Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 66.10; H, 8.64.

B. **From Diethyl 3,6-Dimethyl-*cis*-Δ^4-tetrahydrophthalate** (II).—The crude diol III, prepared from 176 g. (0.659 mole) of II as described above but without the distillation, was acetylated in the same manner as the pure diol III to give 162 g. (92% over-all yield from II) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (IV), b.p. 120° (1.0 mm.), $n^{25}D$ 1.4702.

3,6-Dimethylhexahydrophthalyl Diacetate (V).—In a high pressure hydrogenation bomb were placed 496 g. (1.96 moles) of 3,6-dimethyl-*cis*-Δ^4-tetrahydrophthalyl diacetate (IV) and 50 g. of W-5 Raney nickel catalyst. The hydrogenation was complete in an hour at 75° and 2600 pounds per square inch of hydrogen. The catalyst was removed by filtration, and the filtrate was distilled through a 6-inch, helix-packed column to yield 460 g. (92%) of 3,6-dimethylhexahydrophthalyl diacetate (V), b.p. 133–134° (2.1 mm.), $n^{25}D$ 1.4621.

Anal. Calcd. for $C_{14}H_{24}O_4$: C, 65.60; H, 9.44. Found: C, 65.82; H, 9.53.

3,6-Dimethyl-1,2-dimethylenecyclohexane (I) and 3,6-Dimethyl-1-methylene-2-acetoxymethylcyclohexane (VI).—By the use of the pyrolysis apparatus described previously,[6] 91.5 g. (0.38 mole) of 3,6-dimethylhexahydrophthalyl diacetate (V) was dropped through a helix-packed vertical Vycor tube at a temperature of 515–520° at the rate of 1.5 g. per minute. The addition was conducted in an inert atmosphere by introduction of a slow stream of oxygen-free nitrogen at the top of the column. The pyrolysate was collected in a receiver cooled in a Dry Ice–acetone-bath. The pyrolysis products were dissolved in ether and washed free from acetic acid with distilled water. (Titration of the aqueous washings indicated that 62% of two molar equivalents of acetic acid had been liberated.) The ether solutions were dried over anhydrous magnesium sulfate, and the ether was removed by distillation through a 6-inch, helix-packed column. The residue was fractionated through the same column under reduced pressure to yield 20 g. (42%) of 3,6-dimethyl-1,2-dimethylenecyclohexane (I), b.p. 50° (15 mm.) $n^{25}D$ 1.4682; 28.5 g. (41%) of 3,6-dimethyl-1-methylene-2-acetoxymethylcyclohexane (VI), b.p. 86° (2.0 mm.), $n^{25}D$ 1.4665; and 11.5 g. (12% recovery) of the starting diacetate V. The yield of diene I, based on unrecovered V and VI, was 88%.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 88.38; H, 11.90. Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.62; H, 10.25.

5,8-Dimethyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic Acid (VII).—To a solution of 2.45 g. (0.025 mole) of maleic anhydride in 75 ml. of ether was added 3.40 g. (0.025 mole) of 3,6-dimethyl-1,2-dimethylenecyclohexane (I). After the solution was heated under reflux for 12 hr., the solvent was removed by evaporation to yield 5.3 g. (90%) of the crude white crystalline 5,8-dimethyl-$\Delta^{9(10)}$-octahydronaphthalene-2,3-dicarboxylic acid (VII), m.p. 136–138°. Three recrystallizations from ether produced an analytically pure sample, m.p. 150.5–151°.

Anal. Calcd. for $C_{14}H_{18}O_3$: C, 71.77; H, 7.74. Found: C, 72.02; H, 7.84.

College Park Maryland

[Contribution No. 1341 from the Sterling Chemistry Laboratory of Yale University]

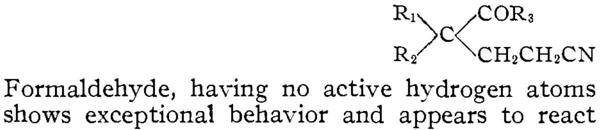
The Reaction of Acrylonitrile with Benzaldehyde under Cyanoethylation Conditions

By Harry H. Wasserman, B. Suryanarayana and David D. Grassetti

Received December 21, 1955

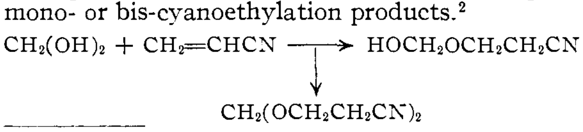
In the presence of Triton B or potassium hydroxide, benzaldehyde reacts with acrylonitrile to form mono- and bis-benzylidene derivatives of β,β'-dicyanodiethyl ether. Other products formed in the presence of potassium hydroxide are α-benzylidene-β-hydroxypropionitrile and β-phenyl-α-formylacrylonitrile. The latter aldehyde is, very probably, formed through an Oppenauer type oxidation of the intermediate unsaturated alcohol. Infrared evidence is presented in support of the assigned structures, and pertinent degradative and synthetic work is described. The stereochemical assignments are based on ultraviolet absorption spectral data.

