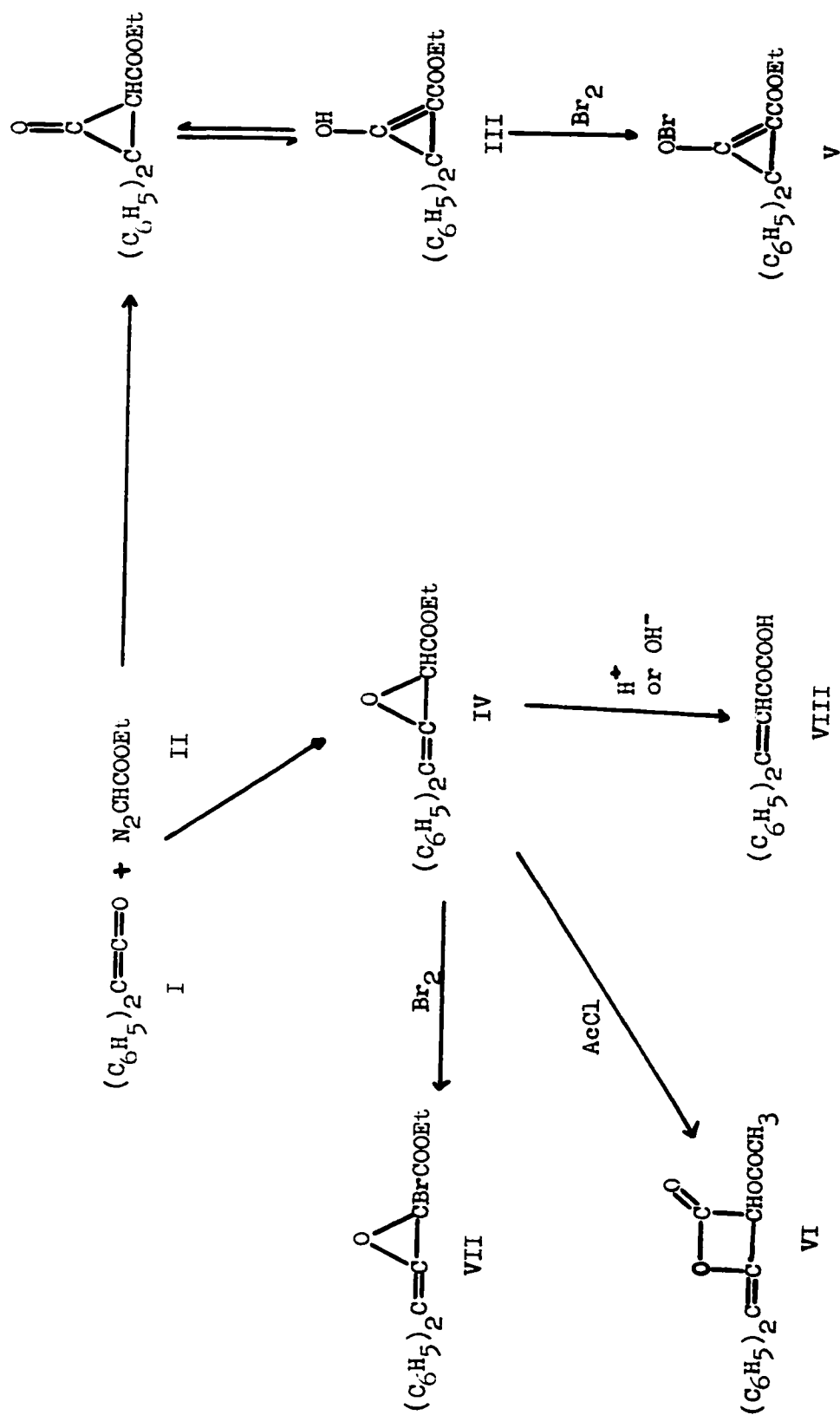
INTRODUCTION

Introduction

In 1921, H. Staudinger and T. Reber (1) investigated the reaction between diphenylketene (I) and ethyl diazoacetate (II). The reaction was reported to proceed vigorously in the cold to give an enol (A), $C_{18}H_{16}O_3$, m.p. 140° , and an isomeric neutral compound (B), m.p. 124° , for which the respective structures (III) and (IV) were proposed. The course of the reaction was envisioned as addition of the diazo compound to the multiple bonds of the ketene followed by loss of nitrogen from the intermediate pyrazolines.

Compound A was characterized as an enol by a deep blue ferric chloride test. It could be titrated with base and was reduced by hydrogen over platinum black to unidentified products. The enol was found to be stable to dilute acid or base but gave resinous products when heated with strong acid or alkali. Prolonged treatment with sodium ethoxide in boiling ethanol gave rise to an acid, m.p. 125° , which was not successfully characterized. It was further reported that the enol took up bromine smoothly in carbon disulfide to give a monobromo substitution product, $C_{18}H_{15}O_3Br$, formulated as the enol hypobromite (V). The bromo derivative would now be considered more likely to be an α -bromo β -keto ester.

Compound B was reported to give a derivative (VI) with acetyl chloride and a monobromo substitution product (VII). The suppression of the olefinic properties of B was rationalized by its similarity to the known $\beta\beta$ -diphenylacrylic acid. Hydrolysis of B gave an acid (C) for which structure (VIII) was proposed. Treatment of C with base or oxidizing agents yielded benzophenone, and esterification of C was found to be difficult. This behavior was compared to that of benzalpyruvic acid



which yields benzaldehyde on treatment with base and esterifies with difficulty.

If compound A had structure III as formulated by Staudinger (1) it would indeed be an interesting molecule since there are no authenticated reports in the literature of the synthesis of anhydrous cyclopropanone or its substituted derivatives. In 1932, Lipp, Buchkremer and Seeles (2) followed the reaction of ketene and diazomethane and obtained hydrated cyclopropanone (1,1-dihydroxycyclopropane) when ketene was in excess. Moisture in the reaction mixture must have accounted for the hydration since in the presence of alcohol the hemiacetal of cyclopropanone was obtained. The anhydrous material was unattainable and the hydrated or alcoholated derivatives were very labile and underwent an exothermic reaction in dilute base to yield propionic acid and its ester respectively. Support for this work was given by Semenow, Cox and Roberts (3) who found evidence for a cyclopropanone intermediate in the formation of cyclobutanone from excess diazomethane and ketene. There have been various reports of other attempts to prepare and isolate pure cyclopropanone (4) but none published have met with success.

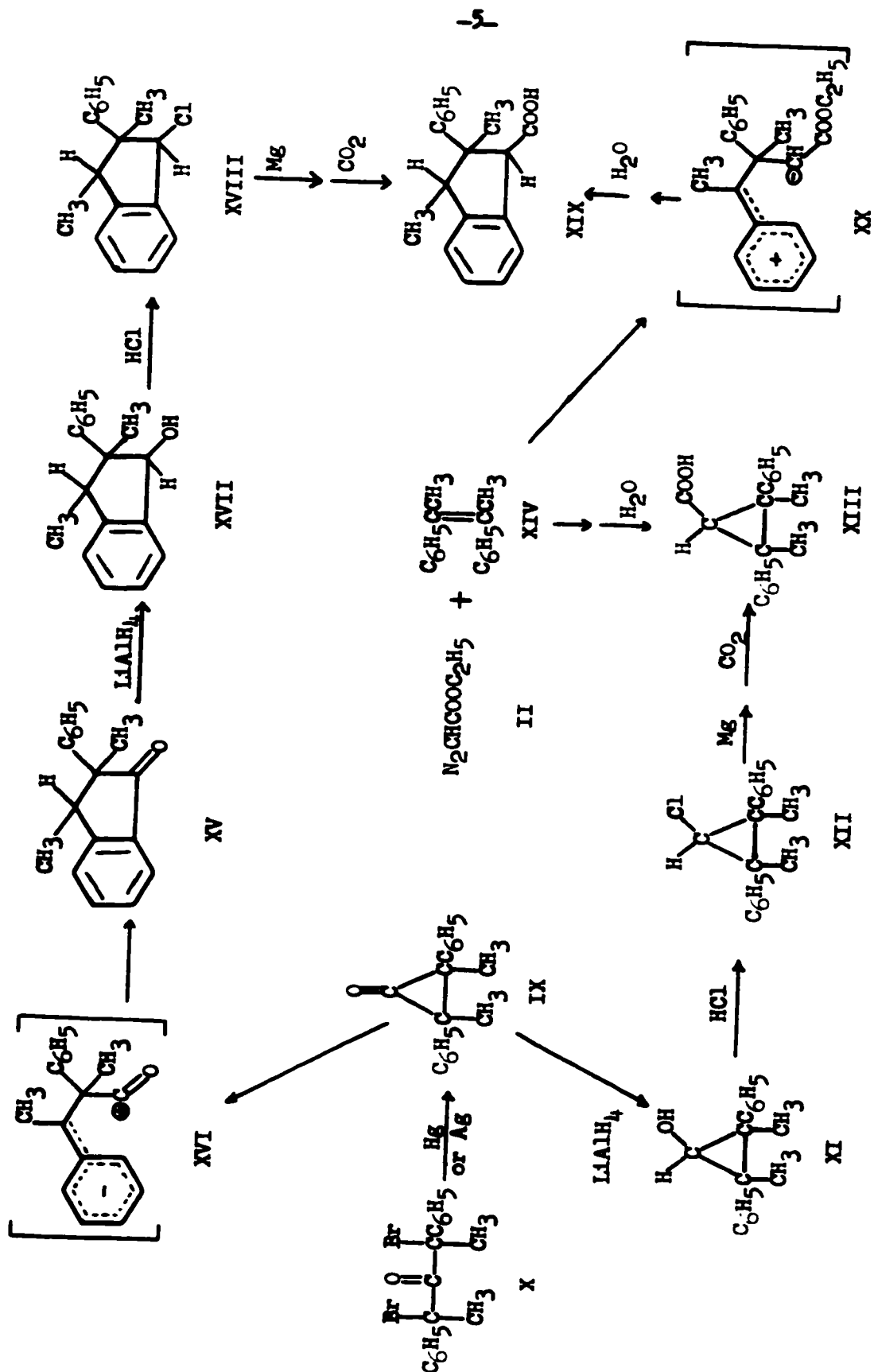
LaForge and Acree (5) have claimed the synthesis of 2-methyl-3-phenylcyclopropanone from the lead tetracetate oxidation of 1-phenyl-1,2-butadiene followed by hydrolysis of the intermediate 1,2-diacetoxy-1-phenyl-2-butene or 2,3-diacetoxy-1-phenyl-1-butene. In view of the mutability of the parent compound (2) and the ready cleavage of the cyclopropanone intermediate proposed by Loftfield (6) in the Favorski reaction, it seems improbable that the structure suggested by LaForge and Acree would be stable to potassium acetate in boiling 90% ethanol, in which the

ketone was supposedly formed. Moreover, it is highly unlikely that cyclization of an α -ketol could be induced under these conditions as the authors claim.

Stodola (7) has suggested that the mesityl α -mesitylvinyl ketone obtained by R. Fuson and co-workers (8) from the base-catalyzed condensation of mesitylacetomesitylene and formaldehyde was in fact 1,2-dimesitylcyclopropanone. This suggestion, based mainly on the lack of reactivity toward potassium permanganate and bromine, may be disregarded in view of the behavior of other highly hindered olefins (9). It would also be quite difficult to envisage a rational mechanism leading to the suggested product.

In 1950, Cogdell and Quayle (10) reported the preparation of 1,2-dimethyl-1,2-diphenylcyclopropanone (IX) from the action of mercury or silver on 2,4-dibromo-2,4-diphenyl-3-butanone (X). Compound IX was characterized by lithium aluminum hydride reduction to the alcohol (XI) which was converted to the chloride (XII) with hydrochloric acid and through the Grignard reagent to the carboxylic acid (XIII) (p-bromophenacyl ester, m.p. 90-92°). Compound XIII was independently synthesized through hydrolysis of the reaction product of cis- α,α' -dimethylstilbene (XIV) and ethyl diazoacetate (II).

In the absence of a report on the experimental conditions and other physical constants one cannot readily judge the validity of this work. In analogy to results of this thesis it might be suggested however that the alleged cyclopropanone was in fact the 2,3-dimethyl-2-phenylindan-1-one (XV) arising from the intermediate IX through a complex zwitterion (XVI). Compounds XI, XII, and XIII would then be the corresponding in-



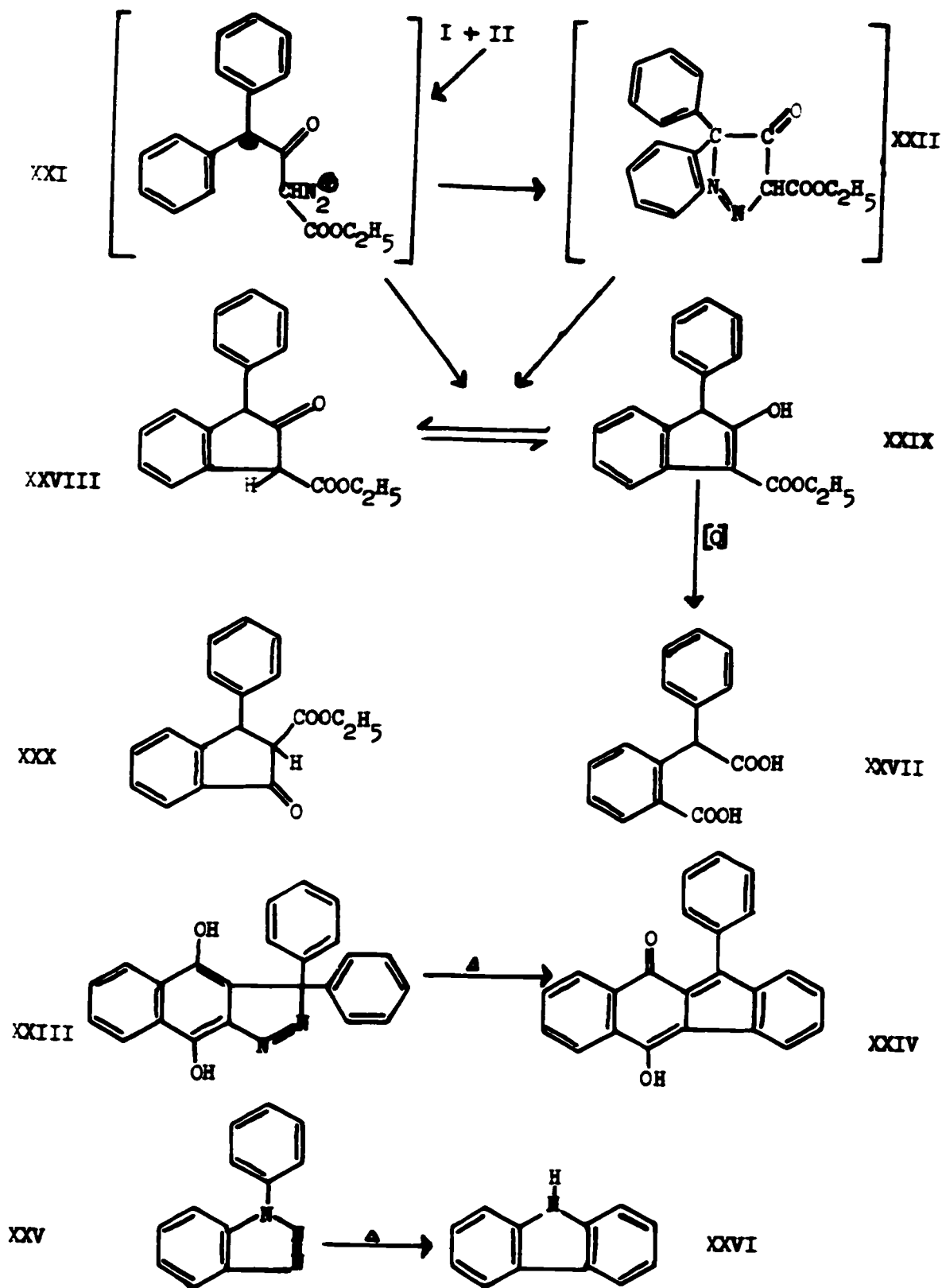
dane derivatives (XVII, XVIII and XIX). The alternate synthesis of XIX would proceed through the complex ion (XX).

The most recent report of a substituted cyclopropanone has been put forth by Jacquier, et al., (11) who claim the synthesis of bicyclo[0,1,4] heptan-7-one and bicyclo[0,1,3] hexan-6-one. Certain aspects of this work, e.g., the reported stability of the supposed cyclopropanone derivatives to methoxide, make one doubt its validity but a critical evaluation must await further details of the experiments.

To date then, the most credible carbonyl substituted cyclopropane is the diphenylcyclopropanone prepared recently by Breslow (12). Here, in contrast to the cyclopropanone, there is considerable resonance stabilization of the closed, conjugated system.

Considering the enol of Staudinger in the light of the foregoing allusions to cyclopropanone derivatives, it appears a priori that structure III might be suspect. In all probability the first attack of the diazo ester is at the central carbon atom of the ketene group giving the zwitterion (XXI), possibly with ring closure to the pyrazoline (XXII). Bader and Ettlinger (13) have shown that loss of nitrogen from a phenyl substituted pyrazoline can lead to attack on an o-position of the benzene ring, demonstrated by pyrolysis of 2,3-(3,3'-diphenylisopyrazolo)-1,4-naphthohydroquinone (XXIII) to 4-hydroxy-9-phenyl-2,3-benzo-1-isofluorenone (XXIV). Further analogy was made to the decomposition of 1-phenyl-benzotriazole (XXV) to carbazole (XXVI), which likewise involves attack at an o-position.

