BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 3501—3504 (1970)

# Liquid Phase Chlorination of Olefins with Cupric Chloride. II. Stereochemistry of the Reactions of 2-Butenes and Cyclohexene

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(Received April 13, 1970)

Chlorination of *cis*-and *trans*-2-butenes with cupric chloride yields a mixture of *meso*- and *dl*-2,3-dichlorobutanes with *meso*/*dl* ratio of about 60/40, which is almost independent of the starting olefin configuration. For cyclohexene, *trans*-1,2-dichlorocyclohexane is accompanied with the *cis*-dichloride, the amount of which depends upon the solvent polarities. In all cases the starting olefins and the product dichlorides are sufficiently stable under the reaction conditions. The results indicate that open ionic intermediates are involved in the chlorination of simple olefins in liquid phase reaction.

The stereochemical sequence of addition of molecular chlorine to olefins in polar media varies with the structure of the substrate. Stereospecific *trans* addition has been observed for the reactions with 2-butenes in acetic acid,[1] di-*t*-butylethylenes in methanol,[2] and 2-pentenes in various polar solvents including acetic acid and methanol.[3] Chlorination of 1-phenylpropenes in acetic acid and in methanol,[1] and phenanthrene[4] or methyl *trans*-cinnamate[5] in acetic acid leads to mixtures of stereoisomeric dichlorides. It is generally accepted that the chlorination of simple alkenes proceeds *via* a chloronium ion intermediate, while that of conjugated olefins occurs *via* an open carbonium ion. The same conclusion has been drawn for non-polar chlorination, evidenced by reactions with 2-butenes,[6] cyclohexene,[7] and *trans*-stilbene.[8]

Similarly, chlorination of 2-butenes with cupric chloride is highly stereoselective in vapor phase reaction.[9] The formation of *cis*-addition products has been attributed to olefin isomerization and interconversion of 2,3-dichlorobutane diastereomers.[10] The chlorination product of cyclohexene with cupric chloride in acetic acid has been reported to be *trans*-dichloride practically with no *cis*-isomer,[11,12] and a bridged type intermediate has been proposed.[13]

However, when 2-butenes were treated with cupric chloride in methanol, isomeric dichlorides were formed where the product composition is almost the same regardless of the starting olefin configuration.[14] The present studies were undertaken in order to obtain further evidence on the stereochemistry of the cupric chloride chlorination in liquid phase. The results with 2-butenes and cyclohexene give a clue to solve the nature of the reaction intermediate.

## Results

Chlorination of either *cis*- or *trans*-2-butene with cupric chloride was carried out in several polar solvents at 100—150°C. The principal products were *dl*- and *meso*-2,3-dichlorobutanes with a small amount of 2-chloro-3-methoxybutanes.[14] The compositions of the dichlorides are shown in Table 1.

Comparing results from the same reaction conditions, we see that the ratios of *meso* to *dl* dichlorides are very similar for both 2-butenes, although slightly larger for *trans*-2-butene. The extent of 2-butene isomerization was too small to account for. Isomerization between the dichlorides was not observed in methanol under the reaction conditions,[14] and no significant variation in the dichloride com-

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[1] R. C. Fahey and C. Schubert, *J. Amer. Chem. Soc.*, **87**, 5172 (1965)

[2] R. C. Fahey, *ibid.*, **88**, 4681 (1966).

[3] M. L. Poutsma and J. L. Kartch, *ibid.*, **89**, 6595 (1967).

[4] P. B. D. de la Mare and R. Koenigsberger, *J. Chem., Soc.*, **1964**, 5327.

[5] M. C. Cabaleiro and M. D. Johnson, *ibid.*, *B*, **1967**, 565.

[6] M. L. Poutsma, *J. Amer. Chem. Soc.*, **87**, 2172 (1965).

[7] M. L. Poutsma, *ibid.*, **87**, 2161 (1965).

[8] S. J. Cristol and R. S. Bly, Jr., *ibid.*, **82**, 142 (1960).