The reactions of acrylonitrile with aldehydes and ketones containing α-hydrogen atoms have been extensively studied by Bruson and co-workers.[1] These reactions, which take place in the presence of alkaline catalysts, involve a Michael type addition of the carbanion to the activated double bond, and result in the attachment of one or more cyanoethyl residues α to the carbonyl group, as shown



$$CH_2{=}CHCN + (R_1)(R_2)CHCOR_3 \xrightarrow{\text{base}} (R_1)(R_2)C(COR_3)(CH_2CH_2CN)$$

Formaldehyde, having no active hydrogen atoms shows exceptional behavior and appears to react through the oxyanion of the hydrated form, giving mono- or bis-cyanoethylation products.[2]



$$CH_2(OH)_2 + CH_2{=}CHCN \longrightarrow HOCH_2OCH_2CH_2CN \qquad \downarrow\ CH_2(OCH_2CH_2CN)_2$$

In the case of aromatic aldehydes such as benzaldehyde, where there is no active hydrogen, reaction with acrylonitrile takes place under the usual cyanoethylation conditions[1] but the nature of the products formed from these reactions has not previously been established. In connection with other studies, we have reinvestigated this reaction, and are now presenting evidence for the structures of the various products formed.

When acrylonitrile is treated in the cold with benzaldehyde (2:1 molar ratio) using *t*-butyl alcohol as solvent,[3] and in the presence of either Triton B (benzyltrimethylammonium hydroxide) or potassium hydroxide, two main products are formed: A, $C_{13}H_{12}N_2O$, and B, $C_{20}H_{16}N_2O$. Other products formed in smaller yields (in the potassium hydroxide catalyzed reaction) are the alcohol C, $C_{10}H_9ON$, and an aldehyde D, $C_{10}H_7ON$.

Products A and B are neutral, show no carbonyl or hydroxyl absorption in the infrared, but do exhibit strong bands in the nitrile region. A has bands at both 2265 and 2224 cm.$^{-1}$, while B shows only 2229 cm.$^{-1}$ absorption. The ultraviolet ab-

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[1] H. A. Bruson and T. W Riener, This Journal, **64**, 2850 (1942); U. S. Patent 2,353,687 (July 18, 1944); *C. A.*, **38**, 6432 (1944).

[2] J. F. Walker, U. S. Patent 2,352,671 (July 4, 1944), *C. A.*, **39**, 223 (1945).

[3] The reaction is carefully maintained at a temperature below 30° to minimize the reaction with solvent.

sorption spectra of both A and B (Fig. 1) show λ_{max} at 275 mμ. The intensity of absorption of B (ϵ_{max} 38,900) is roughly twice that of A (ϵ_{max} 18,620). Hydrolysis of A in ethanolic potassium hydroxide yields β-ethoxypropionic acid. Ozonolysis of B in chloroform and collection of the reaction products in dimedon yields benzoic acid, but no formaldehyde addition product.

The infrared evidence clearly indicates that product A has both a conjugated and an unconjugated nitrile grouping, while B has only conjugated nitrile. These conclusions follow readily from a comparison of the nitrile absorption of compounds A and B with the absorption of model conjugated and unconjugated nitriles, as summarized in Table I. The ultraviolet absorption evidence is also consistent with the fact that there are twice as many chromophoric groupings ($C_6H_5CH{=}\underset{|}{C}$-CN) in B as in A.

Based on the infrared and ultraviolet absorption spectra of compounds A and B, their molecular composition, and a consideration of the more likely reactions between benzaldehyde and acrylonitrile under these conditions, structures I and II (Chart I) were regarded as reasonable possibilities for A and B, respectively. It is known[4] for example that water reacts with acrylonitrile in the presence of alkaline catalysts to form β,β'-dicyanodiethyl ether. Furthermore, when salicylaldehyde is heated with an excess of acrylonitrile in the presence of Triton B, some 3-cyano-1,2-benzopyran (III) can be isolated, along with other products.[5]

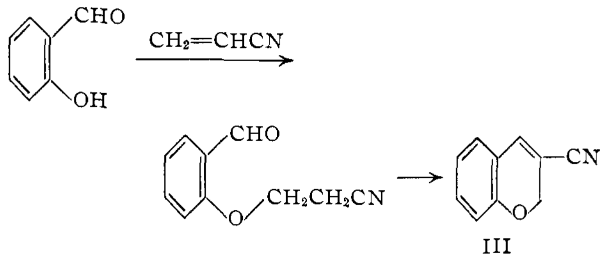


TABLE I

INFRARED ABSORPTION SPECTRA[6]