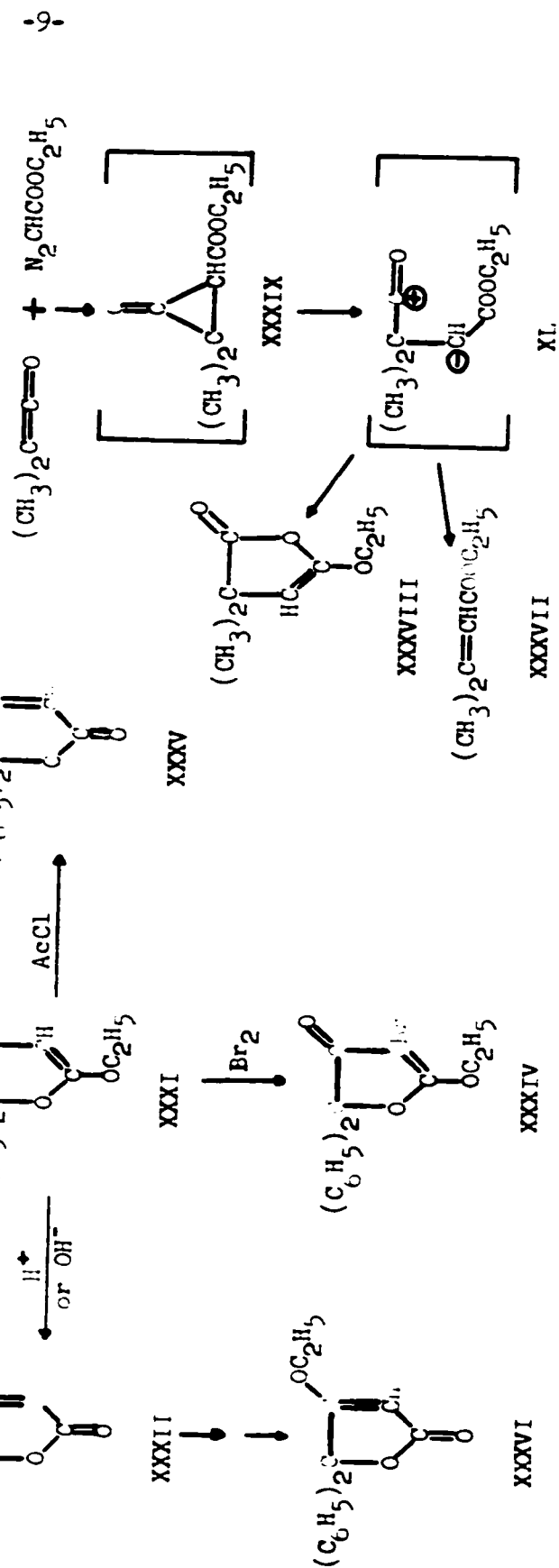
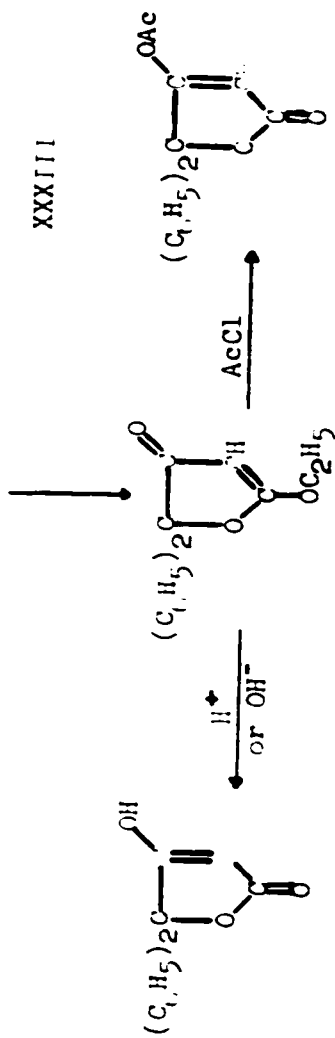
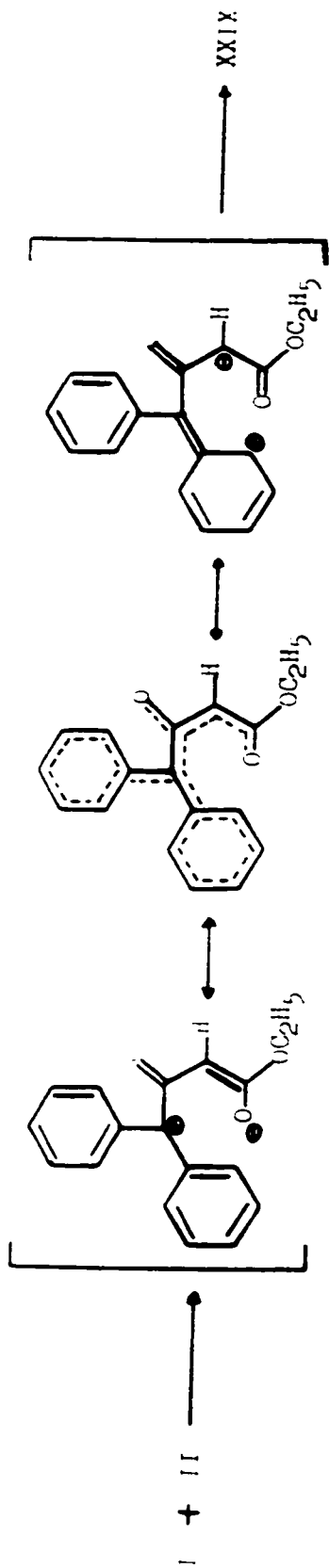
A. H. Hart, in work done at the Rice Institute (1951-1953), repeated the experiments of Staudinger and was able to obtain both reported products from the ketene and diazo ester. He gained further



information on the enol by isolation of α -phenylhomophthalic acid (XXVII), m.p. 170-173°, as a product of oxidation with alkaline 30% hydrogen peroxide. In analogy to the o-rearrangements cited above, the only rational explanation of the oxidation of compound A to XXVII must be that loss of nitrogen from XXI or XXII was followed by attack at an o-position to produce ethyl 2-oxo-1-phenylindan-3-carboxylate (XXVIII) or its enol (XXIX), the correct formulation of A. The isomeric ethyl 3-oxo-1-phenylindan-2-carboxylate (XXX), which would satisfy the observed further transformations, was excluded on the basis of the proposed mechanism. In 1957, a report of the physical properties of XXX (14) confirmed that it was not compound A.

Independent support for the proposed structure XXIX was given by Kende (15), who prepared Staudinger's enol and was able to decarboxylate it to 1-phenyl-2-indanone, thus showing the presence of the indane skeleton as well as the point of attachment of the oxygen function. He was able to show further that the neutral material, m.p. 124°, formulated by Staudinger as the ethylene oxide IV, was in fact the ketene acetal (XXXI) by its facile hydrolysis to β,β -diphenyltetronic acid (XXXII), synthesized from α -chlorodiphenylacetyl chloride and sodium malonic ester. Kende proposed that diazoacetic ester reacts as a nucleophile toward the ketene, followed by loss of nitrogen to give a complex zwitterion (XXXIII). Subsequent collapse of XXXIII can occur in two ways to give either XXIX or XXXI.

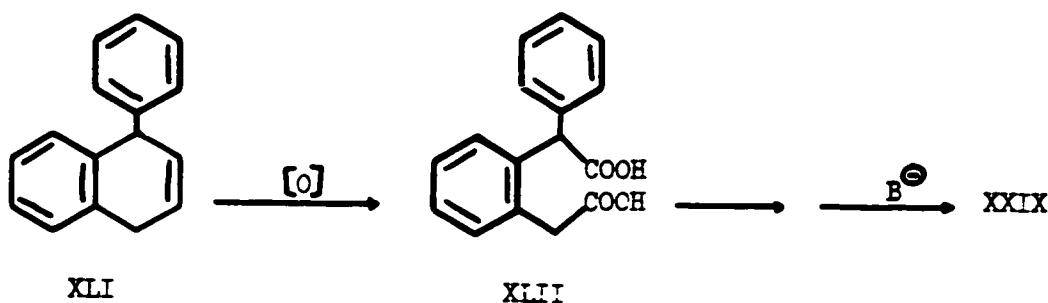
Compound XXXII undoubtedly corresponds to the erroneously presumed benzhydrylidenepyruvic acid VIII of Staudinger while the monobromo substitution product VII can now be reformulated as XXXIV. Rectification



of the β -lactone structure VI on the basis of Kende's work leads to the mixed anhydride (XXXV). The supposed ethyl ester of VIII is amended to the tetrionic acid derivative XXXVI.

Kende also studied the reaction of dimethylketene and ethyl diazoacetate from which he obtained ethyl β,β -dimethylacrylate (XXXVII) and the enol ether of α,α -dimethylsuccinic anhydride (XXXVIII), identified by hydrolysis to α,α -dimethylsuccinic acid. He envisioned the reaction as proceeding through the cyclopropanone (XXXIX) followed by fission to the zwitterion (XL), which could either cyclize directly to XXXVIII or lose carbon monoxide to yield the acrylate. This mechanism is analogous to that proposed (p. 4) in rebuttal of the work of Cogdell and Quayle.

A possible route for an unambiguous synthesis, and therefore proof of structure, of the 2-hydroxy-1-phenylindene-3-carboxylate (XXIX) might start with 1,4-dihydro-1-phenylnaphthalene (XLI) which on oxidative cleavage of the double bond should give rise to α -phenyl- α -benzenediacetic acid (XLII). Esterification of XLII followed by base catalyzed cyclization would be expected to give XXIX. It was the purpose of this research to carry out the indicated scheme as well as to investigate some novel approaches to the synthesis of XLI. The problem was successfully solved.



SECTION I

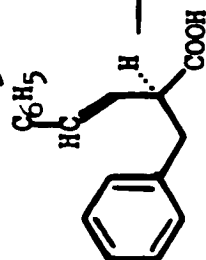
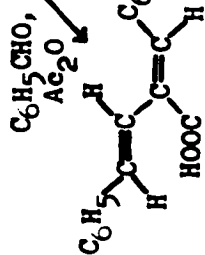
The Synthesis of 1,4-Dihydro-1-phenylnaphthalene

In 1899, Thiele and Meisenheimer (16) first prepared 1,4-dihydro-1-phenylnaphthalene (I). Their synthesis began with styrylacetic acid (II), which was condensed as the sodium salt with benzaldehyde in acetic anhydride to give dibenzalpropionic acid (III), reduced to benzylstyrylacetic acid (IV) with sodium amalgam in alcohol. Compound IV with bromine was converted to 4-phenyl-3-bromo-1,2,3,4-tetrahydro-2-naphthoic acid (V), probably by electrophilic attack of bromine on the double bond to give a bromonium ion (VI), followed by a cyclization of Friedel-Crafts type. The bromo acid was then dehalocarboxylated with base to I. This procedure, with only slight modification (see Experimental), was repeated to obtain authentic I. The structure of I was verified by sulfur dehydrogenation to 1-phenylnaphthalene (VII) and by its ultraviolet spectrum, showing only unconjugated aromatic absorption.

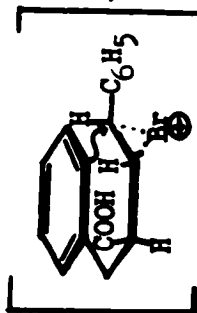
In attempting to obtain I from V and carbonate, Hart (17) isolated a neutral compound (A), supposed without examination to be the desired product. However, it was found in present work that the substance melted at 155-165°, whereas I was known to melt at 50°. The preparation of A could be confirmed, and the material was formulated as 4-phenyl-3-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid lactone (VIII). Structure VIII is based on analogy to the general formation of β -lactones from β -bromocarboxylic acids and weak base (18), and the spectral absorption of A at 5.55 μ (19). Chemical evidence for the proposed structure was obtained by hydrolysis to the known 4-phenyl-3-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid (IX) (16) as well as by pyrolysis to I. The hydroxyl and carbonyl absorption of IX in the solid state showed double



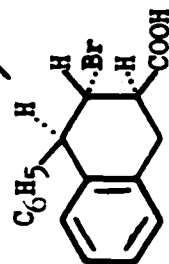
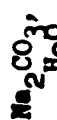
II



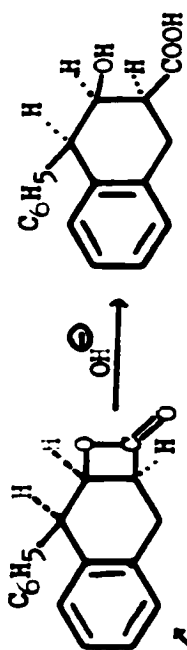
IV



VI



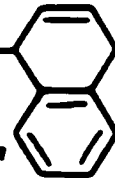
175-195°



IX



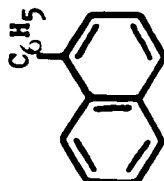
V



I



250°



VII

maxima at 2.80, 3.13 μ and 5.78, 5.89 μ respectively, indicating free as well as hydrogen-bonded functional groups in the crystal, whereas in dioxane solution only single bands appeared at 2.89 and 5.82 μ .

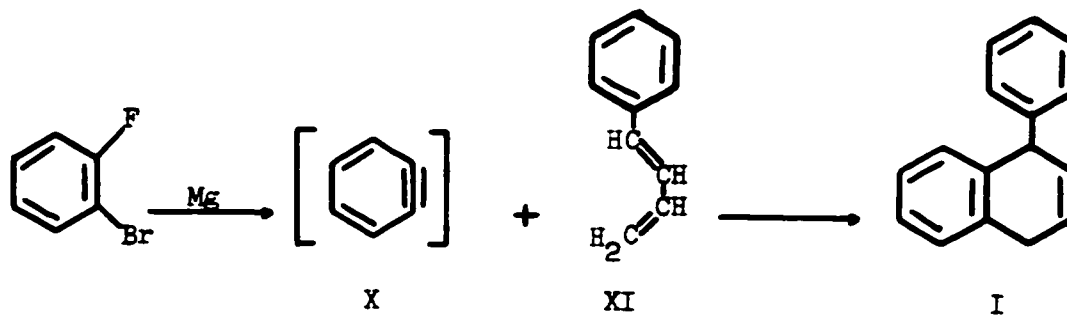
It might be noted here that the β -lactone ring of VIII must, for steric reasons, be cis-fused to the adjacent 6-membered ring and therefore hydrolysis, proceeding through the usual attack on the carbonyl group (20), must lead to a cis-relationship between the hydroxyl and carboxyl groups in IX. Furthermore, the mutual configuration of the bromo and carboxyl groups in V is established as trans to account for the lactone formation, consistent also with trans-elimination to I. The relative configuration of the phenyl group is not known with certainty but if IV is a trans-olefin, as seems likely, and if the brominative cyclization is a trans-concerted process analogous to that proposed by Stork and Burgstahler (21) for formation of cyclic systems from poly-olefins, then the phenyl group is trans to the bromo substituent in V and the stereochemistry of the compounds is that depicted in the structures on page 12.

In preparing I by the process of Thiele and Meisenheimer, an overall yield of 7% was realized in six steps from available starting materials. In the search for an easier route to I, a variety of schemes were investigated with varying success as described below.

Benzyne (X) as a reactive intermediate was first proposed by Wittig (22) in 1942. Good evidence for such a symmetrical intermediate was obtained by Roberts and co-workers (23) when they showed that approximately equal amounts of aniline-1-C¹⁴ and aniline-2-C¹⁴ were obtained by the reaction of chlorobenzene-1-C¹⁴ with potassium amide. Wittig (24) provided an elegant confirmation of his postulate by trapping the benzyne,

from o-bromofluorobenzene and magnesium, through a Diels-Alder reaction with furan to give 1,4-dihydro-1,4-epoxynaphthalene. Other examples of this type of reaction have been reported (25) in which the diene component was cyclopentadiene, cyclohexadiene, N-methylpyrrole or 1,4-diphenyl-2,3-isobenzofuran, and the dienophile was generated from the interaction of o-bromofluorobenzene and magnesium or lithium amalgam, from fluorobenzene and butyllithium, and from o-fluorophenylmagnesium bromide or o-fluorophenyllithium, the latter two compounds being stable only at low temperatures and giving X on warming. The most convenient method to obtain X on a preparative scale is through the reaction of o-bromofluorobenzene and magnesium.

With these analogies in mind, it was felt that I might reasonably be prepared from benzyne and 1-phenyl-1,3-butadiene (XI). The desired compound was in fact obtained from the reaction of o-bromofluorobenzene, magnesium and XI using a little tetrahydrofuran as a solvent. Under the conditions employed, a considerable amount of polymerization of XI was encountered but I could be isolated in 26% yield after distillation and recrystallization.

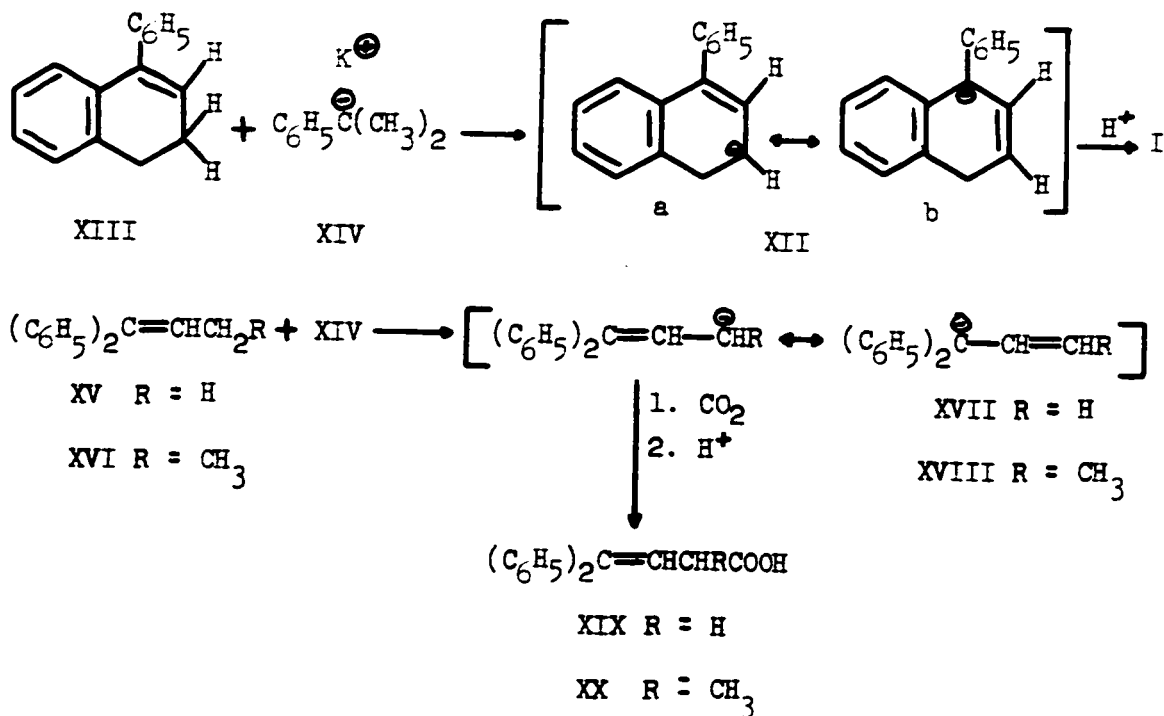


Another synthesis of I was conceived on the possibility of obtaining a mesomeric anion (XII) from the action of base on the readily available 1,2-dihydro-4-phenylnaphthalene (XIII). Compound XIII is certainly more stable than I, by virtue of complete conjugation of the unsaturated system, and under equilibrating conditions, such as in strong acid or base which reacts only partially with the hydrocarbons, one expects XIII to predominate nearly to the exclusion of I. However, if I or XIII were treated with strong enough base in a suitable solvent such that complete ionization to XII were attained, then the highest free electron density should occur near the center of the conjugated system as shown by XII-b. It was speculated that if XII could be generated in solution, rapid acidification under non-equilibrium conditions would lead to protonation at the point of highest electron density, i.e., in the 1-position, to give an appreciable yield of I.

In 1929, Ziegler and co-workers (26) investigated the reaction of phenylisopropylpotassium (XIV) with various unsaturated hydrocarbons. Of interest to the present work was the reaction of XIV with 1,1-diphenyl-1-propene (XV) and 1,1-diphenyl-1-butene (XVI), which are structurally similar to XIII, to give a metathetical transformation to the anions (XVII and XVIII), carbonated to the acids (XIX and XX). That carbonation did not occur at the 1-position of the hydrocarbons is probably due to steric hindrance of that position and protonation might be expected to proceed as indicated above. Conant and Wheland (27) (cf. McEwen (28)) confirmed that the reaction of XIV and XV was essentially complete, finding also that XV was a weaker acid than diphenylmethane. From the similarity of XIII to XV it was expected in the present work that XIV would promote formation of XII.

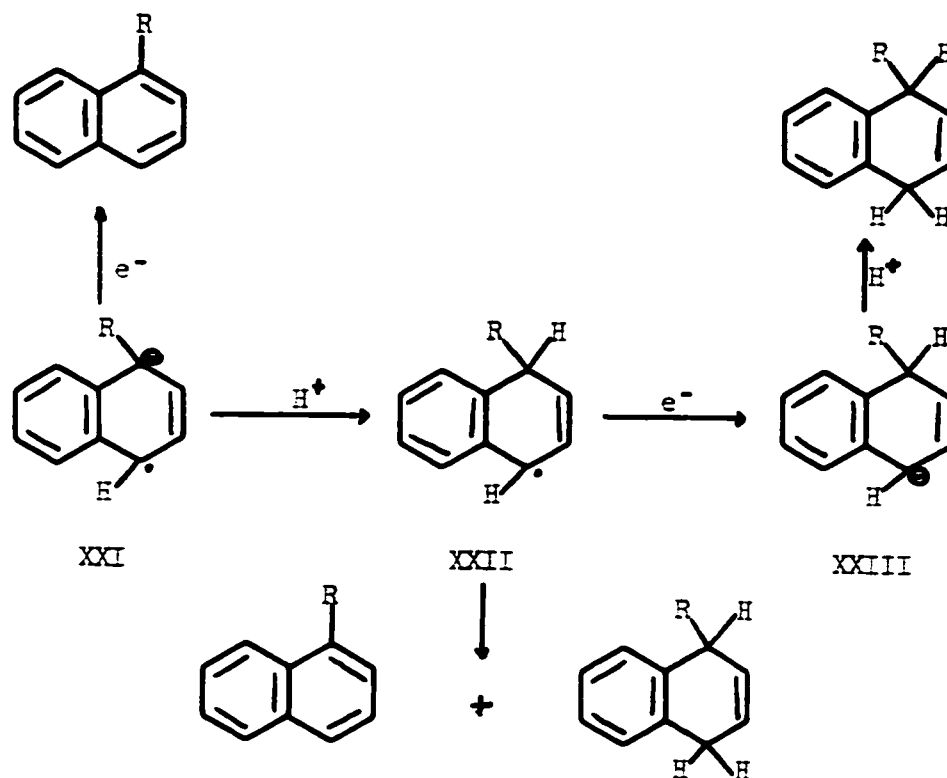
When XIII was treated with an excess of an ethereal solution of XIV, a reaction occurred as evidenced by the color change from deep red to brown with the formation of a precipitate. Irreversible protonation of the products, achieved by slow addition of the reaction mixture to excess acetic acid in ether, gave an oil containing a 12% yield of I. Isolation of I met with difficulty, as indicated in the Experimental Section, and the reported yield is based upon vapor phase chromatographic analysis of the products.

Earlier attempts at bringing about the above transformations employed phenylsodium in toluene as a base. The experiments were hampered by the insolubility of the organometallic compounds in the reaction medium and were inconclusive for lack, at that time, of a suitable means of analysis of the products.



