SYNTHESIS AND REACTIONS OF 2-CYANO-1,3-BUTADIENE

BY

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A.B., University of Minnesota, 1946

THESIS

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I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY NEAL ORIN BRACE

ENTITLED SYNTHESIS AND REACTIONS OF 2-CYANO-1,3-BUTADIENE

BE ACCEPTED* AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

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* Subject to successful final examination in the case of the doctorate.
† Required for doctor's degree but not for master's.

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I. INTRODUCTION

The synthesis of 2-cyano-1,3-butadiene was undertaken in order to provide a quantity of the monomer for polymerization studies. After investigating the various known methods of preparation, it became apparent that a more suitable synthesis giving higher yields was needed. This led to the investigation of several new reactions. The thermal rearrangement of 3-acetoxy-3-cyano-1-butene to 1-acetoxy-3-cyano-2-butene was discovered. The dimerization of acyl cyanides was investigated, and the addition of benzoyl cyanide to aromatic aldehydes was achieved. Finally a dimer of 2-cyano-1,3-butadiene was discovered and a probable structure advanced on the basis of its reactions and physical properties.

II. PART ONE: THE SYNTHESIS OF 2-CYANO-1,3-BUTADIENE; A NEW THERMAL REARRANGEMENT

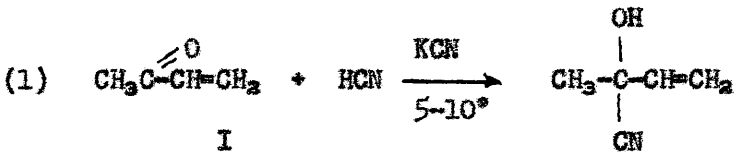
A. Historical

2-Cyano-1,3-butadiene has been prepared previously by two general methods, both appearing in the patent literature. Goodyear workers[1,2] prepared the diene by converting 2-chloro-3-butanone to the 2-acetoxy compound, followed by addition of hydrogen cyanide to the carbonyl group, esterification of this derivative, and subsequent pyrolysis of the 2,3-diacetoxy-2-cyano-butane to 2-cyano-1,3-butadiene. A rather low yield was obtained (about 21 per cent).

Starting with methyl vinyl ketone, duPont chemists[3] obtained 2-cyano-1,3-butadiene by pyrolyzing the acetate ester of the cyanohydrin under carefully controlled conditions.

B. Theoretical

It was proposed to repeat the preparation of 2-cyano-1,3-butadiene from the acetate of methyl vinyl ketone[3] by the following series of reactions:



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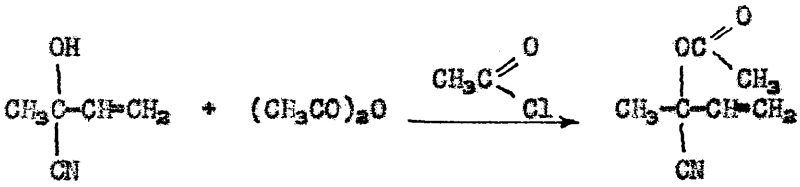

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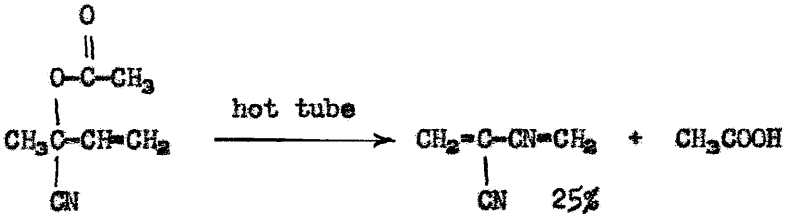
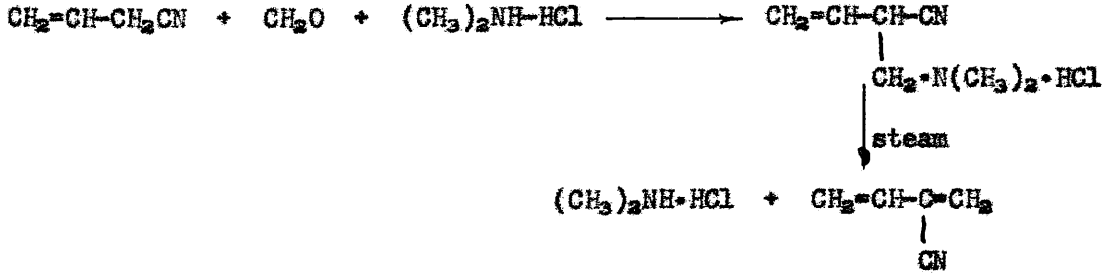
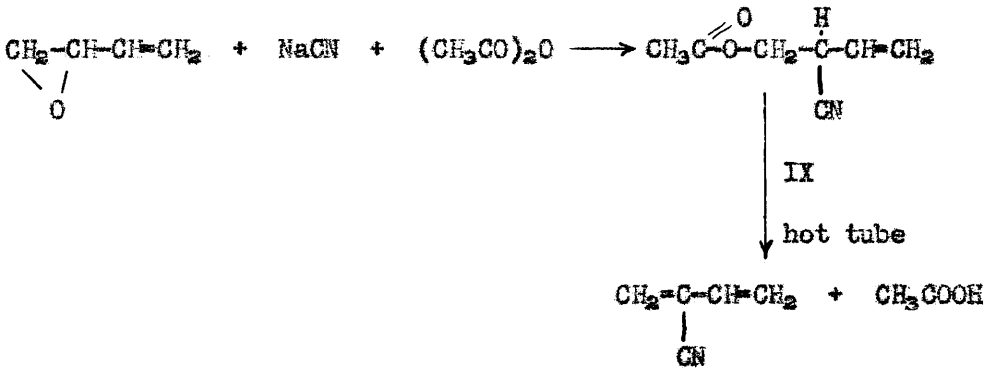


IV

A second scheme involves the Mannich reaction[4] of allyl cyanide with formaldehyde and the decomposition of the Mannich base hydrochloride by steam to 2-cyano-1,3-butadiene.



Another possible route to 2-cyano-1,3-butadiene starts with 3,4-epoxy-1-butene, as outlined below:



The pyrolysis of the acetate of the primary alcohol in this case should proceed without difficulty. The first step in the reaction scheme is analogous to the cleavage of 3,4-epoxy-1-butene with hydrochloric acid reported by Kadesch[5] to give 3-chloro-4-hydroxy-1-butene.

C. Discussion of Results

1. Formation of the Cyanohydrin of Methyl Vinyl Ketone

The cyanohydrin of methyl vinyl ketone[6] was obtained by adding hydrogen cyanide to a benzene solution of the ketone at temperatures between 6-10° using potassium cyanide as a catalyst. Yields of the cyanohydrin were increased when the solvent recovered from the preceding run was used. It was necessary to prepare anhydrous methyl vinyl ketone from the commercially available azeotrope. Careful control of the reaction temperature, rapid stirring, and a rapid addition rate of anhydrous hydrogen cyanide were necessary for success. Temperature is particularly important, since under the conditions of these experiments above 10° hydrogen cyanide adds to give levulinonitrile,[7] and below 6° no addition occurred.

2. Acetylation of Methyl Vinyl Ketone Cyanohydrin

The cyanohydrin of methyl vinyl ketone was readily acetylated by refluxing with acetic anhydride in the presence of acetyl chloride. Sulfuric acid, sodium acetate, or pyridine failed to catalyze this reaction.

3. Benzoylation of Cyanohydrin

The benzoate was also prepared in an analogous manner using benzoyl chloride and pyridine as a catalyst. Attempts to form the benzoyl derivative of the cyanohydrin of methyl vinyl ketone in one step as utilized in the synthesis of 1-cyanobutadiene-1,3[8] resulted only in polymeric products. Similarly attempts to form the cyanohydrin through the intermediate bisulfite addition product resulted in polymeric materials.

4. Pyrolysis of the Acetate

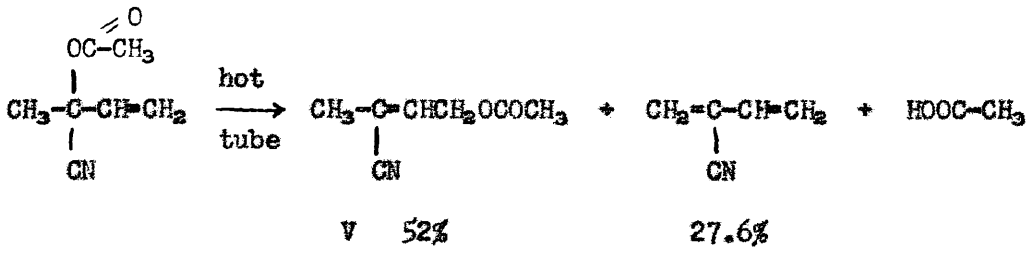
Pyrolysis of the acetyl ester of the cyanohydrin of methyl vinyl ketone was accomplished by passing the ester dropwise through a glass-bead-packed column heated to 465-475°, using a stream of pre-purified nitrogen gas as a diluent. After the acetic acid was removed from the pyrolysate by washing with water, distillation of the organic material yielded 2-cyano-1,3-butadiene in yields of 25 per cent. In addition to the diene, there was obtained an ester which was not the original. Subsequent pyrolysis of the new ester failed to produce any 2-cyano-1,3-butadiene, but the ester was recovered unchanged.

For the pyrolysis of the pure acetate of methyl vinyl ketone cyanohydrin temperatures of 450-475° were found to be optimum, since above 500° considerable charring occurred, and below 450° pyrolysis was incomplete (i.e. unchanged original ester was recovered). A rate of three drops per second or 50 cc. per hour was found to be optimum. The use of other packing materials such as activated alumina (4-8 mesh) or glass helices did not improve the pyrolysis.

Attempts to dehydrate the cyanohydrin of methyl vinyl ketone over activated alumina at 300° failed to give any of the desired 2-cyano-1,3-butadiene. Similarly, when the acetyl derivative of the cyanohydrin was dropped onto fused potassium hydroxide at 300° or fused potassium acid sulfate at 315°, none of the desired diene could be isolated.

5. An Allyl-Type Rearrangement in the Pyrolysis of 3-Cyano-3-acetoxy-1-butene

Physical and chemical methods of analysis showed that the new ester is a rearrangement product of the original ester, and that the following reaction has occurred:

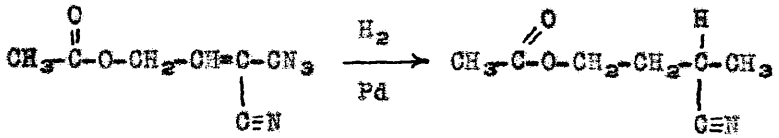


V 52% 27.6%

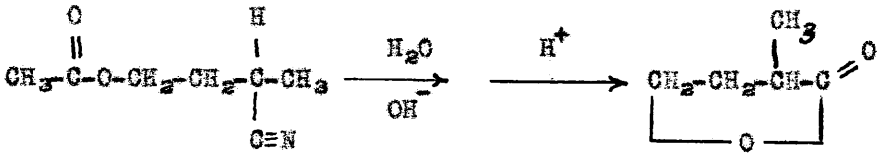
6. Proof of Structure of the New Ester

The new ester obtained by rearrangement boils about twenty degrees higher than the original compound at 20 mm. pressure, has a much higher refractive index and a different odor. When carefully fractionated and analyzed, the unknown ester gives, however, an analysis identical to that of the original acetate. The calculation of molar refractivities both for the original structure and from the physical data of the two compounds shows that the new ester has a molar refractivity about 0.9 unit higher than that of the original. This would indicate a conjugation of unsaturated bonds in the new compound.

