were all combined. The ether was distilled off and the product was distilled at 53–54° at 6 mm. to yield 11.5–11.9 g. (89–92%) of octylamine.

Applicability and By-products.—The General Procedure was successfully applied also to caprinitrile, benzonitrile, *p*-chlorobenzonitrile and butyronitrile with the following respective yields of the corresponding primary amines: 92, 83, 81 and 57%. The low yield of butylamine was probably the result of volatilization of the product when the ether was boiled off through an air condenser, since the vapors emerging instantly turned red litmus paper blue.

In view of the reported reduction of alkyl halides to hydrocarbons,[7] it is worth noting that the reduction of *p*-chlorobenzonitrile gave a good yield of *p*-chlorobenzylamine which, from its boiling range, appeared to be completely free of benzylamine.

It appears likely, however, that complicating side reactions can be expected when this procedure is used for the reduction of nitriles whose α-hydrogen atoms are doubly activated. Phenylacetonitrile, in contrast to all other nitriles worked with, gave a reaction mixture which quickly turned a very dark green when exposed to the atmosphere.

Several of our products were carefully examined before distillation for the presence of secondary amines using the nickel chloride–carbon disulfide test.[8] The results completely substantiated the report[3] that secondary amines are not produced.

Acknowledgments.—The authors are pleased to acknowledge the assistance of Dr. Ellis R. Lippincott who measured and interpreted the infrared spectra of several of our reaction mixtures. Armour and Company kindly furnished the caprylonitrile used in this work. We are also indebted to the University of Connecticut Research Fund for financial assistance.

Summary

1. A procedure, arising from extensive investigations of the reaction conditions, has been described for the reduction of caprylonitrile to octylamine with lithium aluminum hydride. This procedure appears to be widely applicable to other nitriles.

2. In contrast to inferences which may be drawn from the work of others, it has been suggested that only half the hydrogen of lithium aluminum hydride is available for the reduction of the cyano group, when the reaction is carried out below 35°.

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[7] Johnson, Blizzard and Carhart, THIS JOURNAL, **70**, 3664 (1948).

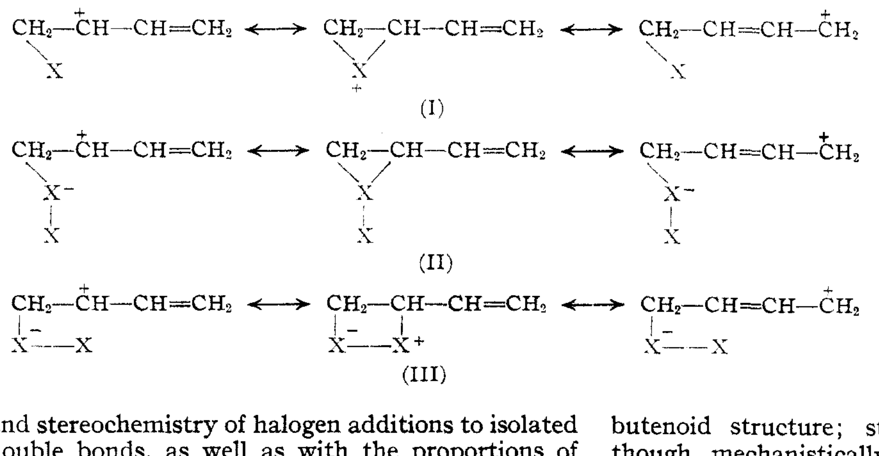
[8] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd ed., 1948, p. 111.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NEW YORK UNIVERSITY]

Stereochemistry of 1,4-Addition. I. The Chlorination of Butadiene[1]

BY KURT MISLOW AND HENRY M. HELLMAN

Addition of halogens to conjugated systems is commonly regarded as a two-stage process[2,3]: electrophilic attack by halogen[4] or halonium ion,[5] followed by nucleophilic attack by halide ion. This view is consistent with the observed kinetics and stereochemistry of halogen additions to isolated double bonds, as well as with the proportions of 1,2- and 1,4-adducts in halogen additions to conjugated double bonds.


