solvent from the filtered solution there was obtained 6.6 g (70%) of 2,4,5-trimethylbenzyl cyanide,[23] bp 105–115° (0.2 mm). Hydrolysis of 5.4 g of the cyanide in 90 ml of 60% sulfuric acid for 15 hr, followed by a conventional work-up, afforded 4.0 g (66%) of pure recrystallized 2,4,5-trimethylphenylacetic acid,[23] mp 128–129°. Esterification by treatment of the acid chloride with ethanol yielded pure VII, bp 90–92° (0.2 mm), in 75% yield.

Anal. Calcd for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found: C, 75.5; H, 8.9.

1,1,1-Trichloro-2-(2,4,5-trimethylphenyl)propane (X).—To a solution of 5.94 g of I in 25 ml of ether was added dropwise with stirring a solution of 0.05 mol of ethylmagnesium bromide in 50 ml of ether. After 15 min the reaction mixture was cooled and treated slowly with ice. The cold ether layer was washed with cold sodium carbonate, and the solvent was removed under reduced pressure in the cold. Infrared examination of the product (mainly VIII) showed that no I was present and OH bands in the $2.8-3.0$-μ region were strong. A solution of this crude carbinol mixture[24] in 75 ml of ether was shaken with cold 3 N hydrochloric acid, and the ether solution was then worked up in the usual way, keeping cool and in the dark. The nmr spectrum indicated that the product contained a preponderance of one (presumably the isomer shown) isomer of IX. No elemental analyses for VIII or IX were attempted because of the sensitivity of these compounds to heat.

The nmr spectrum of IX (which was undoubtedly quite pure) had two multiplets for the vinyl hydrogens, one centered at τ 3.63 (1 H) and one centered at τ 4.40 (2 H). The 4-methyl group appeared as a singlet at τ 8.42 (3 H) and the remaining methyl groups as multiplets centerd at τ 7.90, 8.15, and 8.72 (9 H).

A solution of the above semibenzene IX in 5 ml of hexane was exposed to sunlight for several hours. The solvent was then removed under reduced pressure and the residue distilled to yield 4.35 g (70%) of yellow oil, bp 81–83° (0.1 mm).

A careful fractionation afforded a pure colorless sample of X which had nmr peaks as follows: τ 2.79, 3.20 (1 H each, aromatic), a quartet centered at τ 5.92 (1 H, benzylic); a doublet centered at τ 8.39 (3 H, aliphatic CH_3); a singlet at τ 7.91 (3 H aromatic CH_3); and a partly resolved doublet at τ 7.81 (6 H, aromatic CH_3).

The structure of X was further substantiated by mass spectrophotometry. Molecular ions of weights 264–270 were obtained, the variations being attributable to the chlorine isotopes. No satisfactory elemental analyses for X were obtained owing to the lack of stability. The analyses for C, H, and Cl added to 100%, but the chlorine values were lower than required by the formula $C_{12}H_{15}Cl_3$ owing to loss of HCl.

Registry No.—(+)-I, 16214-72-5; (−)-I, 16214-73-6; (+)-II, 16214-74-7; (−)-III, 16214-75-8; (±)-IV, 16214-76-9; (+)-VI, 16214-77-0; (−)-VI, 16214-78-1; VIII, 16214-79-2; (±)-IX, 16214-80-5; (±)-X, 16214-81-6.

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[23] L. I. Smith and C. W. MacMullen, *J. Amer. Chem. Soc.*, **58**, 629 (1936).

[24] We assume that a mixture of stereoisomeric carbinols was present because of the complexity of the nmr spectrum. In another case[7] only one isomer was formed.