The well known 1,4-reduction of polynuclear aromatic hydrocarbons with metal and a prototropic solvent (29) suggested that I might most conveniently be prepared from XIII by way of 1-phenylnaphthalene (VII). Bamberger and Lodter (30) first used sodium and alcohol to obtain impure 1,4-dihydronaphthalene in 87% yield from naphthalene, while Huckel and Bretschneider (31) report a quantitative yield when the reaction is carried out by addition of the sodium in liquid ammonia and ether at -75° to -65° followed by acidification with methanol. At -60° , 1,4-dihydronaphthalene is isomerized by sodamide to 1,2-dihydronaphthalene, while at -50° or above the dihydro compounds are further reduced to tetralin by excess sodium. Other modifications of this procedure include the use of a co-solvent such as dimethyl ether or ethylene glycol dimethyl ether (32) and the use of alkali metals other than sodium (29).

When the reduction is carried out in an ether (ethylene glycol dimethyl ether, tetrahydrofuran) in absence of a proton source, it probably proceeds (33, 34) by addition of an electron to give the anion radical (XXI), which by acidification in the absence of excess metal is solvolyzed to the radical (XXII). XXII can then couple or more probably disproportionate to starting material and the dihydro derivative. When an acid, e.g., alcohol, is present during the entire reaction and excess metal is employed, then formation of XXI may be followed by addition of a second electron (XXIII) and a proton to give the dihydro compound. The utility of the ethers as co-solvents undoubtedly lies primarily in their ability to promote the formation of XXI, though as diluents they also help by slowing the evolution of hydrogen.



The results of reduction of VII are listed in Table I, excess metal being employed in every case. Sodium reacted with VII in ethylene glycol dimethyl ether as evidenced by the color of the mixture (32). Acidification, accomplished by pipetting acetic acid into the mixture, probably occurred in a partially reversible manner to account for the 1,2-dihydro isomer in the products. If such an acidification is not carried out rapidly, then the first protonation occurs in the presence of the strongly basic sodioaromatic adduct and isomerization to the more stable product may be promoted (cf. 29, 31). However, the possibility that the intermediate anion radical XXI ($R = C_6H_5$) can react at more than one position is not excluded (33).

Table I

Composition of the crude reaction products from the reduction
of 1-phenylnaphthalene *

<u>Reaction conditions</u>	<u>1-phenyl- naphthalene</u>	<u>1,2-dihydro- 4-phenyl- naphthalene</u>	<u>1,4-dihydro- 1-phenyl- naphthalene</u>
Sodium, ethylene glycol dimethylether, rm. temp., followed by acetic acid.	35%	23%	42%
Lithium, ethanol, ammonia, ethylene glycol dimethyl ether, -75°	60%	trace	40%
Sodium, ethanol, -10°	30%	--	70%
Sodium, ethanol, ethylene glycol dimethyl ether, -10° to 0°	--	--	100%
Sodium, ethanol, tetrahydrofuran, -10° to 0°	--	--	100%

* Analyzed by vapor phase chromatography.

Hart (17) tried to effect reduction of VII with sodium in liquid ammonia and ether at -75° to -65° but was unsuccessful. However, in view of the analytical difficulties, an evaluation of his results is uncertain. Thus, in the present work, I could not be isolated from reduction of VII with lithium and ethanol in liquid ammonia and ethylene glycol dimethyl ether at -75° , though it comprised 40% of the crude reaction products analyzed by vapor phase fractionation.

While sodium and alcohol alone reduced 70% of VII to I, the most useful procedure was found to be reduction with sodium in ethylene glycol dimethyl ether or tetrahydrofuran in the presence of ethanol. Under these conditions only one reduction product, namely I, could be detected by vapor phase chromatography and the crude yields based on VII were 91-92%.

Experimental

Styrylacetic acid (4-phenyl-3-butenic acid). The following procedure is a modification of that reported by Linstead and Williams (35) and Vorlander and Strunck (36). A mixture containing 36.07 g. of a 34% ethanolic solution of phenylacetaldehyde (0.102 mole), 10.06 g. (0.097 mole) of malonic acid, 10 ml. of pyridine and 3 drops of diethylamine was heated at reflux under nitrogen for six hours and poured into 100 ml. of 2 N sodium carbonate. The aqueous solution was extracted with 100 ml. of ether and acidified to Congo Red with 10% hydrochloric acid. The precipitate was collected and crystallized from petroleum ether (b.p. 40-60°). Recrystallization gave 5.81 g., m.p. 86.4-87.6° (lit. (35) 87°), plus 1.22 g., m.p. 86-87°, from the mother liquors. The total yield was 45% of the theoretical.

Sodium styrylacetate. The sodium salt may be obtained by neutralization of the acid with aqueous sodium carbonate, but the evaporation to isolate the solid is a nuisance. The following procedure was found more convenient. To a solution containing 16.28 g. (0.101 mole) of styrylacetic acid in 50 ml. of ether was added 0.10 mole of sodium methoxide as a 10% solution in methanol. The fluffy white precipitate was collected and dried in vacuum to give 16.9 g. (92%) of sodium styrylacetate.

Potassium styrylacetate. The potassium salt of styrylacetic acid was precipitated in 71% yield when 5.0 g. of the acid in 15 ml. of ether was added to 1.46 g. of potassium hydroxide in 3 ml. of methanol. The white salt discolored to pink on standing for a few days.

Dibenzalpropionic acid. Preparation of dibenzalpropionic acid according to the method of Thiele (37) led without care to poor yields. The

difficulty arose not in the reaction itself, but rather from the vague description of the procedure for isolation of the acid by extraction with dilute base. The acid was found to be completely soluble in 2-5% sodium hydroxide and could not be extracted from such a solution with ether. However, when the reaction mixture was treated with base, the acid or its salt was readily salted out by the sodium acetate present. For highest recovery of the acid it is desirable first to neutralize the acetic anhydride, then separate the ether-soluble fraction and extract repeatedly with dilute base. The following is a typical procedure.

A mixture of 16.9 g. (0.092 mole) of sodium styrylacetate, 11.6 g. (0.110 mole) of benzaldehyde and 17 g. of acetic anhydride was heated with stirring at 140° for 20 minutes in a round bottom flask fitted with an air condenser and nitrogen inlet. The reaction mixture was poured into 300 ml. of 3% sodium hydroxide, whereupon a crude solid separated in lumps. Ether (150 ml.) was added and the phases were separated. Acidification of the aqueous phase gave a very small amount of yellow precipitate. The ether solution was extracted with six 100-ml. portions of 1 N sodium hydroxide. The extracts on acidification with concentrated hydrochloric acid gave a light yellow precipitate which was combined with the preceding. Recrystallization from ethanol gave 11.9 g. of dibenzalpropionic acid, m.p. $167-170^{\circ}$ (lit. (37) 167°), plus 1.26 g., m.p. $165-167^{\circ}$, from the mother liquors. The carbonyl absorption of a carbon disulfide solution of the acid lay at 5.93μ . The total yield was 49% of the theoretical.

In an analogous experiment starting with 3.24 g. of potassium styrylacetate there was obtained 0.93 g. (23%) of dibenzalpropionic

acid, m.p. 165-169°.

Thiele (37) reported the isolation of 1,4-diphenylbutadiene as a by-product of this reaction. This was confirmed when in one experiment the product insoluble in base was purified by chromatography on alumina and crystallization from methanol and furnished from 6 g. of sodium styrylacetate 0.13 g. of 1,4-diphenylbutadiene, m.p. 151.5-152.5° (lit. (38) 147-148°).

Benzylstyrylacetic acid. Following the procedure of Thiele and Meisenheimer (16), 75 g. of 3% sodium amalgam was added with stirring during 3 hours to 5 g. (0.02 mole) of dibenzalpropionic acid dissolved in 50 g. of ethanol and 7 g. of acetic acid. After removal of part of the ethanol, the product was precipitated by addition of 1% hydrochloric acid and recrystallized from 85% ethanol to give 3.9 g. (77%) of benzylstyrylacetic acid, m.p. 123-125° (lit. (16) 124°).

4-Phenyl-3-bromo-1,2,3,4-tetrahydro-2-naphthoic acid. In accord with Thiele and Meisenheimer (16), a solution of 14.24 g. (0.056 mole) of benzylstyrylacetic acid in 130 ml. of chloroform was cooled to 0° and 2.91 ml. (0.056 mole) of bromine were added with swirling during 5 minutes. After another 5 minutes at 0°, the mixture was cooled to -15° and the precipitate was filtered. More product was obtained by evaporation of the mother liquors to dryness. The combined materials were recrystallized from benzene to give 14.15 g. (76%) of 4-phenyl-3-bromo-1,2,3,4-tetrahydro-2-naphthoic acid, m.p. 204-207° (lit. (16) 204-205°). The carbonyl absorption in a mineral oil mull was at 5.88 μ .

4-Phenyl-3-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid lactone. A

solution of 0.320 g. (3.02 mmole) of sodium carbonate in 50 ml. of water was stirred at room temperature for 36 hours with a solution of 2.005 g. (6.05 mmole) of 4-phenyl-3-bromo-1,2,3,4-tetrahydro-2-naphthoic acid in 100 ml. of ether. A fluffy white precipitate formed immediately in the aqueous phase and then slowly went into solution. The ether was separated, washed with water, dried and evaporated until crystals began to form. After cooling and filtering, 0.386 g. (25%) of 4-phenyl-3-hydroxy-1,2,3,4-tetrahydro-2-naphthoic acid lactone was obtained; m.p. 161-167° dec. (temperature rise 2° per minute). Recrystallization from ether gave material of m.p. 160-168° dec. The carbonyl absorption of an oil mull was at 5.55 μ .

Anal. Calcd. for $C_{17}H_{14}O_2$: C, 81.58; H, 5.64.

Found: C, 81.49; H, 5.58.

When 0.139 g. of the lactone was heated at 175-195° for 0.5 hour, it decomposed with gas evolution to give, after recrystallization from methanol, 57.0 mg. of 1,4-dihydro-1-phenylnaphthalene, m.p. 48.9-49.3°, undepressed by an authentic sample. The infrared spectrum was identical with that of authentic material.

A mixture of 0.099 g. of the lactone, 5 ml. of 0.5% aqueous sodium hydroxide and 2 ml. of ethanol was warmed on the steam bath for 1 hour. Not all of the lactone went into solution so an additional 1 ml. of 4% sodium hydroxide was added and heating was continued for 0.5 hour. On acidification to Congo Red, a white precipitate formed which was separated by extraction with ether. The ether solution was dried over sodium sulfate and evaporated to give 0.104 g. of crude product. Recrystallization from benzene afforded 0.081 g. (76%) of 4-phenyl-3-hydroxy-1,2,3,4-

tetrahydro-2-naphthoic acid, m.p. 199-200° (lit. (16) 194°), neutral equivalent 268 (calcd. 273).

1,4-dihydro-1-phenylnaphthalene from 4-phenyl-3-bromo-1,2,3,4-tetrahydro-2-naphthoic acid. In accordance with the procedure of Thiele and Meisenheimer (16), a mixture of 1.00 g. of the bromo acid and 2 g. of diethylaniline was placed in a flask which was then immersed in an oil bath at 120°. The temperature was slowly raised to 140° and heating was continued about half an hour, until carbon dioxide was no longer evolved. The mixture was poured into 20 ml. of 5% hydrochloric acid and extracted with 50 ml. of ether. After washing with 1% hydrochloric acid, 1% sodium hydroxide and water, the ether solution was dried over sodium sulfate and the solvent removed to give an oily residue. On addition of ca. 4 ml. of methanol and cooling overnight the product crystallized; m.p. 45-47°. Recrystallization from methanol gave 0.275 g. of 1,4-dihydro-1-phenylnaphthalene, m.p. 49.5-50° (lit. (16) 50°). An additional 0.084 g. was obtained from the mother liquors bringing the total yield to 58%. The ultraviolet absorption in methanol exhibited maxima at 205, 264 and 270 ~~mμ~~ (log ε 4.44, 2.85, 2.77) and inflections at 257-259 and 273 ~~mμ~~ (log ε 2.76, 2.53).

1-Phenylnaphthalene (Aldrich Chemical Co.) exhibited maximal absorption in methanol at 224 and 285 ~~mμ~~ (log ε 4.77, 4.02) (lit. (39) 227, 284 ~~mμ~~ (log ε 4.79, 4.05) in hexane), while 1,2-dihydro-4-phenylnaphthalene (see p. 27) showed an inflection at 224 ~~mμ~~ (log ε 4.31) and maximum at 265 ~~mμ~~ (log ε 3.90).

A mixture of 0.488 g. of 1,4-dihydro-1-phenylnaphthalene and 0.084

g. of powdered sulfur was placed in the bottom of a Hickman* tube and heated in a metal bath at 250° for 15 minutes. At first, hydrogen sulfide was evolved. The tube was cooled and evacuated, then warmed slowly. At $124-140^{\circ}$ and 0.2 mm., 0.355 g. of pale yellow oil distilled. The infrared spectrum of this material was superimposable on that of authentic 1-phenylnaphthalene.

1,4-Dihydro-1-phenylnaphthalene from 1-phenyl-1,3-butadiene and o-bromofluorobenzene. 1-Phenyl-1,3-butadiene was prepared according to the procedure of Grummitt and Becker (41). A solution of 18.72 g. of this material in 10 ml. of tetrahydrofuran was added to a flask containing 1.20 g. of magnesium turnings. The mixture was heated under nitrogen to vigorous reflux and, during 15 minutes, 5.01 g. of o-bromofluorobenzene in 10 ml. of tetrahydrofuran was added. After an additional 15 minutes of refluxing, the product was decanted from a little unreacted magnesium, washed with saturated ammonium chloride solution and water and dried over sodium sulfate followed by potassium carbonate. Distillation afforded 2.10 g. of crude material, b.p. $95-123^{\circ}$ at 0.2 mm. Recrystallization from methanol gave 1.52 g. (26%) of 1,4-dihydro-1-phenylnaphthalene, m.p. 51° , undepressed by an authentic sample. The infrared spectrum was identical with that of authentic material.

In a somewhat simpler procedure that afforded a 10-20% yield, all of the reagents were mixed under nitrogen and heated with a small flame until a vigorous reaction set in. The flame was removed until the reaction subsided after 2-10 minutes and, after a short time of additional heating,

* A modification of apparatus reported by Hickman (40), consisting of a 15 mm. glass tube with a bulb blown at the bottom and a second bulb, pushed into an alembic, about 1 inch above.

the product was isolated as above.

1,4-Dihydro-1-phenylnaphthalene from isomerization of 1,2-dihydro-4-phenylnaphthalene. Methyl α -phenylisopropyl ether was prepared from α -methylstyrene (Matheson Co., Inc.) in 40% yield according to the procedure of Ziegler and Dislich (42). Thirty grams of this material, 3 pounds of Mallinckrodt anhydrous ether and 36 ml. of 1:5 sodium potassium alloy reacted to give a 0.084 M solution of phenylisopropylpotassium (26), titrated with 0.1 N hydrochloric acid.

1,2-Dihydro-4-phenylnaphthalene, b.p. 150-155° at 4 mm., n_D^{28} 1.6203, was prepared in 58% yield from α -tetralone following the procedure of Weiss (43) and 10 g. of the hydrocarbon was added to 900 ml. of the organometallic solution. The reagents were thoroughly mixed and allowed to stand overnight whereupon a black gummy precipitate formed and the deep red color of the solution turned brown. With vigorous stirring, 700 ml. of this mixture was slowly added to a solution of 10 ml. of acetic acid in 100 ml. of ether. On contact with the acid, the dark mixture reacted rapidly to give a clear solution plus a precipitate of sodium acetate. The supernatant liquid was separated, washed with 1 N sodium hydroxide, dried over magnesium sulfate and concentrated. Distillation at 0.4 mm. gave 0.208 g., b.p. 110-121°, 1.874 g., b.p. 121-130°, and 0.997 g., b.p. 130-140°. Analysis by vapor phase chromatography disclosed a 12% yield of 1,4-dihydro-1-phenylnaphthalene contained in the first two fractions. It is suggested that the low recovery of hydrocarbon may have been due to addition of the phenylisopropylpotassium across the double bond to give high boiling materials. This is supported by carbonation of a similar reaction mixture, with less

pure hydrocarbon, to give acidic material, m.p. 240-242°, neutral equivalent 344, 352. The material was perhaps not homogeneous but the neutral equivalent is too high for a phenyldihydronaphthoic acid (calc. 250) and suggests a carboxylated adduct of phenylisopropylpotassium and phenyldihydronaphthalene (equiv. wt. 370) (cf. 26, 27, 28).

All of the above operations, from the preparation of the phenylisopropylpotassium through the acidification or carboxylation of the reaction mixture, were carried out in flame dried glass equipment under nitrogen that had been dried and deoxygenated with Fieser's solution or sodium benzophenone ketyl (44-a). Similar experiments using phenylsodium (45) as a base were inconclusive.

Reductions of 1-phenylnaphthalene. a. To a solution of 5 g. (0.0245 mole) of 1-phenylnaphthalene (43) (Aldrich Chemical Co.) in 20 ml. of ethylene glycol dimethyl ether was slowly added 1.5 g. (0.0653 mole) of sodium in small pieces. As the sodium went into solution the color changed to green, red, brown and finally black. After stirring overnight, 5 g. of acetic acid was added followed by water and the products were separated by ether extraction. Evaporation of the ether extracts left 4.75 g. of light colored oil. Vapor phase chromatography resolved three peaks at 16.9, 15.2 and 13.0 minutes, corresponding to a yield of 1.65 g. (33%) of starting material, 1.07 g. (21%) of 1,2-dihydro-4-phenylnaphthalene and 2.03 g. (40%) of 1,4-dihydro-1-phenylnaphthalene.

b. A three-neck, 500 ml., round bottom flask was fitted with a Dry Ice condenser and a Vibramixer and charged with 5 g. of 1-phenylnaphthalene and 25 ml. of ethylene glycol dimethyl ether. After cooling to ca. -75° (Dry Ice), 100 ml. of anhydrous ammonia was condensed

in the flask and 10 ml. of ethanol was added. Since the mixture was not homogeneous, an additional 50 ml. of glycol ether was introduced. Small pieces of lithium ribbon totalling 0.5 g. were added and after 30 minutes the reaction was allowed to warm to room temperature with evaporation of the ammonia. The solution was treated with 5 ml. of acetic acid and then 300 ml. of water and was extracted with one 100-ml. portion and two 50-ml. portions of ether. The combined extracts were washed with base, acid and water, dried over magnesium sulfate and concentrated to 4.46 g. of dark colored oil. Vapor phase chromatography resolved three peaks at 16.8, 15.2 and 13.0 minutes corresponding in yield to 2.68 g. (54%) of starting material, a trace of 1,2-dihydro-4-phenylnaphthalene and 1.79 g. (36%) of 1,4-dihydro-1-phenylnaphthalene.

c. A stirred solution, containing 7.95 g. (0.039 mole) of 1-phenylnaphthalene in 130 ml. of ethanol, was cooled to -10° and during one hour, 7.5 g. (0.325 mole) of sodium was added in small pieces. The solution first turned red, then yellow-brown after ca. thirty minutes as the sodium went into solution. The sodium had not completely reacted after 2 hours so an additional 50 ml. of ethanol was added and after another half an hour the reaction was stopped by the addition of ice. After steam distillation, the distillate was evaporated nearly to dryness and extracted with ether. The extract was combined with an ether extract of the steam-involatile residue, dried over magnesium sulfate and stripped of solvent to give 6.7 g. of crude oily product. Vapor phase chromatography resolved two peaks at 17.2 and 13.4 minutes, corresponding to 30% of starting material and 70% of 1,4-dihydro-1-phenylnaphthalene, or 59% yield of the latter. Crystallization of 4.5 g. of

the crude product from methanol gave 2.0 g. of 1,4-dihydro-1-phenylnaphthalene, m.p. 47.5-49°.

d. To a stirred solution of 5.0 g. (0.025 mole) of 1-phenylnaphthalene, 15 ml. (0.258 mole) of ethanol and 70 ml. of ethylene glycol dimethyl ether, cooled at -10° to 0°, was added 5.60 g. (0.243 mole) of sodium wire during two hours. The solution turned from a pale to a dark yellow and after 9 hours only traces of the sodium were unreacted. Acetic acid (15 ml.) was added followed by 200 ml. of water after some 15 minutes. The solvents were removed under reduced pressure on the steam bath and the residue was extracted with 100 ml. of ether. The extract was washed with base, acid and water, dried over magnesium sulfate and stripped of ether to give 4.67 g. (92%) of pale yellow oil which was analyzed by vapor phase fractionation. One peak was resolved at 13.1 minutes corresponding to 1,4-dihydro-1-phenylnaphthalene. Two recrystallizations of the product from methanol gave 3.38 g. (67%), m.p. 48-50°.

e. Repetition of the reduction with use of 100 ml. of tetrahydrofuran in place of the ethylene glycol dimethyl ether gave 4.59 g. (91%) of gross product, showing one peak in a vapor phase chromatogram. Two recrystallizations from methanol gave 3.08 g. (61%) of 1,4-dihydro-1-phenylnaphthalene, m.p. 47-49°.