(I)
(II)
(III)

In the transition state, according to this approach, the attacking reagent coördinates with one of the terminal double bonds, as illustrated by selected contributing structures (I), (II) and (III).[4] These hybrids will be referred to as terminal.

It is conceivable, on the other hand, that electrophilic attack might occur with the attacking reagent disposed centrally and symmetrically with respect to, and coplanar with, the diene molecule. Such possible transition state hybrids, which will be referred to as frontal, are illustrated by selected contributing structures (IV),[3] (V) and (VI).[6]

The frontal transition states all have the *cis*-2-butenoid structure; stereochemically related, although mechanistically not strictly comparable, transition states are involved in the *cis*-reduction of butadiene,[7] the Diels–Alder synthesis,[8] iron

[1] Presented before the Division of Organic Chemistry, 118th American Chemical Society Meeting, Chicago, Illinois, September 6, 1950.

[2] de la Mare, Hughes and Ingold, *J. Chem. Soc.*, 17 (1948).

[3] de la Mare, *Quart. Revs. (London)*, **3**, 126 (1949).

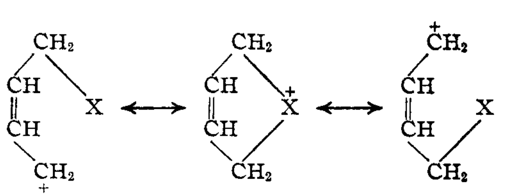
[4] Waters, Caverhill and Robertson, *J. Chem. Soc.*, 1168 (1947).

[5] Roberts and Kimball, THIS JOURNAL, **59**, 947 (1937).

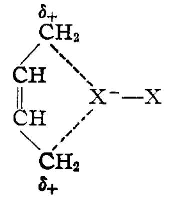
[6] Eyring, Sherman and Kimball (*J. Chem. Phys.*, **1**, 586 (1933)) have proposed a related transition state. Their calculations indicate that one-stage, 1,4-addition is energetically feasible.

[7] Ziegler, *et al.*, *Ann.*, **528**, 101 (1937).

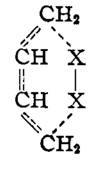
[8] Dewar, "The Electronic Theory of Organic Chemistry," Oxford University Press, New York, N. Y., 1949, p. 150.



(IV)



(V)



(VI)

carbonyl–diene complex formation,[9] and sulfur dioxide addition to butadiene.[10]

It is apparent that the importance of a frontal transition state could be gauged from its stereochemical consequence, *i.e.* the proportion of *cis*-isomer in the kinetically-formed products of 1,4-addition. Evidence in the literature concerning the geometry of 1,4-adducts of halogens to conjugated dienes is scarce. No *cis*-1,4-dibromo-2-butene is reported formed in the bromination of butadiene.[11] However, in the bromination of 2,3-dimethylbutadiene, some of the *cis*-1,4-dibromide is obtained, although this *cis* isomer is thermodynamically unstable with respect to the *trans*-1,4-dibromide.[12] Conceivably a frontal transition state may be involved here. The geometry of 9,10-chlorination adducts of certain anthracene derivatives has been taken as evidence for transannular *cis*-addition of chlorine; presumably a transition state of type (VI) is involved.[13] The formation of a *cis* 1,4-adduct of bromine and cyclopentadiene[14] might be similarly explained. It is noteworthy that in cases where models show the *cis*-2-butenoid structure to be highly strained, as in 2,3-di-*t*-butylbutadiene, the diene does not add sulfur dioxide or maleic anhydride, and it yields a single 1,4-adduct with bromine which has the *trans*-2-butene structure.[15]

