

This absorption is characteristic of the *cis* ethylenic linkage $RCH=CHR'$ in a six-membered ring. Substitution at this linkage increases the frequency to 1681 cm.^{-1} ¹⁴ (1674)^{11,15} as noted in 1-methylcyclohexene spectra ($RR'C=CHR''$). On the basis of relative VPC retention time and spectral evidence only, an unsaturated isomer of component A is suggested as the structure of the second by-product, component B; *i.e.*, 1-methyl-1-cyclohexylcyclohexene-2 or -3.

Since components A and B were only obtained in minute quantities by v.p.c. collection, it was not possible to obtain direct chemical evidence, such as carbon-hydrogen analyses.

Experimental

Infrared spectra were obtained with a Perkin-Elmer Model 21 double-beam infrared spectrophotometer with sodium chloride optics. Frequencies were checked with a polystyrene film reference and estimated to be accurate and reproducible to $0.01\ \mu$. Components A and B were collected in a micro cavity cell (0.05 mm.) and their spectra obtained using a beam condenser attachment. Component C was examined in carbon tetrachloride solution and in a potassium bromide pellet.

Near infrared spectra were run on a Cary Model 14 recording spectrophotometer in liquid sample cells of 1- and 10-mm. path lengths.

The nuclear magnetic resonance spectrum was determined by Varian Associates, Palo Alto, California, on a Varian Model A-60 spectrometer at 60 Mc., with a reported accuracy of $\pm 1\text{ c.p.s.}$ The sample was run in deuteriochloroform solution, with tetramethylsilane as the internal standard.

Vapor phase chromatograms were determined on a Perkin-Elmer Model 154-B Vapor Fractometer, equipped with a 6-ft. column of 16% *m*-bis(*m*-phenoxyphenoxy) benzene on 35-80 mesh Chromosorb W, operating at 164° , outlet flow 100 cc. helium/min., inlet 15 p.s.i.g. Collection of components A and B was made from a 6-ft. column of 20% Apiezon L on 35-80 mesh Chromosorb W, operating at 168° , outlet flow 50 cc. helium/min., inlet 30 p.s.i.g.

1,1'-Dimethylbicyclohexyl.—The Grignard reagent was prepared from 1-chloro-1-methylcyclohexane¹⁶ (245 g., 1.848 moles), magnesium turnings (49.4 g., 2.03 g.-atoms) and 840 ml. of dry ether. Cuprous chloride (11.1 g., 0.112 mole) and copper turnings (12.0 g., 0.189 g.-atom) were added, followed by the dropwise addition of 1-chloro-1-methylcyclohexane (245 g., 1.848 moles) dissolved in 490 ml. of dry ether. The mixture was refluxed for 48 hr. The bulk of the ether was distilled out of the system, being simultaneously replaced with dry toluene. The mixture was refluxed for an additional 8 hr. Hydrolysis was effected by the addition of 490 ml. of saturated aqueous ammonium chloride. The hydrolysate was filtered, and the filter cake was thoroughly washed with ether. The washings were combined with the filtrate, and solvent as well as residual low-boiling disproportionation products were removed by distillation at atmospheric pressure. The residual oil was then carefully distilled from sodium. A series of four distillation cuts were collected, at a high reflux ratio, from $80-96.5^\circ/1\text{ mm.}$, n_D^{20} of liquid cuts 1.4926-1.4965. Distillate collected from $95.5-96.5^\circ/1\text{ mm.}$ solidified in the receiver. The yield of 1,1'-dimethylbicyclohexyl (based on v.p.c.) was 8.6 g., or 2%.

When the reaction was repeated on a 10.6-mole scale, the isolated yield of hydrocarbon of at least 99 area % purity (v.p.c.) was 50 g. (2%), m.p. $42-43^\circ$.

Anal. Calcd. for $C_{14}H_{26}$: C, 86.5; H, 13.5; mol. wt. 194. Found: C, 86.6; H, 13.5; mol. wt. (Rast Method), 191.