The reductions with sodium and ethanol (c-e), with or without the use of an ether co-solvent, are of preparative value.

Analysis of isomerization and reduction products. In some of the procedures described above, the desired 1,4-dihydro-1-phenylnaphthalene was contaminated with the isomeric 1,2-dihydro-4-phenylnaphthalene and

with 1-phenylnaphthalene. Isolation of the desired isomer by conventional means, such as distillation, crystallization and liquid phase adsorption chromatography, was unsuccessful in most of these instances, while the overlapping absorption in the ultraviolet spectrum and the lack of intense characteristic bands in the infrared made analysis of the mixtures by spectroscopic methods difficult and unreliable. Two futile attempts were made at separation by chemical means. In one it was found that none of the components formed a picrate in methanol. In the other a crude mixture of reaction products containing ca. 30% of 1-phenylnaphthalene and ca. 70% of 1,4-dihydro-1-phenylnaphthalene was treated with mercuric acetate in methanol in trying to obtain the methoxymercuriacetate derivative (46). Only an oil was obtained.

Dr. A. Zlatkis, University of Houston, gave generously of his time in first demonstrating the feasibility of using vapor phase chromatographic techniques on these high boiling isomers. A Perkin-Elmer Vapor Fractometer, Model 154, fitted with a Perkin-Elmer column "C"* was found to give adequate resolution (Fig. 1) at 216°, 30 psig. helium. The retention times, measured on the base line at the beginning of each peak, for the known pure compounds were, for 1,4-dihydro-1-phenylnaphthalene 13.6 minutes, 1,2-dihydro-4-phenylnaphthalene 15.2 minutes and 1-phenylnaphthalene 17.0 minutes, while in the actual analyses of reaction mixtures the times varied between 12.8-13.4, 15.2-15.4 and 16.7-17.2 minutes for the respective compounds.

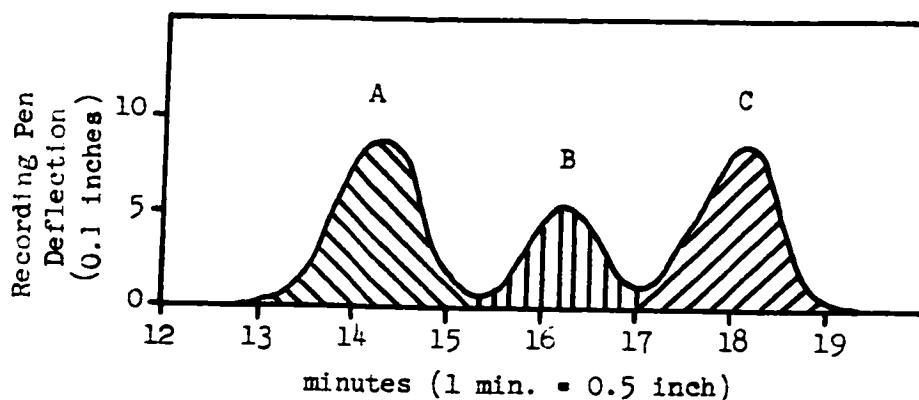
For quantitative measurements, the areas under the peaks were

* Dow Corning 200 silicone oil on fire brick in 2 m. of $\frac{1}{4}$ " stainless steel tubing.

measured by counting the squares on the chart paper and the ratios of these areas were taken as the ratios of the various compounds in the sample under consideration. Since ideal separation was not achieved and the instrument was not calibrated, these measurements can only be considered as close approximations.

Spectral methods. Routine infrared analyses were performed on a single beam recording Model 12C Perkin-Elmer Infrared Spectrophotometer. The ultraviolet absorption was generally determined on a Beckman Model DU Spectrophotometer. For special investigation of absorption below 220 ~~mμ~~ a Cary Model 14 Spectrophotometer was made available through the courtesy of the Welch Foundation.

Figure 1



Resolution of 1,4-dihydro-1-phenylnaphthalene (A), 1,2-dihydro-4-phenylnaphthalene (B), and 1-phenylnaphthalene (C) by vapor phase chromatography.

SECTION II

The Synthesis of Ethyl 1-Phenyl-2-hydroxyindene-3-carboxylate

As set forth in the introduction, the proposed synthesis of ethyl 1-phenyl-2-hydroxyindene-3-carboxylate (I) would proceed by oxidation of 1,4-dihydro-1-phenylnaphthalene (II) to α -phenyl-o-benzenediacetic acid (III), which should yield I on esterification and cyclization.

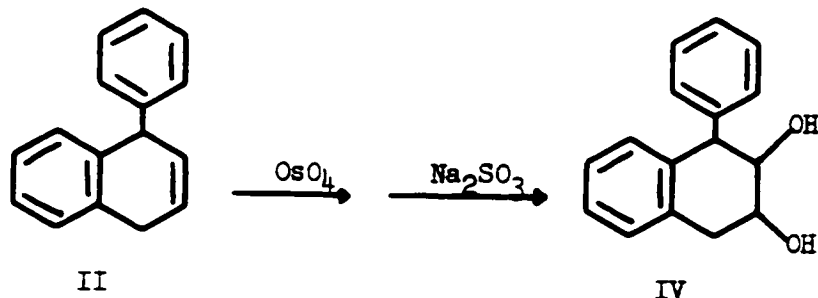
Of the various procedures available for the cleavage of an olefin to a diacid, the use of potassium permanganate was explored first. This reagent in aqueous acetone solution rendered slightly basic with bicarbonate promoted over-oxidation and the only identified acidic product was o-benzoylbenzoic acid, isolated by chromatography on silicic acid. In this and other methods wherein over-oxidation was encountered, it is presumed that intermediate formation of a carbonyl group in the 2 or 3-position could give rise to enolic or phenolic forms with Δ^1 or Δ^3 -bonds.

Milder conditions employing permanganate have been worked out by Lemieux and Rudloff (47) wherein periodate is the cleavage agent with only catalytic amounts of permanganate present. Evidence is given to show that in the first step the permanganate is not reduced below the manganate stage and that the periodate cleaves the intermediate hydroxy ketone. A further stage of oxidation may occur if the cleavage products are susceptible to attack by permanganate. Under these conditions II gave only a small amount of unidentified acidic material while enhanced ultraviolet absorption at 282 ~~m μ~~ in the neutral fraction recovered indicated the probability of some oxidation to 1-phenylnaphthalene or its derivatives.

In a second scheme to cleave the olefinic bond in II, a two-step reaction was contemplated in which 1-phenyl-1,2,3,4-tetrahydronaphtha-

lene-2,3-diol (IV) would be isolated and then oxidized with periodate. Criegee and co-workers (48) have investigated the course of the reaction of osmium tetroxide with an olefin to give the corresponding cis-glycol and this reaction seemed well suited to transform II into IV. The technique of Serini and Logeman (49) was employed in treating II with osmium tetroxide in ether followed by sodium sulfite decomposition of the intermediate osmate ester. The glycol IV was obtained in 59% crude yield and crystallized from ether; m.p. 125° . The substance separated from benzene as a hemisolvate. Aside from the mode of formation, the structure of IV was based on its analysis, typical unconjugated aromatic absorption in the ultraviolet spectrum and its infrared absorption at 2.80μ , in good agreement with the measurements of Kuhn (50) on cis-1,2-glycols. The mutual configuration of the phenyl and hydroxyl groups is probably trans since the intermediate osmate ester would be expected to form on the less hindered side of the ring, and reductive cleavage to the diol would not produce inversion.

Unfortunately the cleavage of the glycol IV with periodate (51) did not proceed as expected. No attempt was made to isolate an intermediate dialdehyde but instead the crude products from sodium periodate oxidation in aqueous methanol were treated directly with silver oxide. The reduction of the silver oxide was evidenced by the formation of a black

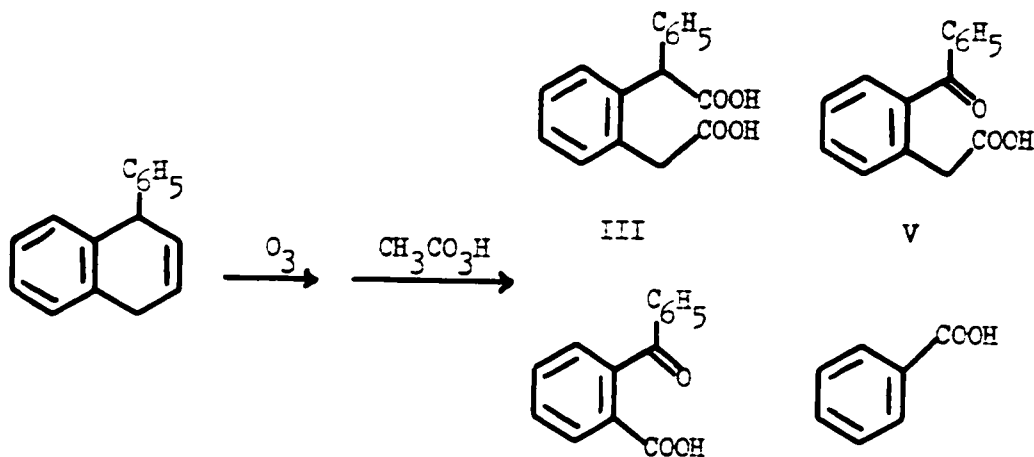


precipitate but the base soluble products of the reaction defied identification. Bamberger and Lüdter (30) have reported the oxidation of 1,2,3,4-tetrahydronaphthalene-2,3-diol to o-benzenediacetic acid with dichromate and sulfuric acid but these conditions were considered too severe in the present case because of the somewhat labile hydrogen in the 1-position. The glycol was found to be resistant to the attack of chromium trioxide-pyridine (52) to the extent that 88% of the starting material was recovered unchanged and this was the total product obtained.

The successful synthesis of α -phenyl-o-benzenediacetic acid (III) was based on the results obtained by Wilms (53) when he investigated the use of peracetic acid as a reagent for the oxidative cleavage of ozonides. He found a 90% yield of adipic acid from the ozonization of cyclohexene in methyl acetate at -50° followed by treatment with 40% peracetic acid. Compound II was ozonized in ethyl acetate at -75° . The products were warmed carefully (see Experimental) with 40% peracetic acid at $50-60^{\circ}$ for twelve hours. Compound III was isolated in 20% yield by chromatography of the crude mixture of oxidation products over silicic acid and crystallization from ethyl acetate and petroleum ether; m.p. 185° . The characterization of III as α -phenyl-o-benzenediacetic acid was based on elementary analysis, neutral equivalent and spectral properties. Carbonyl absorption in mineral oil was at 5.92μ which is typical for the structure indicated (diphenylacetic acid absorbs at 5.90μ), and the ultraviolet spectrum was quite comparable to that of diphenylacetic acid (see Table II).

Other acids found among the ozonization products include benzoic acid, o-benzoylbenzoic acid and o-benzoylphenylacetic acid (V). The

last was previously unknown. It crystallizes from benzene-petroleum ether, m.p. 132° , and was characterized by elementary analysis and spectral properties. Infrared absorption at 5.89 and 6.08 μ is close to that expected for an unconjugated carboxylic acid and a benzophenone system, while the diaryl ketone system shows an ultraviolet maximum at 252 μ ($\log \epsilon$ 4.13), (cf. benzophenone, 254 μ ($\log \epsilon$ 4.27) (39 b)).



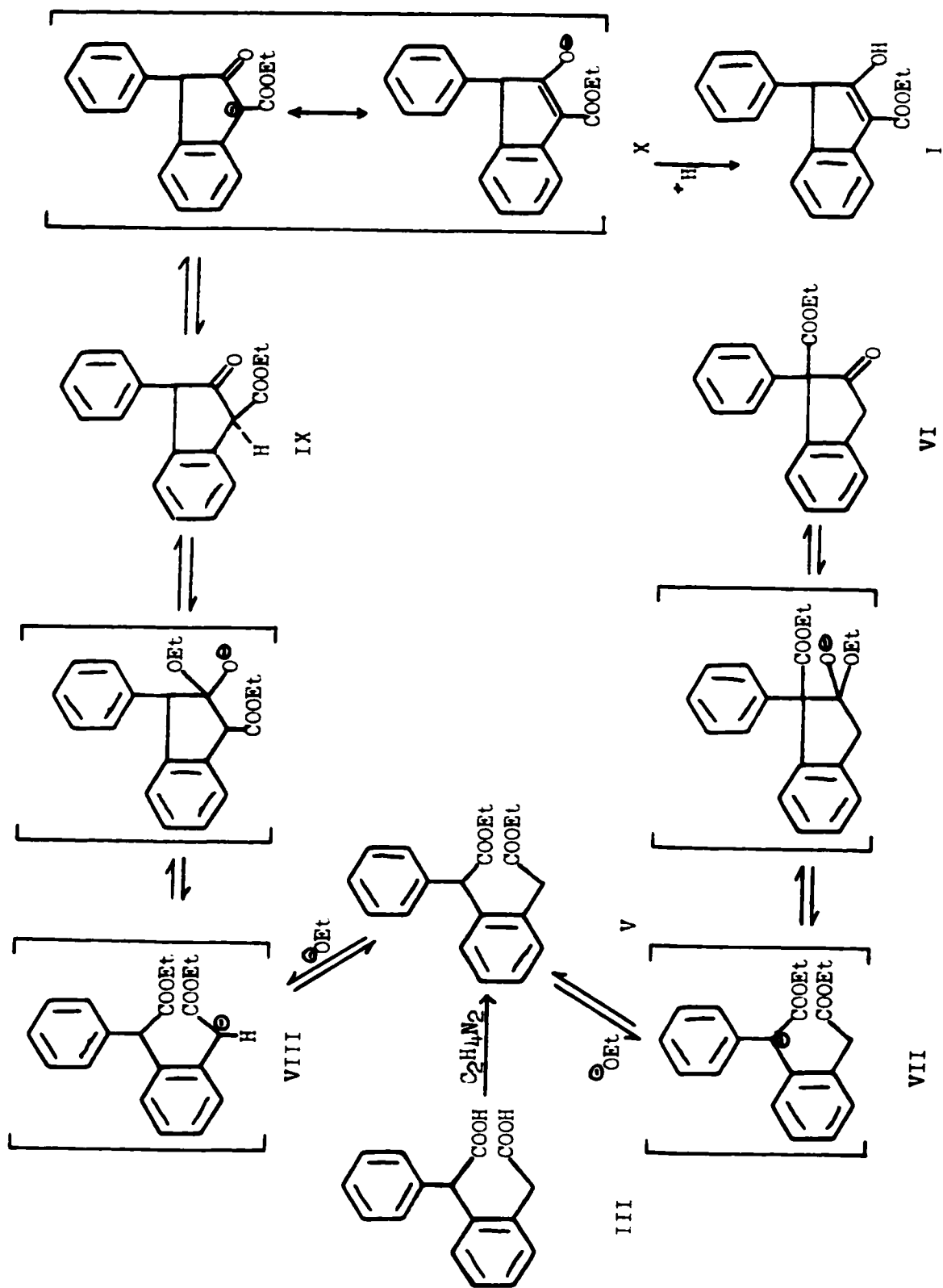
Only one attempt was made to isolate the intermediate ozonide of II. Dr. A. Riebel suggested ozonization in methanol followed by removal of the solvent in air and subsequent treatment of the ozonide with performic acid. In following this procedure a viscous, apparently polymeric, ozonide was obtained upon evaporation of the methanol. Treatment with formic acid and hydrogen peroxide followed by the usual work-up gave nearly equal quantities of III and V. The olefin was recovered unchanged from ozonization in aqueous acetic acid at 0° (54), in which it was only partially soluble, while in a similar experiment wherein ethanol was used as a co-solvent, only a small amount of unidentified acid was obtained along with an 86% weight recovery of neutral material, presumed to be II.

It remained to esterify the diacid III and cyclize to the desired enolic keto ester I. The esterification was accomplished in a straightforward manner by the use of diazoethane in ether solution but no attempt was made to isolate and purify the diethyl α -phenyl-o-benzene-diacetate (V).

In the following step wherein a Dieckmann cyclization (55) is catalyzed by sodium ethoxide, there are two possibilities for ring closure. The first would lead to the undesired ethyl 1-phenylindan-2-on-1-carboxylate (VI) while the second would lead to I. The base catalyzed condensation proceeds reversibly through three discrete steps which involve the formation of an anion by removal of an acidic hydrogen, attack of this anion on a second ester function with loss of alkoxide, and ionization of the resulting β -keto ester.

In the first step, starting with V there is the possibility of forming two anions (VII and VIII). The anion VII should be more stabilized by resonance than VIII and probably will be formed faster, but both VII and VIII will be present in solution. The second step involves cyclization to VI or the keto form (IX) of the desired compound I. In the final stage the α,α -disubstituted β -keto ester VI is unable to form a stabilized enolate anion, whereas IX is a stronger acid than ethanol and in the presence of ethoxide will be converted into the enolate anion X which is stabilized as shown. Thus it is to be expected that in the presence of sodium ethoxide and ethanol the equilibrium will be pushed toward the formation of X to the exclusion of VI and that acidification will lead to the desired compound I.

When the crude ethyl ester V was treated in ethanol with a slight



excess of sodium for twelve hours, there was obtained on acidification and recrystallization from ether a 58% over-all yield from III of pure ethyl 1-phenyl-2-hydroxyindene-3-carboxylate, m.p. 141° . Compound I, obtained in this manner, was shown by an undepressed mixed melting point and by comparison of spectral properties to be identical with a sample of the enol, m.p. 140° , prepared by Hart (17) from diphenylketene and ethyl diazoacetate.

When compound III was first prepared, the ultraviolet spectrum of a sample, shown later by analysis to be impure, had an anomalous absorption maximum at $285\text{m}\mu$. The possibility was considered that this band arose from a similarity to the compounds containing α -phenylcarbonyl groupings that were studied by Kumler, Strait and Alpen (56) (cf. Cookson, et al. (57)). These workers found low intensity maxima at $290\text{-}310\text{m}\mu$ which were attributed to non-conjugated electronic interactions between the aromatic nuclei and carbonyl but not carboxyl groups. To investigate the possibility of this effect in III as well as to lend further support to the ultraviolet characterization of III, the spectra of a number of model compounds were observed from $200\text{ to }400\text{m}\mu$. The compounds investigated and their absorption are listed in Table II. The conjugated and unconjugated acids are clearly distinguishable.

The β -(o-carboxyphenyl)-hydrocinnamic acid (XI) (57a) was prepared by a new method as follows. Treatment of ethyl o-benzoylbenzoate (XII) with ethyl bromoacetate and zinc under Reformatsky conditions led, probably through the hydroxy acid, to ethyl 3-phenylphthalide-3-acetate (XIII). Compound XIII was not purified but was identified by infrared absorption at 5.65 and $5.81\text{m}\mu$ attributable to an α,β -unsaturated

Table II

Ultraviolet Spectra of α -Phenyl-o-benzenediacetic Acid
and Model Compounds

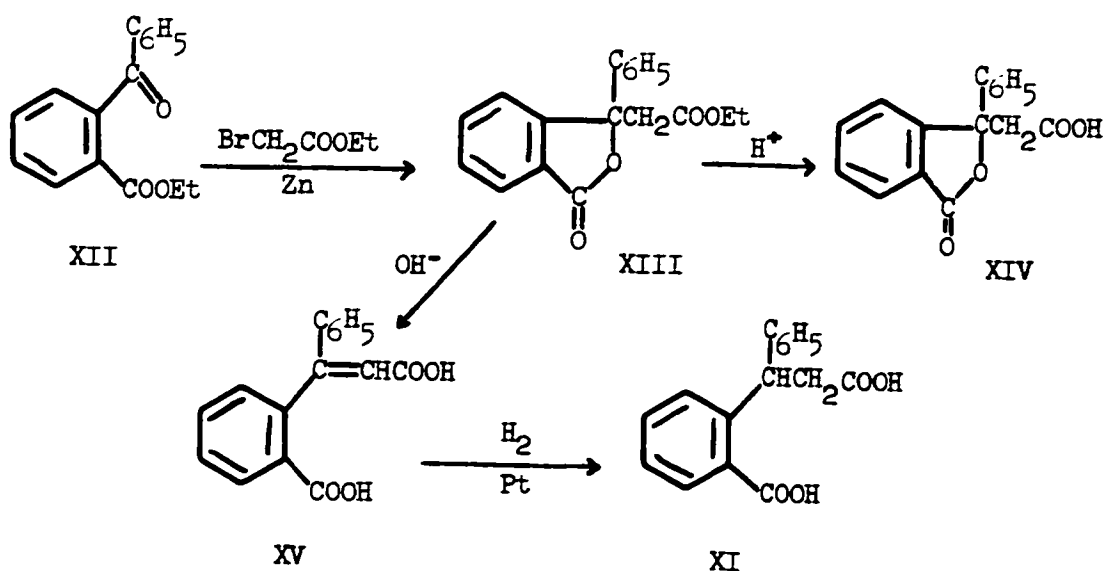
	<u>λ max.</u>	<u>log ϵ</u>	
α -Phenyl- <u>o</u> -benzenediacetic acid	254 max	2.54	*
	258	2.61	
	265	2.56	
	268	2.46	
Diphenylacetic acid	204	4.46	
	248	2.58	
	253	2.68	
	258	2.75	
	265	2.65	
	268	2.46	
<u>o</u> -Benzenediacetic acid	208	3.95	
	257	2.16	*
	261	2.24	
	267	2.12	
<u>o</u> -Benzenediacetonitrile	208	3.95	
	244	2.12	*
	259	2.22	
	265	2.11	
α -Phenylhomophthalic acid	228	4.01	*
	259	3.01	
	278	3.21	
β -(<u>o</u> -Carboxyphenyl)-hydrocinnamic acid	259	3.00	
	278	3.12	
Homophthalic acid	228	3.96	
	276	3.07	

* Inflections.

