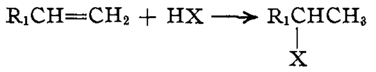
[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Addition of Hydrogen Bromide to α-Ethoxyacrylonitrile

BY CHARLES C. PRICE, EUGENE C. COYNER AND DELOS DETAR

The mode of addition of unsymmetrical reagents to unsymmetrical olefin derivatives has been the subject of a great deal of investigation and there has been much speculation concerning the factors influencing the course of the addition.[1] In general, for the simplest case, $RCH{=}CH_2$, normal addition has been found to obey Markownikoff's rule if R is a group which is also *o,p*-orienting when attached to the benzene ring.



$$R_1CH{=}CH_2 + HX \longrightarrow R_1\underset{\displaystyle X}{\underset{|}{C}}HCH_3$$

(R_1 = alkyl,[2] aryl,[3] halogen,[4] CH_2X,[5] OR[6])

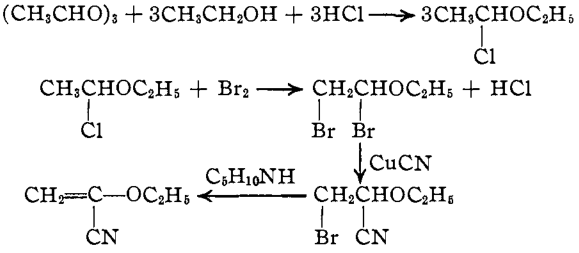
However, if R is a *m*-orienting group in benzene, addition ordinarily occurs in the opposite sense.

$$R_2CH{=}CH_2 + HX \longrightarrow R_2CH_2CH_2X$$

(R_2 = —CHO,[7] —$COCH_3$,[8] —COOH,[9] —COOR,[10] —$CHCl_2$,[11] —NO_2[12])

For certain types of disubstituted olefins, such as $R_1R_2C{=}CH_2$, $R_1CH{=}CHR_1'$ and $R_2CH{=}CHR_2'$, the two substituents would be acting in opposition. One case of the first type is that of methacrylic acid and its esters,[13] in which R_2 is a carboxyl or carbalkoxyl group and R_1 is a methyl group. Since these compounds add hydrogen bromide, for example, in such a manner as to yield the β-bromo derivatives, the carboxyl group evidently has a considerably stronger orienting influence than the methyl group. α-Chloroacrylic acid behaves in a similar manner, yielding α,β-dichloropropionic acid when treated with hydrogen chloride.[14]

The purpose of the present investigation was concerned with the preparation of a similar substance in which a more powerful *o,p*-orienting group was present. We have therefore prepared α-ethoxyacrylonitrile (I) according to the sequence of reactions



$$(CH_3CHO)_3 + 3CH_3CH_2OH + 3HCl \longrightarrow 3CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HOC_2H_5$$

$$CH_3\underset{\displaystyle Cl}{\underset{|}{C}}HOC_2H_5 + Br_2 \longrightarrow \underset{\displaystyle Br}{\underset{|}{C}}H_2\underset{\displaystyle Br}{\underset{|}{C}}HOC_2H_5 + HCl$$

$$\underset{\displaystyle Br}{\underset{|}{C}}H_2\underset{\displaystyle Br}{\underset{|}{C}}HOC_2H_5 \xrightarrow{CuCN} \underset{\displaystyle Br}{\underset{|}{C}}H_2\underset{\displaystyle CN}{\underset{|}{C}}HOC_2H_5 \text{ (II)} \xrightarrow{C_5H_{10}NH} CH_2{=}\underset{\displaystyle CN}{\underset{|}{C}}{-}OC_2H_5 \text{ (I)}$$

I II

β-Bromo-α-ethoxypropionitrile (II) was a colorless liquid which rapidly darkened on standing, even in the cold. On this account, this substance was not ordinarily isolated but was dehydrohalogenated directly to α-ethoxyacrylonitrile (I), a stable, sweet-smelling, colorless, mobile liquid which crystallized at −49.6°.

The unsaturated nitrile absorbed hydrogen bromide so vigorously that cooling was necessary during the operation. The product of the addition was an isomer of II, differing markedly from this compound in its physical properties. It must, therefore, have been α-bromo-α-ethoxypropionitrile (III), a structure which is confirmed by the hydrolysis products, hydrogen cyanide, hydrogen bromide, ethyl alcohol, acetic acid, and traces of ethyl acetate. Rapid hydrolysis of the compound was to be expected since it contains an α-haloether linkage.