Proof of the structure of the new ester (V) was done as follows: Hydrogenation of the olefinic bond using palladium on charcoal as a catalyst gave the saturated ester which was hydrolyzed to the hydroxy acid by refluxing with 20 per cent alkali; then the solution was acidified with dilute sulfuric acid and heated again under reflux to give a lactone. The structure of the lactone which should be α-methyl butyrolactone if the structure postulated for V is correct, was confirmed by preparing the hydrazide derivative which melted at 91°. This is the melting point given in the literature[9,10] for α-methyl-butyrolactone. Isolation of this derivative indicated that the following reactions took place:



V VI



VI VII

7. Pyrolysis of the Benzoate

Pyrolysis of the benzoate of methyl vinyl ketone cyanohydrin gave 2-cyano-1,3-butadiene in yields of only 10 per cent. A further disadvantage was its melting point, 53°, making controlled addition to the pyrolysis tube difficult. In addition to the diene there was obtained by high vacuum distillation of the residue, after the benzoic acid had been washed out, a high boiling fraction, b.p. 150°/1 mm. This compound remained a liquid and gave an analysis close to that of the original benzoate ester. It has not been investigated further, but probably has a structure related to the rearranged acetate.

8. Attempted Mannich Reaction of Allyl Cyanide and Formaldehyde

Other routes to 2-cyano-1,3-butadiene have been investigated. One attractive possibility consists in the formation of the Mannich base hydrochloride from allyl cyanide and formaldehyde which could presumably be decomposed by steam distillation directly to 2-cyano-1,3-butadiene. Several attempts using allyl cyanide and formaldehyde with dimethylamine hydrochloride or piperidine hydrochloride were all unsuccessful, and none of the desired Mannich base hydrochloride was obtained.

9. Cleavage of 3,4-Epoxy-1-butene with Hydrogen Cyanide

By adding sodium cyanide solution to 3,4-epoxy-1-butene and acetic anhydride in ether solution at 3-5°, the acetate ester has been obtained directly in yields of about 45 per cent (based on epoxybutene used up). A side reaction also occurs to form a solid compound, acetyl cyanide dimer, and at temperatures above and below 3-5° this is the only product obtained. The structure of the acetate ester is assumed to be 4-acetoxy-2-cyano-1-butene in analogy to the cleavage of epoxybutene with hydrochloric acid. This structure needs further confirmation.

Similarly benzoyl chloride, sodium cyanide, and 3,4-epoxy-1-butene react at -3 to -5° to give a liquid benzoate ester directly, while at 10° a solid compound is formed which proved to be benzoyl cyanide dimer. Because of the low yields obtained, these reactions were not further pursued. Instead a study of the by-products proved interesting.

D. Experimental

1. Cyanohydrin of Methyl Vinyl Ketone

Apparatus: The reaction flask was a 2-l., three-necked, round-bottomed flask fitted with a mercury-sealed Hershberg stirrer, a gas inlet tube extending to the bottom of the flask, a 50° thermometer, and an outlet tube which was connected to an empty 2-l., round-bottomed flask. This flask was connected to a second 2-l., round-bottomed flask, half filled with concentrated aqueous sodium hydroxide and equipped with an exhaust tube. Preceding the reaction flask was an empty 2-l., round-bottomed flask fitted with a tube connected to the last U-tube of the HCN drying train, and with a glass tube extending to the bottom of the flask. A stopcock was placed between this flask and the reaction flask which could be closed in the event that the evolution of hydrogen cyanide should cease, and the contents of the reaction flask should be drawn back. A tank of nitrogen gas was kept on hand which could be connected to the hydrogen cyanide generating flask and was used to force the benzene solution back into the reaction vessel. Nitrogen gas was used to sweep out the apparatus before and after each run and to make certain that all connections were tight and all tubes open. The entire apparatus was set up in a hood with a good exhaust fan. The hydrogen cyanide was generated according to the Organic Syntheses method.[11]

Purification of Methyl Vinyl Ketone: The azeotrope obtained from duPont containing about 20 per cent water was dried by adding portions of anhydrous potassium carbonate to the cooled liquid with adequate stirring and swirling until the solid no longer caked and an excess of granular potassium carbonate remained. The methyl vinyl ketone was further dried over anhydrous calcium chloride, decanted, and distilled using a water aspirator and a water-cooled condenser. The fraction boiling at 39-40° (100 mm.) was collected in an ice-cooled receiving flask.

Methyl vinyl ketone is a strong lachrymator and vesicant. It may be stored in the icebox for a few days, but should be used as soon as possible, or redistilled prior to use.

Cyanolation: In the reaction flask previously described, were placed 1200 g. of dry benzene and 560 g. (8 moles) of dry, freshly distilled methyl vinyl ketone. The flask and its contents were cooled to 5° with an acetone-Dry Ice bath and maintained between 6-10° throughout the reaction. Eight grams of reagent grade potassium cyanide was added and stirring begun while hydrogen cyanide was bubbled in at a rapid rate for three hours. A total of 10 moles of hydrogen cyanide was used (based on the amount of sodium cyanide solution employed). Thirty-three grams of 85 per cent syrupy phosphoric acid was added (acidity checked with litmus paper) and stirring continued for an additional half hour, after which the reaction mixture was allowed to warm to room temperature and the layers separated.

The benzene solution was decanted into a 2-l., Claisen distilling flask and the solvent removed by distillation at reduced pressure from a water bath heated to 60°. The benzene solvent, rich in methyl vinyl ketone and hydrogen cyanide, was collected in an ice-cooled receiving flask and stored in the icebox until the next run.

The residual oil was poured into a 1-l., round-bottomed, ground-glass flask and distilled at reduced pressure through a 10-in., helix-packed, jacketed column, equipped with a total reflux-partial take-off head. There was obtained 467 g. (4.6 moles) of the cyanohydrin; b.p. 60°/5 mm.; n^{20}_{D} 1.4264; a yield of 60 per cent. Runs using 2 to 5 moles of methyl vinyl ketone consistently gave yields of 60-70 per cent. The optimum yield was obtained when 6 moles of hydrogen cyanide was added over a period of one and one-half hours to 2.64 moles of methyl vinyl ketone.

Temperatures below 5° were found to be too low for addition of hydrogen cyanide and above 5° 1,4-addition to methyl vinyl ketone occurs in the presence of an alkaline catalyst.[7] The water bath must be kept below 60° when removing the solvent and the phosphoric acid layer separated immediately at the end of the run.

2. Acetate of Methyl Vinyl Ketone Cyanohydrin

In a 1-l., round-bottomed, ground-glass flask were placed 428 g. (4.2 moles) of acetic anhydride and 5 g. of acetyl chloride. The flask was equipped with a Y-adapter fitted with a reflux condenser and dropping funnel. After heating to boiling, 388 g. (4.0 moles) of methyl vinyl ketone cyanohydrin was added slowly, and sufficient heat was applied to maintain gentle reflux. About two hours were required for the addition. Heating was continued for one-half hour. Distillation through a 10-in., helix-packed, electrically-heated column yielded 536 g. (96 per cent) of 3-cyano-3-acetoxy-1-butene, b.p. 89-90°/19 mm.; n_D^{20} 1.4270; d_4^{20} 1.0070; M_D calcd. 35.47; M_D found 35.48.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.77; H, 6.50; N, 10.04.

Found: C, 60.53; H, 6.31; N, 10.24.

3. Benzoate of Methyl Vinyl Ketone Cyanohydrin

To a mixture of 31.7 g. (0.3 mole) of methyl vinyl ketone cyanohydrin and 42 g. (0.3 mole) of benzoyl chloride in a 600-ml. beaker cooled in an ice-salt bath was added slowly with stirring 40 g. (0.5 mole) of pyridine, so that the temperature was maintained between 8° and 15°. Care must be taken to keep the mass that forms broken up, or the temperature is difficult to control. After the pyridine had been added, the lumps were broken up and 500 ml. of water added with stirring. The suspended solid was collected on a Buchner funnel and washed with three 500-ml. portions of water. Recrystallization from a water-ethanol mixture yielded 47.5 g. (79 per cent) of the benzoate of methyl vinyl ketone

cyanohydrin, m.p. 49-50°. A small sample was recrystallized from a dioxane-water mixture, m.p. 53.5° and submitted for analysis.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96.

Found: C, 71.44; H, 5.24; N, 6.75.

4. 2-Cyano-1,3-butadiene

Pyrolysis of the acetate of methyl vinyl ketone cyanohydrin was accomplished by passing the material dropwise through a 19-mm. O. D. Pyrex tube packed for a distance of 12 in. with 4-mm. glass beads and heated to 475° by means of an electrically-heated combustion furnace. A rate of one drop/three seconds was maintained at the top. The pyrolysate was collected in a 500-ml. suction flask cooled by a Dry Ice bath, washed with four 100-ml. portions of a saturated solution of sodium chloride, the organic material separated and dried over anhydrous sodium sulfate. A little picric acid (ca. 0.1 g.) was added, and the solution filtered. Distillation was effected through a 4-in., helix-packed column. From 219 g. (1.56 moles) of the acetate there was obtained 34 g. (27.6 per cent) of 2-cyano-1,3-butadiene, b.p. 30-40°/4 mm.; $n^{20}D$ 1.4450.

In addition to the desired diene there was obtained 114.0 g. of an ester that was not the acetate of methyl vinyl ketone cyanohydrin; b.p. 95°/10 mm.; $n^{20}D$ 1.4500; d_4^{20} 1.0280; M_D calcd. 35.47; M_D found 36.36 (exaltation of 0.9).

Anal. Calcd. for $C_7H_9O_2N$: C, 60.27; H, 6.50; N, 10.04.

Found: C, 60.53; H, 6.66; N, 10.29.

5. Identification of the Ester Produced in the Pyrolysis

Hydrogenation of 13.9 g. of the recovered ester dissolved in 100 ml. of absolute ethanol was accomplished in an Adams hydrogenation apparatus at room temperature using as catalyst 1 g. of 10 per cent palladium on charcoal. The

compound absorbed 82 per cent of the theoretical amount of hydrogen. The catalyst was removed by filtration and the ethanol removed by distillation. Distillation of the residue through a 10-in., helix-packed column yielded 8 g. of a saturated derivative; b.p. 110°/18 mm.; n_D^{20} 1.4280.

Anal. Calcd. for $C_7H_{11}O_2N$: C, 59.56; H, 7.86; N, 9.92.

Found: C, 58.89; H, 7.21; N, 9.65.

Six grams of the compound was added to a solution of 5 g. of sodium hydroxide in 20 ml. of distilled water in a 100-ml. round-bottomed flask fitted with a reflux condenser. The mixture was refluxed for two hours, after which it was cooled in an ice-bath and 9 ml. of 50 per cent sulfuric acid slowly added. The acidified solution was again refluxed for two hours. The organic layer was separated, and the aqueous layer extracted with two 15-ml. portions of benzene. The combined extracts and the original layer were dried over anhydrous magnesium sulfate, the drying agent removed by filtration, and the residue distilled through a 6-in. Vigreaux column, giving 2.5 g. of a clear liquid; b.p. 197°; n_D^{20} 1.4320; d_4^{20} 1.0570.

