[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

# The Decomposition of Secondary Alkyl Chlorosulfites. II. Solvent Effects and Mechanisms

BY C. E. BOOZER AND E. S. LEWIS

RECEIVED DECEMBER 2, 1952

The effect of a variety of solvents on the kinetics and stereochemistry of alkyl chloride production from secondary alkyl chlorosulfites has been studied. The steric results vary from clean retention in dioxane to clean inversion in toluene. Tetrahydropyran, tetrahydrofuran, dioxolane, ethylene chloride and ethylene bromide give in this order decreasing degrees of retention; saturated hydrocarbons, acetonitrile, cyclohexanone, thiophene, acetal and acetophenone give low yields of predominantly, but not cleanly inverted chloride. The chlorosulfite disappeared by a first-order reaction, in all solvents in which kinetic measurements were possible, and in the case of isoöctane this was accompanied by an autocatalytic reaction. Three different mechanisms are proposed, all involving the ionization of the sulfur–chlorine bond as the rate determining step, and involving ion-pairs of stable configuration as intermediates.

## Introduction

Previous work on the formation of alkyl chlorides from chlorosulfites showed that intermediates in this reaction must have much ionic character.[1] Ionic intermediates have been proposed for the reaction of 3-chlorobutanol-2[2] with thionyl chloride, and Cram has proposed that ion-pairs are intermediates in the reaction of 3-phenylbutanol-2 with thionyl chloride.[3] Similar cyclic intermediates involving participation of the neighboring chlorine or phenyl were proposed to explain the stereochemical results. Ionic reactions of chlorosulfites of a different sort have been proposed by the English workers,[4] especially with regard to the reactions of α-phenylethanol to give the chloride of inverted configuration.

## Experimental

**Materials.**—Pentanol-2 was purified by distillation of Matheson best grade through an efficient packed column; it boiled at 119.0–119.5° (uncor.) with $n^{20}\text{D}$ 1.4061. The chlorosulfites were prepared as before.[1] The optically active alcohols used were about 10% optically pure, giving rise to chlorides with rotations in most cases of two to three degrees. The ether solvents were purified from commercial materials by boiling under reflux with sodium for many hours, followed by careful fractional distillation. Phillips "Pure grade" 2,2,4-trimethylpentane was stored over sodium and used without other purification. Toluene was Merck Reagent grade, distilled from sodium. Kerosene was purified by extracting it with three portions of fuming sulfuric acid, followed by washing with water and distillation from sodium; it boiled 85 to 95° at 10 mm. The remaining solvents were dried extensively over calcium sulfate, then fractionally distilled. The alcohols were partially resolved *via* the brucine salts of the acid phthalates.[5]

**Product Isolation.**—The methods previously used for isolation of olefins and chlorides were extended. Both 2-chlorobutane and 2-chloropentane were removed from the solvent by distillation through an all-glass, center-rod column of low hold up and high efficiency. Water soluble and acidic materials were then removed by washing with sodium carbonate solution, then the chlorides were dried and redistilled. Rotations were taken at this point and occasionally again after another distillation. The values agreed in these cases to 0.01°. The losses in these isolations are variable, but not large.

**Kinetic Methods.**—The disappearance of chlorosulfite was followed spectrophotometrically as before, and was possible even in toluene solution, by diluting samples of this solution with isoöctane, since the extinction coefficient of the chlorosulfites is much greater than that of toluene at 234 mμ. One run in dioxane was followed in the polarimeter. This was feasible since this reaction going with retention of configuration goes with a change of sign of rotation. Since the precision is low because of thermostating difficulties and gas formation in the polarimeter tube, the method was not applicable to most other solvents, where the change in rotation is smaller.

## Results

The results of the isolation experiments are shown in Table I. The column showing rotation of the alkyl chloride is that calculated on the basis of an optically pure dextrorotatory alcohol, although much less active alcohols of both signs of rotation were actually used. Because of this, the accuracy of these rotations is less than the precision of reading the polarimeter, and the accuracy of these calculated values is about 0.2°. Since the sign of rotation of alcohols and chlorides of the same configuration is the same, a positive rotation shows predominant retention, and negative rotation corresponds to an inverted product. The column headed "% optical purity" gives the per cent. of the rotation of an optically pure chloride. The values used for the rotations of optically pure alcohols and chlorides are given in Table II. These are all taken from the literature and are probably fairly accurate, although the exact values are not pertinent to any of the arguments which follow.