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Reaction of 1,2-Dihaloethanes with Sodium Cyanide

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A well known general method for the preparation of alkyl cyanides is the reaction of sodium or potassium cyanide with an alkyl halide in alcohol solution. Polymethylene dicyanides also may be prepared by this method.¹

The reaction of 1,3-dibromopropane with cyanide ion gives trimethylene cyanide in 86% yield.¹ Reaction of 1-bromo-3-chloropropane with cyanide ion gives 4-chlorobutyronitrile in 70% yield.¹ Thus it is apparent that trimethylene dihalides react with cyanide ion by the stepwise nucleophilic substitution of cyanide ion on the carbon containing halogen. Ethylene dibromide has been treated with cyanide ion to produce succinonitrile in 80% yield.² Although the product corresponding to that produced from the higher polymethylene dihalides is obtained, it has been found that reaction of the ethylene dihalides proceeds by a different path.

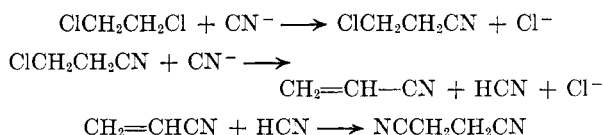
Ethylene dichloride reacted very slowly with sodium cyanide in methanol at 50° . The approximate second-order rate constant was $3.0 \times 10^{-4}\text{ l. mole}^{-1}\text{ hr.}^{-1}$. Reaction of 3-chloropropionitrile, however, was extremely rapid at room temperature, having a rate constant greater than $68\text{ l. mole}^{-1}\text{ hr.}^{-1}$. The products from this latter reaction were acrylonitrile, hydrogen cyanide, and chloride ion. The following, then, represents a more reasonable path by which succinonitrile may be formed from this reaction

(15) Private communication from Prof. R. C. Lord.

(16) H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

(1) R. B. Wagner and H. D. Zook, "Synthetic Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1953, p. 590.

(2) R. B. Wagner and H. D. Zook, *ibid.*, p. 614.



Cyanoethylation of hydrogen cyanide was found to be considerably slower than formation of acrylonitrile from 3-chloropropionitrile and cyanide ion. If separation of acrylonitrile from the reaction mixture at a rate greater than cyanoethylation of hydrogen cyanide could be accomplished, it should be possible to use this reaction as a preparative method for acrylonitrile.

Friedman and Shechter³ have recently shown that the use of dimethyl sulfoxide as solvent greatly enhances the rate of cyanide ion reactions with alkyl halides. Ethylene dichloride, ethylene dibromide, and 1-bromo-2-chloroethane reacted with sodium cyanide in dimethyl sulfoxide in a system placed under vacuum which allowed the acrylonitrile to be flashed from the mixture as it was formed. The following results were obtained.

Ethylene dihalide	% Yield acrylonitrile
$\text{ClCH}_2\text{CH}_2\text{Cl}$	6.4
$\text{ClCH}_2\text{CH}_2\text{Br}$	45.0
$\text{BrCH}_2\text{CH}_2\text{Br}$	82.4

The pressure which could be placed on the system was dependent on the boiling point of the ethylene dihalide. With ethylene dibromide a much lower pressure was possible, resulting in faster rate of removal of acrylonitrile from the reaction mixture and thus higher yield.

Experimental

Rate of Reaction of Sodium Cyanide with Ethylene Dichloride in Anhydrous Methanol.—Sodium cyanide was dissolved in anhydrous methanol at room temperature to prepare an approximately saturated solution. The solution was filtered and added to 0.0500 mole of ethylene dichloride in a 100.0-ml. volumetric flask. Aliquots (10.0 ml.) of this solution were pipetted into separate flasks and these were placed into a constant temperature bath held at $50 \pm 1^\circ$. At various time intervals a sample was removed and the cyanide ion concentration determined by titration with standard silver nitrate solution in the presence of ammonia and potassium iodide.⁴ The following data were obtained.