Anal. Calcd. for $C_5H_8O_2$: C, 59.98; H, 8.05.

Found: C, 59.70; H, 7.73.

A hydrazide of this material was prepared by treating 1.0 g. with 0.5 g. of 85 per cent hydrazine hydrate in 10 ml. of absolute ethanol. The mixture was refluxed for eight hours and the hydrazide isolated by distillation[11a] at reduced pressure; b.p. 72-75°/12 mm. Recrystallization of this material from ethyl acetate yielded white crystals, m.p. 90-91°. This corresponds to the melting point reported by Adams and Rogers,[9] and Cavallito and Haskell,[10] for the hydrazide of α-methyl-butyrolactone.

Anal. Calcd. for $C_5H_{12}O_2N_2$: C, 45.43; H, 9.15; N, 21.20.

Found: C, 45.70; H, 9.00; N, 20.78.

6. Pyrolysis of Benzoate Ester of Methyl Vinyl Ketone Cyanohydrin

Into the hot tube heated to 550° was dropped 169.5 g. of benzoate melted with a heat lamp at a rate of one drop/two sec. using nitrogen gas as a diluent. There was obtained by distillation of the pyrolysis mixture 7 g. of impure 2-cyano-1,3-butadiene, b.p. 24-31°/30 mm. This is 10 per cent of theory. The remaining residue was washed several times with 5 per cent sodium bicarbonate solution, and then two times with 100 cc. of 5 per cent sodium hydroxide solution. The acid-free material was dried over anhydrous sodium sulfate, filtered, and distilled from an oil bath at diminished pressure. A small amount of oil with an ester-like odor, b.p. 73-81°/5 mm. came over first, and then 12 g. of liquid; b.p. 150°/1 mm.; $n^{20}D$ 1.5315. This compound is nearly odorless and remained a liquid.

Anal. Calcd. for $C_{12}H_{11}O_2N$: C, 71.62; H, 5.51; N, 6.96.

Found: C, 70.69; H, 5.28; N, 7.37.

7. Attempted Mannich Reaction Using Allyl Cyanide

In a 200-cc., three-necked, round-bottomed flask fitted with a thermometer and a reflux condenser were placed 22.5 g. (0.33 mole) of allyl cyanide ($n^{20}D$ 1.4079), 25 g. (0.33 mole) of 40 per cent formaldehyde (as formalin) and 27.2 g. (0.33 mole) of dimethyl amine hydrochloride. The mixture was refluxed for twenty-four hours at 60°, and allowed to stand at room temperature for forty-eight hours. The two layers were separated, and the upper layer distilled. There was recovered 10 g. of allyl cyanide; b.p. 114-120°; $n^{20}D$ 1.4060. Some liquid was lost by accident. No amine hydrochloride was obtained.

A second experiment was carried out using the same amounts of allyl cyanide and dimethyl amine hydrochloride with 20 g. (0.66 mole) of paraformaldehyde in 100 cc. of ethanol to which was added 0.75 cc. of concentrated hydrochloric acid. The mixture was refluxed at 80° and stirring maintained for two hours.

Then 600 cc. of boiling acetone was added and the mixture gradually cooled, finally in an ice-salt bath. No precipitate of amine hydrochloride came out. The layers were separated. The lower layer, soluble in water, and which contained the dimethyl amine hydrochloride as well as any of the Mannich base hydrochloride (if present) was steam-distilled. No organic material came over, which it was hoped, would be 2-cyano-1,3-butadiene.

The upper acetone-absolute alcohol layer was distilled. A small fore-run at 65-80° was collected, then 7.3 g. of liquid, b.p. 80-112°, n^{20}_{D} 1.4048, corresponding to impure allyl cyanide.

Piperidine hydrochloride was used as the amine hydrochloride in two experiments, but no Mannich base was obtained. One experiment using dimethyl amine hydrochloride was run in iso-amyl alcohol and refluxed at 150° for one hour, but the amine hydrochloride which crystallized out was identical with the starting material.

Trioxane (the trimer of formaldehyde) was employed in two experiments without success.

8. 2-Cyano-4-acetoxy-1-butene

In a 500-cc., three-necked, round-bottomed flask fitted with a mechanical stirrer, a 50° thermometer and dropping funnel were placed 35 g. (0.5 mole) of 3,4-epoxy-1-butene, 61.2 g. (0.6 mole) of acetic anhydride and 100 cc. (70 g.) of ether. Stirring was started and the flask cooled to 3-5° by an ethanol and Dry Ice bath as 30 g. (0.6 mole) of sodium cyanide in 150 cc. of distilled water was added drop by drop over a period of forty-five minutes. Stirring was continued an additional thirty minutes at 3-5°. The layers were separated, the organic layer dried over anhydrous sodium sulfate, decanted into a Claisen distilling flask and distilled from an oil bath using an ice-cooled receiving flask. There was obtained two fractions, b.p. 30-57° and 55-65° at

atmospheric pressure amounting to 85.3 and 5.5 g., respectively, corresponding to recovered ether-epoxybutene mixture and epoxybutene. Also two ester fractions, 4.6 g. of a liquid, b.p. 67°/3 mm., n^{20}_D 1.4180 and 9.0 g., b.p. 68°/2 mm., n^{20}_D 1.4231. Finally at 82°/6 mm., 5.5 g. of a liquid distilled which solidified on cooling to a white solid, m.p. 69°. This compound has an odor of hydrogen cyanide and acetic anhydride and its melting point is that given in the literature for acetyl cyanide dimer.[13] The yield of acetate ester was 13.6 g. or 45 per cent of the theory (based on the recovery of about 20 g. of epoxybutene). The exact structure of this compound has not been determined as yet.

A similar run at 0-5° using 0.5 mole of potassium cyanide in 60 g. of distilled water gave 10 g. (14 per cent of theory) of a liquid, b.p. 71/3 mm., n^{20}_D 1.4330, and 24 g. of black residue which was not distilled.

The effect of temperature on the reaction was determined at -10°, 0° and 10° using the same amounts of starting materials except the reactions were run in benzene solution. In every case there was obtained only the by-product, acetyl cyanide dimer, in a yield of about 16 g., b.p. 64°/1 mm., n^{20}_D 1.4139, which solidified on cooling to a white solid, m.p. 69°.

9. <u>1-Benzoyloxy-2-cyano-3-butene</u>

This compound was prepared in a manner similar to that of the acetate, using 35 g. (0.5 mole) of 3,4-epoxy-1-butene and 70 g. (0.5 mole) of benzoyl chloride in 100 cc. of dry benzene and adding a solution of 30 g. (0.5 mole) of sodium cyanide in 150 cc. of distilled water drop by drop over a period of twenty minutes. Reaction temperature was -3 to -5°. Stirring was continued an additional twenty minutes.

When the layers were separated and washed with 5 per cent sodium carbonate solution a very stable emulsion formed which would not break until a little ethanol was added. Distillation gave 23.5 g. of liquid, b.p. 50-65°

corresponding to recovered epoxybutene, 34.5 g. of ethyl benzoate, b.p. 58°/10 mm., n_D^{20} 1.5030, and finally 17.7 g. of the benzoate ester of the cyano-alcohol; b.p. 95-96°/0.5 mm.; n_D^{20} 1.5162. This is 17.5 per cent of the theory (or 55 per cent based on the amount of 3,4-epoxy-1-butene actually used up).

The effect of temperature was investigated. At 0° or 2-3° no benzoate ester could be isolated; at 10° no ester was obtained, but instead 70 g. of a very high boiling, viscous, yellow liquid was obtained which distilled at 150°/1 mm. and solidified on cooling to a solid, m.p. 95°. Analysis of this compound showed it to be an isomer of benzoyl cyanide, and the melting point corresponds to that of the dimer described in the literature.[14,15] Benzoyl cyanide melts at 32°.

Anal. Calcd. for $C_{16}H_{10}O_2N_2$: C, 73.30; H, 3.85; N, 10.64.

Found: C, 72.75; H, 3.66; N, 10.48.

III. PART TWO: THE STRUCTURE OF BENZOYL CYANIDE DIMER AND THE ADDITION OF BENZOYL CYANIDE TO AROMATIC ALDEHYDES

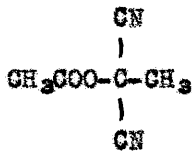
A. Historical

Acetyl and benzoyl cyanide dimers are well-known compounds of long standing. Hubner[16] first reported the preparation of acetyl cyanide dimer, but its structure was not correctly determined until Brunner[17] studied this compound and assigned to it a structure which has been confirmed by later workers.[18,19]

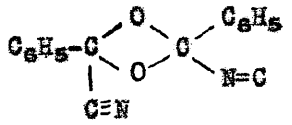
Similarly benzoyl cyanide dimer was discovered by Wache,[15] but its structure remained unknown until Diels and Pillow[14] advanced a structure based on certain derivatives they obtained. Bardroff[18] called into question the structure of benzoyl cyanide dimer postulated by Diels and Pillow[14] but did not investigate the compound further.

B. Theoretical

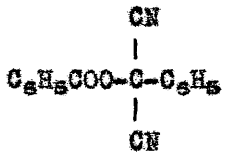
The structure of acetyl cyanide dimer (I) is shown below along with the structure of benzoyl cyanide dimer (II) postulated by Diels and Pillow.



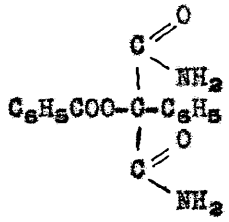
I



II



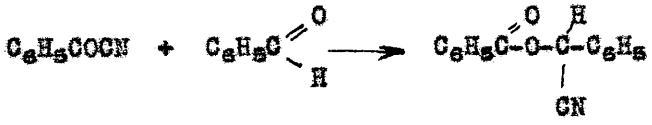
III



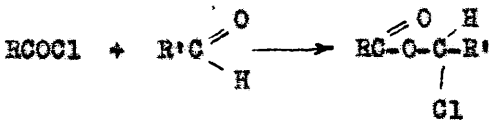
IV

The analogy between structures (I) and (III) should be borne out by infrared absorption spectra as well as the isolation of a diamide of each compound. The diamide of acetyl cyanide dimer was reported by Bardroff[18] and its structure proved.

The reaction of benzoyl cyanide with benzaldehyde was investigated in order to confirm in a different way the structure for benzoyl cyanide dimer (III) which was believed to be more satisfactory than that advanced by Diels and Pillow (Structure II). This reaction may be formulated as follows:



and is analogous to the reaction discovered by Adams and his students[20] some years ago.



in which an acid chloride adds to the reactive carbonyl group of an aliphatic or aromatic aldehyde.

C. Discussion of Results

1. The Formation of Acetyl and Benzoyl Cyanide Dimers

The reaction of 3,4-epoxy-1-butene with saturated aqueous sodium cyanide solution and acetic anhydride at various temperatures gave as a by-product "acetyl cyanide dimer", which is actually α-methyl- α-acetoxy-malononitrile. Similarly benzoyl chloride, 3,4-epoxy-1-butene and saturated aqueous potassium cyanide solution at 10° gave "benzoyl cyanide dimer".