Studies on the Bromination of Isoprene

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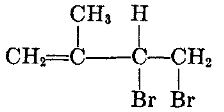
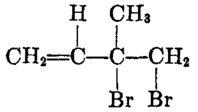
A study of the bromination of isoprene under various conditions is reported. Although previous reports stated that bromination of isoprene gave exclusively *trans*-1,4-dibromo-2-methyl-2-butene (**4**), it has been shown that, depending on the conditions, varying amounts of the following dibromides are also formed: *cis*-1,4-dibromo-2-methyl-2-butene (**3**), 3,4-dibromo-3-methyl-1-butene (**2**), and 3,4-dibromo-2-methyl-1-butene (**1**). The formation of **1**, **3**, and **4** was confirmed by comparison with authentic isomers, using infrared and vpc analysis. The unambiguous syntheses of **3** and **4** are reported. The presence of **2** was based on infrared and vpc studies, and on its rearrangement to **3** and **4**. The equilibration mechanism probably involves a covalent transition state in which the rearranging bromine atom is attached to carbon atoms at both ends of the allylic system, as proposed by Hatch, *et al.*, for the equilibration of 3,4-dibromo-1-butene and *trans*-1,4-dibromo-2-butene. In the addition of bromine to isoprene, in nonpolar solvents, it is suggested that π complexes (four of them are possible from attack of bromine on either end of the *s-cis* and *s-trans* forms of the isoprene molecule) are initially formed that break down to give bromonium ions in which the charge is highly dispersed across the whole allylic system. The bromonium ions from the *s-cis* and *s-trans* forms of isoprene would give **3** and **4**, respectively, by attack of tribromide ion on the terminal, vinyl carbon atom. Dibromide **2** (or **1**, depending on which end of the isoprene molecule was originally attacked) could be formed by opening of the three-membered ring.

Several researchers have reported that the product obtained from the bromination of isoprene is exclusively 1,4-dibromo-2-methyl-2-butene,[1] and that it has the *trans* configuration.[2,3] While studying the allylic diazide, prepared from isoprene dibromide, we became suspicious that this dibromide was not exclusively the *trans* isomer.[4] In order to establish the composition of the dibromide product from isoprene and to begin a mechanistic investigation of diene bromination, of which little is known, we undertook a study of the bromination of isoprene. Theoretically four dibromides, whose structures are shown below, are possible from the addition of bromine to isoprene. The formation of tetrabromide would be expected to be minimal since butadiene is reported to give no tetrabromide[5] and 2,3-dimethyl-1,3-butadiene in only small amounts.[6]



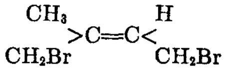
$$\begin{array}{ccccc} & \mathrm{CH_3} & & \mathrm{H} & \\ & | & & | & \\ \mathrm{CH_2{=}} & \mathrm{C} & \text{——} & \mathrm{C} & \mathrm{—CH_2} \\ & & & | & | \\ & & & \mathrm{Br} & \mathrm{Br} \end{array}$$

1



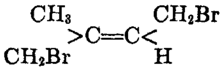
$$\begin{array}{cccc} & \mathrm{H} & \mathrm{CH_3} & \\ & | & | & \\ \mathrm{CH_2{=}C} & \mathrm{—} & \mathrm{C} & \mathrm{—CH_2} \\ & & | & | \\ & & \mathrm{Br} & \mathrm{Br} \end{array}$$

2



$$\begin{array}{ccc} \mathrm{CH_3} & & \mathrm{H} \\ & \mathrm{>C{=}C<} & \\ \mathrm{CH_2Br} & & \mathrm{CH_2Br} \end{array}$$

3



$$\begin{array}{ccc} \mathrm{CH_3} & & \mathrm{CH_2Br} \\ & \mathrm{>C{=}C<} & \\ \mathrm{CH_2Br} & & \mathrm{H} \end{array}$$

4

Results and Discussion

The results of our study on the bromination of isoprene under various conditions are shown in Table I. The percentages of the dibromides were determined by

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[1] H. Staudinger, O. Muntwyler, and O. Kupfer, *Helv. Chim. Acta*, **5**, 756 (1922).

[2] A. A. Petrov, *J. Gen. Chem. USSR*, **13**, 741 (1943).

[3] Y. M. Slobodin, *ibid.*, **24**, 444 (1954).

[4] C. A. VanderWerf and V. L. Heasley, *J. Org. Chem.*, **31**, 3534 (1966).

[5] L. F. Hatch, P. D. Gardner, and R. E. Gilbert, *J. Amer. Chem. Soc.*, **81**, 5943 (1959).

