with a side arm carrying a serum bottle cap. Samples were removed periodically by means of a hypodermic syringe, added immediately to water,[25] and the organic layer analyzed by infrared. A small, positive pressure of nitrogen in the reaction flask prevented contamination of the reaction with atmospheric moisture during sampling.

The reactions plotted in Fig. 1–3 were run with the same prepared catalyst solution in order to avoid any complications arising from differences in the composition of the catalyst. A solution of 4.35 g. (8.1 mmoles) of Al_2Br_6 in 30 ml. of carbon disulfide was treated with 0.140 g. (7.7 mmoles) of water. The mixture was shaken thoroughly and forced with nitrogen through a sintered glass funnel. The clear, yellow catalyst solution was stored in a flask fitted with a serum bottle cap, and aliquots were removed as required with a hypodermic syringe. Isomerizations were carried out in 100-ml. serum bottles. The bromotoluene and solvent, if any, were weighed into the bottle, a serum bottle cap applied and a weighed amount of the above catalyst solution was added from a syringe. Samples were removed by means of a syringe and added to water plus enough carbon disulfide to form a solution of appropriate concentration for infrared analysis. The carbon disulfide layers were separated, dried with anhydrous magnesium sulfate, and analyzed.

Analyses.—The concentrations of the bromotoluene isomers were estimated by quantitative analysis of infrared spectra recorded from carbon disulfide solution on a Perkin-Elmer Infracord spectrometer, Model 137. The out-of-plane hydrogen deformation frequencies at 13.4, 13.0, and 12.5 μ were used for determination of *o*-, *m*-, and *p*-bromotoluene, respectively. Mixtures containing largely a single isomer were run at two concentrations. Alternatively, in mixtures containing only small amounts of the *o*- and *m*-isomers, *p*-bromotoluene was determined at 9.9 μ. When no other materials were present, known mixtures could be determined to ±2% of the amount present. Toluene was similarly estimated from its absorption peak at 13.7 μ. Large amounts of toluene caused interference with the *o*-bromotoluene absorption, and the two were determined by means of simultaneous equations.

o-Bromotoluene could also be estimated by gas chromatography, using a 150 ft. × 0.010 in. capillary column coated with Ucon LB-550-X and operated at 100°. About one third of the samples in the runs shown in Fig. 1–3 were checked in this manner and the agreement with infrared analyses was excellent. Separation of *m*- and *p*-bromotoluene by gas chromatography was not obtained.

Reaction mixtures in which 5% or more disproportionation had occurred could not be analyzed without first removing the dibromotoluenes formed (analysis of the entire mixture gave high values for the *p*-isomer). This was accomplished either by fractional distillation or by preparative scale v.p.c. (5 ft. × 1/2 in. column packed with Ucon LB-550-X on Chromosorb P). When distillation was used, each fraction was analyzed by infrared and the fractions analyzed contained at least 96% of the monobromotoluenes present before distillation. The preparative v.p.c. method was used also to check a number of reaction mixtures which had been analyzed directly by infrared. The agreement obtained (Table II) indicated that there was no serious interference in the total reaction mixture.

TABLE II

COMPARISON OF DIRECT ANALYSIS OF REACTION MIXTURES AND ANALYSIS AFTER PREPARATIVE V.P.C.

	o	*m*	*p*
Before v.p.c.	37.7	45.9	16.4
After v.p.c.	38.0	45.0	17.0

TABLE III

COMPARISON OF V.P.C. AND INFRARED ANALYSES OF BROMOTOLUENE ISOMERIZATION MIXTURES

V.p.c. (wt. %)			Infrared (wt. %)	
Toluene	Bromotoluene	Dibromotoluene	Toluene	Bromotoluene[a]
1.2	98.3	. . .	1.0	99.0
25.9	74.1	. . .	25.3	74.7
. . .	65.4	34.6	. . .	61.5
6.9	72.9	20.2	6.6	71.8

[a] Sum of analyses for the three individual isomers.