The cyanide was readily detected by a Prussian blue test and the Volhard titration of the cyanide and bromide resulting from hydrolysis actually served as a useful means of analysis for the halogen and cyanide content of the addition product. Ethyl alcohol was identified by conversion to the 3,5-dinitrobenzoate, acetic acid by conversion to the *p*-bromophenacyl ester and ethyl acetate by its boiling point, its refractive index and its characteristic odor.

In every instance, the low-boiling α-bromo addition product (III) was accompanied by a small amount (up to 20%) of higher-boiling substance

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(1) (a) Markownikoff, *Ann.*, **153**, 256 (1870); *Compt. rend.*, **81**, 668 (1875); (b) Wagner and Laytzeff, *Ann.*, **179**, 324 (1875); (c) Michael, *J. prakt. Chem.*, **60**, 341 (1879); *Ber.*, **39**, 2138 (1906); (d) Cuy, THIS JOURNAL, **42**, 503 (1920); (e) Lucas and Jameson, *ibid.*, **46**, 2475 (1924); (f) Kharasch and Reinmuth, *J. Chem. Ed.*, **8**, 1703 (1931).

(2) Berthelot, *Ann. chim.*, [7] **4**, 104 (1895).

(3) Schramm, *Ber.*, **26**, 1710 (1893).

(4) Réboul, *Ann.*, **155**, 212 (1870).

(5) Réboul, *Ann. chim.*, [5] **14**, 461 (1878); Michael, *Ber.*, **39**, 2787 (1906).

(6) Wislicenus, *Ann.*, **192**, 106 (1878).

(7) Nef, *ibid.*, **335**, 219 (1904).

(8) Bayer and Co., German Patent 233,519.

(9) Wislicenus, *Ann.*, **166**, 1 (1873).

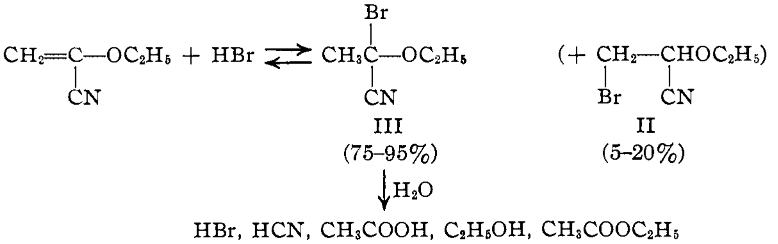
(10) Flürscheim, *J. prakt. Chem.*, [2] **68**, 349 (1903).

(11) Prins, *ibid.*, [2] **89**, 421 (1914).

(12) Wieland and Sakellarios, *Ber.*, **52**, 901 (1919).

(13) See Price and Coyner, THIS JOURNAL, **62**, 1306 (1940).

(14) Werigo and Melikoff, *Ber.*, **10**, 1499 (1878); Otto and Beckurtz, *ibid.*, **18**, 239 (1885).



$$CH_2{=}\underset{CN}{C}{-}OC_2H_5 + HBr \rightleftarrows CH_3\overset{Br}{\underset{CN}{C}}{-}OC_2H_5 \qquad (+\ \underset{Br}{CH_2}{-}\underset{CN}{C}HOC_2H_5)$$

III (75–95%) II (5–20%)

$$\downarrow H_2O$$

$$HBr,\ HCN,\ CH_3COOH,\ C_2H_5OH,\ CH_3COOC_2H_5$$

which corresponded in physical properties to the β-bromo isomer (II).

Addition of two equivalents or more of hydrogen bromide to the unsaturated nitrile yielded a solid product which was insoluble in ether and other inert organic solvents but which dissolved readily in water. Its properties and analyses indicated it to be a mixture of the mono- and dihydrobromides[15] of the bromonitrile (III).

The addition of hydrogen bromide to the unsaturated nitrile has been indicated as a reversible reaction since, on standing, the pure addition product (III) forms a precipitate of the nitrile hydrobromides with the liberation of the unsaturated nitrile (I). This reaction made isolation of an entirely pure sample of α-bromo-α-ethoxypropionitrile very difficult, since some elimination of hydrogen bromide occurred on distillation, even at room temperature under diminished pressure. The addition product was therefore always contaminated by traces of the starting material as is clearly indicated by the analytical data and physical properties.

Addition of hydrogen bromide to α-ethoxyacrylonitrile to yield α-bromo-α-ethoxypropionitrile as the principal product is evidence that the ethoxyl group exerted a more powerful directing influence than the nitrile group. The simultaneous formation of small amounts of the β-bromo isomer indicates that the difference is small.