[9] R. P. Arganbright and W. F. Yates, *J. Org. Chem.*, **27**, 1205 (1962).

[10] P. P. Nicholas and R. T. Carroll, *ibid.*, **33**, 2345 (1968).

[11] K. Ichikawa, S. Uemura, T. Hiramoto and Y. Takagaki, *Kogyo Kagaku Zasshi*, **71**, 1657. (1968).

[12] S. Uemura, T. Hiramoto, Y. Takagaki and K. Ichikawa, *ibid.*, **72**, 2390 (1969).

[13] S. Uemura, Y. Takagaki and K. Ichikawa, *ibid.*, **72**, 2577 (1969).

[14] T. Koyano. This Bulletin, **43**, 1439 (1970).

TABLE 1. CHLORINATION OF 2-BUTENES

| Solvent | Dielectric constant[15] | Additive | Temp. (°C) | Time (hr) | Dichloride (%) | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | | from *cis* | | from *trans* | |
| | | | | | *meso* | *dl* | *meso* | *dl* |
| Acetic acid | 6.2 (20°) | | 150 | 2 | 58.2 | 41.8 | 63.8 | 36.2 |
| 1-Octanol | 10.3 (20°) | | 150 | 2 | 53.5 | 46.5 | 54.8 | 45.2 |
| 1-Butanol | 17.1 (25°) | | 150 | 2 | 57.7 | 42.3 | 62.9 | 37.1 |
| Methanol | 32.6 (25°) | | 150 | 2 | 61.0 | 39.0 | 65.7 | 34.3 |
| | | $H_2O$ (10%) | 150 | 2 | 61.4 | 38.6 | — | — |
| | | $H_2O$ (20%) | 150 | 2 | 63.3 | 36.7 | — | — |
| | | LiCl* | 150 | 2 | 63.7 | 36.3 | — | — |
| | | | 120 | 2 | 63.4 | 36.6 | — | — |
| | | | 120 | 5 | 63.7 | 36.3 | — | — |
| | | | 100 | 5 | 66.5 | 33.6 | — | — |
| Nitromethane | 35.9 (30°) | | 150 | 2 | 58.3 | 41.7 | 64.1 | 35.9 |

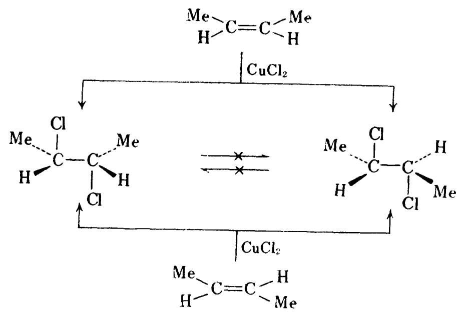
500 m*l* glass-lined autoclave, 2-butene 0.30 mol, $CuCl_2$ 0.045 mol, solvent 150 m*l*
* 0.045 mol

TABLE 2. CHLORINATION OF CYCLOHEXENE

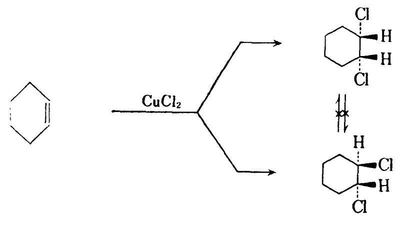
| Solvent | Dielectric constant[15] | Additive | Dichloride (%) | |
|---|---|---|---|---|
| | | | *trans* | *cis* |
| Acetic acid | 6.2 (20°) | | 87.6 | 12.4 |
| 1-Butanol | 17.1 (25°) | | 91.0 | 9.0 |
| Ethanol | 24.3 (25°) | | 95.6 | 5.4 |
| Methanol | 32.6 (25°) | | 96.0 | 4.0 |
| | | $H_2O$ (10%) | 96.6 | 3.4 |
| | | $H_2O$ (20%) | 100 | trace |
| Nitromethane | 35.9 (30°) | | 96.1 | 3.9 |

50 m*l* glass sealed tube, cyclohexene 0.01 mol, $CuCl_2$ 0.01 mol, solvent 30 m*l*, 150°C, 2 hr

position with the reaction time was observed, *e.g.*, in the case of *cis*-2-butene at 120°C. It appears that the results reflect the kinetically controlled product composition.