[6] O. J. Sweeting and J. R. Johnson, *ibid.*, **68**, 1057 (1946).

vpc analysis. The identity of each isomer, with the exception of **2**, was based on comparison of retention times and infrared spectra with those of authentic samples. The structure of **2** was confirmed by its infrared spectrum and by the fact that it rearranged to give **3** and **4**. The synthesis of **1** has already been reported.[2] The unambiguous syntheses of **3** and **4**, reported here for the first time, are discussed in the Experimental Section.

TABLE I
ADDITION OF BROMINE TO ISOPRENE UNDER VARIOUS CONDITIONS

Solvent	Temp, °C	Dibromides, % 1	2	3	4
Chloroform	25	5	14	8	73
Chloroform	0	3	21	5	71
Chloroform	−45	1	20	3	76
n-Pentane	25	12	4	10	74
n-Pentane	0	6	9	7	78
n-Pentane	−45	3	14	3	80
Carbon tetrachloride	25	8	5	10	77
1,2-Dichloroethane	25	5	6	11	78

The rearrangement of **4** at 25° was studied in various solvents. The percentages of the dibromides at equilibrium are indicated in Table II.

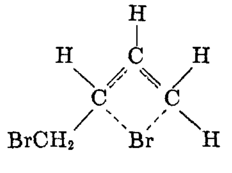
TABLE II
EQUILIBRATION OF *trans*-1,4-DIBROMO-2-METHYL-2-BUTENE[a] AT 25°

Solvent	Dibromides, % 1	2	3	4
Carbon tetrachloride	7	Trace	23	70
Chloroform	3	Trace	4	93
n-Pentane	10	Trace	21	69
1,2-Dichloroethane	5	Trace	21	74
Neat	5	Trace	21	74

[a] Although only the equilibration of **4** was studied, all of the other dibromides (**1**, **2**, and **3**) were observed to rearrange under somewhat different conditions, and undoubtedly would have given the same percentages of dibromides at 25°. The rearrangements of **1**, **2**, and **3** are discussed in greater detail in the Experimental Section.

One observation that can be made from the data in in Tables I and II is that the *trans*-1,4-dibromo-2-methyl-2-butene mentioned in previous reports contained significant quantities of other isomers, the percentages of which depended on the method of synthesis and isolation, and how long the dibromide was allowed to stand.

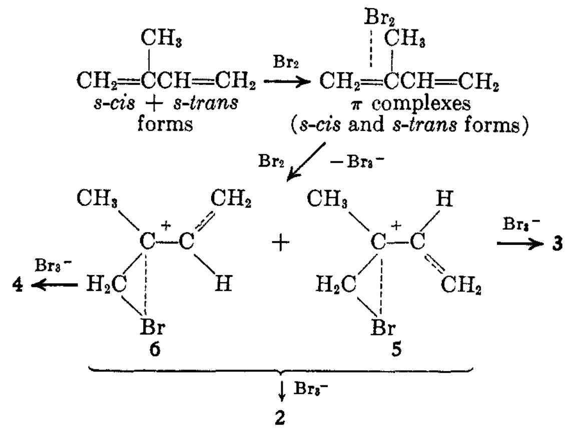
The results of the bromination of butadiene, reported by Hatch and coworkers,[5] and our results on the bromination of isoprene differ mainly in that butadiene gives no *cis*-1,4-dibromide, neither during bromination nor equilibration, and much larger quantities of vicinal dibromide. Hatch, *et al.*,[5] in discussing the mechanism of the addition of bromine to butadiene suggested that the transition states for addition of bromine to the diene and equilibration of the dibromide isomers are probably identical, and can be represented