	Unconjugated	Conjugated
β-Hydroxypropionitrile	2265	
β-Bromopropionitrile	2270	
β,β'-Dicyanodiethyl ether	2265	
1,4-Dicyano-n-butane	2265	
Acrylonitrile		2249
β-Bromo-α-benzylidenepropionitrile (V)		2234
1,4-Dicyano-1,4-dibenzylidene-n-butane (VIII)		2222
A (β,β'-Dicyano-α-benzylidenediethyl ether) (I)	2265	2224
B (β,β'-Dicyano-α,α'-dibenzylidenediethyl ether) (II)		2229
C (β-Hydroxy-α-benzylidenepropionitrile) (IV)		2224
D (β-Phenyl-α-formylacrylonitrile) (VI)		2249

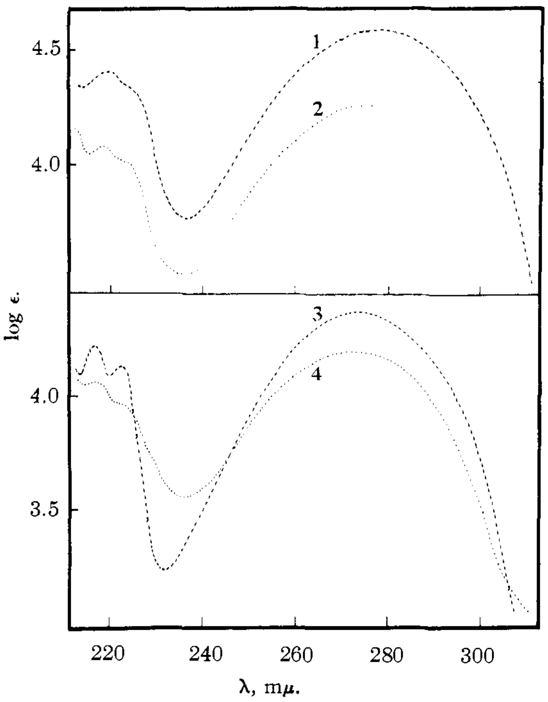
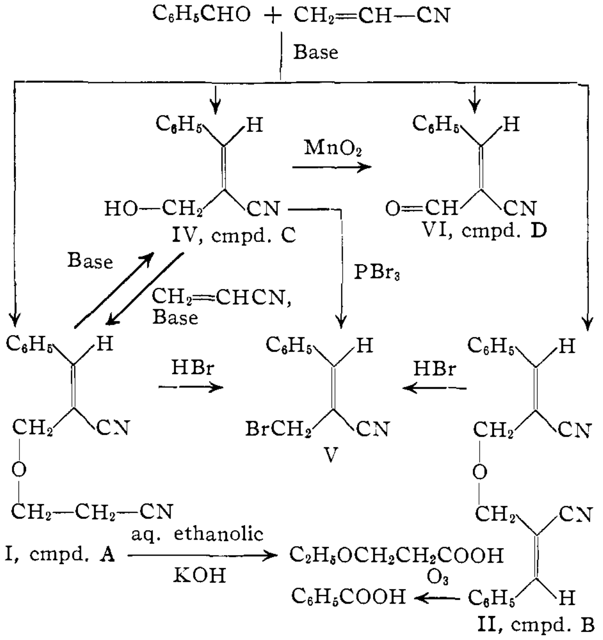


Fig. 1.—Ultraviolet absorption spectra in 95% ethanol: 1, compound B (II); 2, compound A (I); 3, *trans*-cinnamonitrile; 4, compound C (IV).

CHART I



Proof that substances A and B are correctly represented by structures I and II, respectively, is given below. It will also be shown that the alcohol C is IV, and the aldehyde D is VI.

Reaction of both compounds A and B with hydrogen bromide in glacial acetic acid led to the same bromide, $C_{10}H_8NBr$, m.p. 54–55°, exhibiting a conjugated nitrile band in the infrared (Table I). That this bromide has the structure V was shown by its preparation in the following way. β-Hydroxypropionitrile was condensed with benzaldehyde in the

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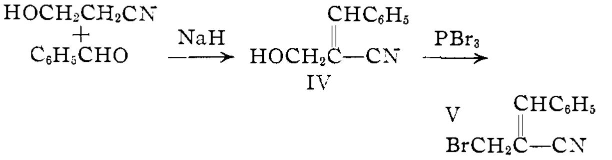
[4] H. A. Bruson and T. W. Riener, THIS JOURNAL, 65, 23 (1943).