We have reinvestigated the chlorination of butadiene.[16] In this system the stability of 1,2- and 1,4-adducts permits investigations not complicated by facile anionotropic rearrangements. Chlorination in the dark at Dry Ice temperatures yielded *trans*-1,4-dichloro-2-butene as the only 1,4-adduct. Its structure was proved by converting it to *trans*-2-butene by reduction with lithium aluminum hydride. Supplementary evidence for the *trans*-configuration of the chlorination product exists in the stereospecific oxidation of that compound to the *meso*- and *dl*-1,4-dichlorobutane-2,3-diols with peroxyformic acid and potassium permanganate, respectively.[16d]

It seemed possible that the *trans*-dichloride, presumably the thermodynamically more stable form, was produced by rearrangement from kinetically-formed *cis* isomer. In order to avoid the possible isomerizing action of acids, the chlorination, which is always accompanied by copious formation of hydrogen chloride, was repeated in the presence of an excess of pyridine. The infrared spectrum of the resulting compound indicates that the product still has the *trans* configuration (Fig. 1). The possibility that the *cis* compound isomerized under the conditions of preparation and isolation, was further reduced by a study of the properties of *cis*-1,4-dichloro-2-butene. This compound was prepared from *cis*-2-butene-1,4-diol and phosphorus trichloride in the presence of pyridine. The structure of the *cis* dichloride was proved by reduction to *cis*-2-butene, with lithium aluminum hydride. The *cis* dichloride remained unchanged on heating at 100°. Its chlorination product did not yield any of the solid tetrachloride,[16a] m.p. 72°, which is produced when the *trans* isomer is further chlorinated.[16c] This eliminates the possibility of isomerization by chlorine.

It has therefore been demonstrated that the kinetically-controlled product of the 1,4-addition of chlorine to butadiene has the *trans* configuration. *The electrophilic reagent (chlorine) can coördinate with only one double bond of butadiene at a time, and not with both simultaneously.* In the terminal transition state which obtains, the configuration of the 4-carbon system will be *trans*.

The explanation of this result may be found in the steric interference of the terminal hydrogen atoms[17]; possibly, also, the small tendency for chloronium ion formation[18] makes contributing structures, such as (IV), with their relatively large C–Cl distances, unstable compared to (I).

These questions are being further pursued in a study of the geometry of chlorination products of related dienes.

Experimental[19]

***cis*-1,4-Dichloro-2-butene.**—*cis*-2-Butene-1,4-diol, b.p. 114° (4 mm.), $n^{25}D$ 1.4776, was obtained by the hydrogenation of 2-butyne-1,4-diol[20] in methanol over Raney nickel at atmospheric pressure and room temperature.[11] A solution of 26.0 g. (0.30 mole) of the *cis*-diol and 13.7 g. of pyridine was added slowly to 32.8 g. (0.24 mole) of phosphorus trichloride while the reaction mixture was kept cold in an ice-bath. The product was extracted with ether, and the ether layer washed with 5% sodium carbonate and dried over sodium carbonate. The solvent was stripped and the product fractionated through a 30-cm. helix-packed column to yield 10.3 g. (28%) of *cis*-1,4-dichloro-2-butene, b.p. 22.5° (3 mm.), 152.5° (758 mm.), m.p. −48°, $n^{25}D$ 1.4887, d^{25}_{4} 1.188, M_D calcd., 29.95; found, 30.35.

Anal. Calcd. for $C_4H_6Cl_2$: C, 38.43; H, 4.84; Cl, 56.72. Found: C, 38.26; H, 4.90; Cl, 56.97.

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[9] Reihlen, *Ann.*, **482**, 161 (1930). It is uncertain whether butadiene forms cyclic pentagonal platinum complexes (Hel'man, *Compt. rend. Acad. Sci. U. R. S. S.*, **23**, 532 (1939)).

[10] *E.g.* Backer, Strating and Kool, *Rec. trav. chim.*, **58**, 778 (1939).

[11] Valette, *Ann. chim.*, [12] **3**, 644 (1948).