Time, hr.	[CN ⁻] mole/l.
0	1.088
28.5	1.009
48.0	0.940
148.0	.724
192.5	.652

From these data the approximate second-order rate constant was evaluated as 3.0×10^{-4} l. mole⁻¹ hr.⁻¹.

Reaction of Sodium Cyanide with 3-Chloropropionitrile.—A saturated solution of sodium cyanide in methanol was

prepared and added to 0.0500 mole of 3-chloropropionitrile in a 100.0-ml. volumetric flask at room temperature. The concentration of sodium cyanide was approximately 1.0 M. Immediately a precipitate began to form and after 5 min. the precipitation appeared to be complete. An aliquot of the liquid portion of the reaction mixture was analyzed for cyanide ion and the solution was found to be 0.946 M in cyanide ion. The mixture was filtered and the precipitate was found to be practically pure sodium chloride. Analysis of the liquid portion of the reaction mixture by vapor phase chromatography revealed that the solution contained no 3-chloropropionitrile but contained 0.0425 mole of acrylonitrile.

Preparation of Acrylonitrile from Ethylene Dibromide and Sodium Cyanide.—A flask was fitted with a stirrer, an inlet through which solid could be added in small portions, and a reflux condenser with the exit leading through a Dry Ice trap to a vacuum pump. In the flask were placed 500 ml. of dimethyl sulfoxide and 187.8 g. (1.00 mole) of ethylene dibromide. The mixture was heated to 100° and the pressure lowered until refluxing in the reflux condenser was vigorous (74 mm.). Solid sodium cyanide (25.8 g., purity 95%, 0.500 mole) was added in small portions during a period of 32 min. After addition was complete, the pressure was lowered and heating continued until there was nothing passing into the Dry Ice trap. From the Dry Ice trap was obtained 121.1 g. of liquid. By vapor phase chromatographic analysis of this liquid, it was found to be a solution of 10.9 g. (0.206 mole) of acrylonitrile in ethylene dibromide. This corresponds to 82.4% yield to acrylonitrile based on consumed sodium cyanide.

The same procedure carried out on 1-bromo-2-chloroethane and ethylene dichloride gave, respectively, 45.0 and 6.4% yield of acrylonitrile.

The column used for vapor phase chromatographic analysis was an 8 ft. \times $\frac{3}{16}$ in., stainless steel tube packed with a composition of Celite and tricresyl phosphate which was 30% tricresyl phosphate. The area under the acrylonitrile peak in the chromatograms was measured with a planimeter and compared to a calibration curve.

The Base-catalyzed Isomerization of Allyl to Propenyl Sulfides

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The fact that allyl sulfides will isomerize to their propenyl analogs under the influence of base has been shown previously by Tarbell and co-workers.^{1,2} In view of recent investigation on the base-catalyzed isomerizations of allyl to propenyl ethers,³⁻⁵ 1- to 2-olefins,⁶ and allyl- to propenylamines,⁷ it was of interest to extend the investigation on the allyl sulfide isomerizations. In particular, it was

(1) D. S. Tarbell and M. A. McCall, *J. Am. Chem. Soc.*, **74**, 48 (1952).

(2) D. S. Tarbell and W. E. Lovett, *ibid.*, **78**, 2259 (1956).

(3) C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961).

(4) T. J. Prosser, *ibid.*, **83**, 1701 (1961).

(5) D. M. Simons and J. J. Verbanc, *J. Polymer Sci.*, **44**, 303 (1960).

(6) A. Shriesheim, J. H. Hofmann, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **83**, 3731 (1961).

(7) C. C. Price and W. H. Snyder, *Tetrahedron Letters*, **2**, 69 (1962).

(3) L. Friedman and H. Shechter, *J. Org. Chem.*, **25**, 877 (1960).

(4) H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., Princeton, N. J., 1940, p. 186.