[5] G. B. Bachman and H. A. Levine, *ibid.*, 70, 599 (1948).

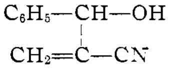
[6] All the spectra were taken in chloroform solution (0.1-mm. cell thickness) using a Perkin–Elmer model 21B infrared spectrophotometer. The positions of all nitrile bands determined in this work were calibrated with the carbon dioxide spectrum.

presence of sodium hydride to form an unsaturated alcohol, assigned the structure IV (*vide infra*). Further treatment of IV with phosphorus tribromide led to a bromide which was identical with the degradation product V.



$$\underset{\text{C}_6\text{H}_5\text{CHO}}{\overset{\text{HOCH}_2\text{CH}_2\text{CN}}{+}} \xrightarrow{\text{NaH}} \underset{\text{IV}}{\text{HOCH}_2\overset{\overset{\text{CHC}_6\text{H}_5}{\|}}{\text{C}}\text{—CN}} \xrightarrow{\text{PBr}_3} \underset{\text{V}}{\text{BrCH}_2\overset{\overset{\text{CHC}_6\text{H}_5}{\|}}{\text{C}}\text{—CN}}$$

It is pertinent to point out at this stage of the structure proof that the preparation of the unsaturated alcohol IV, outlined above, does not distinguish between the primary alcohol IV and an alternative possibility, the secondary alcohol, IVa.



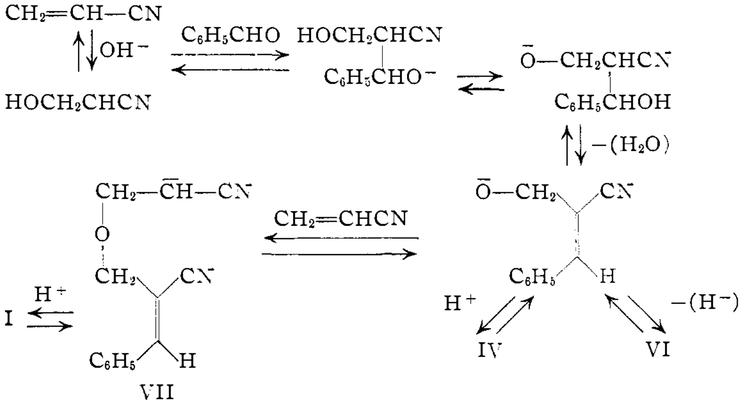
$$\begin{array}{l}\text{C}_6\text{H}_5\text{—CH—OH}\\ \qquad\quad |\\ \text{CH}_2\text{=C—CN}\end{array}$$

IVa

The latter structure can be considered, *a priori*, to be unlikely, in view of the fact that ozonolysis of compound B (which can be cleaved to the same bromide as is formed from the unsaturated alcohol) gives no evidence for a terminal methylene group. The following additional evidence clearly rules out the alcohol IVa as a possibility: (i) The ultraviolet absorption spectrum of the alcohol (λ_{max} 273 mμ, log ϵ 4.18) corresponds very closely (Fig. 1) to the spectrum[7] of *trans*-cinnamonitrile[8] (λ_{max} 273 mμ, log ϵ 4.36) both compounds apparently incorporating the common chromophoric grouping $\text{C}_6\text{H}_5\text{—CH=}\underset{|}{\text{C}}\text{—CN}$. Structure IVa should, on the other hand, show much weaker absorption in the ultraviolet corresponding to a superposition of acrylonitrile absorption[9] (λ_{max} 214–217 mμ, log ϵ 1.70) and that of benzyl alcohol[10] (λ_{max} 259 mμ, log ϵ 2.27). (ii) Oxidation of the unsaturated alcohol using freshly precipitated manganese dioxide[11] led smoothly to an unsaturated aldehyde VI (Chart I) (carbonyl absorption at 5.85 μ, positive Schiff test). The aldehyde VI was shown to be identical with compound D isolated from the original benzaldehyde–acrylonitrile reaction mixture. Reaction of β-hydroxy-α-benzylidenepropionitrile with acrylonitrile in the presence of potassium hydroxide led readily to compound A. This separate preparation of A lends strong support to structure I, and is also good evidence for the intermediacy of the alcohol IV in the formation of both I and II during the benzaldehyde–acrylonitrile reaction.