Attempts to polymerize α-ethoxyacrylonitrile by heating with aqueous potassium persulfate for four days, by heating with aluminum chloride for one day and by exposure to ultraviolet light in the presence of benzoyl peroxide for two weeks failed to yield any polymer; the nitrile was apparently unaffected.

Experimental

α-Chloroethyl ethyl ether,[16] b. p. 90–93° (740 mm.), 40–43° (60 mm.), was brominated[17] to give an 82% yield of α,β-dibromoethyl ethyl ether, b. p. 75–79° (20 mm.). Replacement of the α-halogen was accomplished using essentially the procedure of Lingo and Henze.[18] A solution of 300 g. of the dibromoether in 500 cc. of absolute ether was refluxed with 150 g. of cuprous cyanide for four hours. The copper salts were removed by filtration and the solution distilled. Approximately half the material boiled at 66–80° (8 mm.), n^{20}_D 1.4532–1.4577. The β-bromo compound boiled at 90–91° (16 mm.), 83° (8 mm.) and 62° (4 mm.), n^{20}_D 1.4618. After standing three days, a sample of β-bromo isomer was refractionated. Approximately half boiled at about 50° (4 mm.), n^{20}_D 1.4495. The remainder was unchanged **β-bromo-α-ethoxypropionitrile** (II), b. p. 62–63° (4 mm.), n^{20}_D 1.4618; d^{20}_{20} 1.430; M^{20}_D (calcd.) 34.44; M^{20}_D (found) 34.23.

Anal. Calcd. for C_5H_8NOBr: Br, 44.94. Found: Br, 44.91, 45.05.

An ice-cold ether solution of β-bromo-α-ethoxypropionitrile was treated with a 20% excess of piperidine. The bulky, crystalline precipitate of piperidine hydrobromide was removed by filtration and the solution was distilled. The product, **α-ethoxyacrylonitrile** (I), was a stable, colorless liquid with a pleasant sweet odor; b. p. 133–135°, 63° (60 mm.), f. p. −49.6°, n^{20}_D 1.4170, d^{20}_{20} 0.9090; M^{20}_D (calcd.) 26.21; M^{20}_D (found) 26.86. The exaltation in molecular refraction is because of conjugation in the molecule.

Anal. Calcd. for C_5H_7ON: N, 14.43. Found: N, 14.10.

The conversion of α-chloroethyl ethyl ether to α-ethoxyacrylonitrile was ordinarily carried out more conveniently and in better yield without isolating the relatively unstable intermediates. When the reaction was carried out in this manner the average over-all yield for bromination, treatment with cuprous cyanide and dehydrohalogenation was 40%.

Addition of Hydrogen Bromide.—Hydrogen bromide was generated by dropping bromine into tetralin or naphthalene; it was washed by bubbling through tetralin. The gas was passed through weighed samples of 7–10 g. of the unsaturated nitrile (I) until one to one and one-half equivalents of hydrogen bromide had been absorbed. The material was then fractionally distilled under diminished pressure. The receiver was kept in a dry-ice–acetone bath to ensure condensation and to prevent undue decomposition of the unstable product. For the seven experiments carried out in this manner the yield of α-bromo-α-ethoxypropionitrile was usually about 75–80%; in one case it was 95%. This substance was a colorless, lachrymatory liquid which fumed in the air. The physical properties of the purest samples were: b. p. 44–45° (13 mm.); 29° (4 mm.); n^{20}_D 1.4478–1.4479; d^{20}_{20} 1.333–1.334; M^{20}_D (calcd.) 34.44; M^{20}_D (found) 35.70.

Anal. Calcd. for C_5H_8NOBr: Br, 44.94; CN, 14.61. Found: Br, 44.10.

A sample with n^{20}_D 1.4441; d^{20}_{20} 1.291; M^{20}_D 36.63, was dissolved in 10% sodium hydroxide and the cyanide and

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[15] Hantzsch (*Ber.*, **64**, 667 (1931)) has observed the formation of such salts for several simple nitriles.

[16] Swallen and Boord, THIS JOURNAL, **52**, 654 (1930).

[17] Lewis, Dykstra and Boord, *ibid.*, **52**, 3400 (1930).

[18] Lingo and Henze, *ibid.*, **61**, 1574 (1939).

bromide titrated with thiocyanate by the Volhard method. The proper ratio (1:1) of bromide to cyanide was found.

Anal. Found: Br, 40.4, 40.0; CN, 12.97, 12.84.

Determination of halogen in a similar sample (n^{20}_D 1.4437; d^{20}_{20} 1.285; M^{20}_D 36.80) by means of sodium in liquid ammonia[19] gave the same halogen analysis, indicating that the hydrolysis above was quantitative.