It seems reasonable to assume that the transition state involved in the rearrangements of **1**, **2**, **3**, and **4** is essentially identical with that reported by Hatch, *et al.*[5] (shown above) for the butadiene dibromides. However, we would like to suggest that an entirely different mechanism is involved in the addition of bromine to isoprene (and perhaps other dienes). In order to discuss this mechanism, the recent studies by Buckles and coworkers[7] on the addition of bromine to an olefin (specifically *cis*- and *trans*-stilbene) must be considered. These authors have shown that the initial step in the addition of bromine to an olefin in a nonpolar solvent involves initial formation of a π complex that breaks down to give a bromonium ion, which is subsequently opened to give a dibromide. They[7] also state that, in a solvent with a low dielectric constant, the system is most stable when the charge is dispersed over a large area (a three-membered bromonium ion), rather than when it is localized on a single carbon atom (a carbonium ion). Hence, *cis*-stilbene undergoes a reaction with bromine to give exclusively *dl*-α,α^1-dibromobibenzyl. Formation of *meso*-α,α^1-dibromobibenzyl would have indicated the presence of a carbonium ion.

Perhaps isoprene (*s-cis* and *s-trans* forms), as does a monoolefin, undergoes reaction with bromine in a nonpolar solvent (*n*-pentane) to form π complexes (Scheme I). The resulting bromonium ions (**5** and **6**) should be most stable if the charges were dispersed over the whole allylic system. The extended π bonding in the bromonium ions would prevent rotation around the 2,3-carbon bond. Dibromide **2** could be formed from both **5** and **6**, by opening of the three-membered ring; **3** and **4** would result from attack of the tribromide ion on the terminal vinyl carbon atom of **5** and **6**, respectively.[8] If the equations in Scheme I correctly represent the mechanism for addition of bromine to isoprene, then the amount of **3** and **4** formed on bromination may reflect the ratio of *s-cis* and *s-trans* forms of isoprene existing at a particular temperature. The results in Table

SCHEME I



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[7] (a) R. E. Buckles, J. M. Bader, and R. J. Thurmaier, *J. Org. Chem.*, **27**, 4523 (1962); (b) R. E. Buckles, J. L. Miller, and R. J. Thurmaier, *ibid.*, **32**, 888 (1967).

[8] It seems doubtful that **3** and **4** are formed by rearrangement of **2** since it is reasonably stable under the reaction conditions. For example, after refluxing in carbon tetrachloride for 16 hr, **2** had rearranged only 60%. Since a typical bromination experiment requires about 1 hr, often at low temperatures, little rearrangement should have occurred. Small amounts of bromine or hydrogen bromide did not seem to significantly increase the rate of rearrangement.

I seem to indicate this relationship inasmuch as the increase in formation of **3** from lower to higher temperatures is in line with an increase in concentration of the less stable form of the diene (*s-cis*) at higher temperatures. The work by Buckles, *et al.*,[7] indicates that the charge should become more localized as the polarity of the solvent increases (*n*-pentane to chloroform). Again, the results in Table I confirm this, since the percentage of **2** is significantly higher in chloroform than *n*-pentane at all temperatures.[9]

Additional evidence for this mechanism comes from studies on the reaction of N-bromosuccinimide with isoprene in water. We have determined that the product from this reaction is exclusively 1-bromo-2-methyl-1-buten-2-ol.[10] No 4-bromo-2-methyl-2 buten-1-ol was detected. N-bromosuccinimide probably functions as a source of bromine, in low concentration, which attacks isoprene to give the π complex. In the polar solvent (H_2O) the π complex breaks down to give the localized carbonium ion (tertiary carbon atom) which subsequently bonds with water to give the bromohydrin. Bromonium ion formation seems doubtful since it would be opened mainly at the primary carbon atom to give 2-bromo-2-methyl-3-buten-1-ol, which undoubtedly would rearrange slowly to 4-bromo-2-methyl-2-buten-1-ol.

Attack by bromine at the opposite end of the isoprene molecule, *via* the same type of mechanism, would lead to **1** and also **3** and **4**. Attack seems to occur mainly on the double bond with the methyl group.[10]

Experimental Section[11]

Materials.—Unless otherwise indicated the solvents and reagents were obtained commercially in high purity. The isoprene, furnished by Phillips Petroleum, polymerization grade, was shaken with sodium bisulfite to remove peroxides, distilled immediately prior to use, and carefully isolated from oxygen.[12]

Bromination of Isoprene. General Procedure.—To 6.8 g (0.10 mol) of isoprene in 100 ml of solvent in a nitrogen atmosphere at the selected temperature was added dropwise with stirring 16.0 g (0.10 mol) of bromine. The solvent was removed at low pressure with no heat applied. The dibromides were analyzed without distillation. It was confirmed that the dibromides were not lost during solvent removal. Although the total yield of dibromides was not determined, it is probably quite good since little residue was observed on a few samples that were distilled.