A summary of the reactions involved in the characterization of compounds A, B, C and D is given in Chart I. Attempts to prepare the dibenzylidene derivative B (II) by the reaction of benzaldehyde with A (I) or with β,β'-dicyanodiethyl ether in the presence of a variety of bases led only to elimination reactions forming alcohols. In Williamson type reactions whereby the bromide V was refluxed with the sodium or potassium salt of the alcohol IV, small amounts of compound B were formed, as shown by the infrared spectra of the crude reaction mixtures. The pure dibenzylidene derivative II could not, however, be isolated in this way.[12]

A reaction scheme for the formation of the products I, IV and VI is outlined below. Further condensation of the intermediate anion VII with benzaldehyde, followed by dehydration, would lead to the bis-benzylidene derivative II. Formation of the aldehyde VI by an oxidation–reduction reaction, involving the alcohol IV and benzaldehyde in base, may be pictured in terms of an Oppenauer type hydride ion shift.[13] There are many analogies for the involvement of benzaldehyde in this sort of oxidation, as in the Cannizzaro reaction, and in the conversion of benzaldehyde to a mixture of benzophenone and benzyl alcohol by the action of phenylmagnesium bromide.[14]



Stereochemistry.—In formulating the reaction products I, II, IV and VI (Chart I) all structures are written with a *trans* arrangement of phenyl and cyano groups about the double bond. This stereochemical assignment is based on the ultraviolet absorption spectra of compounds A, B and C, all of which contain a strong band at 273 mμ. The latter absorption corresponds very closely to that of *trans*-cinnamonitrile (Fig. 1). *Cis* compounds in this series show weaker absorption at lower wave lengths.[15]

Acknowledgment.—This investigation was supported by a research grant (G-4072) from the National Institutes of Health, Public Health Service.

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[7] Pure *trans*-cinnamonitrile, m.p. 22.5–23.5°, n^{20}_{D} 1.6030 (G. B. Kistiakowsky and W. R. Smith, THIS JOURNAL, **58**, 2428 (1936), report m.p. 22°, $n^{20.2}_{D}$ 1.6031), was obtained from commercial cinnamonitrile by fractional distillation.

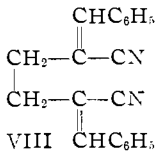
[8] M. Coenen and M. Pestemer, *Z. Elektrochem.*, **57**, 785 (1953).

[9] M. T. Rogers, THIS JOURNAL, **69**, 2545 (1947).

[10] T. W. Campbell, *et al.*, *ibid.*, **69**, 880 (1947).

[11] J. Attenburrow, *et al.*, *J. Chem. Soc.*, 1094 (1952).

[12] From one such reaction mixture, the coupling product VIII was isolated. The latter must have been formed by a Wurtz type of reaction involving the bromide V and unreacted potassium metal.



$$\begin{array}{l}\qquad\ \ \text{CHC}_6\text{H}_5\\ \qquad\quad \|\\ \text{CH}_2\text{—C—CN}\\ |\\ \text{CH}_2\text{—C—CN}\\ \qquad\quad \|\\ \qquad\ \ \text{CHC}_6\text{H}_5\end{array}$$

VIII

[13] W. v. E. Doering and T. C. Aschner, THIS JOURNAL, **75**, 393 (1953).

[14] J. Marshall, *J. Chem. Soc.*, **107**, 520 (1915).

[15] Whereas *trans*-cinnamic acid absorbs at λmax 273 mμ, log ϵ 4.32, the corresponding *cis*-cinnamic acid absorbs at λmax 264 mμ, log ϵ 3.98 (A. Smakula and A. Wasserman, *Z. physik. Chem.*, **155A**, 353 (1931)).

Experimental[16]

Reaction of Acrylonitrile with Benzaldehyde in the Presence of Potassium Hydroxide.—Acrylonitrile (106 g., 2 moles) was added dropwise during 40 minutes to a stirred mixture of freshly distilled benzaldehyde (106 g., 1 mole), *t*-butyl alcohol (100 g.) and a 30% solution (5 ml.) of potassium hydroxide in methanol. The mixture was maintained below 30°, and, after stirring for 8 hours, it was acidified to *p*H 3 with 10% hydrochloric acid, diluted with excess ether, and washed repeatedly with water. The ether solution was dried over sodium sulfate, and, on evaporation, yielded a brown oil (200 g.) which was fractionated *in vacuo*. The yellow oil which boiled at 200–240° (0.5 mm.) was redistilled *in vacuo*, and three main fractions were collected: 1, 18.5 g., b.p. 145–180°; 2, 45 g., b.p. 180–210°; and 3, 27.1 g., b.p. 220–240°.

Fraction 1 solidified partially; the colorless solid (3.5 g.) (compound **D**) was collected by filtration, and crystallized four times from a mixture of benzene and petroleum ether (60–75°), m.p. 99–100°. It gave a positive test with Schiff reagent.