2. Identification of Benzoyl Cyanide Dimer

In an effort to identify this by-product a derivative was prepared by hydrolysis with sulfuric acid which was found by analysis to be a diamide of benzoyl cyanide dimer. It melted at 203.5°, whereas Diels and Pillow[14] reported that only a monoamide could be obtained which melted at 174-177°.

Infrared absorption spectra (Figure 1a and b) of benzoyl cyanide dimer and acetyl cyanide dimer show them to be analogous in structure, and there is no evidence for the oxygen bridge of structure (II).

3. Infrared Absorption Spectra of Benzoyl Cyanide and Acetyl Cyanide Dimers, The Diamide of Benzoyl Cyanide Dimer, and Acetyl and Benzoyl Cyanide

Dr. Foil A. Miller and Mrs. J. L. Johnson determined the infrared spectra and made the following statement concerning them:

"Comparison of the spectra (Figure 1a and b, curves C and D) of the two dimers indicates that they have analogous structures. Both show weak -C≡N absorption (2256 $cm.^{-1}$) and strong C=O stretching frequencies (1746 and 1767 $cm.^{-1}$). The fact that the C=O band of the benzoyl cyanide dimer (curve D) is 20 $cm.^{-1}$ lower than that of the acetyl cyanide dimer (curve C) indicates that it is conjugated with the phenyl group. In the spectrum of the diamide of the benzoyl cyanide dimer (curve E) the C≡N absorption is absent and strong amide

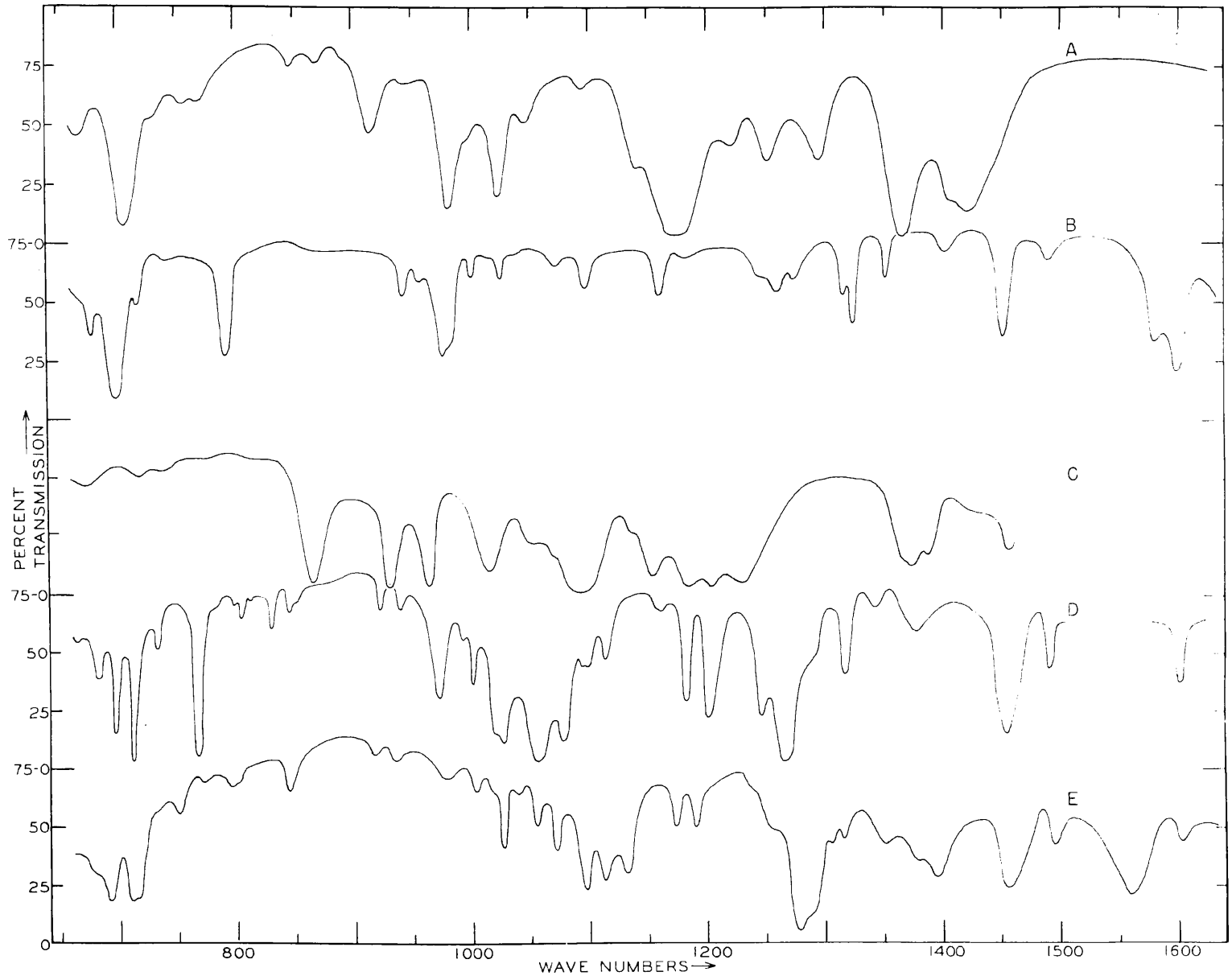

A
B
C
D
E
75
50
25
75-0
50
25
75-0
50
25
75-0
50
25
0
PERCENT TRANSMISSION
800
1000
1200
1400
1500
1600
WAVE NUMBERS

Figure .c

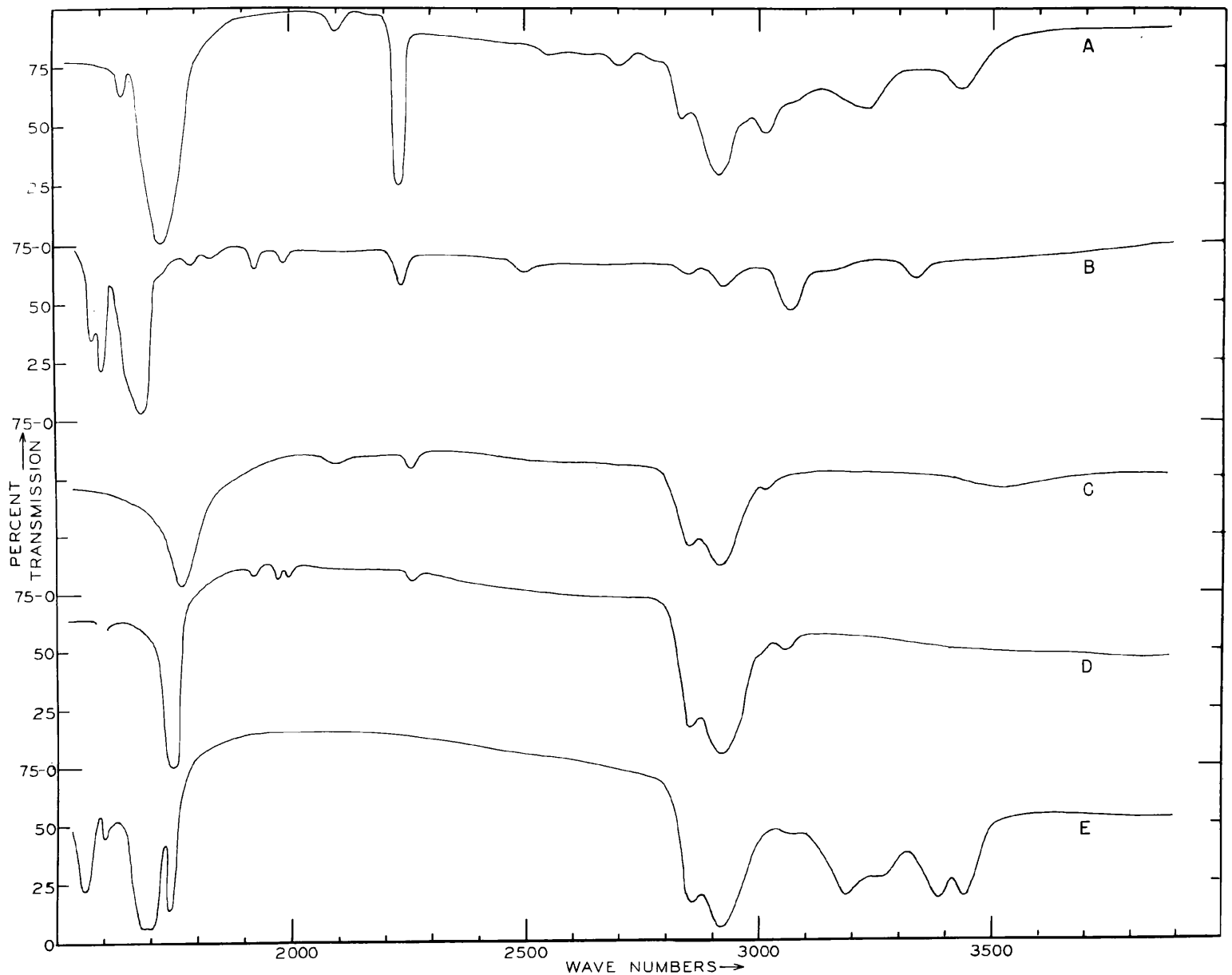
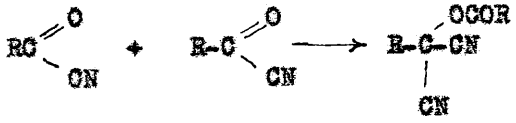

A
B
C
D
E
75
50
25
75-0
50
25
75-0
75-0
50
25
75-0
50
25
0
PERCENT TRANSMISSION
2000
2500
3000
3500
WAVE NUMBERS

Figure 1b

C=O absorption (1675 - 1700 cm.$^{-1}$) appears in addition to the C=O frequency found in the original compound. A complex series of N-H stretching frequencies also appears between 3190 and 3450 cm.$^{-1}$. Both these spectra (curves D and E of Figure 1) show the characteristic carbon-carbon stretching frequencies of the phenyl group at 1493 and 1602 cm.$^{-1}$. The presence of two strong bands around 700 cm.$^{-1}$, where the mono-substituted phenyl group absorbs, indicates two types of mono-substitution, e.g. $C_6H_5C(=O)-$ and $C_6H_5C(-)-$. The remainder of the strong absorption bands in the spectra (from 800 - 1400) are due to vibrations of C-O, C-C, C-N linkages and extensive parts of the molecules. These frequencies are too greatly affected by slight changes in structure to be of any value in interpretation.

"The infrared absorption curves of acetyl (curve A) and benzoyl (curve B) cyanide both show a C N stretching frequency at 2235 cm.$^{-1}$ and ketone C=O around 1700 cm.$^{-1}$. This is at a lower frequency in the benzoyl where it is more highly conjugated. Characteristic phenyl frequencies appear in (B) at 1600, 1580, 1490 cm.$^{-1}$ and at 700 cm.$^{-1}$ for the mono-substituted phenyl group. Typical of methyl ketones, except acetone, the acetyl cyanide absorbs in the CH_3 region (1370 cm.$^{-1}$) and has a strong band around 1170 and one between 700 and 800 cm.$^{-1}$."