Dibromotoluene was determined by v.p.c. (10 ft. × 1/4 in. column, Dow Corning silicone oil 550 on Celite, 170°), relating peak area to mole % by means of correction factors determined from known mixtures.[26] At the same time, toluene and bromotoluene could be readily determined and the values compared with those obtained by infrared. The agreement (Table III) served as a further check on the reliability of the infrared analyses.

Acknowledgment.—The authors are indebted to Professor J. C. Martin of the University of Illinois and Professor H. M. Walborsky of Florida State University for very stimulating discussions of the mechanism and to Mr. F. L. Beman and Dr. G. A. Olah for making the results of their investigations available prior to publication.

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(25) Equivalent results could be obtained from the aluminum cloride-catalyzed reactions by adding the reaction mixture directly to carbon disulfide, filtering, and recording the infrared spectrum of the filtrate.

(26) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31** (2), 230 (1959).

The *cis–trans* Isomerization of Some Simple Ethylene Derivatives

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The position of the *cis–trans* equilibrium has been determined for four simple chlorinated propenes (III–VI) and two substituted acrylonitriles. Equilibrium was approached from each isomer by the familiar bromine-catalyzed isomerization. The amount of *cis* isomer present at equilibrium is discussed in terms of favorable dipole–dipole interactions between dissimilar substituents.

Although considerable information is available concerning the relative stabilities of the *cis* and *trans* forms of the dihaloethylenes[2,3] and of a number of olefins,[4] very little is known about isomerization of halogenated propenes, butenes, etc., in which the double bond carries both alkyl and halogen substituents. Harwell and Hatch[5] found that the equilibrium mixture of 1-bromopropenes contained 68% of the *cis* and 32% of the *trans* isomer at 0–100°. Predominance of the *cis* form at equilibrium has also been reported qualitatively for 1-iodopropene[2] and 1-chloropropene.[6]

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(1) Present address: Department of Chemistry, Albion College, Albion, Mich.

(2) H. G. Viehe, *Chem. Ber.*, **93**, 1697 (1960).

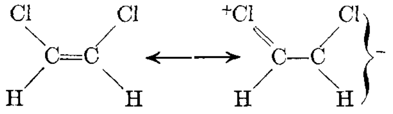
(3) (a) A. R. Olson and W. Maroney, *J. Am. Chem. Soc.*, **56**, 1322 (1934); (b) R. E. Wood and R. G. Dickinson, *ibid.*, **61**, 3259 (1939).

(4) For leading references see M. S. Newman, "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 340–344.

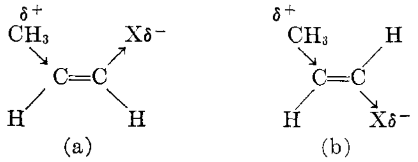
(5) K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).

(6) M. Craen dissertation, Univ. Brüssel, 1924, p. 45; quoted by Viehe ref. 2.

In the dichloroethylenes, predominance of the *cis* isomer has been explained[7] on the basis of contributions from the resonance form Ib and its symmetrical equivalent. It is tempting to attribute the sizeable negative charge on chlorine in Ib to participation of the chlorine d-orbitals.[8] However, the recent observation that *cis*-difluoroethylene also predominates over the *trans* isomer at equilibrium is not consistent with d-orbital resonance being required for such stabilization. The stability of *cis*-1-bromopropene (IIa) is more readily rationalized in terms of permanent dipoles, as shown in II. The closer proximity of the opposed dipoles in IIa than in IIb would be expected to favor the *cis* isomer, IIa.