The stereochemistry of chlorination of cyclohexene with cupric chloride was also studied at 150°C (Table 2). The reaction products were mainly dichlorides with small quantities of by-products which were not analyzed. The composition of dichlorides was determined by means of gas chromatography. The results with two different columns (C and D) coincided well with each other (within a variation of 0.5%), proving the identity of *cis*-dichloride. The portion of *cis* compound increases with decrease in polarity of the solvent. In this case also no isomerization occurred between two isomeric dichlorides at 150°C in the presence of cupric chloride, so that the *cis* dichloride must have been formed directly from the starting olefin.



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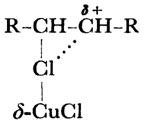
[15] N. A. Lange, "Handbook of Chemistry," 10th Ed., McGraw-Hill Book Co., New York, N. Y. (1967), p. 1234.

## Discussion

The lack of stereospecificity in the results cannot be ascribed to prior isomerization of the olefin or to secondary isomerization of the product dichlorides, since the olefins and the dichlorides have been shown to be stable under the reaction conditions. The results of the 2-butene chlorination are most reasonably interpreted by an assumption that the intermediate consists of two convertible isomeric species, one being the precursor to the *meso* dichloride and the other to the *dl* compound, the composition of which is the same for both starting *cis*- and *trans*-olefins. This can only be attained by rotation along the central C=C bond of the substrate. Therefore, the intermediate complex resembles an open type cation, in which the rotation is faster than the attack of second chlorine to establish an equilibrium, rather than a bridged chloronium ion. Radical mechanisms are improbable in such polar solvent reactions in the presence of oxygen and in the dark.

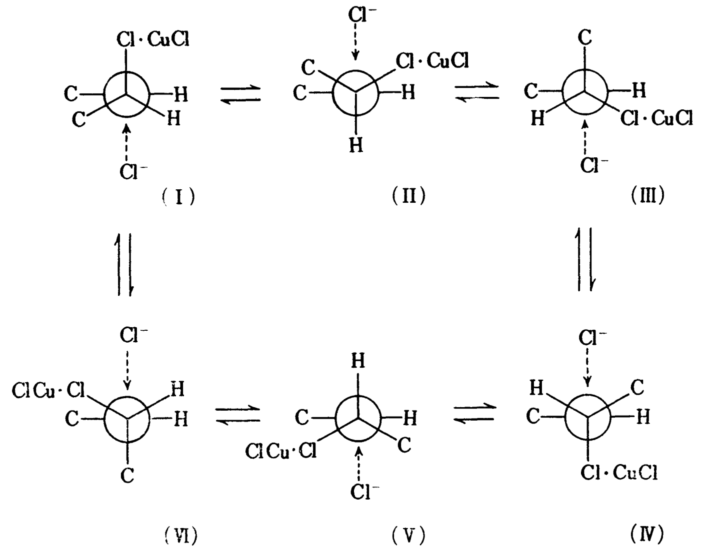
There is a tendency that *dl* formation is comparatively favored in less polar solvents, obviously in the hydroxylic series. The reason for the slight discrepancy in acetic acid and nitromethane is not clear, but it is probably due to their somewhat different solvent characters.[*1]

The chlorine species in the reaction intermediate should not be a free cationic chlorine as is suggested in the addition of a chlorine molecule to simple alkenes[1–3] where a strong chlorine bridging is characteristic. Thus, when chlorine of cupric chloride attacks olefin in an electrophilic manner, a fairly large interaction can be expected between the attacking chlorine and the remaining CuCl group. Then, because of some electron cloud localization on Cl–CuCl bond, polarizability of the chlorine is decreased, which is reflected in almost no bridging interaction to the cationic center and leaves the intermediate open enough for free rotation. However, a faint bridging might still exist in view of the slight preference for *trans* addition, which appears in the slightly larger *meso*/*dl* ratio for *trans*-2-butene than for *cis*-2-butene reaction.