All spectra were observed in 0.01 N methanolic hydrogen chloride with the exception of o-benzenediacetonitrile which was observed in methanol.

γ -lactone (phthalide) and a carboxylic ester group. The ultraviolet absorption of XIII rose monotonically to shorter wave lengths with an inflection at 270-285 μ . Acid hydrolysis of XIII gave 3-phenylphthalide-3-acetic acid (XIV), m.p. 183 $^{\circ}$, characterized by carbonyl absorption at 5.87 and 3.3-3.5 μ corresponding to the carboxylic acid as well as a peak at 5.72 μ attributable to the lactone group. Preparation of XIV in another way has been reported in a patent (57b).

Saponification of XIII with sodium hydroxide gave β -(o-carboxyphenyl)-cinnamic acid (XV), configuration unknown, m.p. 194 $^{\circ}$ dec. The neutral equivalent and analysis were in accord with structure XV, while the ultraviolet absorption at 264 μ (log ϵ 4.06) was in good agreement with the structurally analogous γ,γ -diphenylitaconic acid, inflection 228 μ (log ϵ 4.20), maximum 264 μ (log ϵ 3.98) (39c). Compound XV could be reduced catalytically over platinum to β -(o-carboxyphenyl)-hydrocinnamic acid (XI), m.p. 156 $^{\circ}$.



Experimental

Oxidations of 1,4-Dihydro-1-phenylnaphthalene. A series of experiments were carried out in the attempt to oxidize 1,4-dihydro-1-phenylnaphthalene to α -phenyl-o-benzenediacetic acid. The results of these experiments are indicated below.

Since in every case a crude mixture of acidic products was obtained, it was found necessary to employ adsorption chromatography to isolate the various compounds produced. In the general procedure followed, silicic acid (Mallinckrodt, 100 mesh, activated 1 hour in air at 200°), corresponding to forty times the weight of the material to be chromatographed, was slurried in petroleum ether and poured into a glass column. The column was fitted with a stopcock and cotton plug at the bottom and was chosen of such a size that the height of the silicic acid when packed was approximately ten times the diameter. The solvents used, in order of increasing polarity, were reagent grade carbon tetrachloride, chloroform and ether.

The material to be chromatographed was taken up in a convenient amount, 2-3 ml., of the least polar solvent or solvent combination in which it would dissolve and was added to the top of the column. The material was eluted with increments of solvent corresponding approximately to the volume of the adsorbent. Each fraction eluted was immediately evaporated to dryness and weighed. When the weight of two successive fractions was approaching zero, the content of the more polar component in the eluting solvent was increased by 10%. This was continued until all the material had been eluted from the column or until a final wash with 4-6 fractions of ether.

Ozonolysis. In a modification of the general procedure of Wilms (53), a solution of 1.06 g. (0.00515 mole) of 1,4-dihydro-1-phenylnaphthalene in 20 ml. of ethyl acetate was cooled in a Dry Ice-acetone bath. Ozone, generated in 0.02 cu. ft./min. of anhydrous oxygen at 8 psig. by a Welsbach Corporation Laboratory Ozonator, Model T-23, 115 v. AC, was bubbled through the solution for 30 minutes (equivalent to 2 g. of ozone). Two milliliters of 40% peracetic acid* (0.0105 mole) were added and the mixture was warmed slowly to 50°. The heating bath was removed, the pressure was reduced to water pump vacuum and the solution was concentrated to ca. 4 ml. The vessel was cooled further to ca. -20° before releasing the vacuum and 4 ml. of 40% peracetic acid (0.0210 mole) were added. The resulting solution was warmed at 50-60° for 12 hours.

The solution was diluted with 10 ml. of ethyl acetate and extracted with two 25-ml. portions of 5% ferrous sulfate solution that had been slightly acidified with sulfuric acid. Removal of the solvent under reduced pressure gave 0.902 g. of straw colored oil. By chromatography, as described above, 0.282 g. (20%) of crude α -phenyl-o-benzenediacetic acid was obtained in three fractions eluted with 10% ether in chloroform. Repeated recrystallization from ethyl acetate-petroleum ether gave rosettes, m.p. 184.5-185.2°, with carbonyl absorption at 5.92 μ (mineral oil mull), and ultraviolet absorption maxima in 0.01 N methanolic hydrogen chloride at 258, 265 and 268 μ (log ϵ 2.61, 2.56 and 2.46).

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135.

Found: C, 71.18; H, 5.21; neut. equiv., 137.

* Becco Chemical Division, Food, Machinery and Chemical Corporation, Buffalo, N.Y. Manufacturer's analysis: 40% peracetic acid, 5% hydrogen peroxide, 39% acetic acid, 1% sulfuric acid, 13% water.

In a typical experiment where Wilms' procedure was closely followed, 0.254 g. of starting material was ozonized and treated with peracetic acid for 12 hours at 50° as above. The reaction mixture was then heated to 95° for 10 min. to destroy the excess peracid and concentrated in vacuo. This procedure led to a dark oil which yielded 0.064 g. of crude product, m.p. 180-183°, on chromatographic separation.

Care must be exercised when concentrating solutions known or suspected to contain peracetic acid. If all of the peracid is not evaporated, rapid and sometimes violent decomposition may occur when the vacuum is released at or above room temperature. This can be avoided by releasing the vacuum only after cooling to ca. -20° when partial evaporation is required, by destroying the peracid first in dilute solution at 90-100°, or by destroying the peracid with ferrous sulfate before concentration.

Ozonolysis of 1.08 g. of 1,4-dihydro-1-phenylnaphthalene for 15 minutes at -80° in 50 ml. of methanol yielded, on removal of the solvent in a stream of air at 30°, a white viscous residue. This residue was dissolved in 25 ml. of 85% formic acid and 2 ml. of 30% hydrogen peroxide and refluxed for 45 minutes. Removal of the solvent under reduced pressure left 0.877 g. of dark oil. By chromatographic separation in the usual manner, 0.261 g. of o-benzoylphenylacetic acid was eluted in the eighth fraction of chloroform and 0.177 g. of α -phenyl-o-benzenediacetic acid was eluted with 10% ether in chloroform.

The o-benzoylphenylacetic acid was recrystallized from benzene-petroleum ether; m.p. 132°; carbonyl absorption, 5.89 and 6.08 μ (mineral oil mull); ultraviolet absorption maximum, 252 $m\mu$ (log ϵ 4.13) in ethanol.

Anal. Calcd. for $C_{15}H_{12}O_3$:

C, 74.98; H, 5.04.

Found:

C, 75.20; H, 4.89.

Potassium permanganate oxidation. 1,4-Dihydro-1-phenylnaphthalene readily discolored permanganate solutions. However, chromatographic separation of the products from two experiments wherein 0.5 g. of this material was treated with 1 g. of potassium permanganate in a basic aqueous acetone solution gave only 0.0224 g. of crude o-benzoylbenzoic acid. The product was characterized by conversion to anthraquinone with concentrated sulfuric acid (44b).

Following the procedure of Lemieux and Rudloff (47), 0.495 g. of 1,4-dihydro-1-phenylnaphthalene was oxidized in aqueous pyridine with 150 ml. of a solution that was 0.09 M in periodic acid, 0.10 M in sodium hydroxide and 0.001 M in potassium permanganate. No rigorously identified material was obtained but increased ultraviolet absorption at 282 ~~nm~~ indicated the presence of 1-phenylnaphthalene or its derivatives in the neutral extracts.

Osmium tetroxide oxidation. Following a procedure analogous to that of Serini and Logemann (49), a solution containing 0.805 g. (0.00391 mole) of 1,4-dihydro-1-phenylnaphthalene in 50 ml. of ether was added to 1.019 g. (0.00401 mole) of osmium tetroxide in 50 ml. of ether. After 45 hours at room temperature, 10 g. of sodium sulfite in 25 ml. of ethanol and 100 ml. of water were added. The mixture was heated on the steam bath for 2 hours, filtered and the precipitate washed with 50 ml. of ethanol and 25 ml. of water. The ethanol was evaporated from the combined filtrates and washings and the solution was extracted with 100 ml. of chloroform. Removal of the chloroform under reduced pressure left a

brown liquid which crystallized on standing. The material was taken up in ether from which it crystallized in small pellets, m.p. 123-124°. The crude yield was 0.554 g. (59%). Further recrystallization from ether gave pure 1-phenyl-1,2,3,4-tetrahydronaphthalene-2,3-diol, m.p. 125°. Infrared absorption at 2.80 μ was typical of a cis-1,2-glycol (50). The ultraviolet spectrum showed typical unconjugated aromatic absorption with maximum at 262 μ (log ϵ 2.72) in ethanol.

Anal. Calcd. for $C_{16}H_{16}O_2$: C, 79.97; H, 6.71.

Found: C, 79.78; H, 6.62.

On recrystallization from benzene, the glycol took up one half mole of benzene of crystallization to give clear needles that changed to an opaque white at 82-90° before melting sharply at 125°.

Anal. Calcd. for $C_{16}H_{16}O_2 \cdot \frac{1}{2}C_6H_6$: C, 81.69; H, 6.86; C_6H_6 , 13.98.

Found: C, 81.66; H, 6.89; C_6H_6 , 15.06.

The crystals lost solvent and became an opaque white powder when dried at 80° in vacuo. The powder on recrystallization afforded unchanged glycol.

Ethyl 1-phenyl-2-hydroxyindene-3-carboxylate. To 0.122 g. (0.45 mmole) of α -phenyl-o-benzenediacetic acid in 2 ml. of ethanol was added a fivefold excess of diazoethane (58) in 15 ml. of ether. A reflux condenser and nitrogen inlet were attached and 10 ml. of anhydrous benzene was introduced. The orange color of the diazoethane was gone in ca. 0.5 hour. Sodium (0.11 g., 0.48 mmole) was added and the flask warmed in an oil bath at 55° for 12 hours. After adding 1 ml. of acetic acid and 50 ml. of ether, the solution was washed with 225 ml. of 3% sodium carbonate in six portions. The carbonate solutions were acidified with hydrochloric

acid and extracted with ether. Drying over sodium sulfate and removal of the solvent gave 92.9 mg. (73%) of crystalline material, m.p. 135-139°. Three recrystallizations from ether gave 73.5 mg. of pure ethyl 1-phenyl-2-hydroxyindene-3-carboxylate, m.p. 141.1-141.8°. The melting point of a mixture of this material with that obtained by Hart (17) from diphenylketene and ethyl diazoacetate was 140.9-141.6°. The infrared and ultraviolet spectra of the two materials were identical with maxima at 3.33, 3.37, 6.08 ~~μ~~ (carbon disulfide solution); 3.12, 3.39, 6.01 ~~μ~~ (potassium bromide disk); 235, 276, 284 ~~μ~~ (log ϵ 4.18, 3.81, 3.78) in ethanol; 237, 277, 284, 308 ~~μ~~ (log ϵ 4.18, 3.65, 3.64, 3.41) in 0.01 N methanolic hydrogen chloride; 223, 284, 328 ~~μ~~ (log ϵ 4.28, 4.31, 3.61) in 0.015 N methanolic sodium hydroxide.

3-Phenylphthalide-3-acetic acid. Five grams of o-benzoylbenzoic acid underwent smooth esterification on heating with 50 ml. of ethanol and 2 ml. of concentrated sulfuric acid to yield 4.69 g. of ethyl o-benzoylbenzoate, m.p. 56-57° after crystallization (lit. (58) 58°), with infrared absorption at 5.84 and 6.00 ~~μ~~ (carbon disulfide solution).

Ethyl o-benzoylbenzoate (3.97 g.), 150 ml. of benzene and 2 ml. of ethyl bromoacetate were mixed and 2 g. of granular zinc (cleaned with 10% hydrochloric acid, water, acetone and ether) was added with a small crystal of iodine. Upon heating with the steam bath for a short time, the iodine color disappeared and a vigorous reaction set in. With continued refluxing on the steam bath, a total of 30 g. of zinc was added during 3 hours. After the first half hour, an oil separated out and caused the zinc to collect in lumps but was redissolved by addition of 15 ml. of tetrahydrofuran. A small crystal of iodine was added every

hour during the reaction and an additional 2 ml. of ethyl bromoacetate was added after the first 1.5 hours.

The reaction was cooled, a few drops of acetic acid were added and the supernatant liquid was decanted from the unreacted zinc. The zinc was washed with benzene and a few drops of acetic acid and the washings combined with the previous solution. Two hundred milliliters of water were added and the mixture was acidified with acetic acid. The organic phase was separated, the aqueous phase was washed with two 50-ml. portions of benzene and the organic materials were combined. After washing with 5% ammonium hydroxide until the washings were clear, then with water and finally drying over magnesium sulfate, the solvent was evaporated to leave 4.23 g. of crude ethyl 3-phenylphthalide-3-acetate, with infrared absorption at 5.65 and 5.81 μ (carbon disulfide solution).

On heating 0.432 g. of the crude ester with 5 ml. of acetic acid and 3 ml. of 10% hydrochloric acid for 1.5 hours on the steam bath, followed by separation of the acidic material with 5% sodium carbonate in the conventional manner, 0.139 g. of 3-phenylphthalide-3-acetic acid was obtained. Repeated recrystallization from chloroform gave the pure compound, m.p. 182.5-183° (lit. (57b) 175-177°), with infrared absorption at 5.75 and 5.87 μ (mineral oil mull), and ultraviolet absorption maxima at 276 and 281 μ (log ϵ 3.12, 3.13) in ethanol.

Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51.

Found: C, 71.81; H, 4.71.

β -(o-Carboxyphenyl)-cinnamic acid. A solution containing 0.474 g. of the crude ethyl 3-phenylphthalide-3-acetate and 0.150 g. of sodium hydroxide in 5 ml. of methanol and 5 ml. of water was heated at reflux

on the steam bath for 1.5 hours. The solution was poured into 100 ml. of water, carefully neutralized to litmus with dilute hydrochloric acid and extracted with 50 ml. of ether. The aqueous phase was acidified to Congo Red and extracted twice more with 50 ml. of ether. The second extracts were dried and concentrated to give 0.349 g. of oil, which deposited 0.156 g. of crude product from ether-petroleum ether. Recrystallization from aqueous methanol gave pure β -(o-carboxyphenyl)-cinnamic acid, m.p. 193.8-194.8° dec., with infrared absorption at 5.86 and 6.22 μ (mineral oil mull), and ultraviolet absorption at 264 μ (log ϵ 4.06) in ethanol. Anal. Calcd. for $C_{16}H_{12}O_4$: C, 71.63; H, 4.51; neut. equiv., 134.

Found: C, 71.63; H, 4.58; neut. equiv., 135.5.

β -(o-Carboxyphenyl)-hydrocinnamic acid. β -(o-Carboxyphenyl)-cinnamic acid (0.273 g.) was dissolved in 50 ml. of acetic acid-ethanol containing a few drops of 10% hydrochloric acid and hydrogenated over 0.306 g. of platinum oxide. Filtration, followed by evaporation of the solvent on the steam bath led to 0.326 g. of oil which was chromatographed in the usual manner over silicic acid. The material eluted with chloroform containing 5-40% ether was crystallized from carbon tetrachloride; m.p. 158°. A high neutral equivalent (185) suggested that partial esterification had occurred during evaporation of the solvents from the reaction mixture. Saponification of the products followed by chromatography over silicic acid gave the free acid which was recrystallized from benzene-ligroin; m.p. 161-162°. After 24 hours at 80° in vacuo over phosphorus pentoxide, the substance melted at 155.8-156°, *with infrared absorption at 5.79 and 5.96 μ (mineral oil mull), and ultraviolet absorption maxima at 259 and 278 μ (log ϵ 3.00 and 3.12) in 0.01 N

* (lit. (57a) m.p. 155-157°)

methanolic hydrogen chloride.

Anal. Calcd. for $C_{16}H_{14}O_4$: C, 71.10; H, 5.22; neut. equiv., 135.

Found: C, 70.76, 71.07; H, 5.40, 5.64; neut. equiv., 135.

o-Benzenediacetonitrile. Obtained from Aldrich Chemical Co. and recrystallized from ethanol; m.p. $59.5-60^{\circ}$ (lit. (59) 60°). The substance exhibited ultraviolet maxima at 208, 259 and 265μ (log ϵ 3.95, 2.22, 2.11) in methanol.

o-Benzenediacetic acid. Prepared from o-benzenediacetonitrile by bubbling hydrogen chloride through a methanolic solution of the dinitrile and saponifying the methyl ester with aqueous sodium hydroxide. Recrystallization from ether gave pure material, m.p. $150-150.9^{\circ}$ (lit. (30) 150°), neutral equivalent 98 (calcd. 97), with ultraviolet maxima at 208, 261 and 267μ (log ϵ 3.95, 2.24, 2.12) in 0.01 N methanolic hydrochloric acid.

Homophthalic acid. Prepared from homophthalic anhydride (Aldrich Chemical Co.) by hydrolysis in 10% hydrochloric acid and recrystallized from water to give pure material, m.p. $180-180.5^{\circ}$ (lit. (30) $180-181^{\circ}$), neutral equivalent 91 (calcd. 90), with ultraviolet maxima at 228 and 276μ (log ϵ 3.96, 3.07) in 0.01 N methanolic hydrochloric acid.

PART TWO

INTRODUCTION

Introduction

There are three general mechanisms for the initiation and propagation of polymer chains. These entail radical, cationic and anionic processes. The most thoroughly studied of these have been radical and cationic processes which are widely employed in the polymerization of unsaturated monomers such as halogenated olefins, olefinic hydrocarbons and acrylic acid derivatives.

Base catalysis has been employed to a considerable extent in condensation polymerizations but has only been brought under close scrutiny for addition polymerization during the past decade. Beaman (60) has investigated the anionic polymerization of methacrylonitrile using such initiators as sodium, triphenylmethylsodium and Grignard reagents, while more recently, the polymerization of acrylonitrile by alkoxides has been reported by Zilka and co-workers (61). Other olefins, e.g., styrene (62), isoprene (63) and butadiene (64), have been subjected to base initiated polymerization but in general a strong base such as an organo-alkali compound or alkali metal is required and the products are of low molecular weight. The facility with which an olefin of the type $\text{CH}_2=\text{CRR}'$ undergoes anionic polymerization depends on the nature of the groups R and R', one of which must be capable of stabilizing a negatively charged intermediate. The more electronegative the R groups, the easier the polymerization. If R or R' is hydrogen, then cross linking is to be expected in base from removal of a proton since this generates a new active site in the polymer chain.

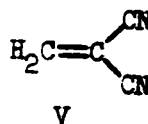
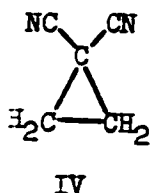
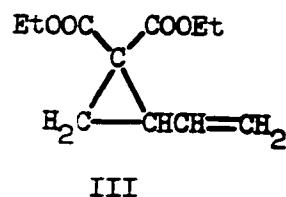
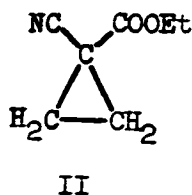
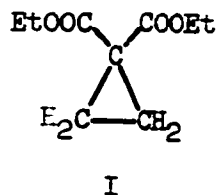
In 1953, Ettlinger (65) undertook a study of the transformation of carbocyclic compounds to open-chain polymers by additive ring fission.