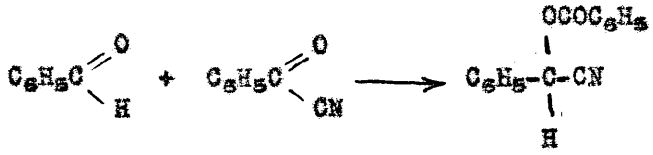
Thus the dimers have the structure that might be expected if one acyl cyanide molecule adds to the carbonyl group of another molecule.



4. <u>The Addition of Benzoyl Cyanide to Benzaldehyde and Anisaldehyde</u>

It has been found that benzoyl cyanide will indeed add to the active carbonyl group of an aromatic aldehyde in the presence of catalytic amounts of

aqueous potassium hydroxide. This furnishes a convenient method of converting an aromatic aldehyde to the benzoate of the corresponding cyanohydrin.



The reaction works well with benzaldehyde and anisaldehyde, but has not been successfully extended to aliphatic aldehydes or any ketones.

D. Experimental

1. Acetyl Cyanide Dimer and Benzoyl Cyanide Dimer

α-Acetoxy-α-methylmalononitrile was obtained by high vacuum distillation of the residue of a reaction employing acetic anhydride and aqueous potassium cyanide as clear liquid, b.p. 82°/6 mm., which on cooling solidified to a white solid, m.p. 69°, having an odor reminiscent of hydrogen cyanide and acetic acid. The solid was crystallized from aqueous alcohol solution. Brunner[17] gives the melting point for acetyl cyanide dimer as 69°.

Anal. Calcd. for $C_5H_6O_2N_2$: C, 52.17; H, 4.38; N, 20.29.

Found: C, 52.01; H, 4.18; N, 20.28.

Similarly, α-benzoyloxy-α-phenylmalononitrile was obtained by distillation at diminished pressure of the residue of a reaction employing benzoyl chloride and aqueous potassium cyanide as a yellow, viscous liquid, b.p. 150°/1 mm., which solidified on cooling to a white solid, m.p. 95°. The solid was recrystallized from alcohol, m.p. 95°.

Anal. Calcd. for $C_{18}H_{10}O_2N_2$: C, 73.30; H, 3.85; N, 10.64.

Found: C, 72.75; H, 3.66; N, 10.48.

2. α-Phenyl-α-benzoyloxymalonamide

Two grams of α-benzoyloxy-α-phenylmalononitrile was placed in a 125-ml. Erlenmeyer flask and dissolved in 10 ml. of concentrated sulfuric acid. As a few drops of water were added the temperature rose to 85°. The flask was cooled in an ice bath, and a white solid separated out as 100 ml. of water was slowly added with stirring. The solid was collected on a Buchner funnel and washed with cold water. The material was recrystallized from 100 ml. of benzene containing a small amount of alcohol. The recrystallized material, after drying at 65°, melted at 185-190°. After further recrystallization from benzene containing a little alcohol and ether, the solid melted at 203.5-204.5° (uncorr.).

Anal. Calcd. for $C_{16}H_{14}O_4N_2$: C, 64.42; H, 4.73; N, 9.39.

Found: C, 64.60; H, 4.90; N, 9.20.

3. Acetyl Cyanide and Benzoyl Cyanide

Acetyl cyanide was prepared from cuprous cyanide and acetyl bromide according to the directions given by Migrdichian,[21] and benzoyl cyanide by the method given in "Organic Syntheses".[22]

4. Benzoate of p-Methoxybenzaldehyde Cyanohydrin

Three grams (0.023 mole) of benzoyl cyanide and 3 g. (0.023 mole) of anisaldehyde were mixed in a 50-ml. glass-stoppered bottle, and 6 ml. of 10 per cent aqueous potassium hydroxide solution was added. The bottle was shaken about ten minutes. An emulsion formed first, and later a viscous yellow oil settled out. The aqueous layer was decanted and the residual oil crystallized from alcohol. There was obtained 2.8 g. (46 per cent of the theory) of a solid, m.p. 64-65°; the mother liquor contained additional material which did not crystallize. Recrystallization of the solid did not change the melting point.

A mixed melting determination with an authentic sample of the benzoate of p-methoxybenzaldehyde cyanohydrin (m.p. 64-65°) prepared by the method of Francis and Davis[23] showed no depression. These authors gave the value of 66-67° for the melting point of this compound.

Anal. Calcd. for $C_{16}H_{13}O_3N$: C, 71.91; H, 4.86; N, 5.24.

Found: C, 72.09; H, 4.78; N, 5.14.

5. Benzoate of Benzaldehyde Cyanohydrin

In a 50 ml. glass-stoppered bottle were placed 2 g. (0.015 mole) of benzoyl cyanide, 1.6 g. (0.015 mole) of benzaldehyde, and 6 ml. of 5 per cent aqueous potassium hydroxide. The bottle was shaken for about fifteen minutes and a white solid ball formed. The aqueous solution was decanted, and the solid was

recrystallized from alcohol. There was obtained 0.45 g. of the benzoate of benzaldehyde cyanohydrin, m.p. 59°, and 0.3 g. of a white solid, m.p. 121° (probably benzoic acid). From the mother liquor there was obtained by further evaporation 1.3 g. of solid, m.p. 54-55°, making total yield of 49 per cent of theory of the benzoate of benzaldehyde cyanohydrin. Recrystallization of the material melting at 59° did not change its melting point. The compound was submitted for analysis.

Anal. Calcd. for $C_{15}H_{11}NO_2$: C, 75.93; H, 4.67; N, 5.90.

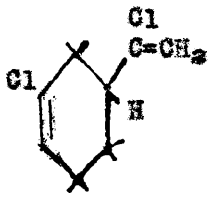
Found: C, 76.03; H, 4.73; N, 5.91.

Francis and Davis[23] report the melting point of the benzoate ester of benzaldehyde cyanohydrin as 63-64°.

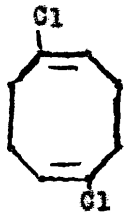
IV. PART THREE: THE DIMERIZATION OF 2-CYANO-1,3-BUTADIENE AND THE STRUCTURE OF THE DIMER

A. Historical

The dimerization of dienes to yield cyclic compounds is a well-known general reaction. Butadiene, the simplest diene, dimerizes by a Diels-Alder condensation to 1-vinyl-Δ^3-cyclohexene,[24] and 2-chloro-1,3-butadiene, the chloro-analog of 2-cyano-1,3-butadiene, has been shown to dimerize in two different ways, yielding a six- and an eight-membered ring compound[25,26] (Structures I and II).



I

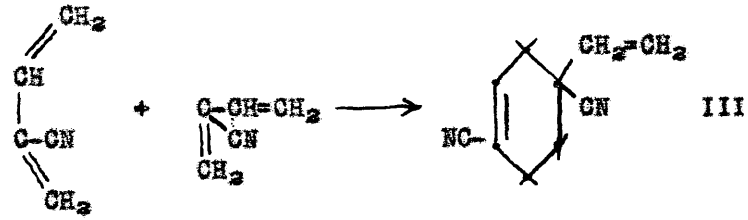


II

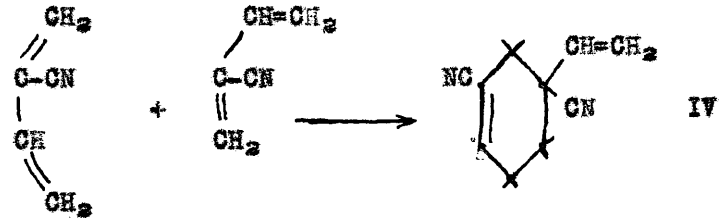
B. Theoretical

1. The Possible Structures of the Dimer

The formation of the dimer of 2-cyano-1,3-butadiene by a Diels-Alder condensation may occur in the following ways:

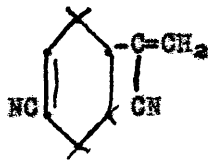
(1) 

III

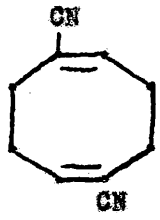
(2) 

IV

One molecule of 2-cyano-1,3-butadiene, with the nitrile-activated double bond, acts as the dienophile and thus permits the facile addition of another molecule of the diene to give one or both of the two isomers shown (III and IV). The formation of dimers analogous in structure to those found in the still residues of 2-chloro-1,3-butadiene[26,27] cannot be excluded, although it would be difficult to understand how addition across the unactivated ethylenic bond would occur (under the very mild conditions in which the dimerization of 2-cyano-1,3-butadiene had taken place) in preference to the nitrile-activated double bond. Thus, structures (V) and (VI) are also possible, but not probable:

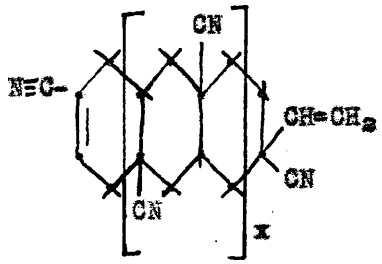


V



VI

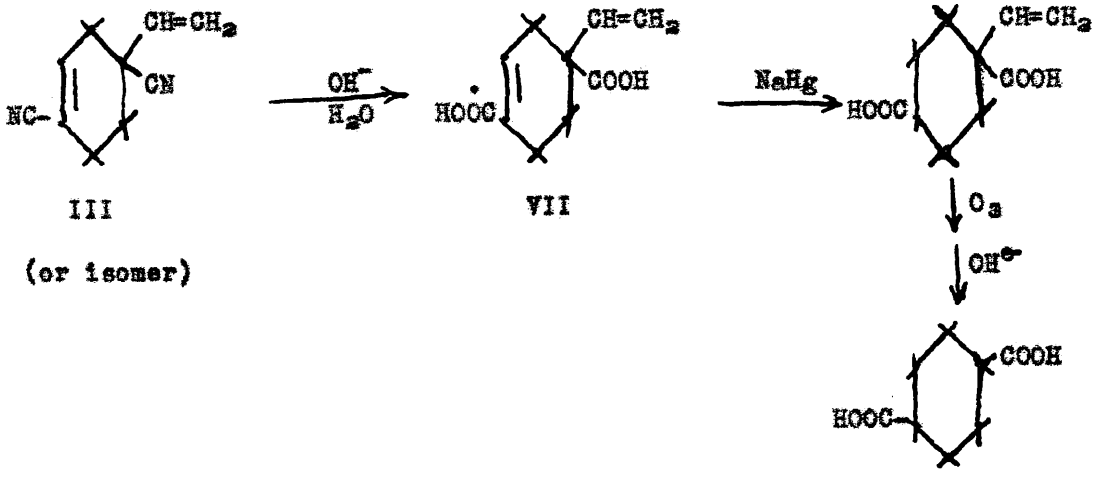
Either structure (III) or (IV) with its nitrile-activated double bond in the ring, possess the structural requirement for further 1,4-addition of 2-cyano-1,3-butadiene in the Diels-Alder manner, which presumably could give rise to a new type of polymer having the structure:



Thus a determination of the structure of the dimer may throw some light on the structure of the polymer of 2-cyano-1,3-butadiene.

2. Proposed Methods of Proof of Structure

The method originally proposed to convert the dimer to a known derivative involves the sodium amalgam reduction of the double bond α-β to the activating group, shown below for structure (III). This partially hydrogenated derivative could then be converted to a known cyclohexane dicarboxylic acid by ozonolysis and decarboxylation of the resulting substituted malonic acid.