Anal. Calcd. for $C_{10}H_7ON$: C, 76.42; H, 4.49; N, 8.91; mol. wt., 157. Found: C, 76.43; H, 4.45; N, 9.02; mol. wt., 144 (Rast).

The 2,4-dinitrophenylhydrazone of the aldehyde from fraction 1 crystallized from glacial acetic acid in elongated orange plates, m.p. 274–275°.

Anal. Calcd. for $C_{16}H_{11}N_5O_4$: C, 56.97; H, 3.29. Found: C, 57.25; H, 3.35.

Further fractionation of fraction 2 gave a small amount (1 g.) of a low boiling liquid (135–145°, 0.3 mm.) (compound C) which was shown to be β-hydroxy-α-benzylidenepropionitrile by comparison of the infrared spectrum with that of an authentic sample prepared by a different route (see below). The main portion of fraction 2 on refractionation, gave a light yellow liquid, b.p. 170° (0.3 mm.) (compound A).

Anal. Calcd. for $C_{13}H_{12}ON_2$: C, 73.54; H, 5.70; N, 13.20; mol. wt., 212.3. Found: C, 74.05; H, 5.68; N, 13.00; mol. wt., 225 (Rast).

Fraction 3 solidified completely, and was recrystallized from ethanol forming colorless needles, m.p. 73° (compound B).

Anal. Calcd. for $C_{20}H_{16}ON_2$: C, 79.97; H, 5.37; N, 9.33; mol. wt., 300.4. Found: C, 80.23; H, 5.32; N, 9.28; mol. wt., 277 (Rast).

Alkaline Hydrolysis of Compound A.—A mixture of compound A (25 g.) and 350 ml. of 15% potassium hydroxide in 80% ethanol was refluxed for 50 hours. The cooled mixture was poured into water, acidified with hydrochloric acid and extracted three times with ether. The oily, red product obtained after removal of ether was dissolved in an excess of 10% aqueous sodium hydroxide and the tarry impurities were removed by ether extraction. The solution was acidified, and the oil thus obtained was separated by means of ether extraction, removal of solvent and distillation *in vacuo*. The major fraction was a colorless, nitrogen-free liquid (9 g.), b.p. 74° (0.5 mm.). It was acidic, and gave negative tests for the presence of unsaturation. A mixture of the acid (0.5 g.) and *p*-toluidine (1.5 g.) was heated in an oil-bath at 190° for 30 minutes, cooled and acidified with dilute hydrochloric acid. The *p*-toluidide of β-ethoxypropionic acid which separated, was crystallized from aqueous ethanol, m.p. 59–60°.

Anal. Calcd. for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found: C, 69.75; H, 8.45; N, 6.68.

The free acid was found to be identical with β-ethoxypropionic acid by comparison of its infrared spectrum with that of an authentic sample prepared by the action of sodium ethoxide on β-bromopropionic acid.

Ozonolysis of Compound B.—A solution of compound B (1.18 g.) in chloroform (40 ml.) was ozonized for 4 hours while cooling in an ice-bath. At the end of this time, the solution was treated with 20 ml. of water, and the chloroform was removed under reduced pressure at room temperature. The resulting aqueous solution was diluted with 250 ml. of water and distilled. The distillate (200 ml.), on treatment with dimedon did not yield an addition product (showing the absence of formaldehyde). The residue, on cooling, deposited a crystalline product, m.p. 121° (0.45 g., 50% yield), identified as benzoic acid by a mixture melting point determination.

β-Bromo-α-benzylidenepropionitrile (V) from Compounds A and B.—(a) A mixture of compound A (6.75 g.), glacial acetic acid (90 ml.), and 48% hydrobromic acid (50 ml.) was refluxed for two hours, cooled to room temperature, and poured over ice. The white precipitate thus obtained was collected, washed with water, and dried. Recrystallization from petroleum ether (60–100°) yielded a colorless compound (2.1 g.), m.p. 50–55°. On extracting with warm petroleum ether (60–100°) and cooling, colorless needles were deposited, m.p. 54–55°.

Anal. Calcd. for $C_{10}H_8BrN$: C, 54.08; H, 3.63; N, 6.31; Br, 35.99. Found: C, 54.22; H, 3.71; N, 6.59; Br, 35.98.

(b) A mixture of compound B (5.5 g.), glacial acetic acid (90 ml.), and 48% hydrobromic acid (40 ml.) was refluxed for two hours, cooled to room temperature and poured over crushed ice (300 g.). The colorless precipitate was collected, washed with water, and dried (6.5 g.), m.p. 40° (unsharp). After two crystallizations from petroleum ether (60–100°) colorless needles, m.p. 54–55°, were obtained. The infrared spectrum of this compound is identical with that of the bromide obtained in the procedure described in (a) above.