This type of polymerization had never been accomplished, though lactones (66), lactams (67) and epoxides (68) had been converted to polyesters, polyamides and polyethers respectively. The known fission of the ring in diethyl cyclopropane-1,1-dicarboxylate (I) and ethyl 1-cyanocyclopropane-1-carboxylate (II) by sodium malonate and sodium cyanoacetate (69) as well as the analogy of a cyclopropane ring to a double bond suggested the possibility of anionic polymerization of suitable cyclopropanes.

In pursuing this line of endeavor, Ettlinger prepared the 1,1-dicarbethoxy-2-vinyl (III), 1,1-dicarbethoxy, 1,1-cyanocarbethoxy and 1,1-dicyano (IV) derivatives of cyclopropane, the last of which was previously unknown. Only the vinylcyclopropane diester underwent polymerization with benzoyl peroxide. At 75°, a clear viscous polymer was obtained with the cyclopropane ring apparently still intact. The other derivatives were stable to benzoyl peroxide at 100-130°.

Further investigation showed that diethyl cyclopropane-1,1-dicarboxylate would not polymerize over sodium at 105° or 215°, though the cyano ester polymerized with a sodium dispersion in 10 minutes at 100° and the dinitrile likewise polymerized in 4 hours at 75°. Both polymers had crystalline character as shown by X-ray diffraction, the former being a friable brown mass that fused and decomposed at 240°, the latter an infusible, pale yellow powder decomposing at 320°. The cyano ester polymer was soluble in warm dimethylformamide from which it could be precipitated with methanol as a stiff gel. No solvent was found for the dinitrile polymer.

Gilbert and co-workers (70) in 1954 reported the anionic as well



as the homolytic polymerization of vinylidene cyanide (V). The monomer polymerizes slowly in the presence of benzoyl peroxide but reacts rapidly in the presence of catalytic amounts of water, alcohol, amines or ketones. The resulting polymer, which reverts to the monomer on heating to 160°, was shown to have crystalline character by X-ray diffraction and was found to be soluble in dimethylformamide, tetramethylurea, tetramethylenesulfone and triethyl phosphate. It is interesting that this material, which differs from that of Ettlinger by only one methylene group in the chain, regenerates the monomer on heating and is found soluble in dimethylformamide while the polydicyanocyclopropane exhibits neither of these properties. The 1,5-spacing of the nitrile groups in the polyvinylidene cyanide undoubtedly allows a reverse Michael reaction on heating, analogous to the well known behavior of 1,5-dicarbonyl compounds, but the solubility of the polymer would appear to be due to an unexplained difference in its crystalline properties compared to the other dinitrile polymer.

The initial purpose of the present work was to reinvestigate the

anionic polymerization of 1,1-dicyanocyclopropane and to find a solvent for the polymer which might facilitate the determination of its physical properties and might be utilized in the formation of films or fibers. The search for a solvent was fruitless, though information was gained on polymerization conditions and on the molecular weight of the polymer and a new polymer was prepared from methyl 1-cyanocyclopropane-1-carboxylate.

SECTION I

Anionic Polymerization

Ethyl cyanoacetate is alkylated readily by ethylene dibromide in the presence of sodium ethoxide to give ethyl 1-cyanocyclopropane-1-carboxylate in 51% yield. Since ethyl sodiocyanoacetate is not very soluble in ethanol, the reaction is carried out in refluxing absolute alcohol by adding the ethoxide and cyano ester from separate funnels to a solution of the bromide, which constitutes in effect the addition of the sodium salt of the cyano ester. Along with the cyclopropane derivative there is obtained considerable quantities of ethyl 2-imino-3-cyanocyclopentane-1-carboxylate (VI) which is left as a residue on distillation of the products. This by-product has been shown by Thorpe (69) to arise from cyclization and decarbethoxylation of diethyl α,α' -dicyano-adipate (VII) which is formed by attack of the ethyl cyanoacetate ion on the intermediate ethyl β -bromoethylcyanoacetate (VIII) or by fission of the cyclopropane derivative with the same ion. The extent of this side reaction can be minimized by avoiding high concentrations of the cyano ester anion. This is accomplished by the very slow addition of one equivalent of base along with the cyano ester followed by slow addition of the second equivalent of base. Under these conditions the most probable course of the reaction is formation of the monoalkylated cyano ester in the first stage with cyclization to the cyclopropane derivative in the second. The path of the reaction is indicated by the scheme on the following page.

The ethyl 1-cyanocyclopropanecarboxylate obtained in the above manner has previously been difficult to purify. The alkylated ester cannot be separated from ethyl cyanoacetate by fractionation since they

boil at 212° and 208° respectively. Thorpe's (71) procedure for removal of the ethyl cyanoacetate by treatment of the crude mixture with sodium ethoxide followed by immediate hydrolysis of the salt and separation of the cyclopropane derivative was ineffective and, Ettlinger (65) found fractional extraction with base to be unsatisfactory. Previous investigators were forced to rely on elementary analyses to determine the state of purity. It has now been found that quantitative analysis of impurities is feasible with vapor phase chromatography. The distillate from a typical preparation of the alkylated ester was fractionated at 130° over a polyethylene glycol stationary phase and shown to contain ca. 2% of ethyl cyanoacetate along with ca. 2% of an unidentified impurity. The problem of purification has now also been solved with the discovery that the cyclopropane derivative could be crystallized from ether at low temperatures. Recrystallization from ether gave clear prisms, m.p. 12.8° , demonstrated to be pure by vapor fractionation as well as by elementary analysis.

The previously unknown methyl 1-cyanocyclopropane-1-carboxylate (IX) was prepared in an analogous manner from methyl cyanoacetate and ethylene bromide, though the yield was lower, 28%. Purification was effected by recrystallization from ether to give clear prisms, m.p. $31.5-32.8^{\circ}$, b.p. $111-112^{\circ}$ at 27 mm.

Either of the alkylated cyano esters underwent amination with concentrated ammonia to furnish 1-cyanocyclopropane-1-carboxamide (X). Crude starting material was satisfactory in this reaction since the amide, m.p. 160° , could be easily purified by recrystallization from water. The methyl ester gave somewhat better yields (89%) than the

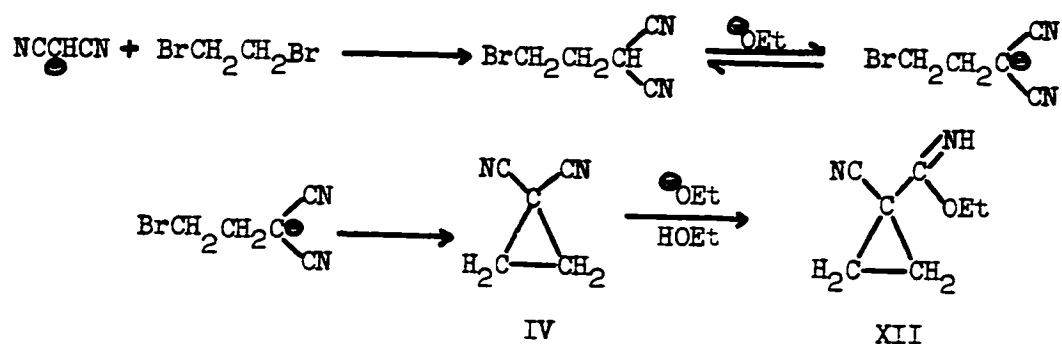
ethyl ester (74%) but the low yield in preparation of the former offset this advantage. The failure to obtain quantitative yields is probably due to some ring fission in the presence of the concentrated base.

1,1-Dicyanocyclopropane was prepared according to the method of Ettlinger (65), who found the cyano amide to be more satisfactory as starting material than cyclopropane-1,1-dicarboxamide both because of easier preparation and more facile dehydration. Thus the cyano amide undergoes dehydration with phosphorus pentoxide at 170-220° under reduced pressure to give the dinitrile. A 41% yield was realized after redistillation. The material obtained in this manner readily underwent anionic polymerization as indicated below but, though no change in physical properties was observed, on prolonged standing (3 months) it was found necessary to redistill the dinitrile to get reasonable conversions to polymer.

The known ease of dialkylation of malononitrile suggested that the 1,1-dicyanocyclopropane might more readily be obtained by direct alkylation of the dinitrile, though the higher reactivity conferred by the two more strongly electronegative groups could lead to a predominance of the iminocyclopentane derivative analogous to that obtained from the cyano esters. When an alcoholic solution of sodium malonitrile was slowly added to a refluxing solution of ethylene dibromide in alcohol, followed by a second equivalent of sodium ethoxide, the product, b.p. 110-112° at 25 mm., showed infrared absorption at 3.03, 3.24, 3.39, 4.50 and 6.09 μ . Treatment with 1 N hydrochloric acid gave ethyl 1-cyanocyclopropane-1-carboxylate, identified by spectral comparison with an authentic sample, while 1 N sodium hydroxide converted the compound

into 1-cyanocyclopropane-1-carboxylic acid (XI) which was characterized by its melting point, 148-149° (lit (72) 149°), and by infrared absorption at 3.20, 4.46 and 5.79 μ corresponding to a carboxylic acid and a nitrile group.

The elementary analysis for the product from above agreed with $C_7H_{10}N_2O$, while the infrared absorption cited suggests the presence of an imido ester and a nitrile function. These properties, coupled with the facile hydrolysis to known cyclopropane derivatives, indicated clearly that, instead of the dinitrile, the ethyl 1-cyanocyclopropane-1-carboximidate (XII) was obtained. This is in agreement with the known tendency of malononitrile derivatives to give stable imido esters in ethanolic sodium ethoxide (73). The probable course of the reaction is as follows.



Having obtained the desired monomers, a study of polymerization conditions was undertaken with the first goal an initiator that would not be expected to cause far reaching side effects. It also seemed desirable to use an initiator that would not introduce any new functional group into the polymer. The results are to be found in the Experimental Section, Table V.

In the absence of an initiator none of the monomers would polymerize at temperatures up to 150°. The ethyl cyano ester was used in the pre-

liminary work due to its ready availability and was found to undergo rapid and apparently complete conversion to a pale brown friable polymer with sodium dispersion or sodium hydride. The strength of these bases permitted polymerization of even the crudest monomer presumably because any traces of acidic inhibitors present are completely neutralized. The likelihood of attack on the nitrile or ester functions with subsequent chain branching led to a abandonment of these initiators.

Sodium ethoxide seemed to be a capricious initiator and required temperatures above 150° to induce polymerization. This same statement is applicable to the sodium salt of ethyl cyanoacetate though polymerization could be promoted at 180° . The presence of active sites in the crude polymer from one such preparation was demonstrated by using the crude polymer to initiate conversion of a fresh sample of monomer to polymer. After washing and drying the polymer was inactive.

The initiator, meeting all the desired conditions, that was finally decided upon for general use was potassium cyanide. It promoted polymerization at 150° in 4 hours in all three of the monomers at hand and the lack of discoloration in the products indicated that no great side reaction was taking place. In using the dry salt, the polymerization was carried out under heterogeneous conditions. To attain a homogeneous reaction triethylamine was employed as an initiator and was found to give very rapid and complete conversion of the monomer but the product was highly discolored.

The possibility then suggested itself that perhaps a co-solvent would enhance the activity of one of the dry initiators. This idea was verified with the use of potassium carbonate which gave no poly-

merization with the dinitrile alone but served as an initiator when the monomer was dissolved in dimethylformamide. Further investigation showed that the monomers were stable to heating in a non-acidic solvent and it became apparent that the enhancement of polymerization by a co-solvent depended on its ability to dissolve the initiator. A number of co-solvents were tried with potassium cyanide and the effects on the yield from the dinitrile are shown in Table VI (Experimental).

Having determined that polymerization in a solvent was practical, and indeed advantageous, the effect of the cyanide concentration in dimethylformamide and dimethyl sulfoxide was subjected to a preliminary investigation. It was found that the conversion to polymer increased from 0 to 80-100% on varying the sodium cyanide concentration from 0 to 0.001% as shown in Table VII (Experimental). More accurate data was obtained during the molecular weight determinations (Table III) and is graphically depicted in Fig. 2. The conversion to polymer is observed to rise rapidly at first and levels off somewhat after 0.0005% of sodium cyanide is added. This behavior indicates that some termination step occurs to the active center in the chain. Otherwise complete conversion should be observed in every case. The nature of the termination is purely speculative other than that it must involve an acidic center. It could very well be water because no attempt was made to rigorously exclude moisture though the materials were carefully dried and distilled before use.

All of the polymers obtained from the various cyclopropane derivatives were superficially quite similar, being powders ranging from pale yellow to white in color. Both of the polycyano esters were soluble in

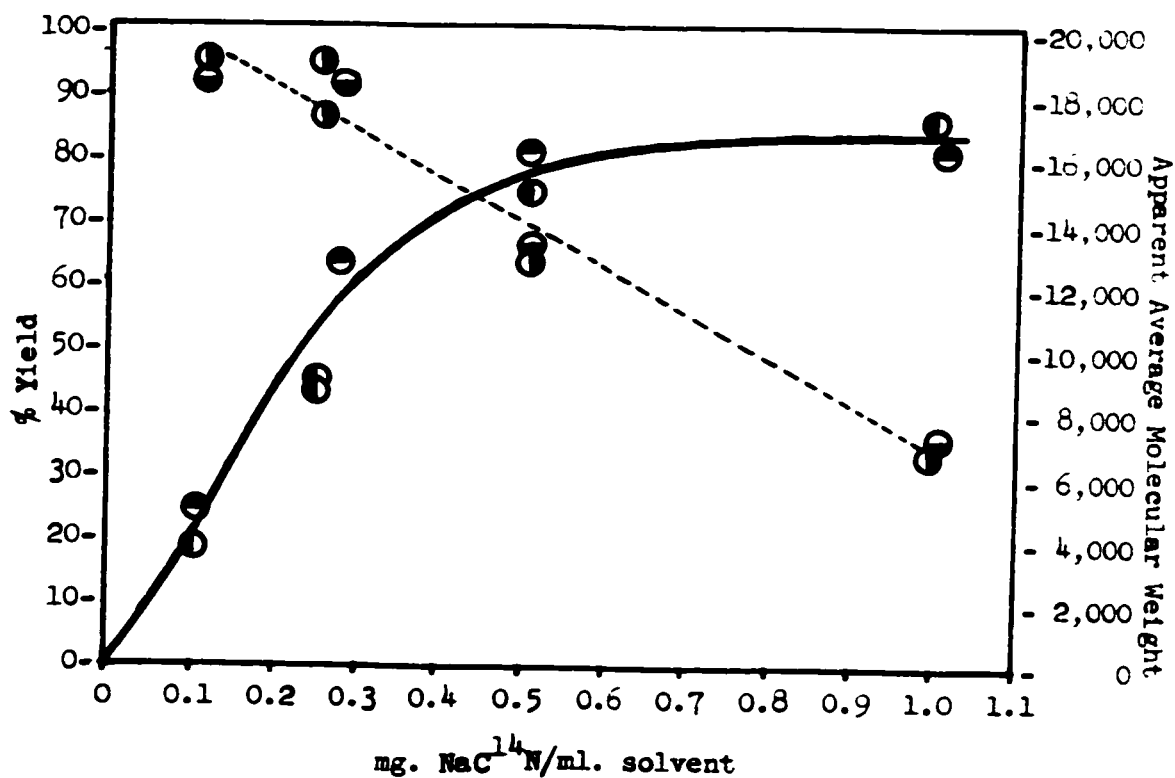
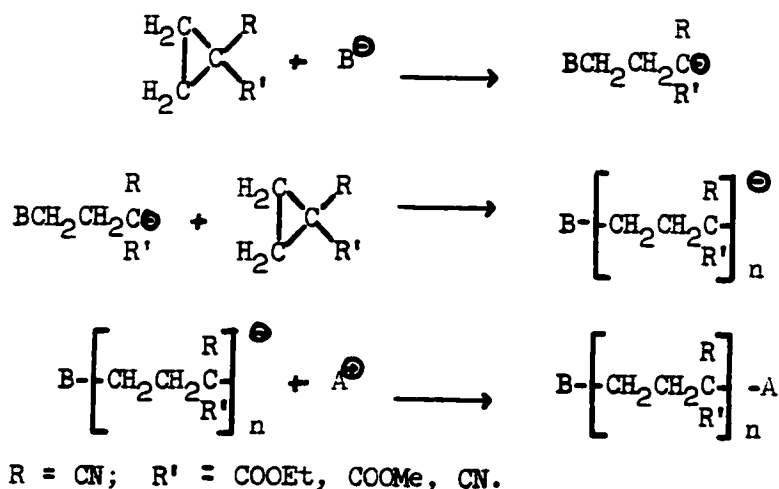


Figure 2. Effect of cyanide concentration on % yield and apparent average molecular weight of poly-1,1-dicyanocyclopropane: — % Yield, ○ in dimethylformamide, ● in dimethyl sulfoxide; --- Average molecular weight, ○ in dimethylformamide, ● in dimethyl sulfoxide.

hot dimethylformamide or dimethyl sulfoxide from which they were precipitated as a stiff gel with methanol or ether. Air drying of the gel led to a clear, brittle, discontinuous film that powdered with ease and fused with decomposition at ca. 250° (see Table V). Fig. 3 (a-b) shows the X-ray diffraction patterns of the powders indicating a high degree of crystallinity.

The infrared spectra had peaks at 4.50 and 5.78-5.79 μ indicative of the nitrile and ester functions but notably absent was the peak at 3.24 μ , corresponding to the cyclopropane methylene groups, that was clearly resolved in the monomers. Also there was no indication in the spectra of triazine rings. The absence of cyclopropane rings in the polymers substantiates the proposition that the polymerization proceeds through an additive ring fission as follows.



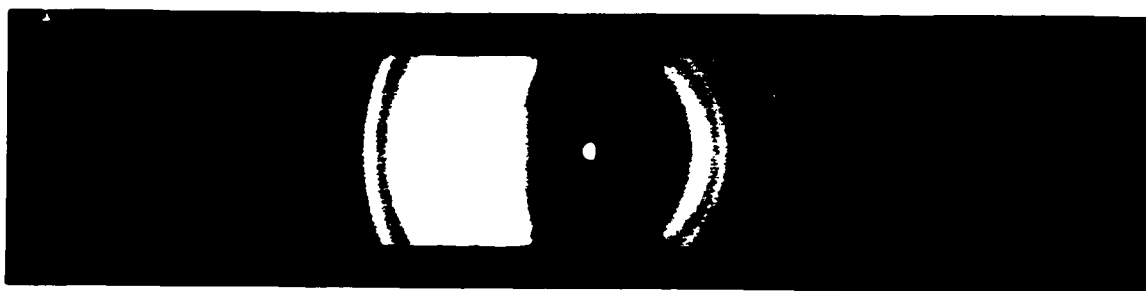
A number of unusual solvents were tried with the dinitrile polymer but neither solvation nor swelling was observed. A list of the solvents tried is given in Table VIII (Experimental). These particular materials were investigated after a survey of the literature indicated their

Figure 3

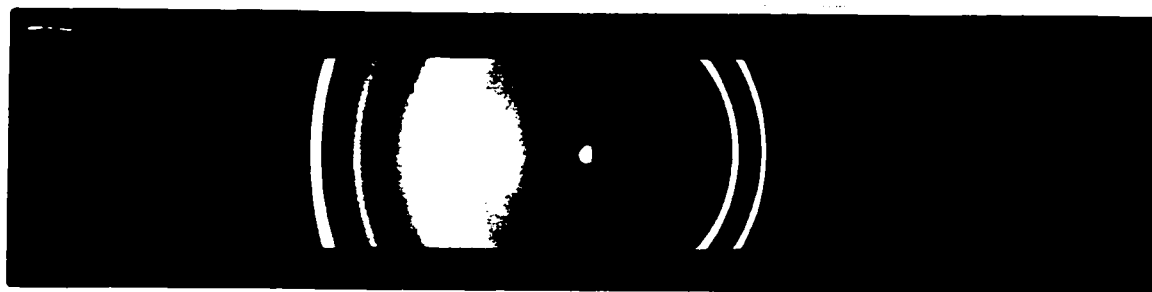
X-Ray Diffraction of Polymers



a. Ethyl 1-Cyanocyclopropane-1-carboxylate Polymer
(Table Vk)



b. Methyl 1-Cyanocyclopropane-1-carboxylate Polymer
(Table Vm)



c. 1,1-Dicyanocyclopropane Polymer
(Table Vo)

utility as solvents for polyacrylonitrile and the previously mentioned polyvinylidene cyanide. The low solubility of polyacrylonitrile in ordinary solvents such as alcohols and ketones has been ascribed by Waltcher (74) to the presence of α -hydrogen atoms since polymethacrylonitrile (60) is readily soluble. This hypothesis would appear to be incorrect in view of the present work (cf. polyvinylidene cyanide (70)) and the molecular bonding forces might better be imputed to an interaction between nitrile groups. X-Ray diffraction (Fig. 3,c) shows the polycyclopropanedinitrile to be crystalline. It is infusible and only slowly browns at 300°.