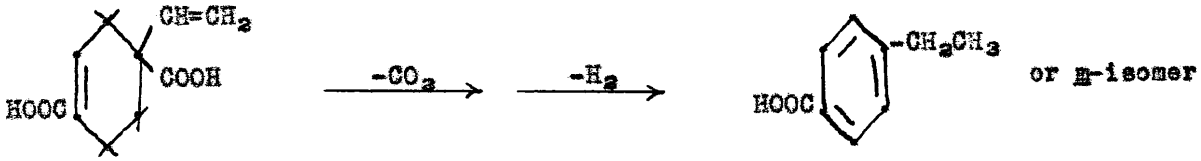


III

(or isomer)

VII

A second method of attack is to dehydrogenate and partially decarboxylate the unsaturated dibasic acid (VII) to a known aromatic derivative:



VII

(or isomer)

3. Physical Evidence

The physical evidence obtained from the infrared absorption spectra of the dimer should reveal the presence of two different nitrile groups in the case of structures (III) and (IV), but in structures (V) and (VI) both nitrile groups are conjugated with a double bond. A confirmatory check is possible with the spectra of the di-ester derivative of the dimer. A comparison of the observed and calculated molar refractivities for the liquid di-ester will also indicate the extent of conjugation in this compound by the amount of exaltation of the molar refractivity found from the physical data and calculated by the formula[28]

$$M_D = \left(\frac{n^2-1}{n^2+2}\right)\left(\frac{m}{d}\right)$$

where n = refractive index, m = molecular weight, and d = density.

C. Discussion of Results

1. Formation of the Dimer

2-Cyano-1,3-butadiene dimerizes very readily. There was isolated a crystalline compound, m.p. range 30-40°, from a sample of monomer containing a little picric acid as inhibitor and which had been stored in the icebox for some time. This compound had a molecular weight of 146 as determined by the freezing point of acetic acid. The theoretical molecular weight of the dimer is 158.2.

2. Crystallization of the Pure Compound

The dimer was later distilled under reduced pressure, but analysis showed some decomposition had occurred. Attempts to recrystallize the pure compound from various solutions were at first unsuccessful, yielding only yellow oils, but later it was found possible to obtain the pure dimer as white needles, m.p. 55°, from dilute aqueous alcohol solution. Repeated crystallizations of the material remaining in the mother liquors yielded only the same compound, and no evidence for isomers was found.

3. Chemical and Physical Properties of the Dimer

The dimer of 2-cyano-1,3-butadiene has two olefinic bonds as shown by hydrogenation using 10 per cent palladium on charcoal in an Adams hydrogenation apparatus at room temperature. It does not decolorize bromine in chloroform solution, but does readily decolorize dilute aqueous potassium permanganate solution when the compound is dissolved in acetone. Ultraviolet absorption indicates the double bonds are not in conjugation with each other. Infrared absorption (Figure 2, curve A) reveals the presence of two different nitrile groups with absorption at 2243 and 2220 $cm.^{-1}$ (i.e. unconjugated and conjugated with a double bond), and two double bond frequencies, 1639 and 1649 $cm.^{-1}$, indicating a conjugated and an unconjugated double bond.

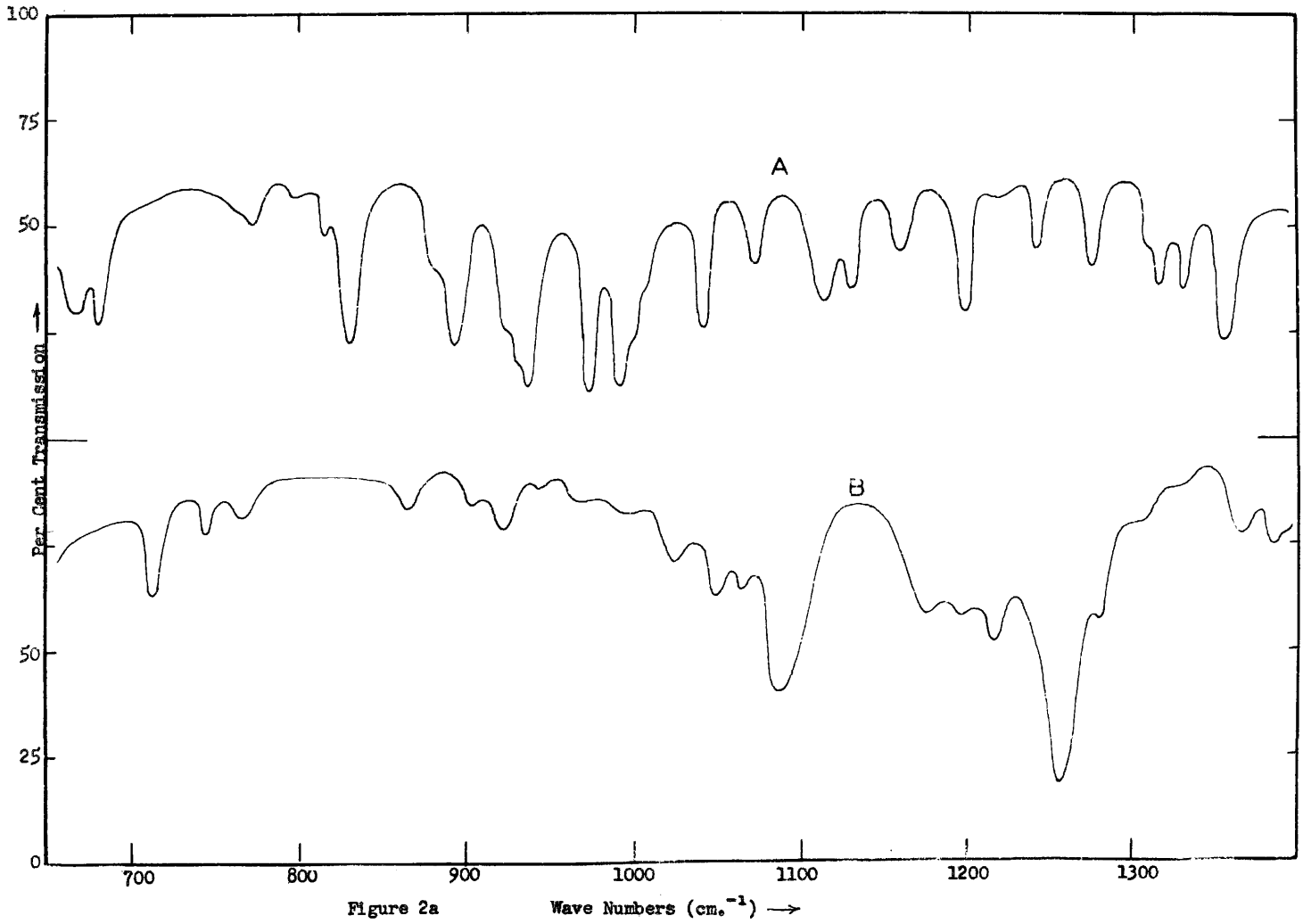

100
75
50
Per Cent. Transmission
A
B
50
25
0
700
800
900
1000
1100
1200
1300
Wave Numbers (cm.$^{-1}$) →

Figure 2a

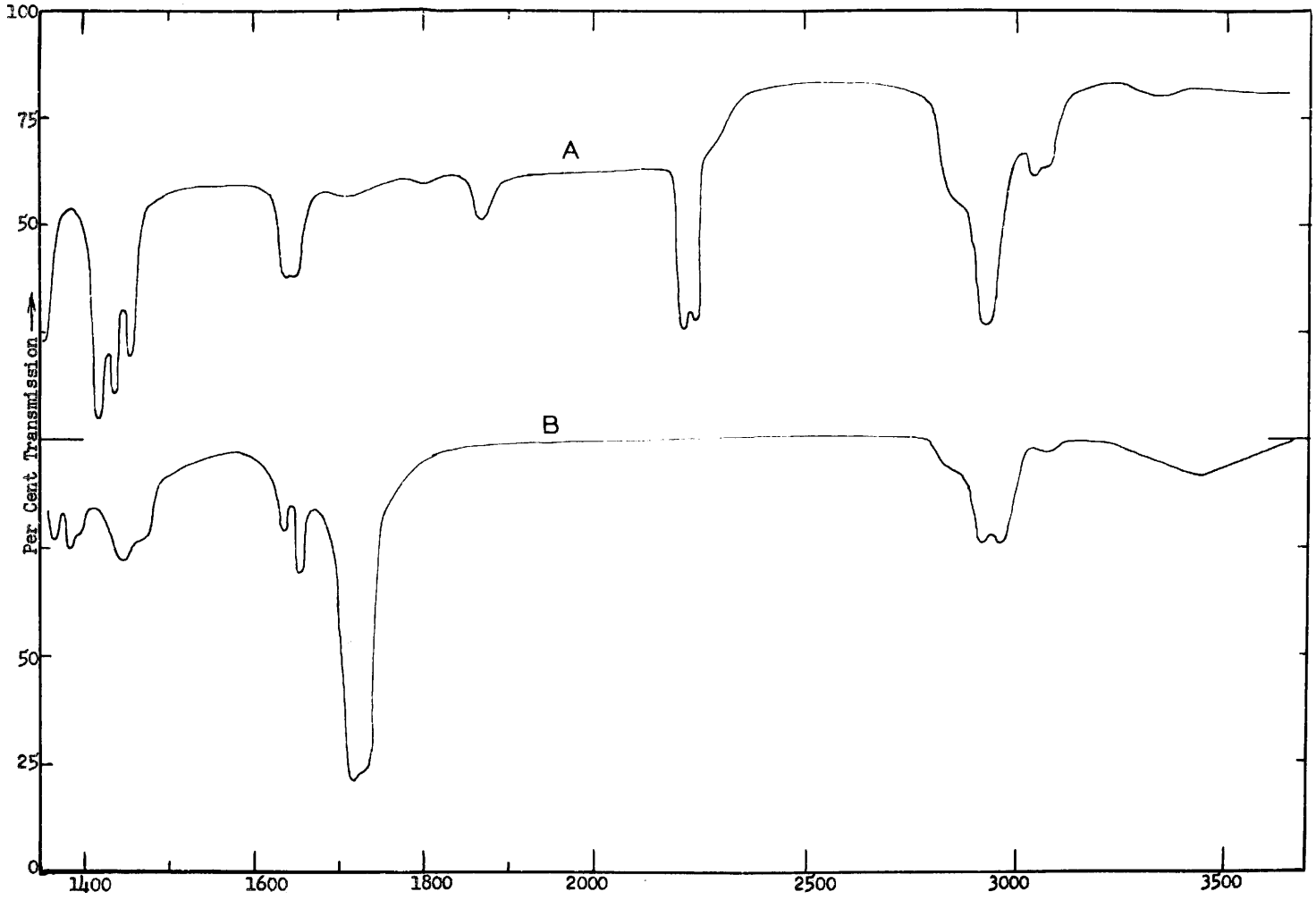

100
75
50
Per Cent Transmission →
A
B
50
25
0
1400
1600
1800
2000
2500
3000
3500
Wave Numbers (cm.$^{-1}$) →

Figure 2b

The compound is soluble in alcohol, chloroform, benzene, acetic acid, ether, and acetone, and insoluble in water, cyclohexane, and Skellysolve B.