Procedure for Analysis of the Dibromides.—The vpc analysis of the dibromides was done with an Aerograph 90 P-3 chromatograph under the following conditions: flow rate (He), 495 cc/min; column length and diameter, 6 ft × 0.25 in.; column temperature, 60°; column composition, 2.5% SE-30 on 60–80 mesh DMCS Chromosorb W. Under these conditions the retention times of **1**, **2**, **3**, and **4** are, respectively, 100, 83, 204, and 260 sec. A 10% solution of the dibromides in *n*-pentane gave the best analysis.

As nearly as could be determined, none of the dibromides rearranged on the column. However, **2** rearranged approximately 5% while passing through the considerably warmer detector.

The percentages of dibromides were based on their adjusted areas in the chromatograms. The adjustments were based on the following determinations: ratio of A_3/A_4 divided by W_3/W_4 is equal to 1,[13] and the ratio A_1/A_4 divided by W_1/W_4 is equal to 0.84. The area/weight ratio for dibromides **1** and **2** was assumed to be unity on the basis of their similar molecular structures.

Owing to the baseline drift, resulting from the high flow rate, the extreme sensitivity and other factors, the accuracy of the experimental results probably does not exceed ±(percentage of dibromide × 0.05).

The Authentic Isomers.—*trans*-1,4-Dibromo-2-methyl-2-butene (**4**) and *cis*-1,4-dibromo-2-methyl-2-butene (**3**) were synthesized from *trans*- and *cis*-2-methyl-2-butene-1,4-diol by a reaction with PBr_3 according to the method of Valette.[14] The boiling points for **3** and **4** are approximately 48–50° (0.1–0.2 mm). The boiling point of the dibromide mixture from isoprene is essentially identical with this. The infrared spectra of authentic **3** and **4** were nearly identical. Both showed a powerful absorption band at 1200 and the C–Br absorption bands at 550 and 628 cm^{-1}, respectively.[15] The structures of **3** and **4** were confirmed by the fact that, when they were heated at 100° in a sealed tube, each rearranged to give a mixture of approximately 26% **3** and 74% **4**, with small amounts of **1** and **2**.

trans-2-Methyl-2-butene-1,4-diol was prepared by the reduction of diethyl mesaconate[16] with aluminum hydride[17] in the following manner. Diethyl mesaconate (24.1 g, 0.129 mol) in tetrahydrofuran (130 ml) was added to 300 ml of 0.863 *M* aluminum hydride. Methanol was added to destroy the excess hydride, and a 60% potassium sodium tartrate solution was used to decompose the addition complex. After removal of the solvent, distillation of the remaining liquid resulted in three fractions, the highest boiling of which, bp 96–98° (0.10 mm), showed a powerful OH absorption band[15] from 3300 to 3400 cm^{-1} with essentially no carbonyl absorption. The yield was approximately 15%. Treatment of this compound with PBr_3 as indicated above, resulted in pure **4**.

cis-2-Methyl-2-butene-1,4-diol was prepared from citraconic anhydride and aluminum hydride with the same ratio of reagents as described in the preparation of the *trans* diol. The *cis* diol, which was obtained when the addition complex was destroyed with potassium sodium tartrate, contained some impurities since the infrared spectrum showed, in addition to the OH absorption band, a carbonyl band which could not be removed by distillation. Vpc analysis on a Polypak column confirmed these impurities. However, when this impure *cis* diol was treated with PBr_3, **3** was obtained without contamination.