An indication that partial solvation might take place in dimethylformamide is given by the electron micrographs in Fig. 4 and 5. The unquestionably fibrous nature of the material in Fig. 4 is subdued in Fig. 5, the latter material having been heated in the solvent for a longer period of time. It is suggested that partial recrystallization may have occurred under these conditions. If this contention is correct then it also accounts for the apparent difference in Figs. 6 and 7 showing polymers formed in dimethyl sulfoxide and it might further be suggested from comparison of Figs. 4 and 6 that dimethyl sulfoxide is the better of the two "solvents".

The dinitrile polymer does dissolve slowly in warm sulfuric acid from which it can be precipitated by water or ether. However, the white powdery material recovered differs from the original polymer in that the infrared spectrum indicates complete conversion of the nitrile groups to amides.

Since conventional molecular weight determinations require solutions

Figure 4

Electron Micrograph ($\times 60,000$, 1 mm. = 167 Å) of 1,1-Dicyanocyclopropane
Polymerized One Hour at 125° in Dimethylformamide (Table VIIId).



Figure 5

Electron Micrograph ($\times 30,000$, 1 mm. = 333 Å) of 1,1-Dicyanocyclopropane
Polymerized Six Hours at $50-110^{\circ}$ in Dimethylformamide (Table VIc).



Figure 6

Electron Micrograph ($\times 30,000$, 1 mm. = 333 Å) of 1,1-Dicyanocyclopropane
Polymerized One Hour at 125° in Dimethyl Sulfoxide (Table VIIh).

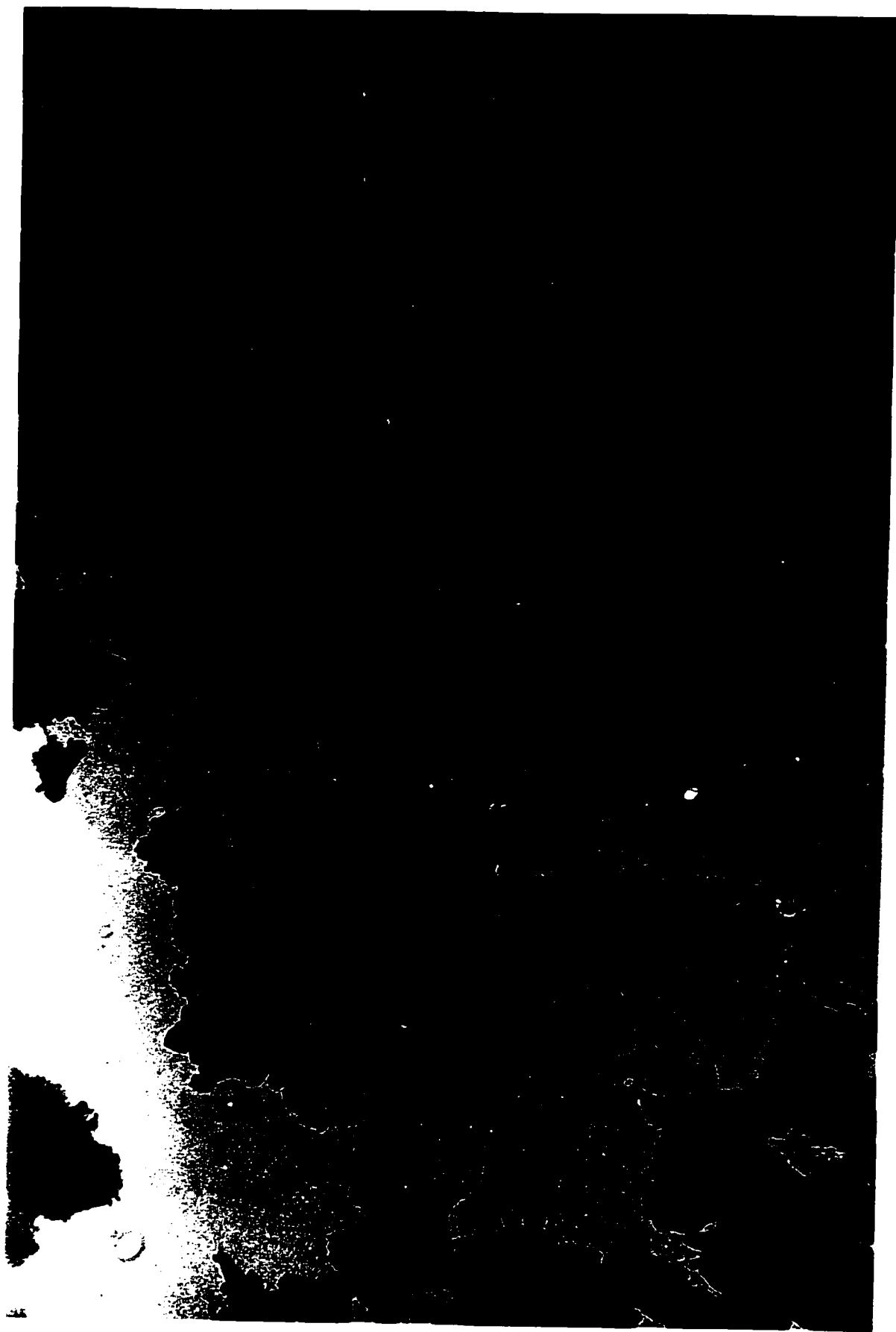


Figure 7

Electron Micrograph ($\times 30,000$, 1 mm. = 333 Å) of 1,1-Dicyanocyclopropane
Polymerized Six Hours at $50-110^{\circ}$ in Dimethyl Sulfoxide (Table VIb).



of the material under consideration, they were not applicable to the dinitrile polymer. There is the possibility that the nitrile groups could be converted into esters to confer solubility on the polymer but there would be no assurance that other changes had not occurred during the transformation. It is presumed that the simple mechanism set forth on page 63 applies to the dinitrile as well as to the cyano esters. If this scheme is correct and does not involve chain transfer or other initiation and propagation steps then each molecule of polymer will contain one mole of the initiating species. Determination of the end groups per mole would then give a measure of the average molecular weight of the polymer. This was in fact accomplished by the use of sodium cyanide- C^{14} as initiator followed by counting the radioactivity imparted to the resulting polymer. The insolubility of the material necessitated the use of suspension counting techniques which had been previously worked out by White and Helf (75). As set forth in Table III and Fig. 2, the average molecular weight of the dinitrile polymer varied from 6,800 to 19,000 depending on the concentration of initiator used. If chain transfer occurred during the polymerizations, the molecular weights determined in this manner would be high, whereas entrainment of cyanide- C^{14} would make them low.

In a similar manner the average molecular weights of the cyano esters were determined (Table III) but the results were not so satisfactory. The lack of consistency in the yields and molecular weights might be attributed to the solubility of both the initiator and polymer in the solvents employed thereby leading to incomplete separation and isolation under the same conditions that were satisfactory for the

Table III

Molecular Weight Determinations

Monomer*	Solvent*	Initiator mg. NaC^{14}N ml.	Time	T°C	Yield	Molecular Weight
C	DMF	0.11	2 hrs.	100	19.4%	19,000 g./mole
C	DMF	0.25	2 hrs.	100	44%	19,000
C	DMF	0.25	2 hrs.	100	45%	17,200
C	DMF	0.50	2 hrs.	100	76%	12,800
C	DMF	1.00	2 hrs.	100	88%	6,800
C	DMS	0.11	2 hrs.	100	24.4%	18,400
C	DMS	0.25	2 hrs.	100	53%	32,800**
C	DMS	0.28	2 hrs.	100	63%	18,400
C	DMS	0.50	2 hrs.	100	81%	15,200
C	DMS	1.01	2 hrs.	100	82%	7,200
C	Succino- nitrile	2.5	19 hrs.	100	18%	15,200**
C	None	5 mg.***	3 hrs.	150	7.3%	8,070
A	DMF	0.50	$\frac{1}{2}$ hr.	100	3.9%	5,920
A	DMS	0.50	$\frac{1}{2}$ hr.	100	52%	20,000
B	DMF	0.50	$\frac{1}{2}$ hr.	100	33%	13,400
B	DMS	0.50	$\frac{1}{2}$ hr.	100	26%	6,480
B	None	5 mg.***	$7\frac{1}{2}$ hrs.	100- 150	5.5%	4,330

* DMF = dimethylformamide; DMS = dimethyl sulfoxide; A = ethyl 1-cyanocyclopropane-1-carboxylate; B = methyl 1-cyanocyclopropane-1-carboxylate; C = 1,1-dicyanocyclopropane. In all runs 0.2 g. of monomer and 2 ml. of solvent were employed.

** Omitted from Fig. 2.

*** Dry initiator added to 0.2 g. of monomer.

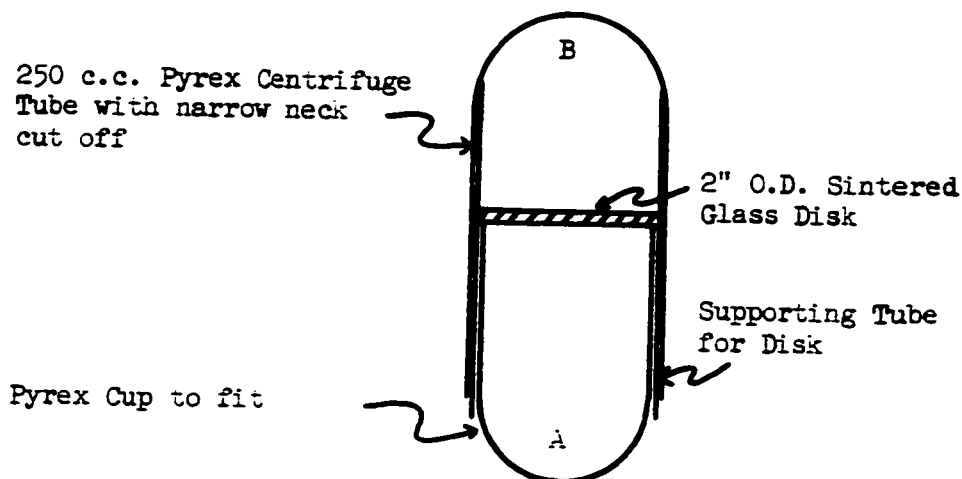
dinitrile. Further work would undoubtedly lead eventually to consistent results and in this case it would prove interesting to determine the molecular weights by conventional methods as well, perhaps in dimethylformamide, in order to obtain an evaluation of the radioactive tracer technique. This would in turn shed light on whether chain transfer or other processes were occurring in the polymerization.

Experimental

Ethyl 1-cyanocyclopropane-1-carboxylate. Following the procedure of Ettlinger (65), a solution of 545 g. of ethylene dibromide in 2 l. of absolute ethanol was stirred under nitrogen and refluxed while from separate funnels 270 g. of ethyl cyanoacetate and a solution of 50 g. of sodium in 600 ml. of ethanol were added proportionately during 4 hours. The pH was checked frequently throughout the addition with Universal Indicator paper and remained between 7 and 9, the final pH being 7. A second, equal portion of sodium in ethanol was added over a 6-hour period so that pH 9 was never exceeded. After standing overnight at room temperature, the sodium bromide precipitate was filtered from the strawberry colored solution and the ethanol was largely removed under reduced pressure. The residue was taken up in ether, washed with water, dried and concentrated. Distillation gave 154 g. of ethyl 1-cyanocyclopropane-1-carboxylate, b.p. 112-114° at 26 mm., n_D^{25} 1.4404. The yield was 51% of the theoretical.

The material obtained in this manner was suitable for use in preparing 1-cyanocyclopropane-1-carboxamide but was shown by vapor phase chromatography to contain ca. 2% of an unidentified impurity along with ca. 2% of ethyl cyanoacetate, both of which could be removed by recrystallization from ether. To accomplish this, a modified Craig tube as illustrated in Fig. 8 was employed. The solvent and material to be crystallized were placed in cup A and the sintered plate with cup B was fitted on top as shown. The apparatus was sealed from moisture by attachment of two rubber balloons and was cooled in a Dewar flask with Dry Ice. When crystallization was complete the apparatus was inverted

Figure 8



and centrifuged at -20° in a refrigerated centrifuge, used by courtesy of Dr. J. Daugherty.

By this technique, 35.0 g. of the distillate from above was crystallized from 50 ml. of ether to give 28 g. of product which was recrystallized twice more from 25 ml. of fresh ether and yielded 25 g. of ethyl 1-cyanocyclopropane-1-carboxylate, contaminated only with traces of ether and moisture. The product was taken up in ether, dried over sodium sulfate and the solvent was removed on a Rinco evaporator at 24 mm. up to a temperature of 70° . Vapor phase chromatography showed no traces of impurities in the material thus obtained; m.p. 12.8° ; $n_D^{26.5}$ 1.4388. The infrared absorption in the pure liquid and in carbon disulfide was at 3.24, 4.50 and 5.79μ .

Anal. Calcd. for $C_7H_9NO_2$: C, 60.42; H, 6.52.
Found: C, 60.24; H, 6.38.

Methyl 1-cyanocyclopropane-1-carboxylate. Four hundred and fifty grams of ethylene bromide was dissolved in 3 l. of anhydrous methanol and stirred and refluxed under nitrogen. From separate funnels, 198 g. of methyl cyanoacetate and 44 g. of sodium in 500 ml. of methanol were added proportionately during 5 hours. The basicity never exceeded pH 9. A second, equal portion of sodium in methanol was added during the next 5 hours with the addition rate being such that pH 9 was not exceeded. Reflux was continued for an additional 10 hours, the methanol was mostly distilled and the residue taken up in ether and water. The ether was separated, dried and concentrated. Distillation of the residue gave 67.9 g. (28%) of methyl 1-cyanocyclopropane-1-carboxylate, b.p. 108-112° at 27 mm., which was suitable for conversion to the amide.

Further purification could be effected by recrystallization from ether and redistillation to give a product of m.p. 31.5-32.8°, b.p. 111-112° at 27 mm., n_D^{28} 1.4439. The infrared absorption of the pure liquid was at 3.24, 4.50 and 5.78 μ .

Anal. Calcd. for $C_5H_7NO_2$: C, 57.59; H, 5.64.

Found: C, 57.52; H, 5.86.

1-Cyanocyclopropane-1-carboxamide. The amide was prepared by essentially the procedure of Carpenter and Perkin (72). A mixture of 112 g. of ethyl 1-cyanocyclopropane-1-carboxylate and 350 ml. of concentrated aqueous ammonia was shaken, allowed to stand overnight, chilled and filtered to give 95 g. of crude product, m.p. 152-159°. Recrystallization from 200 ml. of water afforded 65.6 g. (74%) of 1-cyanocyclopropane-1-carboxamide, m.p. 160-162° (lit. (72) 160°).

In like manner, from 2.54 g. of methyl 1-cyanocyclopropane-1-

carboxylate and 10 ml. of concentrated aqueous ammonia was obtained 1.98 g. (98%) of the amide.

1,1-Dicyanocyclopropane. Following the procedure of Ettlinger (65) (cf. 76), 30 g. of 1-cyanocyclopropane-1-carboxamide, 60 g. of phosphorus pentoxide and 170 ml. of tricresyl phosphate were thoroughly mixed and heated under water pump vacuum. A vigorous reaction set in at 170° and the distillate was collected up to a bath temperature of 220°. Redistillation to remove a little sublimed amide gave 10.4 g. (41%) of 1,1-dicyanocyclopropane, b.p. 106-107° at 25 mm., n_D^{25} 1.4445 (lit. (65) m.p. 16-16.5°). The infrared absorption was identical with that of authentic material, being at 3.24, 3.35 and 4.48 μ in the pure liquid.

Vapor phase chromatography. To determine the purity of the various monomers employed in this work, the materials were analyzed by vapor phase chromatography with a Perkin-Elmer Model 314 Vapor Fractometer. A variety of column packings were investigated in the search for adequate resolution. The columns were made up in the following manner.

The desired quantity of adsorbent (stationary phase) was dissolved in a suitable, low boiling solvent (ether, petroleum ether, methanol or acetone) and added to a dilute slurry of the supporting medium (Johns-Manville 30-60 mesh C-20 Fire-brick or Chromosorb) in a round bottom flask. The solvent was then removed under water pump vacuum until the supporting medium became friable. A convenient straight length of $\frac{1}{4}$ " copper tubing was plugged loosely for ca. 1 cm. at one end with glass wool and connected by a short piece of rubber tubing to a funnel at the other end. While rapidly tapping the tubing in a vertical position with a flexible steel spatula, the packing was charged through the funnel until the tube was full. After removing the funnel, about 1 cm. of the column

packing was shaken from the open end and the tube plugged with glass wool. The tubing was bent to a U-shape so the ends could be attached to the fittings in the fractometer and finally the loose ends of the glass wool plugs were fire polished in a soft flame so that the fibers would not foul the flow system of the instrument.

A list of the columns prepared in this manner and an indication of their utility for the analysis of ethyl 1-cyanocyclopropane-1-carboxylate, methyl 1-cyanocyclopropane-1-carboxylate and 1,1-dicyanocyclopropane is presented in Table IV. The prime impurity to be analyzed in the case of the esters was ethyl or methyl cyanoacetate which was one of the starting materials in their preparation. The references to resolution and separation refer to this material only since the other impurities that were resolved were not identified.

Ethyl 1-cyanocyclopropane-1-carboximidate. To a stirred, refluxing solution of 100 g. (0.535 mole) of ethylene bromide in 500 ml. of ethanol was added, during 5 hours, a solution of 10 g. (0.435 mole) of sodium and 30 g. (0.455 mole) of malononitrile in 350 ml. of ethanol. The rate of addition was such that the pH did not exceed 9. After standing overnight at room temperature, the solution was again heated to reflux, 10 g. of sodium in 250 ml. of ethanol was added during 4 hours and refluxing was continued for an additional 2 hours, at the end of which the pH was 9. The reaction was cooled, neutralized with formic acid, filtered and concentrated to ca. 100 ml. A little sodium bromide was filtered and the solution further concentrated to a dark oil which was taken up in ether and water. The ether phase was separated, dried, concentrated, and distilled under water pump vacuum

Table IV
Vapor Phase Chromatography of Monomers

<u>Column Length</u>	<u>Stationary Phase</u>	<u>Remarks</u>
2.0 m.	Didcyl phthalate*	Poor resolution.
2.0 m.	20% Dow Corning 550 silicone oil on fire-brick.	Poor resolution.
1.0 m.	Tide**	No separation.
2.0 m.	Tide**	Partial separation.
2.0 m.	20% Carbowax 1500*** on fire-brick.	Low flow rate gave excessive retention time at low temperature; Ethyl cyanoacetate decomposed on column at 220°.
0.6 m.	20% Carbowax 1500 on fire-brick.	No separation.
1.5 m.	30% Carbowax 1500 on Chromosorb.	Good resolution obtained at 130°, 30 psig. helium; Retention times were: 1,1-Dicyanocyclopropane.....14.5 min. Methyl 1-cyanocyclopropane-1-carboxylate.....15.0 min. Ethyl 1-cyanocyclopropane-1-carboxylate.....19.0 min. Methyl cyanoacetate.....20.0 min. Ethyl cyanoacetate.....24.0 min.

* Perkin-Elmer column "A".

** Procter & Gamble; No added supporting medium.

***Carbide and Carbon Chemical Co., polyethylene glycol.

to give 11.9 g. (35%) of crude product. Redistillation afforded 10.5 g. (31%) of ethyl 1-cyanocyclopropane-1-carboximidate, b.p. 110-112° at 25 mm., n_D^{25} 1.4568. Infrared absorption occurs in the pure liquid or a carbon disulfide solution at 3.03, 3.24, 3.39, 4.50 and 6.09 μ . The ultraviolet absorption in ethanol was at 245 $m\mu$ ($\log \epsilon$ 1.77).

Anal. Calcd. for $C_7H_{10}N_2O$: C, 60.85; H, 7.30; N, 20.28.
Found: C, 60.49; H, 7.21; N, 20.12.

The material thus obtained reacted slowly with potassium permanganate in acetone, gave a yellow precipitate with ferric chloride in alcohol and rapidly gave a pale yellow precipitate with bromine in carbon tetrachloride.