4. Saponification of the Crude Dimer

Saponification of the crude dimer with 35 per cent aqueous sodium hydroxide solution yields only one unsaturated dibasic acid (m.p. 235°) with a neutral equivalent of 100.4. The theoretical value for the dibasic acid corresponding to the structures (I) to (IV) is 98.1. The unsaturated acid decolorizes dilute aqueous potassium permanganate solution only when the test is carried out in alcohol, according to the suggestion of Ipatieff,[28] and does not give a positive test in acetone solution. A quantitative hydrogenation of the unsaturated acid using 10 per cent palladium on charcoal catalyst showed two double bonds to be present.

5. Attempted Sodium Amalgam Reduction of Unsaturated Dibasic Acid

Several attempts to carry out the reduction using 2 per cent sodium amalgam with either an aqueous solution of the sodium salt of the acid at a pH of 9-9.5 or a dilute aqueous alcohol solution of the sodium salt of the acid failed. The compound recovered was identical (melting point and mixed melting point) with the starting material. Evidently the olefinic bond must be more highly activated (i.e. phenyl and carboxyl groups as in cinnamic acid) for the reduction to take place readily.

6. An Attempted Sulfur Dehydrogenation

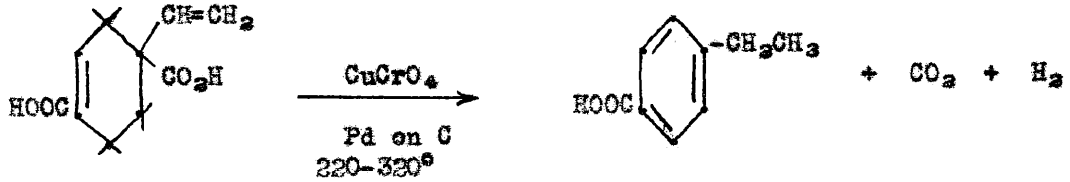
An attempt to convert the acid (m.p. 235°) to an aromatic derivative by dehydrogenation with the theoretical amount of sulfur[30] was unsuccessful. A small amount of orange-colored solid was distilled out of the melt at 0.1 mm. pressure. This material was alkali-soluble, but attempts to crystallize a pure

compound from either aqueous acetic acid or aqueous alcohol solutions yielded only gummy precipitates.

7. Catalytic Dehydrogenation

A catalytic dehydrogenation with 10 per cent palladium on charcoal catalyst and a small amount of copper chromite catalyst to promote decarboxylation of the tertiary carboxyl group yielded p-ethyl benzoic acid.

Isolation of this derivative shows the following reaction has occurred:



VII VIII

8. Esterification of the Unsaturated Dibasic Acid

The diethyl ester (IX) of the unsaturated acid was obtained by sulfuric acid catalyzed esterification with absolute ethanol.[31] The equilibrium was displaced by azeotropic distillation of the water-benzene-ethyl alcohol ternary mixture over a period of several hours.

VII IX

9. Molar Refractivities of the Di-ester

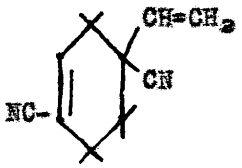
Using the values for atomic refractivities given in Shriner and Fuson[28] the theoretical molecular refractivity was calculated to be 67.04. The observed molecular refractivity as calculated by the Lorenz-Lorentz equation[28] is

$$M_D = \left(\frac{2.1906 - 1}{2.1906 + 2}\right)\left(\frac{252.30}{1.0639}\right) = 67.38$$

using the data obtained from a pure sample of the compound. The exaltation of 0.34 may be attributed to the presence of the double bond conjugated with the ester group, but is hardly large enough to indicate the presence of two negative (electron-attracting) groups conjugated with double bonds. Infrared absorption maxima (Figure 2, curve B) occur at 1636 and 1654 cm.$^{-1}$, indicating a conjugated and an unconjugated double bond, and at 1715 and 1730 cm.$^{-1}$, indicating a conjugated and an unconjugated ester group.

10. Assignment of Structure to the Dimer

Accordingly structure (III) is assigned to the dimer of 2-cyano-1,3-butadiene as the most probable structure on the basis of the chemical and physical evidence.



III

This structure is compatible with the physical and chemical evidence so far obtained. No evidence was found for the eight-membered ring compound, structure (VI). Failure to obtain any α-carboxy-styrene in the dehydrogenation of the unsaturated acid, as well as the facile formation of the dimer even at

low temperatures appears to be convincing evidence that the Diels-Alder condensation has involved the nitrile-activated rather than the unsubstituted ethylenic bond. This is borne out by the infrared absorption spectra and the molar refractivity of the di-ester derivative.

One may perhaps speculate that the <u>para</u> rather than the <u>meta</u> isomer was produced by the Diels-Alder condensation, because the <u>para</u> compound, being more symmetrical, would be more insoluble, have a higher melting point, and thus separate out of the equilibrium mixture at 5°. It would be of interest to determine the products of the dimerization of 2-cyano-1,3-butadiene at higher temperatures.

D. Experimental

1. Dimer of 2-Cyano-1,3-butadiene

A sample of 57 g. of the monomer, containing a little picric acid as polymerization inhibitor, when stored in the icebox at 5° for about three months, had solidified to the extent of about 75 per cent. When warmed up to room temperature the solid dissolved, but after the remaining monomer was removed by distillation, the residual viscous oil (ca. 40 g.) crystallized when cooled, m.p. range 30-40°.

In another instance the solid residue remaining in a bottle of 2-cyano-1,3-butadiene (containing picric acid as inhibitor) which had been stored in the icebox for about six months was scraped out and placed in a small ground-glass distilling flask. The dimer was distilled under high vacuum through an 8-in., helix-packed column. There was obtained 4.2 g. of liquid, b.p. 110-112°/1 mm., which solidified on standing to a white solid, m.p. range 30-40°. A brown, semi-viscous liquid which remained in the flask became spongy when cooled but was interspersed with crystallites.

An analysis of the liquid, b.p. 110-112°/1 mm. was obtained.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71.

Found: C, 74.46; H, 5.94; N, 16.74.

The sample grew darker in color on standing.

Crystallization of this compound from dilute alcohol was done in the following way. The crude dimer was dissolved in alcohol, treated with Darco, and filtered. The filtrate was evaporated and a few milliliters of water added until the solution began to get cloudy at 50°. When cooled to room temperature, the solution was seeded with a small crystal previously obtained and placed in the icebox. The mass of crystals which formed was collected on a Buchner funnel, washed with very dilute alcohol, and air-dried, m.p. 54-54.5°. Further similar

treatment of the filtrate (omitting the Darco) yielded three more crops of crystals. The third crop, which melted over the range of 44-51° was contaminated with some of the residual oil, but the fourth crop was colorless and melted at 54-55°. In another experiment crystals were obtained which melted at 55-56°; analysis of this material, in constrast to the compound which had merely been distilled, agreed well with the theory.

Anal. Calcd. for $C_{10}H_{10}N_2$: C, 75.92; H, 6.37; N, 17.71.

Found: C, 75.92; H, 6.53; N, 17.67.

The dimer is soluble in dioxane, absolute ethanol, acetic acid, acetone, benzene, and ether, gives a cloudy solution with methanol, and is insoluble in water, cyclohexane, and Skellysolve B. The dimer decolorized dilute potassium permanganate solution rapidly when dissolved in acetone; a blank run on the acetone did not decolorize permanganate.

2. Molecular Weight Determinations

The molecular weight of the dimer was determined cryoscopically by means of the depression of the freezing point of glacial acetic acid. A depression of 0.6° was obtained by dissolving 1.12 g. of the solid in 50.0 g. of glacial acetic acid. Using the equation[32] $T = \frac{c}{P} M$ where T is the constant for 100 g. of solvent (39 for glacial acetic acid), c is the depression of the freezing point, P is the weight of the solute in 100 g. of solvent and M is the molecular weight, mol. wt. $= T\frac{P}{c} = \frac{39 \times 2.24}{0.6} = 146.$

The molecular weight of the dimer was also determined by measurement of the elevation of the boiling point of benzene. Using a Beckmann thermometer the boiling point of 10 ml. of benzene was determined after equilibrium was established, 0.097 g. of the solid dimer was added and the boiling point was again determined after several minutes. An elevation of $0.21 \pm 0.02°$ occurred.

Using the formula[33]

$$\text{mol. wt.} = \frac{1000 \times K \times g}{s \times T}$$

where K = molal boiling constant of benzene = 2.67

g = grams of solute

s = grams of solvent

T = elevation of boiling point

$$\text{Mol. Wt.} = \frac{1000 \times 2.67 \times 0.097}{8.79 \times 0.21} = 141$$

The calculated molecular weight of a dimer is 158.20.

3. Hydrogenation of 2-Cyano-1,3-butadiene Dimer

In order to determine the number of double bonds in the dimer, 4.0 g. (0.0254 mole) of the solid (from the previous distillation, b.p. 110-112°/1 mm.) and 1.0 g. of 10 per cent palladium on charcoal catalyst were placed in a hydrogenation bottle along with 50 cc. of absolute ethanol and hydrogenation was carried out at 25° in an Adams hydrogenation apparatus at 40 pounds initial hydrogen pressure. This amount of material would require a pressure drop of 11.5 pounds if two double bonds were present in the dimer. An initial drop of 2.5 pounds occurred in the first three minutes of shaking; the hydrogen up-take became slower, with a total of 8 pounds of pressure drop occurring in forty minutes. The hydrogenation was continued for a total of eighteen and one-half hours, until a 10-pound pressure drop had occurred. This corresponds to 87 per cent of the theory for two double-bonds.

The hydrogenated compound was obtained by high vacuum distillation after first removing the catalyst by filtration and the ethanol by distillation at 30 mm. pressure. There was obtained 1.5 g. of liquid, b.p. 115-118°/1 mm. which

solidified on cooling to a white solid which would not decolorize dilute potassium permanganate solution. The solid was submitted for analysis.

Anal. Calcd. for $C_{10}H_{14}N_2$: N, 17.27. Found: N, 15.95.

4. Saponification of the Dimer of 2-Cyano-1,3-butadiene

A solid acid derivative of the dimer has been obtained by hydrolysis of the nitrile groups using 4.5 g. (0.0286 mole) of the crude solid with 6.7 g. (0.12 mole) potassium hydroxide in 30 cc. of water. The mixture was heated under reflux for one hour, during which time ammonia could be detected. Then 0.5 g. of additional potassium hydroxide was added and refluxing was continued four hours until no more ammonia could be detected. One gram of Darco was added to the resulting orange solution, which was then filtered. The solution was cooled in ice and acidified with 50 per cent sulfuric acid. The precipitated acid was collected on a Buchner funnel, redissolved in 95 per cent ethanol, and concentrated some by evaporation; then water was added and the solution was allowed to crystallize at room temperature. The first crop of crystals, silvery-white leaflets, amounted to 0.3 g., m.p. 235-236° (sintered 230°). By further evaporation of the filtrate and crystallization from dilute alcohol solution a total of 2.6 g. of solid (ca. 50 per cent of theory), m.p. 235-236°, was collected. A portion of material was lost when a solution boiled over.