The *cis* diol was obtained in much higher purity, but in very low yield, by decomposing the addition complex with 50% sodium hydroxide. The infrared spectrum of this diol showed no carbonyl absorption band, and was strikingly similar to the spectrum of the *trans* diol. The boiling point of the *cis* diol is approximately the same as for the *trans* diol.

Dibromides **3** and **4** and *cis*- and *trans*-2-methyl-2-butene-1,4-diol showed weak C=C absorption bands in the neighborhood of 1675 cm^{-1}. In addition to the similar OH and C=C absorption bands, the *cis* and *trans* diol showed the following principal bands (cm^{-1}), respectively: 2940, 2875, 1460, 1380, 1040, and 1009 and 2930, 2875, 1450, 1380, 1065, and 1000.

Identification of the Dibromides Isomers Formed on the Bromination of Isoprene.—The chromatogram of the appro-

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[9] Other factors may be involved in the increase of **2** in chloroform, since bromination in dichloroethane, which has a higher dielectric constant than chloroform, does not lead to a significant increase in **2**. Also, **1** does not show the same increase in going from *n*-pentane to chloroform.

[10] E. J. Reist, I. G. Junga, and B. R. Baker [*J. Org. Chem.*, **25**, 1673 (1960)] confirmed that the epoxide from this bromohydrin product is primarily 3,4-epoxy-3-methyl-1-butene (91%); they did not identify the impurity, although it was likely 3,4-epoxy-2-methyl-1-butene. A. A. Petrov [*J. Gen. Chem. USSR*, **13**, 481 (1943)], in a very similar reaction (using N-bromoacetamide instead of N-bromosuccinimide), established that the bromohydrin product is 1-bromo-2-methyl-3-buten-2-ol. Nmr studies by us on the product from isoprene, water, and N-bromosuccinimide confirm the exclusive formation of 1-bromo-2-methyl-3-buten-2-ol.

[11] Boiling points are uncorrected.

[12] If this procedure was not followed rigorously, drastically different results were obtained, probably owing to radical reactions, caused by peroxides.

[13] This ratio was determined early in the study under identical conditions except the column did not contain dichlorodimethylsilane. The slight column change should not effect this ratio.

[14] A. Valette, *Ann. Chim.*, **3**, 644 (1948).

[15] For a discussion of the positions of absorption bonds in the infrared, see L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1957.

[16] The diethyl mesaconate was prepared from highly purified mesaconic acid, ethyl alcohol, and sulfuric acid. Under these acidic conditions, rearrangement around the olefinic bond could occur. However, vpc analysis of the diethyl mesaconate indicated only one compound, presumably diethyl mesaconate.

[17] For the preparation of aluminum hydride, see H. C. Brown and N. M. Yoon, *J. Amer. Chem. Soc.*, **88**, 1464 (1966). Lithium aluminum hydride was employed, under various conditions, for the reduction of diethyl mesaconate, but without success.

priate bromination product (example *n*-pentane, 25°) showed four peaks. The second, third, and fourth peaks were identified as **1**, **3**, and **4**, respectively, on the basis that the retention time and infrared spectrum[18] of each was identical with that of the appropriate authentic isomer. The second and third peaks were further confirmed as **1** and **3** by heating samples of them at 100° and observing that they rearranged to essentially the same mixtures as reported for authentic **3** and **4**.

The dibromide corresponding to the first peak in the chromatogram and assigned structure **2** was isolated from the dibromide mixture (*n*-pentane, 25°) by low temperature fractional distillation. It was assigned structure **2** on the basis that its infrared spectrum showed the terminal vinyl absorption bands[15] at 930 and 990 cm^{-1}, and that it rearranged[8] on refluxing to **3** and **4**.

The Equilibration Studies.—Solutions of approximately 15% **4** in the solvents listed in Table II were allowed to stand at room temperature (approximately 25°) for about 6 months. Analyses at the end of 3- and 6-month periods were essentially the same. As indicated, the equilibration of **4** without a solvent was studied. The essentially pure **4** used in the equilibration study was prepared by recrystallization of the product obtained from the bromination of isoprene at −45°. The recrystallization was carried out in *n*-pentane at Dry Ice temperatures. Vpc analysis indicated that only traces of the other dibromides remained. The **4** prepared in this manner was used in the equilibration studies without distillation since distillation sometimes resulted in rearrangement. We are unable to account for the fact that distillation of **4**, purified by recrystallization, did not always result in rearrangement. However, equilibration studies in $CHCl_3$ on a sample of **4**, prepared in this way and distilled without rearrangement, gave identical results with that of undistilled **4**.