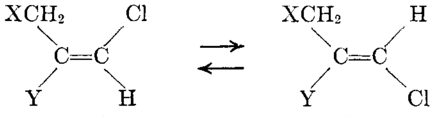
Ia Ib



(a) (b)

II. X = Br
III. X = Cl

In the present study, the simple mono-, di-, and trichloropropenes (III–VI) have been equilibrated at or near room temperature and the *cis–trans* compositions at equilibrium determined for each pair of compounds. The isomerizations were readily effected by treating each individual isomer with a trace of bromine[9] and exposing the samples to direct sunlight.[10] Data illustrating the approach of IIIa and IIIb to an equilibrium mixture of the two are shown in Table I. After fifteen hours the reaction mixtures gave identical analyses, indicating an equilibrium composition of 75% *cis*- and 25% *trans*-1-chloropropene. The increased *cis* content in III, relative to that reported for the corresponding bromo compound, II, may be ascribed to either of two factors: (1) the smaller chlorine atom should result in less steric interference in the *cis* isomer, and (2) the slightly greater electronegativity of chlorine should increase the importance of the dipole–dipole interaction in IIIa relative to IIa.



(a) (b)

III. X = H, Y = H
IV. X = H, Y = Cl
V. X = Cl, Y = H
VI. X = Cl, Y = Cl

TABLE I

ISOMERIZATION OF *cis*- AND *trans*-1-CHLOROPROPENE

0.7 mole % Br_2, 30–35°, direct sunlight

Time, hr.	0	2	4.5	8.5	15
% *cis*	97	82	77	76	75.8
% *trans*	3	18	23	24	24.2
% *cis*	20	48	70	74.5	75.7
% *trans*	80	52	30	25.5	24.3

Equilibrium data for each of the chloropropenes (III–VI) are summarized in Table II. As expected replacement of one of the methyl hydrogens in III by a chlorine atom (V) resulted in a decrease in the amount of *cis* isomer present at equilibrium. Again, it is not known whether the change in equilibrium composition is a result of steric or electronic factors.[11] The 1,2-dichloropropene isomer with the two chlorine atoms *cis*-oriented (IVb) was found to be favored at equilibrium, in spite of the fact that the equilibrium *cis:trans* ratio in the dichloroethylenes[3a] (70:30) is slightly less than in the 1-chloropropenes (75:25).

TABLE II

cis–trans EQUILIBRIA IN SIMPLE CHLOROPROPENES

Compound	Temp., °C.	% composition at equilibrium[a] *cis* (a)	*trans* (b)
1-Chloropropene (III)	30	75.5	24.5
1,2-Dichloropropene (IV)	45[b]	39	61
1,3-Dichloropropene (V)	30	56.5	43.5
1,2,3-Trichloropropene (VI)	30	20	80
1,2,3-Trichloropropene (VI)	80[b]	22	78
1,2,3-Trichloropropene (VI)	140[b]	24	76

[a] Established by 1% or less of bromine; sunlight catalysis. [b] Mercury lamp used as ultraviolet source.

1,2,3-Trichloropropene (VI) was studied over a temperature range of >100° (Table II). From a plot of $\ln K$ *vs.* $1/T$ (Fig. 1), the following approximate values for the enthalpy and entropy of the isomerization VIa $\rightleftarrows$ VIb were obtained: $\Delta H = -270$ cal./mole; $\Delta S = 2.0$ e.u. The free energy difference at 80°, calculated directly from the equilibrium constant, was almost exactly 1 kcal./mole.

The limited information available in the literature indicates that the thermodynamically more stable isomers of III and VI are not the major products obtained from elimination reactions of the corresponding chloropropanes. Dehydrochlorination of 1,2-dichloropropane over activated carbon at 200–260° produced IIIa and IIIb in yields of 37 and 43%, respectively,[12] while the same dehydrochlorination with 15% caustic at 125° produced IIIa and IIIb in a ratio of 45:55, but in unspecified over-all yield.[13] Similarly, treatment of 1,2,2,3-tetrachloropropane with potassium hydroxide[14] yielded 32% VIa and 26% VIb. In each of the above examples, the isomer obtained in higher yield was the less stable isomer.[15] In the present work, 1,2,2-tri-

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(7) K. S. Pitzer and J. L. Hollenberg, *J. Am. Chem. Soc.*, **76**, 1493 (1954).