β-Hydroxy-α-benzylidenepropionitrile (IV).—A well-cooled mixture of benzaldehyde (212 g., 2 moles), β-hydroxypropionitrile (142 g., 2 moles) and anhydrous dioxane (2.5 l.) was kept in an atmosphere of nitrogen during stirring. To the above mixture, sodium hydride (96 g., 4 moles) was added during four hours, and the thick yellow mixture thus obtained was stirred overnight. The excess sodium hydride was then decomposed by cautious addition of ice-cold water with stirring, and the mixture was then acidified (litmus) using 10% aqueous hydrochloric acid. To the solution was added 1500 ml. of ether, and the ether layer was separated, washed with aqueous sodium carbonate followed by water, and then dried over anhydrous sodium sulfate. Removal of ether from the solution yielded a dark brown oil (125 g.). This oil was fractionated *in vacuo* using a Vigreux column. The fractions boiling below 110° (0.2 mm.) consisted largely of the starting materials as shown by their infrared spectra. The fraction, b.p. 135–140° (0.2 mm.) (60 g.), showed a distinct hydroxyl band and a single conjugated nitrile band in the infrared.

Anal. Calcd. for $C_{10}H_9ON$: C, 75.45; H, 5.70; N, 8.80. Found: C, 75.68; H, 5.62; N, 8.80.

Conversion of β-Hydroxy-α-benzylidenepropionitrile to the Bromide (V).—A solution of phosphorus tribromide (8.3 g., 0.03 mole) in carbon tetrachloride (25 ml.) was added during 1 hour to a well-cooled and stirred solution of β-hydroxy-α-benzylidenepropionitrile (14.3 g., 0.09 mole) in carbon tetrachloride (50 ml.). The mixture was gradually heated to the boiling point and refluxed for one additional hour. The solvent was then removed under reduced pressure, and the residue was extracted with ether. The ether extract was washed with ice-cold aqueous sodium bicarbonate (5%) followed by water and dried over anhydrous sodium sulfate. Removal of the ether yielded a yellow oil (19 g.) which solidified on standing in the refrigerator. One crystallization from a mixture of benzene and petroleum ether (60–75°) gave a pure sample, m.p. 54°, found to be identical (mixture melting point and infrared spectra) with the bromo derivative obtained by the HBr cleavage of both compounds A and B as described above.

Attempted Williamson Synthesis of β,β′-Dicyano-α,α′-dibenzylidenediethyl Ether (Compound B).—Potassium sand (0.98 g., 0.025 mole) was prepared in 40 ml. of dry dioxane in an atmosphere of nitrogen. The mixture was cooled to room temperature and a solution of β-hydroxy-α-benzylidenepropionitrile (4.5 g.) in dioxane (25 ml.) was added dropwise during 15 minutes. After stirring for one hour longer, a solution of β-bromo-α-benzylidenepropionitrile (5.5 g., 0.025 mole) in dioxane (30 ml.) was gradually added. The mixture was slowly heated to boiling, refluxed for two hours, and filtered hot in order to remove the potassium bromide which had separated. The solvent was removed from the filtrate under reduced pressure and the brown oil thus obtained, was distilled *in vacuo*. The viscous yellow oil boiling at 220–235° (0.5 mm.) was collected. Although no pure crystalline product could be obtained from this reaction mixture the infrared spectrum of the oil is remarkably similar to that of compound B.

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(16) All m.p.'s are uncorrected.

In another run using benzene as a solvent, the fraction boiling at 220–260° (0.5 mm.) solidified to a crystalline mass which gave colorless needles from ethanol. The elementary composition of these crystals corresponds to 1,4-dicyano-1,4-dibenzylidenebutane.

Anal. Calcd. for $C_{20}H_{16}N_2$: C, 84.48; H, 5.67; N, 9.85. Found: C, 84.37; H, 5.43; N, 9.99.

β-Phenyl-α-formylacrylonitrile (Independent Preparation of Compound D).—A mixture of β-hydroxy-α-benzylidenepropionitrile (0.20 g.), freshly precipitated manganese dioxide (2.0 g.) and carbon tetrachloride (12 ml.) was stirred at room temperature for two hours. The mixture was filtered to remove the excess manganese dioxide and the latter washed with a mixture of carbon tetrachloride and chloroform. The combined filtrates on evaporation *in vacuo* gave a lustrous white residue (0.16 g., 80% yield) which crystallized from benzene–petroleum ether in colorless needles, m.p. 97–99°, and was found to be identical with compound D (VI) by mixture melting point and infrared spectra.