Registry No.—Isoprene, 78-79-5; **3**, 16526-18-4; **4**, 16526-19-5.

Acknowledgment.—Acknowledgment is made to the Research Corporation and the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

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[18] A small sample of each isomer was isolated from the gas chromatograph. These samples were used to make the infrared spectra. The spectra were identical with the spectra of the authentic isomers, except for some very minor impurity peaks in the latter.

The Chlorination of Olefins with Cupric Chloride. A Comparative Study of *trans*-Ethylene-d_2 and *cis*- and *trans*-2-Butene

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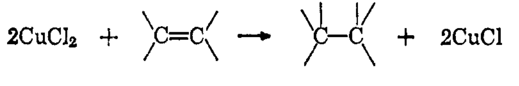
Received December 13, 1967

The chlorination of olefins at 320° with cupric chloride does not always proceed with a high degree of *trans* addition. Although both *cis*- and *trans*-2-butene chlorinate by largely *trans* addition, the chlorination of *trans*-ethylene-d_2 is nearly random. The order of stereoselectivity is *cis*-2-butene > *trans*-2-butene ≫ *trans*-ethylene-d_2. The random chlorination of *trans*-ethylene-d_2 occurs during the product-forming step. Neither ethylene-d_2 nor product isomerization is responsible. However, most of the randomly chlorinated product from *cis*- and *trans*-2-butene can be explained by 2-butene isomerization and the interconversion of the 2,3-dichlorobutane diastereomers. The greater stereoselectivity in the chlorination of *cis*- over *trans*-2-butene is mainly due to the isomerization of *meso*- into *dl*-2,3-dichlorobutane. At 320°, this isomerization occurs approximately 1.4 times faster than the isomerization of *dl*- into *meso*-2,3-dichlorobutane. Evidence is also presented which shows that cupric chloride and not chlorine is the chlorinating agent. The mechanism of this reaction is discussed in terms of chloronium ion and radical intermediates.

The literature contains several examples of the use of cupric chloride as a versatile chlorinating agent for a variety of organic molecules.[1–4] Undoubtedly, the most extensive industrial application of this chemistry of cupric chloride is in so-called "oxychlorination" reactions. This is a vapor phase reaction normally carried out at temperatures of 220–330°.[5] In this process, cupric chloride chlorinates the double bond of the olefin and in turn is reduced to cuprous chloride. Cuprous chloride is then reoxidized with hydrogen chloride and oxygen, and the process is repeated many times.



$$2CuCl_2 + >C{=}C< \longrightarrow >C(Cl){-}C(Cl)< + 2CuCl \quad (1)$$

$$2CuCl + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O \quad (2)$$

This paper deals with the mechanism of the olefin chlorination step (eq 1). Arganbright and Yates recently reported on the chlorination of *cis*- and *trans*-2-butene with cupric chloride supported on pumice.[1] They found that at 290° this reaction proceeds with a high degree of *trans* addition. In this present work, we have extended the study of olefin chlorination with cupric chloride with the objective of answering the following questions. (1) Do olefin substituents greatly influence the stereochemistry of this reaction? Specifically, is the chlorination of the simplest olefin, ethylene, also highly stereoselective? (2) Why is the chlorination of *cis*-2-butene more stereoselective than *trans*-2-butene? (3) Is elemental chlorine involved in this reaction?

Results

Both *cis*- and *trans*-ethylene-d_2 were required for this study. They are conveniently synthesized by the stereospecific reduction of acetylene-d_2.[6] We confirmed the stereochemistry of these reductions by infrared spectroscopy. The characteristic bands for *cis*- and *trans*-ethylene-d_2 appear at 842 and 987 cm^{-1}, respectively.[7,8]

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