(8) *Cf.* G. Cilento, *Chem. Rev.*, **60**, 147 (1960).

(9) *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 302–308.

(10) At elevated temperatures a General Electric AH-4 mercury lamp was used as the source of ultraviolet radiation.

(11) Some indication as to which factor, if either, is dominant might be obtained by comparing the equilibrium composition on V with that of 1-chloro-3-fluoro-1-propene. When substituted for chlorine, fluorine, being smaller but more electronegative, should increase the equilibrium *cis* content if steric factors are dominant but decrease the *cis* content if the strength of the C_2–C_3 dipole is of primary importance.

(12) E. Galitzenstein and C. Woolf, *J. Soc. Chem. Ind.*, **69**, 298 (1950).

(13) G. W. Hearne, T. W. Evans, H. L. Yale, and M. C. Hoff, *J. Am. Chem. Soc.*, **75**, 1392 (1953).

(14) L. F. Hatch, J. D'Amico, and E. V. Ruhnke, *ibid.*, **74**, 123 (1952).

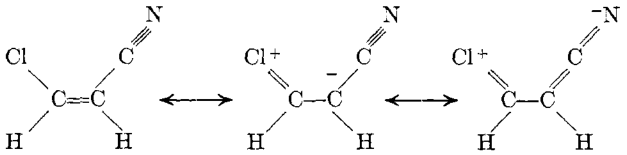
(15) The fact that IIIb and VIa were the major products isolated does not necessitate their being the kinetically favored products of dehydrochlorination, since preferential reaction of IIIa or VIb (*e.g.*, by further dehydrochlorination) could lead to their partial destruction and inversion of the major product.

chloropropane was treated with half an equivalent of potassium hydroxide in methanol at 40°. The ratio of IVb to IVa varied from 0.75 after 18% reaction to 0.5 at 65% reaction. By extrapolating to zero time, it is inferred that the initial product of the elimination reaction contained *ca.* 55% IVa and 45% IVb. Thus, the kinetically favored product in this case is not the more stable of the two isomers.

The *cis–trans* isomerization of crotonitrile (VII) and 3-chloroacrylonitrile (VIII) have also been investigated, and in both cases, the *cis* isomer was found to predominate. Equilibration of each of the crotononitrile isomers by the method of Walling and Helmreich[16] produced a mixture containing 57 ± 2% VIIa and 43 ± 2% VIIb at 80°.[17] Starting with either pure *trans*-3-chloroacrylonitrile (VIIIb) or a 50:50 mixture of VIIIa and VIIIb, isomerization by the light-catalyzed bromine method yielded the two isomers, VIIIa and VIIIb, in a ratio of 69:31. Although in the absence of data for the isomerization of a mixture rich in VIIIb we cannot be certain that the 69:31 ratio represents equilibrium, the true equilibrium mixture can contain no less than the 69% *cis* isomer obtained above. The predominance of *cis*-crotononitrile (VIIa) at equilibrium was anticipated on the basis of the same type of dipole–dipole interaction discussed for the halopropenes, since the highly electronegative cyano group has been substituted for the electron-withdrawing halogen of II or III. Rationalization of the high proportion of *cis*-3-chloroacrylonitrile (VIIIa) at equilibrium is more difficult, since the dipoles of the two substituents normally operate in the same direction. In order to have an attractive dipole–dipole interaction, the contributions of resonance forms B and C would have to be large enough to reverse the normal sense of the carbon–chlorine dipole, resulting in the positive end toward chlorine.[19] Alternatively, the simple dipole hypothesis may not be sufficient to explain the various equilibrium compositions.