Formation of β-Hydroxy-α-benzylidenepropionitrile (IV) from Compound A (I).—A mixture of benzaldehyde (21.2 g.), compound A (12.4 g.), *t*-butyl alcohol (35 ml.) and a solution (3 ml., 30%) of potassium hydroxide in methanol was stirred at 40–50° for 5 hours and allowed to stand overnight. It was then neutralized with dilute hydrochloric acid (10%) and extracted with ether. The ether layer was washed repeatedly with water and dried over anhydrous sodium sulfate. The oil obtained after removal of ether was distilled *in vacuo* to yield recovered benzaldehyde (14 g.) and an oil (2 g.), b.p. 150° (0.3 mm.). The infrared spectrum of the latter shows characteristic absorption of hydroxyl and conjugated nitrile groups and corresponds exactly to the spectrum of β-hydroxy-α-benzylidenepropionitrile (IV). The alcohol IV was also obtained when the above reaction was carried out in the presence of sodium ethoxide or sodium hydride in dioxane.

Conversion of Compound C (IV) to β,β'-Dicyano-α-benzylidenediethyl Ether (I).—Acrylonitrile (0.53 g.) was added dropwise to a stirred mixture of β-hydroxy-α-benzylidenepropionitrile (1.59 g.) and one drop of 20% potassium hydroxide solution, at 40°. The temperature was maintained at 40–42° for one hour longer and the stirring was continued at room temperature for 24 hours. The mixture was neutralized with dilute hydrochloric acid, and the product isolated by ether extraction. The yellow oil thus obtained was distilled *in vacuo* and the fraction b.p. 155–175° (0.5 mm.) (0.55 g.) was collected. Redistillation of this fraction yielded a pure sample, b.p. 175–180° (0.5 mm.), which was shown to be identical (infrared spectra) with compound A.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XL. *cis–cis-* and *cis–trans*-1,3-Cycloöctadiene from Cycloöcten-3-yldimethylamine[1]

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Application of the Hofmann exhaustive methylation procedure to cycloöcten-3-yldimethylamine has been shown to yield a mixture of 1,3-cycloöctadienes. The mixture was separated by extraction with 20% aqueous silver nitrate into the *cis–trans* isomer (15%), soluble in the silver nitrate solution, and the *cis–cis* isomer (41%), which was insoluble. Cyclooctan-3-yldimethylamine oxide on heating formed *cis–cis*-1,3-cycloöctadiene (50%) by elimination of N,N-dimethylhydroxylamine. O-Cycloöcten-3-yl-N,N-dimethylhydroxylamine also was formed to the extent of approximately 19% by rearrangement of the cycloöctenyl group from the nitrogen to the oxygen atom.

1,3-Cycloöctadiene has been prepared by dehydrobromination of 3-bromocycloöctene with quinoline and also by application of the Hofmann exhaustive methylation procedure to cycloöcten-3-yldimethylamine. Since the properties of the 1,3-cycloöctadiene from the two methods of preparation were different, it was suggested that the product of the exhaustive methylation reaction contained the less stable *cis–trans* isomer in addition to the *cis–cis* isomer.[3] Evidence supporting this view has been reported recently. The mixture was treated with phenyl azide and with hexachlorocyclopentadiene; derivatives of the more reactive (presumably *cis–trans*) isomer were formed in amounts corresponding to the presence of 10% in one experiment and 30% in another.[4]

In the present work, the method previously used for the separation of *cis-* and *trans*-cycloöctene[5] has been applied successfully to the separation of the mixture of 1,3-cycloöctadienes prepared by the Hofmann exhaustive methylation route. The thermal decomposition of cycloöcten-3-yldimethylamine oxide also has been investigated.

Cycloöcten-3-yltrimethylammonium hydroxide was prepared by a method described previously[3] and decomposed by distillation under reduced pressure. The distillate was extracted with 20% (by weight) aqueous silver nitrate, and the fraction that was insoluble in this reagent was distilled. In this way *cis–cis*-1,3-cycloöctadiene, with an infrared spectrum essentially identical with a sample prepared by dehydrobromination of 3-bromocyclooctene, was isolated in 41% yield. Addition of ammonium hydroxide to the silver nitrate extract formed an unstable hydrocarbon, C_8H_{12} (I), in 15% yield. This hydrocarbon had a characteristic unpleasant odor resembling that of cyclopentadiene. It was found necessary to protect the hydrocarbon I from atmospheric oxygen and to determine physical properties and carry out reactions immediately with freshly prepared material, because of the rapidity with which it polymerized. The hydrocarbon could not be stored at −80° without change in its index of refraction, but it formed a more stable crystalline 1:1 adduct with silver nitrate from which it could be regenerated by addition of ammonium hydroxide.

The structure of the hydrocarbon I was de-

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(2) United States Rubber Co. Fellow, 1954–1955.

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