In a second experiment 3.6595 g. of the dimer was saponified by heating with 15 g. of sodium hydroxide in 50 cc. of water over a period of fourteen and one-half hours while the vapors coming off were tested for the presence of ammonia. The alkaline solution was added slowly with very rapid stirring by an air-driven motor to a solution of 41.5 cc. of 12 N hydrochloric acid and 50 cc. of water in a 250-cc. beaker. The precipitated acid was collected on a Buchner funnel, washed with distilled water and dried in an oven at 55° for two hours; m.p. 231-232°

(sintered 229°). The yield was 3.0881 g. or 70.5 per cent of the theory. The acid was recrystallized from alcohol-water solution, m.p. 235°.

Analysis of the recrystallized acid was obtained.

Anal. Calcd. for $C_{10}H_{12}O_4$: C, 61.21; H, 6.17.

Found: C, 60.80, 60.73; H, 6.11, 6.34.

The unsaturated acid is soluble in alcohol and hot water, and sparingly soluble in ether, benzene, and acetone. It decolorizes dilute potassium permanganate solution when dissolved in 95 per cent ethanol. It does not decolorize bromine in carbon tetrachloride solution.

5. Attempted Sodium Amalgam Reduction of the Unsaturated Acid

The unsaturation present in the case of structures (III) and (IV) is of two types, with one of the double bonds $\alpha-\beta$ to a nitrile group. The unsaturated acid derived from either of these structures, then, should have its $\alpha-\beta$ double bond reduced by sodium amalgam without affecting the unconjugated double bond. However, when this was attempted, according to the method of Bachmann, Cole, and Wilds,[34] the recovered material had a melting point only one degree lower than the starting material (234-235°), and a mixed melting point was identical.

The attempted reduction was repeated, using 10 per cent aqueous alcohol instead of water and at a temperature of 50° instead of 20°, but again the recovered acid had the same melting point (234°) as the starting material. The quantities of material used in both cases were 0.196 g. (0.001 mole) of unsaturated acid, 1.5 g. of potassium hydroxide in 15 cc. of solution and 12 g. of 2 per cent sodium amalgam. The solution was shaken for fifteen minutes.

A third attempt followed the directions given by Gattermann,[35] in which the sodium amalgam is added portionwise to a solution of the acid in

alkali just basic to phenolphthalein indicator (pH:9-9.5) . The recovered product was identical with the starting material.

6. Neutralization Equivalent of the Unsaturated Acid

Using phenolphthalein as indicator, 0.0981 g. (0.000500 mole) of the unsaturated acid required 10.15 cc. of 0.09625 N sodium hydroxide solution. This is 0.9769 milli-equivalents. Hence, the neutralization equivalent equals $\frac{.0981}{.9769 \times 10^{-3}} = 100.4$. If dibasic, the molecular weight is 200.8 (calculated for the unsaturated dibasic acid, 196.20).

7. Quantitative Determination of the Number of Double Bonds in the Unsaturated Acid by Hydrogenation

A hydrogenation apparatus designed to measure quantitatively the amount of hydrogen taken up by an unsaturated compound consisting of a gas buret connected with a ground glass hydrogenation bottle in a shaker was used in this experiment. There were placed in the bottle 50 cc. of absolute ethanol, 0.5 g. of 10 per cent palladium on charcoal and 0.1962 g. (0.001 mole) of the unsaturated acid. The system was evacuated and filled with hydrogen twice, the volume of hydrogen at 737 mm. pressure and 23.8° was noted and shaking begun. In one minute 53.5 cc. of hydrogen was absorbed before stopping the shaker. The gas buret was refilled and shaking was resumed. In the next hour and twenty minutes, 42.9 cc. of hydrogen at 23° and 742 mm. was absorbed, making a total of 96.4 cc. of hydrogen.

In a blank determination, 0.500 g. of 10 per cent palladium on charcoal in 50 cc. of absolute alcohol took up 40 ± 2 cc. of hydrogen at 22° and 749 mm. pressure. This is equivalent to 42 cc. at 742 mm. and 23°. In other words, the unsaturated compound itself required only about 54 cc. of hydrogen. The amount calculated for two double bonds is 50.0 cc. at 23.8° and 742 mm.

8. Dehydrogenation of the Unsaturated Acid With Ten Per Cent Palladium on Charcoal

In an 18 x 150 mm. Pyrex test tube were placed 1.00 g. (0.00510 mole) of the unsaturated acid, 0.100 g. of 10 per cent palladium on charcoal catalyst, and 0.01 g. of copper chromite catalyst. The materials were mixed and the test tube closed with a one-hole rubber stopper fitted with a 6-in. length of glass tubing. The tube was connected by means of rubber tubing to a U-shaped capillary glass tubing immersed in a pan of water and extending part way up into a 50-cc. buret filled with water and standing in the water.

The evolved gas was collected in the buret and the volume, temperature, and pressure of the gas noted as the dehydrogenation was carried out. As one buret became filled with gas another was put in its place and filled with water by suction.

The test tube was placed in a Wood's metal bath heated with a Bunsen burner to an initial temperature of 220°. Gas bubbles began to appear after a few minutes heating, and as they began to slacken, the temperature of the bath was raised over a period of four hours; the final temperature was 320°. A total volume of 163.5 cc. of gas at standard temperature and pressure (corrected for water vapor pressure) was collected. The theoretical amount of hydrogen at standard temperature and pressure is 114 cc. for 0.00510 mole. An equal amount of carbon dioxide should be evolved, but it is very soluble in water (90 cc. per 100 cc. of water at 20°) and only a portion of it was collected (ca. 50 cc. by difference).

The catalyst and product were washed out with distilled ether and the catalyst filtered off. The residue remaining after the ether was evaporated solidified when chilled in the icebox.

The alcohol solution was treated with Darco, filtered, and the solution saturated by adding water at the boiling point. Two successive attempts

at crystallization yielded only gummy precipitates. The alcohol solution was transferred to a 10-cc. distilling flask, the alcohol removed, and the residue subjected to distillation at reduced pressure. Only a drop or two collected in the side-arm (b.p. 145-150°/19 mm.), but when the distilling flask cooled, solid crystals appeared on the sides. The crystals were scraped out, and weighed 0.053 g.; m.p. 98-105°. When recrystallized from alcohol-water solution, m.p. 112°. The literature gives 110-111°[36] and 112-113°[37] for the melting point of p-ethyl benzoic acid; m-ethyl benzoic acid melts at 47°.

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71.

Found: C, 71.50; H, 6.99.

9. Esterification of the Unsaturated Dibasic Acid

In a 50-cc., ground-glass, round-bottomed flask attached to a 2-ft., water-cooled condenser were placed 0.98 g. (0.005 mole) of the unsaturated acid (m.p. 235°), 5 cc. of absolute alcohol (0.085 mole) and 2 drops of concentrated sulfuric acid. The reactants were refluxed on the steam bath for four hours. Then 10 cc. of benzene was added, the water-cooled condenser replaced by a 10-in. Vigreaux column and a total reflux partial take-off head and the solution heated under practically total reflux as the azeotropic mixture of alcohol, benzene, and water was taken off at 65-72° over a period of four and one-half hours. The remaining traces of benzene and alcohol were removed by distillation under water pump pressure.

The residue was dissolved in 50 cc. of distilled ether and washed three times with 15-cc. portions of 5 per cent aqueous potassium hydroxide solution, dried over anhydrous sodium sulfate, filtered and distilled under reduced pressure in a 10-cc. distilling flask. The ester boiled at 131-33°/3 mm. and amounted to 15-20 drops, n_D^{20} 1.4801; d_4^{20} 1.0639; M_D calcd. 67.04; M_D found 67.38 (exaltation of 0.34).

The distilled ester is soluble in alcohol, ether, and chloroform; insoluble in dilute potassium hydroxide and 10 per cent sodium bicarbonate solution. The ester decolorizes dilute aqueous potassium permanganate solution, but does not decolorize bromine in chloroform solution.

The ester was submitted for analysis as the diethyl ester of the unsaturated dibasic acid.

Anal. Calcd. for $C_{14}H_{20}O_4$: C, 66.64; H, 7.99.

Found: C, 66.54; H, 7.95.

Acidification of the potassium hydroxide wash solution with concentrated hydrochloric acid gave 0.128 g. of recovered acid, m.p. 233-234°.

V. SUMMARY

Several routes to the synthesis of 2-cyano-1,3-butadiene were investigated, but the only practicable method was found to be the pyrolysis of the acetate of methyl vinyl ketone cyanohydrin, though even here it was shown that the major product is an isomeric ester formed by an allyl-type rearrangement and 2-cyano-1,3-butadiene is obtained in yields of only about 30 per cent. The Mannich reaction of allyl cyanide with formaldehyde and dimethyl amine hydrochloride could not be successfully achieved. The cleavage of 3,4-epoxy-1-butene with sodium cyanide and acetic anhydride or benzoyl chloride gave poor yields (30-40 per cent) of the corresponding esters of the cyano-alcohol under all conditions investigated. The dimers of acetyl and benzoyl cyanide were obtained as by-products in these reactions.

While the structure of acetyl cyanide dimer is well established that of benzoyl cyanide dimer previously advanced by Diels and Pillow is inconsistent with the isolation of a diamide and with the now-known infrared spectrum of this compound. The infrared spectra of acetyl and benzoyl cyanide dimers are quite analogous. A more satisfactory structure, analogous to that of acetyl and other alkyl cyanide dimers, is suggested for benzoyl cyanide dimer.

This structure suggests that the dimer has been formed by the addition of one molecule of benzoyl cyanide to the carbonyl group of another molecule. It was found that benzoyl cyanide will indeed add to the active carbonyl group of an aromatic aldehyde in the presence of aqueous potassium hydroxide.

A dimer of 2-cyano-1,3-butadiene was discovered and its structure elucidated. The dimerization occurred under very mild conditions, suggesting a Diels-Alder condensation of one molecule of the monomer across the nitrile-activated ethylenic bond of another molecule. This condensation was shown to have taken place to yield the *para* isomer, 1-vinyl-1,4-dicyano-Δ^4-cyclohexene.

The dinitrile was saponified and the resulting dibasic acid was simultaneously partially decarboxylated and dehydrogenated to p-ethyl benzoic acid. Further confirmation of the structure postulated for the dimer of 2-cyano-1,3-butadiene was obtained from the infrared spectrum of this compound which showed two different nitrile groups to be present, indicating one double bond is conjugated and the other is not conjugated with a nitrile group, and showed also a conjugated and an unconjugated double bond. The infrared absorption spectrum of the diester was analogous.

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VITA

The author was born twenty-six years ago in Osceola, Wisconsin, and attended the public schools there, graduating from high school in May, 1940. After two years of college at the State Teachers College, River Falls, Wisconsin, and somewhat more than a year at the University of Minnesota where he majored in organic chemistry and minored in physics and mathematics, there followed a period of service of thirty-three months in the U. S. Army Air Corps. He was discharged as a First Lieutenant at Camp Grant, Illinois, on March 16, 1946, and immediately began his studies at the Graduate School in the University of Illinois. In the meantime upon recommendation of the Dean of the School of Science, Literature and The Arts in the University of Minnesota he was graduated with the degree of Bachelor of Arts, cum laude, in June of 1946 in absentia. He has been employed as a part time Special Research Assistant on the Government Synthetic Rubber Research Program from March, 1946, to August, 1948.

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