(a) *cis* (*b*) *trans*

VII. X = CH_3
VIII. X = Cl



A B C

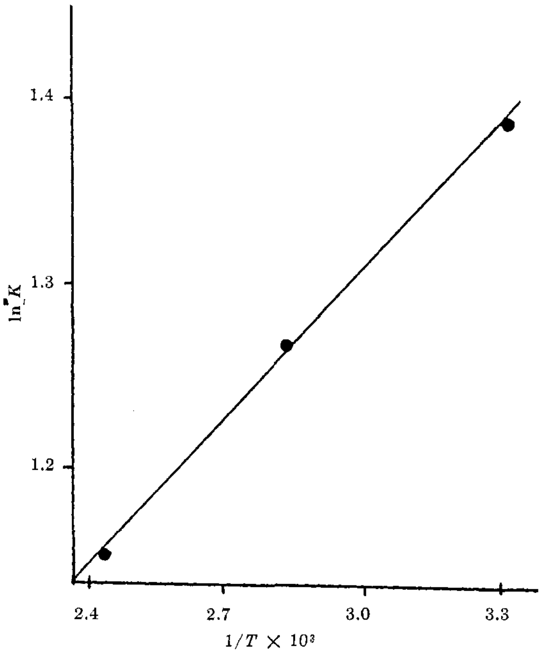
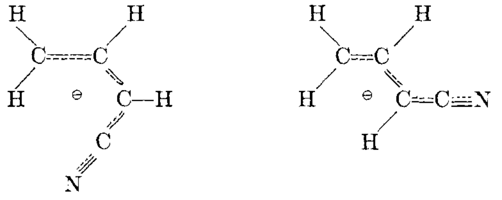


Fig. 1.—Temperature dependence of equilibrium constant for VIa ⇄ VIb.

In the preparation of crotononitrile by treatment of 3-butenenitrile with dilute sodium hydroxide,[20] the *cis* isomer predominated[21] over the *trans* by a factor of 2.5. Preferential formation of *cis* olefins in the base-catalyzed isomerization of allyl derivatives has been observed in other systems[22] and has been ascribed to cyclic coordination of the cation. In the crotononitrile system, the geometry of the intermediate anion, IX, does not offer the possibility of ready chelate formation in either the *cis* or *trans* configuration. It may be that IXa is more stable than IXb for reasons similar to those responsible for the relative stabilities of the *cis*- and *trans*-crotononitriles themselves. On the other hand, the more rapid formation of *cis*-crotononitrile may not reflect a difference in stabilities or rates of formation of the intermediate anions (IXa and IXb), but a difference in the rates of protonation of IXa and IXb on the terminal carbon atom.



IXa IXb

Experimental

1-Chloropropene (III).—Commercial 1-chloropropene (Dow Chemical Co.) was distilled through a 6-ft. Podbelniak column and the fractions analyzed by vapor phase chromatography (silicone rubber on Chromosorb W column, 10 ft. × 1/4 in., operated at 40°). *cis*-1-Chloropropene (IIIa), b.p. 30.5° (751 mm.), $n^{25}\mathrm{D}$ = 1.4026 [lit.,[23] b.p. 32° (747 mm.), $n^{20}\mathrm{D}$ = 1.4053] contained *ca.* 1% 2-chloropropene and < 1% *trans*-1-chloropropene. *trans*-1-Chloropropene (IIIb), b.p. 37.0° (745 mm.),

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[16] C. Walling and W. Helmreich, *J. Am. Chem. Soc.*, **81**, 1144 (1959).

[17] The energy difference between VIIa and b is thus calculated to be only 0.2 kcal./mole. A difference of 1.9 kcal. had previously been assigned[2] on the basis of combustion data.[18]

[18] P. Bruylants and A. Christiaen, *Bull. Soc. Chim. Belges*, **34**, 144 (1925); see also J. Timmermans, "Physico-Chemical Constants," Elsevier Publishing Co., Inc., New York, N. Y., 1950, p. 542.