[12] Sweeting and Johnson, THIS JOURNAL, **68**, 1057 (1946).

[13] Bergmann and Weizmann, *ibid.*, **60**, 1801 (1938); Bergmann, "Isomerism and Isomerization of Organic Compounds," Interscience Publishers, Inc., New York, N. Y., 1948, Ch. 3.

[14] Farmer and Scott, *J. Chem. Soc.*, 172 (1929); Blomquist and Mayes, *J. Org. Chem.*, **10**, 134 (1945).

[15] Backer, *Rec. trav. chim.*, **58**, 643 (1939).

[16] (a) Muskat and Northrup, THIS JOURNAL, **52**, 4043 (1930); (b) Petrov and Sopov, *J. Gen. Chem.* (*U. S. S. R.*), **15**, 981 (1945), *C. A.*, **40**, 6406 (1946); (c) Pudovic, *J. Gen. Chem.* (*U. S. S. R.*), **19**, 1179 (1949), *C.A.*, **44**, 1005 (1950); (d) Owen, *J. Chem. Soc.*, 241 (1949).

[17] *Cf.* Dewar, ref. 8, p. 154.

[18] Winstein, Grunwald and Ingraham, THIS JOURNAL, **70**, 821 (1948).

[19] Microanalyses by Drs. D. Clegg and F. Buhler.

[20] We are indebted to Dr. A. Nease of General Aniline and Film Corp. for samples of 2-butyne-1,4-diol.

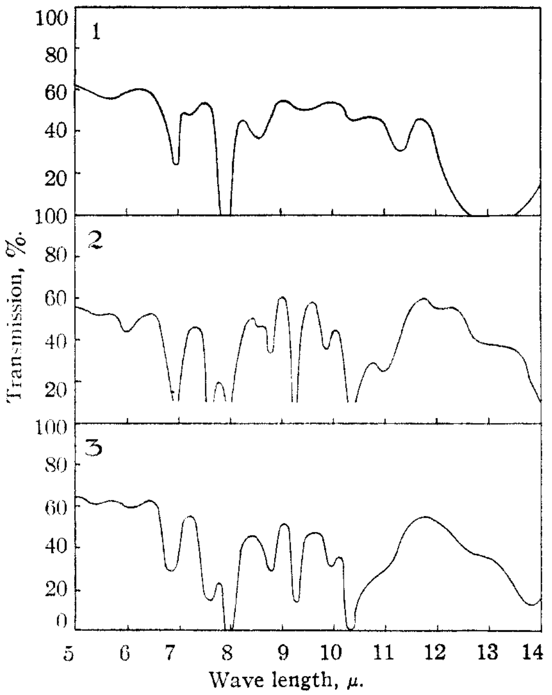

Fig. 1.—(1) *cis*-1,4-dichloro-2-butene, (2) *trans*-1,4-dichloro-2-butene, (3) 1,4-addition product from the chlorination of butadiene in pyridine.

The infrared spectrum[21] is shown in Fig. 1 (curve 1).

Upon being heated at 100° for 7 hours the compound became yellow but melting point and refractive index remained unchanged. Chlorination in carbon tetrachloride at 0° in the dark yielded a mixture from which no solid tetrachloride could be isolated.

***trans*-1,4-Dichloro-2-butene.**—The chlorination apparatus consisted of a 500-ml. flask immersed in Dry Ice–acetone, and was equipped with a stirrer and two gas inlets. Butadiene (99.6%, passed over potassium hydroxide) and chlorine (dried over sulfuric acid) were passed simultaneously into 150 g. of carbon tetrachloride, in the dark. The use of calibrated flowmeters permitted regulation of the quantities reacted (volume ratio $C_4H_6:Cl_2$ 3:1). The product was fractionated at reduced pressure through a 75-cm. helix-packed column, and the isolated 1,4-dichloro-2-butene was redistilled through a Hypercal Podbielniak Column at 55.5° (20 mm.). The properties of the compound are in substantial agreement with reported values:[15] b.p. 155.5° (758 mm.), m.p. +1°, $n^{25}D$ 1.4871, d^{25}_4 1.183, M_D calcd., 29.95; found, 30.40.