Anal. Found: Br, 39.9, 41.0.

In three of the seven addition reactions, an appreciable portion (*ca.* 20%) of the hydrogen bromide addition product boiled at a considerably higher temperature (b. p. 83° (14 mm.), 65° (4 mm.)) and had a considerably higher index of refraction (n^{20}_D 1.4618–1.4697). These are properties which correspond to β-bromo-α-ethoxyacrylonitrile.

When about two moles of hydrogen bromide was passed into α-ethoxyacrylonitrile a light tan powder separated. This material was insoluble in ether but dissolved readily in water, forming a solution which reduced silver nitrate to silver. The powder was washed with ether, dried and analyzed.

Anal. Calcd. for $C_5H_8NOBr \cdot HBr$: Br, 61.72. Calcd. for $C_5H_8NOBr \cdot 2HBr$: Br, 71.48. Found: Br, 67.1, 68.3, 66.6.

The average of these halogen analyses, 67.4%, corresponds to 1.48 moles of hydrogen bromide per mole of bromonitrile.[15]

This same powder precipitated from distilled samples of either α- or β-bromo-α-ethoxypropionitrile on standing, even in a dry-ice–acetone bath in the case of the α-isomer. Evidently the bromonitrile was slowly converted to the unsaturated nitrile by loss of hydrogen bromide which then combined with more of the bromonitrile to yield the insoluble nitrile hydrobromides.

Hydrolysis of **α-bromo-α-ethoxypropionitrile** (III) proceeded vigorously when water was added or when the nitrile was poured into water. The essentially quantitative progress of the hydrolysis is indicated by the analyses above for halogen and cyanide on an alkaline hydrolysis mixture. The presence of cyanide ion was further proved by the formation of a copious precipitate of Prussian blue. When a sample of α-bromo-α-ethoxypropionitrile (2 g.) was carefully hydrolyzed by dropwise addition of water at 0°, the hydrolysis mixture extracted with ether, dried and distilled, a few tenths of a cubic centimeter of liquid with the characteristic odor of ethyl acetate was obtained, b. p. 75–90°, n^{19}_D 1.3728. The corresponding properties for ethyl acetate are b. p. 77°, n^{19}_D 1.3722.

A 10-g. sample of the bromonitrile was hydrolyzed with cold alkali and a small portion distilled. Treatment of the distillate with 3,5-dinitrobenzoyl chloride yielded a small amount of crystals, m. p. 89°. Ethyl 3,5-dinitrobenzoate melts at 93°.[20] The alkaline hydrolysis mixture was then acidified with phosphoric acid and distilled. The distillate was neutralized with sodium hydroxide and treated with *p*-bromophenacyl bromide.[20] A copious precipitate of the *p*-bromophenacyl ester of acetic acid was obtained, m. p. 84–85°.[20]

Summary

α-Ethoxyacrylonitrile has been prepared from α,β-dibromoethyl ethyl ether by treatment with cuprous cyanide followed by dehydrohalogenation.

Addition of hydrogen bromide to α-ethoxyacrylonitrile yielded principally α-bromo-α-ethoxypropionitrile, indicating that the ethoxyl group was a more potent factor than the nitrile group in directing addition to the carbon–carbon double bond.

Attempts to polymerize α-ethoxyacrylonitrile by aqueous potassium persulfate, by aluminum chloride and by benzoyl peroxide and ultraviolet light failed.

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(19) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

(20) Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Mechanism of the Peroxide-Catalyzed Polymerization of *d*-*s*-Butyl α-Chloroacrylate[1]

BY CHARLES C. PRICE AND ROBERT W. KELL

The kinetics of the benzoyl peroxide-catalyzed polymerization of *d*-*s*-butyl α-chloroacrylate have been investigated in dilute dioxane solution at several temperatures between 26 and 68°, making use of the polarimetric technique for following the polymerization recently reported by Marvel, Dec and Cooke.[2] The reaction proceeded smoothly under these conditions and the rate could be conveniently and accurately followed by this method since the specific rotation of the monomer was twice that of the polymer.

The *d*-*s*-butyl α-chloroacrylate was prepared according to the directions of Marvel, Cooke and Dec,[2] b. p. 70–71° (23 mm.), n^{20}_D 1.4360. It was stored over hydroquinone and samples were twice redistilled immediately before use since the uninhibited monomer polymerized appreciably in a few days at room temperature. Two samples

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[1] Presented before the division of Organic Chemistry at the St. Louis meeting of the American Chemical Society, April 9, 1941.

[2] Marvel, Dec and Cooke, THIS JOURNAL, **62**, 3499 (1940).