[19] This hypothesis leads to the prediction that in 2-methyl-3-chloroacrylonitrile the isomer with chlorine and methyl *trans*-oriented should predominate by more than the 70:30 ratio found for VIII. Experiments to test this prediction are planned.

[20] R. A. Letch and R. P. Linstead, *J. Chem. Soc.*, 443 (1932).

[21] Correction was made for a small amount of *cis–trans* isomerization occurring after the allylic rearrangement.

[22] T. J. Prosser, *J. Am. Chem. Soc.*, **83**, 1701 (1961); C. C. Price and W. H. Snyder, *ibid.*, **83**, 1773 (1961); A. Schriesheim, J. F. Hofmann, and C. A. Rose, Jr., *ibid.*, **83**, 3731 (1961).

$n^{25}\mathrm{D}$ 1.4025 [lit.,[23] b.p. 36.7° (747 mm.), $n^{20}\mathrm{D}$ 1.4054] contained < 1% *cis*-1-chloropropene. These fractions were used as standards for infrared analyses of mixtures of IIIa and IIIb using absorption maxima at 13.24 and 12.50 μ, respectively.

1,2-Dichloropropene (IV) was prepared from 1,2,2-trichloropropane by treatment with one equivalent of sodium ethoxide in ethanol for 15 hr. at 40°. Distillation through a 4-ft. modified Vigreux column furnished two fractions (in addition to a small intermediate cut).

Isomer	% yield	B.p., °C. (750 mm.)	Lit.,[24] b.p., °C. (atm.)	% purity
IVa	44	74.8–75.0	75	98
IVb	20	91.0–91.8	92	95

Each isomer was examined by vapor phase chromatography (10 ft. × $^1/_4$ in. Carbowax 20M on Chromosorb W column at 85°) and the purity of each sample calculated from peak areas, using a small correction factor[25] calculated from known mixtures. Compositions of unknown mixtures were determined in the same manner.

1,3-Dichloropropene (V) (Shell Development Co.) was fractionally distilled to obtain fractions enriched in the individual isomers. Analysis of the fraction of b.p. 109–111° (755 mm.), $n^{25}\mathrm{D}$ 1.4682, by gas chromatography (10 ft. × $^1/_4$ in. silicone rubber column at 100°) indicated 77% Va and 23% Vb. Similarly, the fraction, b.p. 114–115 (755 mm.), $n^{25}\mathrm{D}$ 1.4718, analyzed 89% Vb and 11% Va. For the pure isomers, Hatch[26] reported: Va, b.p. 104.3°, $n^{20}\mathrm{D}$ 1.4682; Vb, b.p. 112.0°, $n^{20}\mathrm{D}$ 1.4730. Mixtures were analyzed by gas chromatography, assuming peak areas proportional to per cent composition.

1,2,3-Trichloropropene (VI) (Dow Chemical Co.) was distilled through a 4-ft. glass-helices column yielding VIa and VIb free of impurities (by gas chromatography). VIa, b.p. 75–75.5 (100 mm.), $n^{25}\mathrm{D}$ 1.4960 [lit.,[14] b.p. 75° (100 mm.), $n^{25}\mathrm{D}$ 1.4956]; VIb, b.p. 87° (100 mm.), $n^{25}\mathrm{D}$ 1.5023; [lit.,[14] b.p. 87° (100 mm.), $n^{25}\mathrm{D}$ 1.5020]. Mixtures of the two isomers were analyzed by gas chromatography (10 ft. × $^1/_4$ in. silicone rubber column, 150°).