$$\begin{array}{l} \qquad\quad\;\; \delta+ \\ \text{R-CH-CH-R} \\ \qquad | \;\, \cdot^{\cdot^{\cdot}} \\ \qquad \text{Cl} \\ \qquad | \\ \quad \delta\text{-CuCl} \end{array}$$

Among six possible relative configurations of the intermediate complexes of free rotation, III and IV are assumed to be the most stable rotamers as the *dl* and the *meso* precursors, respectively, since they are less crowded and suffer less interference between the substituents than the other four. The less polar the solvents, the larger the interaction between Cl and CuCl in attacking $CuCl_2$ should be, due to disadvantage in charge separation. Therefore, in such cases, the bulkiness of the first attacking group increases, so that IV would have a tendency to shift toward III owing to increasing steric repulsion between Cl–CuCl group and methyl group on the adjacent carbon. Thus, the *meso* dichloride formation becomes less favorable in less polar solvents.



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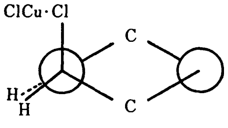
[*1] In acetic acid, there is some evidence that it reacts on cupric chloride to form copper(II) acetate by releasing hydrogen chloride.[12] On the other hand, methanolysis of cupric chloride is improbable and no green solid (Cu(OMe)Cl)[16] or blue solid (Cu$(OMe)_2$)[16,17] was detected in the reaction mixture.

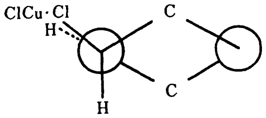
16) C. H. Brubaker, Jr., and M. Wicholas, *J. Inorg. Nucl. Chem.*, **27**, 59 (1965).

17) G. Costa, A. Camus and N. Marsich, *ibid.*, **27**, 281 (1965).

The formation of some *cis*-1,2-dichlorocyclohexane from cyclohexene strongly suggests that the intermediate complex is also of an open type. By analogy with photochlorination of chlorocyclohexane,[*2] the intermediate may assume an *axial* conformation (VII) rather than an *equatorial* one (VIII). The latter is unfavoravle because of repulsion between eclipsing Cl–CuCl group and hydrogen. Thus, chloride ion[*3] attacks VII preferentially from the *axial* side to yield the *trans* product, since the two incoming chlorine species are farther apart in transition state than in the case of an *equatorial* attack. However, in less polar solvents, increasing tightness of Cl–CuCl bond causes the first attacking group to be more bulky. As a result of greater repulsion between Cl–CuCl group and *axial* hydrogens on the ring, some inversion (or distortion) toward the *equatorial* conformation (VIII) would occur. In VIII, the difference in steric requirements between *axial* attack and *equatorial* attack is not pronounced and *cis* compound would result from the *axial* attack.



(VII)



(VIII)

## Experimental

**Materials.** *cis*- and *trans*-2-Butenes (pure grade, Takachiho Chemical Industrial Co.) were used. Cyclohexene (Koso Chemical Co.) was distilled under $N_2$ after drying over $Na_2SO_4$, which was gas chromatographically pure. Cupric chloride was of anhydrous GR grade (Koso). Methanol (GR, Koso) was distilled from $Mg(OMe)_2$, and acetic acid (GR, Koso) from $B(OAc)_3$[19] under $N_2$. The other solvents were commercially available purest reagents, distilled prior to use. Authentic *meso*- and *dl*-2,3-dichlorobutanes were synthesized by addition of chlorine to *trans*- and *cis*-2-butenes.[20] *trans*-1,2-Dichlorocyclohexane was prepared by chlorine addition to cyclohexene,[21] and *cis*-dichloride was prepared by chlorination of *trans*-2-chlorocyclohexanol[22] with $SOCl_2$[21].