Anal. Calcd. for $C_4H_6Cl_2$: C, 38.43; H, 4.84; Cl, 56.72. Found: C, 38.35; H, 4.86; Cl, 56.65.

The infrared spectrum is shown in Fig. 1 (curve 2).

The chlorination was repeated in a mixture of 70 g. of carbon tetrachloride and 70 g. of pyridine; in this case the reaction mixture was alkaline on completion of the reaction. The liquid was decanted from the heavy precipitate of pyridine hydrochloride and gum, washed with water, 10% acetic acid, and sodium carbonate solution. The liquid was dried over sodium carbonate and distilled to give *trans*-1,4-dichloro-2-butene (Fig. 1, curve 3).

On being heated for 6 days at 100°, the *trans* compound suffered discoloration, but the refractive index and the melting point remained unchanged. Chlorination in carbon tetrachloride at 0° in the dark yielded the solid tetrachloride, m.p. 72–73° from petroleum ether (repd.[16a] m.p. 72°).

Reduction of the 1,4-Dichloro-2-butenes.—A solution of 3.0 g. (0.024 mole) of *trans*-1,4-dichloro-2-butene in 25 ml. of tetrahydrofuran was added to a refluxing suspension of 0.6 g. (0.075 mole) of lithium hydride and 0.5 g. (0.013 mole) of lithium aluminum hydride in 25 ml. of tetrahydrofuran, while vigorous stirring was maintained. The evolved 2-butene was collected in a trap kept at Dry Ice temperature. Refluxing was continued for another half hour and the collected 2-butene was then brominated with a solution of 3.9 g. (0.024 mole) of bromine in 10 ml. of chloroform. Excess bromine was removed by shaking with 5% sodium bisulfite solution. Following removal of the chloroform, the product was distilled at reduced pressure to give 40–60% yields of *meso*-2,3-dibromobutane.

The same procedure, using *cis*-1,4-dichloro-2-butene, gave comparable yields of *dl*-2,3-dibromobutane.

The 2,3-dibromobutanes were identified by their refractive indices, and their rate constants of reaction with iodide ion at 75° in 99% methanol.[22] The product obtained from *trans*-1,4-dichloro-2-butene had $n^{25}D$ 1.5090; K_2 0.0515, 0.0509 (repd.[22] for *meso*-2,3-dibromobutane: $n^{25}D$ 1.5092, K_2 0.0544); the product derived from the *cis* isomer had $n^{25}D$ 1.5120; K_2 0.0280, 0.0284 (repd.[22] for *dl*-2,3-dibromobutane: $n^{25}D$ 1.5125, K_2 0.0297).

Acknowledgments.—The authors wish to express their gratitude to Research Corporation which made this investigation possible by a grant-in-aid, and to Dr. Edwin R. Buchman for helpful and stimulating discussions.

Summary

The *cis* and *trans* forms of 1,4-dichloro-2-butene have been prepared, and their configurations proved by conversion to the respective 2-butenes.

The 1,4-addition of chlorine to butadiene yields the *trans* isomer exclusively, under conditions not conducive to *cis–trans* isomerization. This result indicates that chlorine coördinates with only one double bond of butadiene in the transition state, and not with both double bonds simultaneously. The transition state hybrid accordingly, is terminal, and not frontal.

NEW YORK 53, N. Y. RECEIVED JULY 13, 1950

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[21] The infrared spectra were kindly determined and interpreted by Mr. H. A. Miller. A Perkin-Elmer Model 12-C instrument with sodium chloride cells was employed.

[22] Dillon, Young and Lucas, THIS JOURNAL, **52**, 1953 (1930).