Chloropropene Isomerizations.—The general procedure involved addition of *ca.* 1 mole % bromine to the desired chloropropene isomer in a small, glass-stoppered flask. The flasks were placed in direct sunlight and samples removed periodically with a microsyringe for gas chromatographic analysis. Although the bromine color disappeared very rapidly, isomerization continued as long as the samples were irradiated. Data for a typical run are shown in Table I. The ease of isomerization under these conditions varied in the order V > VI > III > IV. When gas chromatographic analysis indicated that the reaction mixtures from a pair of isomers were identical, the samples were analyzed by the methods described above to determine the equilibrium compositions. When a mercury lamp was used (Table II), the samples were placed in a Pyrex tube adjacent to the lamp and immersed in a suitable refluxing coolant. Analyses of starting and equilibrium compositions at 30° for each pair of isomers are summarized in Table III.

TABLE III

EQUILIBRATION OF CHLOROPROPENES AT 30°

Compound	*cis*:*trans* ratio[a] Initially	After equilibration
1-Chloropropene (III)	97:3	75:25
	20:80	75.8:24.2
1,2-Dichloropropene (IV)[b]	98:2	41.8:58.2
	5:95	38.6:61.4
	58:52	38.8:61.2
1,3-Dichloropropene (V)	77:23	56.9:43.1
	11:89	56.2:43.8
1,2,3-Trichloropropene (VI)	100:0	20.4:79.6
	0:100	19.8:80.2

[a] The designations *cis* and *trans* refer to the hydrogen on C-1 and the hydrogen or chlorine on C-2. [b] Equilibrated at 45°.

***cis*- and *trans*-Crotononitrile.**—A mixture of 67.6 g. of 3-butenenitrile and 150 ml. of 1 *N* sodium hydroxide was stirred for 18 hr. at 30°. The organic layer (65.8 g.), containing 68% *cis*- and 32% *trans*-crotononitrile, was dried over magnesium sulfate and distilled through a 30-cm. Holzmann column. The lowest boiling fraction (6.6 g., b.p. 109–109.5°) and highest boiling fraction (7.6 g., b.p. 116.5–120°) showed 80% *cis*- and 80% *trans*-crotononitrile, respectively. (Analysis by gas chromatography on a 10 ft. × $^1/_4$ in. Tide column; confirmed by quantitative infrared spectral analysis.)

Crotononitrile Isomerizations.—A solution of 5.4 g. of the appropriate crotononitrile mixture, 0.53 g. of *n*-octyl mercaptan and 0.41 g. of 2,2′-azobisisobutyronitrile was heated 3.5 hr. at 80°. Analysis of the total reaction mixture by gas chromatography gave the results shown below. No attempt was made to obtain a more accurate estimate of the equilibrium.

Starting crotononitrile	Product crotononitrile
81% *cis*, 19% *trans*	59% *cis*, 41% *trans*
20% *cis*, 80% *trans*	55% *cis*, 45% *trans*

3-Chloroacrylonitrile was obtained through the courtesy of R. M. Nowak of the Physical Research Laboratory, The Dow Chemical Co. The *trans* isomer, m.p. 42–44° (lit.,[27] m.p. 45–46°), was estimated to be >98% pure by gas chromatography. The second sample, liquid at room temperature, showed 58% *cis* and 42% *trans*, by gas chromatography and nuclear magnetic resonance. Equilibration at 30° by the method used for the chloropropenes produced a 69:31 mixture of *cis*- and *trans*-3-chloroacrylonitrile from either sample.

Acknowledgment.—The author is very grateful to Dr. R. M. Nowak for supplying samples of 3-chloroacrylonitrile.

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(23) M. S. Kharasch, H. Engelmann, and F. R. Mayo, *J. Org. Chem.*, **2**, 288 (1937).

(24) L. C. Leitch, *Can. J. Chem.*, **31**, 385 (1953).

(25) A. E. Messner, D. M. Rosie, and P. A. Argabright, *Anal. Chem.*, **31** (2), 230 (1959).

(26) L. F. Hatch and A. C. Moore, *J. Am. Chem. Soc.*, **66**, 285 (1944).

(27) E. Gryszkiewicz-Trochimowski, W. Schmidt, and O. Gryszkiewicz-Trochimowski, *Bull. soc. chim. France*, 593 (1948).