**Analytical Methods.** The reaction products were analyzed by gas chromatography with He as a carrier gas. The apparatus, column and temperature were as follows. For dichlorobutanes: (A) Shimadzu GC-2C, dioctyl sebacate (plus sebacic acid) on Chromosorb W, 120°C; (B) Shimadzu GC-4APT, Igepal CO-990 on Diasolid L, 100°C. For dichlorocyclohexanes: (C) the same as B, 180°C; (D) Shimadzu GC-4APT, Ucon -50-HB5100 on Chromosorb P, 160°C. For analysis of 2-butenes: (E) Shimadzu GC-3AH, propylene carbonate plus glutaronitrile on Chromosorb W, room temp.

**Reaction of 2-Butenes.** In a 500 m*l* glass-lined autoclave (with a glass-coated thermo-well and an agitator made of Ta metal) were placed cupric chloride (6.05 g, 0.045 mol) and solvent (150 m*l*), and after slight evacuation on cooling 2-butene (*ca.* 17 g, 0.30 mol) was introduced from a pressure bottle. The autoclave was heated in an oil bath (+1.0°C) with stirring. After the reaction, the autoclave was cooled to room temperature and the reaction solution was immediately subjected to gas chromatographic analysis. The results were shown in Table 1.

When *cis*-2-butene (containing 0.4% *trans*) was reacted with cupric chloride in methanol at 150°C for 2 hr, the waste gas consisted of 97.1% *cis* and 2.9% *trans*. For *trans*-2-butene (100% *trans*) under the same reaction conditions, the composition of the waste gas was 99.0% *trans* and 1.0% *cis*.

**Reaction of Cyclohexene.** Cyclohexene (0.82 g, 0.01 mol), cupric chloride (1.34 g, 0.01 mol) and solvent (30 m*l*) were sealed in a 50 m*l* glass tube, which was then placed in a 500 m*l* autoclave. The autoclave was heated at 150°C (±1.0°C) with an oven for 2 hr with shaking (75/min). The reaction solution was taken out and analyzed by gas chromatography. The results are summarized in Table 2.

**Stability of Dichlorocyclohexane.** *trans*-1,2-Dichlorocyclohexane (1.53 g, 0.01 mol) was treated with cupric chloride (1.34 g, 0.01 mol) in methanol or acetic acid (30 m*l*), being placed in a 50 m*l* glass sealed tube, at 150°C for 2 hr with shaking. No *cis*-1,2-dichlorocyclohexane was detected in the reaction mixture by gas chromatography. Similarly, when a mixture (*cis* 47.1%, *trans* 52.9%) of dichlorides (0.51 g, 3.3 mmol) in methanol (10 m*l*) was heated with cupric chloride (0.45 g, 3.3 mmol) or cuprous chloride (0.33 g, 3.3 mmol) in a 15 m*l* glass sealed tube at 150°C for 8 hr, no fluctuation of the composition of dichlorides was observed.

The author is indebted to Professor Naoki Inamoto for valuable discussions and also to Dr. Shozo Wada for encouragement in this work.

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[*2] 2-Chlorocyclohexyl radicals were discussed in literature.[18] The present intermediate should resemble this radical closely because of its open chain character.

18) G. A. Russell, A. Ito and R. Konaka, *J. Amer. Chem. Soc.*, **85**, 2988 (1963).

[*3] From analysis of the kinetic data, the second chlorinating species is very likely chloride ion (unpublished result).

19) L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., D. C. Heath Co., Boston (1955), p. 281.

20) H. J. Lucas and C. W. Gould, Jr., *J. Amer. Chem. Soc.*, **63**, 2541 (1941).

21) B. Carroll, D. G. Kubler, H. W. Davis and A. M. Whaley, *ibid.*, **73**, 5382 (1951).

22) M. S. Newman and C. A. VanderWerf, *ibid.*, **67**, 233 (1945).