When 1 g. of ethyl 1-cyanocyclopropane-1-carboximidate was shaken with 10 ml. of 1 N hydrochloric acid it went into solution and immediately thereafter an oil separated. The mixture was warmed on the steam bath for a short time and extracted with ether. Separation and concentration of the ether gave 0.904 g. of ethyl 1-cyanocyclopropane-1-carboxylate, having infrared absorption identical to that of an authentic sample.

One gram of the imido ester went rapidly into solution on shaking with 10 ml. of 1 N sodium hydroxide. After warming a short time on the steam bath, the solution was acidified to Congo Red and extracted with ether. Evaporation of the ether gave 0.527 g. of crystalline solid. Recrystallization of a portion of this material from ether gave 1-cyanocyclopropane-1-carboxylic acid, m.p. 148-149° (lit. (72) 149°). The infrared absorption in perchlorobutadiene was at 3.20, 4.46 and 5.79 μ . The cyanoacid could be sublimed on the steam bath at ca. 1 mm. to give amorphous material, m.p. 147-149°.

Initiators. A number of polymerizations were carried out in the search for a suitable anionic initiator. Table V lists the results of these experiments which were performed in the following general manner. About 0.5 g. of the monomer was placed in a 10 x 75 mm. test tube along with a pinch (ca. 5 mg.) of the dry initiator or one drop of the initiator if it was a liquid or dispersion. The tube was stoppered, placed in an oil bath at the desired temperature and shaken or stirred occasionally for the indicated period of time. Unless otherwise denoted, the mixture was taken up in ca. 10 ml. of dimethylformamide, filtered and cooled.

In the case of the cyano ester polymers, which were soluble in the amide, the filtrate gelled on cooling. The gel was boiled with 40 ml. of methanol or ether to dissolve the dimethylformamide and precipitate the polymer, which was collected by filtration and dried at 80° in vacuum. The dinitrile polymer, being insoluble in the amide, was collected as a precipitate from the hot dimethylformamide, boiled with 40 ml. of methanol, filtered and dried as above.

Infrared spectra. All of the polymers obtained from 1,1-dicyanocyclopropane had similar infrared absorption with a sharp peak at 4.48-450 μ corresponding to the nitrile stretching vibration and a strong band at 7.65 μ . All of these polymers also exhibited variable, weak absorption at 2.96 and 6.08 μ characteristic of amide absorption, the intensity being greatest when the polymerization was carried out in a solvent. The presence of these bands is presumed due to a bit of hydrolysis of the nitrile groups during polymerization since moisture was not rigorously excluded.

The polymers obtained from ethyl 1-cyanocyclopropane-1-carboxylate

Table V

Anionic Initiators

Monomer*	Initiator	T °C	Time	Melting Point of Polymer	Remarks
a. A	None	190	1 hr.		No polymerization.
b. A	Sodium dispersion in toluene	150	5 min.	235° dec.	Complete polymerization.
c. A	Polymer from b.	150	30 min.		No polymerization.
d. A	Sodium hydride	150	30 min.	265-275° dec.	Complete polymerization.
e. A	Sodium ethoxide	100-150	3 hrs.		No polymerization.
f. A	Sodium ethoxide	190	1.5 hrs.		Crude monomer employed; no polymerization.
g. A	Sodium ethoxide	130-190	4 hrs.	250° dec.	Polymerized. A similar sample did not polymerize on standing at rm. temp. for 12 hrs. before heating.
h. A	Ethyl sodium- cyanoacetate	150	2.5 hrs.		Old sample of initiator used; no polymerization.
i. A	Ethyl sodium- cyanoacetate	130-190	3.75 hrs.	255° dec.	Polymerized. A similar sample polymerized at 180° during 1 hr.
j. A	Crude polymer from i.	180	2.5 hrs		Polymerized

(continued)

See footnotes on p. 83.

Table V (contd.)

Monomer*	Initiator	T °C	Time	Melting Point of Polymer	Remarks
k. A	Potassium cyanide	150	4.3 hrs.	250°	Polymerized.
l. B	None	150	5.5 hrs.		No polymerization.
m. B	Potassium cyanide	150	3.5 hrs.	255°	Gelled after 15 min. at 150°; nearly complete polymerization.
n. C	None	150	5.5 hrs.	**	Slight trace of polymerization.
o. C	Potassium cyanide	150	3.5 hrs.	**	Clouded at once and became stiff after 15 min.
p. C	Potassium cyanide	110-120	24 hrs.	**	Carried out in a sealed tube; some polymerization.
q. C	Sodium hydride	150	5 hrs.	**	Complete polymerization.
r. C	Potassium carbonate	135-145	1 hr.	**	No polymerization.
s. C	Potassium carbonate	145	2 hrs.	**	Polymerized in 2 ml. of dimethylformamide; polymer isolated after dilution with methanol.
t. C	Triethylamine	135	20 min.	**	Very rapid and complete polymerization.

(continued)

See footnotes on p. 83.

Table V (contd.)

<u>Monomer*</u>	<u>Initiator</u>	<u>T°C</u>	<u>Time</u>	<u>Melting Point of Polymer</u>	<u>Remarks</u>
u. C	Triethylamine	rm. T.	1 hr.	**	No polymerization in 2 ml. of dimethylformamide.
v. C	Triethylamine	70-80	30 min.	**	Warmed slowly to 70° in 2 ml. of dimethylformamide whereupon turbidity appeared; polymer isolated after additional 30 min. by dilution with methanol.

* A = Ethyl 1-cyanocyclopropane-1-carboxylate.

B = Methyl 1-cyanocyclopropane-1-carboxylate.

C = 1,1-Dicyanocyclopropane.

** All the dinitrile polymers were infusible. They slowly browned at 300°.

and from methyl 1-cyanocyclopropane-1-carboxylate exhibited fairly uniform absorption at 4.50 and 5.78-5.79 μ , characteristic of the nitrile and ester groups respectively.

All of the infrared data were obtained on the solid polymers in mineral oil or perchlorobutadiene mulls with a recording, single beam, Perkin-Elmer Model 12C infrared spectrophotometer.

Solvent effects. To determine the effect of various solvents on the polymerization of 1,1-dicyanocyclopropane, 0.2 g. of the monomer was dissolved in 2 g. of each of the solvents to be tried, about 5 mg. of potassium cyanide was added and the mixture was placed in an oil bath at 50°. The temperature was slowly raised to 110° during 70 minutes and heating was continued at this temperature for a total of 6 hours. The polymer was collected by boiling the reaction mixture with 25 ml. of methanol for 5 minutes and filtering. The percent conversion to polymer is listed in Table VI along with the time and temperature range until the first appearance of turbidity in the solution.

Cyanide concentration effects. The solubilities of sodium cyanide and potassium cyanide in dimethylformamide and dimethyl sulfoxide were determined by diluting aliquots of saturated solutions with water and titrating with silver nitrate according to the method of Liebig. The dimethylformamide was purified by distillation after shaking with potassium hydroxide pellets and lime. The dimethyl sulfoxide was shaken with potassium hydroxide pellets and distilled*. The saturated solutions were found to contain 1.00 mg. of potassium cyanide per milli-

* Attempted drying with barium oxide led to rapid, exothermic decomposition.

Table VI

Solvent Effect on Polymerization

	<u>Solvent</u>	<u>Yield</u>	<u>Appearance of Turbidity</u>
a.	None	3.1%	5 min., 50-60°
b.	Dimethyl sulfoxide	92%	10 min., 50-65°
c.	Dimethylformamide	82%	12 min., 50-65°
d.	Succinonitrile	48%	14 min., 50-65°
e.	Triethyl phosphate	28%	60 min., 50-100°
f.	Dimethylcyanamide	15%	25 min., 50-65°
g.	Nitromethane	Slowly discolored, no polymerization.	
h.	Ethylene carbonate	Slowly discolored, no polymerization.	

liter of dimethylformamide, 5.88 mg. of sodium cyanide per milliliter of dimethylformamide, 3.69 mg. of potassium cyanide per milliliter of dimethyl sulfoxide and 23.0 mg. of sodium cyanide per milliliter of dimethyl sulfoxide. Treatment of 1,1-dicyanocyclopropane with any of these solutions at 100° promoted rapid polymerization.

In a series of determinations, 0.2 g. samples of 1,1-dicyanocyclopropane were dissolved in 2 ml. of dimethylformamide or dimethyl sulfoxide containing various amounts of sodium cyanide. The solutions were heated at 125° to induce polymerization and the polymer was isolated by diluting the reaction mixture with 25 ml. of methanol, boiling for a few minutes and filtering. The results are noted in Table VII.

Solubility. The polymers obtained from ethyl 1-cyanocyclopropane-1-carboxylate or methyl 1-cyanocyclopropane-1-carboxylate were completely soluble in boiling dimethylformamide or dimethyl sulfoxide. The

Table VII

Cyanide Concentration Effects on 10% Solutions of 1,1-Dicyanocyclopropane in Dimethylformamide and Dimethyl sulfoxide at 125°

	<u>Solvent</u>	<u>mg. NaCN/ml. of Solvent</u>	<u>Time</u>	<u>Yield</u>
a.	Dimethylformamide	0.0	2 hrs.*	0
b.	Dimethylformamide	0.022	5 hrs.	trace
c.	Dimethylformamide	0.24	5 hrs.	14%**
d.	Dimethylformamide	0.99	1 hr.	102%
e.	Dimethyl sulfoxide	0.0	3 hrs.	0
f.	Dimethyl sulfoxide	0.020	3 hrs.	trace
g.	Dimethyl sulfoxide	0.22	5 hrs.	60%
h.	Dimethyl sulfoxide	1.0	1 hr.	79%***

* 150°

** Some loss during work up.

***Centrifuged.

solutions set on cooling to a stiff gel, from which the polymer could be recovered by treatment with hot methanol or ether and filtration.

The solubility of the polymer obtained from 1,1-dicyanocyclopropane was examined in a number of solvents and solvent combinations by mixing 10-15 mg. of the dry polymer with 0.5 to 2 ml. of the solvent and heating to the boiling point or at least 180°. Table VIII lists the non-solvents that were tried.

Fifty milligrams of the dinitrile polymer did not dissolve in 0.5 ml. of concentrated sulfuric acid during 1 hour at room temperature. On warming to 70° the material went into solution during ca. 30 minutes with gas evolution. The clear solution was cooled, poured into 20 ml. of water and centrifuged. After washing with water, acetone and methanol

Table VIII

Non-solvents for Polydicyanocyclopropane

Dimethylformamide	Tetramethylurea
N-Methylformamide	Morpholine
N-Methylacetamide	N-Acetylmorpholine
N,N-Dimethylacetamide	N-Nitrosomorpholine
N-Methylpropionamide	Tricresyl phosphate
Succinonitrile	Perchlorobutadiene
Lactonitrile	<u>sym</u> -Tetrachloroethane
Ethylene carbonate	Ethylene glycol dimethyl ether
Dimethylcyanamide	Methyl cyanoacetate
Triethyl phosphate	1,3-Diaminopropan-2-ol
Tetramethylene sulfone	Acetonitrile
Dimethyl sulfoxide	Ethylenediamine
2-Cyanopyridine	Chloroacetic acid
Nitromethane	Trichloroacetic acid
Potassium thiocyanate aqueous, concentrated	Concentrated nitric acid
1:1 Concentrated nitric acid and nitromethane	
1:1 Resorcinol and succinic anhydride	
1:1 Formic acid and ethylene carbonate	
1:1 Tricresyl phosphate and succinonitrile	
1:1 Tricresyl phosphate and 2-cyanopyridine	
5-25% Succinic anhydride in nitromethane	
5-50% Dimethylformamide, formic acid, 2-cyanopyridine, ethylene carbonate or tetramethylene sulfone in nitromethane	

there remained a white powdery polymer that exhibited infrared absorption in mineral oil at 2.96-3.18 and 6.06 μ . When a solution of polymer in acid (70 mg. in 1 ml.) was instead poured into ether (50 ml.), the recovered material (103 mg.) had similar characteristics.

Average molecular weight determinations. To ascertain the average molecular weight of the polymer from 1,1-dicyanocyclopropane, the polymerization was initiated with sodium cyanide- C^{14} dissolved in dimethylformamide or in dimethyl sulfoxide. The resulting mixture was poured into 25 ml. of methanol, boiled 5 minutes, filtered and washed with 75 ml. of methanol and dried. By the addition of 25 mg. of sodium cyanide to the methanol-diluted material and titration of the washings with alcoholic silver nitrate, it was determined that the free cyanide was removed by washing with ca. 50 ml. of methanol. The carbon-14 content and the apparent average molecular weight of the polymers thus prepared was determined as described below. These results are listed in Table III along with similar determinations on the polymers from ethyl 1-cyanocyclopropane-1-carboxylate and methyl 1-cyanocyclopropane-1-carboxylate.

The counting procedure employed was similar to the suspension counting in scintillating gels described by C. G. White and S. Helf (75). The assistance of Dr. E. S. Lewis in this work is gratefully acknowledged.

Counting equipment. A Tricarb liquid scintillation counter (Model 314, Packard Instrument Company, LaGrange, Illinois) was used to obtain all counting data by courtesy of the Robert A. Welch Foundation. All determinations were made with lower and upper discriminators fixed at

10 and 50 volts respectively to maintain low background and enable counting at a well defined peak. At these settings a homogeneous C^{14} internal standard counts at 55% efficiency.

The refrigerated shielded sample system and dual photomultipliers were maintained at -10° .

Homogeneous internal standard. Benzoic- C^{14} acid* dissolved in toluene was used as a homogeneous internal standard. Its absolute activity as determined by the manufacturer was 5230 dpm/mg.

Scintillators. For counting materials that were soluble in toluene, such as the standard, a solution of 4 g. of 2,5-diphenyloxazole (PPO) and 0.1 g. of 1,4-di[2-(5-phenyloxazolyl)] benzene (POPOP) in 1 liter of toluene was employed. Hereinafter, this scintillator solution will be referred to as SS.

Materials that were insoluble in SS were counted in a Thixcin R scintillator solution (TSS) prepared by mixing 12.5 g. of Thixcin** and 500 ml. of SS in a Waring blender for 3 minutes. The resulting TSS was a clear, opalescent, thixotropic gel.

Counting procedure. The sample to be counted was weighed or pipetted into a Kimble Opticlear 7-dram vial fitted with a polyethylene cap. Ten milliliters of SS or 10 g. of TSS were added and the vial was capped and shaken to thoroughly mix or disperse the sample. The vial was then placed in the refrigerated compartment of the scintillometer for at least 1 hour before counting and 15 minutes was allowed to elapse before counting after the sample was momentarily exposed to light during transfer to the sample chamber. The peak counting efficiency was de-

* NES-1 Benzoic- C^{14} acid, Lot No. 25-95-4, New England Nuclear Corporation, Boston 18, Massachusetts.

** Baker Castor Oil Co., New York, N.Y.

terminated on the low energy scaler by one minute counts at different high voltage tap settings and the sample was then counted at peak efficiency for such a time that not less than 1,000 counts were recorded. The counting efficiency in each determination was established by the subsequent addition of a measured amount of homogeneous internal standard and recounting. The counting efficiency is then given by

$$100 \times \frac{\text{cpm with standard} - \text{cpm without standard}}{\text{dpm of standard introduced}} = \% \text{ Efficiency}$$

and the molecular weight of the polymer is given by

$$\frac{\text{mg. polymer}}{\text{cpm observed}} \times \frac{\% \text{ Efficiency}}{100} \times \frac{\text{dpm}}{\text{mg. NaC}^{14}\text{N}} \times \text{M.W. of NaCN} = \text{M.W.}$$

Suitable corrections were applied to compensate for background scintillation as determined on blanks containing only 10 ml. of SS or 10 g. of TSS.

It was found that a standard benzoic-C¹⁴ acid sample was counted with an efficiency of 55% in SS, 54% in TSS and 32% in TSS containing 100 mg. of non-radioactive polymer. The 32% efficiency observed in this one case is quite low compared to thirteen cases involving radioactive polymer in which the counting efficiency varied between 41 and 54%. The variations are attributed to the color and degree of subdivision rather than to the weight of polymer counted.

Sodium cyanide-C¹⁴. One and one tenth milligram of Nenex-21 Sodium cyanide-C¹⁴, 21,000 dps/mg.*, and 26.9 mg. of reagent grade sodium cyanide were dissolved in a small amount of methanol and the solution was evaporated to dryness under nitrogen. The residue was dried for 15 minutes

* New England Nuclear Corp., Boston 18, Massachusetts

at 110°. To determine the absolute activity of the material, solutions were made in dimethylformamide (DMF) or dimethyl sulfoxide (DMS) and aliquots were counted as above in TSS.

<u>Solution</u>	<u>cpm/ml.</u>	<u>Efficiency</u>	<u>dpm/ml.</u>	<u>dpm/mg. NaC¹⁴N</u>
0.5008 mg. NaC ¹⁴ N/ml. DMF	12,455	50%	25,500	49,900
0.5043 mg. NaC ¹⁴ N/ml. DMS	12,518	49%	24,910	50,600

The average value of 50,250 dpm/mg. NaC¹⁴N was used in all subsequent calculations.

Example of molecular weight determination. 1,1-Dicyanocyclopropane (0.198 g.) was dissolved in 2 ml. of dimethylformamide containing 0.25 mg. of sodium cyanide-C¹⁴ per milliliter and heated 2 hours at 100° and the polymer was isolated as described above. The yield was 89.9 mg. (45%) of polymer, weighed into a counting vial. Ten grams of TSS were added and the mixture was shaken thoroughly and placed in the scintillometer.

The peak efficiency was determined by one-minute determinations of the counting rate for the polymer as listed below and the High Voltage Tap was set at 5 in all subsequent determinations.

High Voltage Tap	4	Counting rate per minute	4663
" " "	5	" " " "	6091
" " "	6	" " " "	6052

Ten separate one-minute determinations of the counting rate for the polymer are tabulated below.

6318	6150	6220	6259	6307
6338	6205	6281	6170	6127

From these determinations \bar{x}_n^2 was calculated as follows (77).

$$\chi_n^2 = \frac{(N_1 - \text{Av.})^2 + (N_2 - \text{Av.})^2 + \dots + (N_n - \text{Av.})^2}{(\text{av.}/t)}$$

N = one determination of the counting rate.

Av. = average of n determinations.

t = counting time for each determination.

$$\chi_{10}^2 = 7.9$$

Chi-square is a measure of the probability that the variations in a series of counting determinations are due to the randomness of the disintegration process. The value 7.9 for ten determinations indicates a probability between 0.9 and 0.1 ($4.2 < \chi^2 < 14.6$) that the determinations exhibit Poisson distribution (77) and therefore the instrument could be assumed to be operating properly.

The remainder of the counting rate determinations and calculations were as follows.

Background (10 g. of TSS)	
HVT5	399 counts/20 min. = 20 cpm.
Polymer	61,880 counts/10 min. = 6,188 cpm.
Polymer corrected for background	6,168 cpm.
Polymer + ^{6,046} dpm.	
Benzoic-C ¹⁴ acid Std.	91,142 counts/10 min. = 9,114 cpm.
Polymer and Std. Corr. for background	9,094 cpm.

$$\text{Efficiency} = \frac{100 \times 9,094 - 6,168}{6,046} = 48\%$$

$$\text{M.W.} = \frac{89.9}{6,188} \times \frac{48}{100} \times \frac{50,250 \text{ dpm}}{\text{mg. NaC}^{14}\text{N}} \times \frac{49.01 \text{ g.}}{\text{mole NaCN}} = 17,200$$

Electron Micrographs. The electron micrographs in Figures 4-7 were kindly produced by R. H. Morriss, the Rice Institute. The polymer sample was dispersed by shaking in water, a drop of the dispersion was evaporated on a carbon membrane and the micrograph taken with a Phillips, Type E. M. 100-A electron microscope.

X-Ray powder diffraction patterns. The X-ray powder patterns shown in Figure 3 were magnanimously provided by R. F. Scheuerman, the Rice Institute. They were taken on a powder wedge using copper K_{α} radiation and a nickel filter with a Norelco XRD apparatus. The lattice spacings are given in Table IX.

Table IX

Lattice Spacings in Polymers of the Type $(-\text{CH}_2\text{CH}_2\text{CCNR}-)_n$.

<u>Line No.</u>	<u>R = COOEt</u>	<u>R = COOMe</u>	<u>R = CN</u>
1.	9.1479 Å	7.9215 Å	5.8011 Å
2.	5.7192	6.4768	4.8490
3.	4.4800	5.5552	3.6745
4.	3.7951	4.4401	3.1291
5.	3.1530	3.7760	2.8932
6.	2.3052	2.4249	2.7248
7.	1.9576	2.1771	2.4224
8.			2.0026

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