TABLE I

STEREOCHEMICAL RESULTS OF THE DECOMPOSITION OF CHLOROSULFITES IN VARIOUS SOLVENTS

| Solvent | Alkyl group | RCl, % | Olefin, % | Temp., °C. | $[\alpha]^{27}\text{D}$ of RCl | Optical purity, % |
|---|---|---|---|---|---|---|
| Dioxane | Butyl | 50 | .. | 62 | +32.6 | 96.5 |
| Dioxane | Pentyl | 46 | 20 | 76 | +41.9 | 98.5 |
| Tetrahydropyran | Butyl | 40 | .. | 62 | +33.0 | 98.2 |
| Ethylene chloride | Butyl | 10 | .. | 76 | +18.5 | 55 |
| Tetrahydrofuran | Octyl | 34 | 56 | 71 | +12.5 | 35 |
| Ethylene bromide | Pentyl | 30 | 40 | 62 | +16.1 | 32 |
| Dioxolane | Octyl | 11 | 52 | 74 | + 7.2 | 20 |
| Acetophenone | Octyl | 15 | .. | 77 | − 6.5 | 18 |
| Acetal | Octyl | 9 | 29 | 77 | − 9.6 | 27 |
| Cyclohexanone | Butyl | 40 | .. | 78 | −12.2 | 36 |
| Isoöctane | Octyl | 38 | 15 | 100 | −15.3 | 43 |
| Thiophene | Octyl | 27 | 38 | 74 | −17.6 | 49 |
| Acetonitrile | Butyl | 30 | .. | 62 | −21.6 | 64 |
| Dioxane + $10^{-3}$ $M$ $C_5H_5N \cdot HCl$ | Butyl | 51 | .. | 30.5 | −22.7 | 67 |
| Kerosene | Octyl | 20 | .. | 111 | −28.0 | 78 |
| Toluene | Butyl | 50 | .. | 62 | −32.0 | 95 |
| No solvent | Octyl | 60 | .. | 70 | −33.2 | 93 |

---

[1] E. S. Lewis and C. E. Boozer, THIS JOURNAL, 74, 308 (1952).

[2] H. J. Lucas and C. W. Gould, *ibid.*, 63, 2541 (1941).

[3] D. J. Cram, *ibid.*, 75, 332 (1953).

[4] W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937).

[5] R. N. Pickard and J. Kenyon, *ibid.*, 99, 45 (1911).

TABLE II

ROTATIONS OF OPTICALLY PURE ALCOHOLS AND CHLORIDES

| Alkyl group | $[\alpha]_D$ alcohol | $[\alpha]_D$ chloride |
|---|---|---|
| 2-Butyl | 13.52 at 27°[5] | 33.8 at 25°[6] |
| 2-Pentyl | 13.44 at 27°[5] | 42.46 at 20°[7] |
| 2-Octyl | 9.51 at 26°[5] | 35.8 at 20°[8] |

There is an error in the yields of chloride and especially in the stereochemical result in the reactions using the 2-octyl compound. The 2-octyl chlorosulfite decomposes perceptibly at temperatures necessary to distil it, giving a distillate significantly contaminated with chloride of extensively inverted configuration. The last entry in Table I shows the result of this decomposition without solvent. Thus the product of any reaction of 2-octyl chlorosulfite contains some inverted chloride present when the reaction was started. The yield of chloride is thus slightly high, and the extent of inversion is also too high, especially when the yield is low. This effect is virtually absent with the other two chlorosulfites, since nearly clean retention was observed with both, showing less than 1% contamination. The previously reported analysis of the butyl compound also showed freedom from contamination.

In addition to the solvents mentioned in Table I, several others gave no alkyl chloride. Only 2-pentene was isolated from the pentyl compound in di-*n*-butyl ether; no alkyl halide could be isolated from decompositions in diisoamyl ether, butyl bromide and nitrobenzene. In nitromethane, the butyl compound gave rapidly an unidentified white crystalline solid, m.p. 144–146°, and in dimethylformamide the reaction was too violent to encourage further study.

The first-order rate constants for the disappearance of chlorosulfite are given in Table III. Some runs essentially duplicate our previous results and conditions, although improved techniques make the new values more accurate. The values previously reported at the lower temperature are in error due to concentration of the solution by solvent evaporation. The new values have been reproduced at different nitrogen flows, all lower than those used previously. The heat of activation now calculated by the Eyring equation[9] in dioxane over a temperature range of about 35° is 20.5 kcal./mole. Only in isoöctane was there a poor fit to first-order kinetics under some conditions. In this solvent a first-order plot showed a marked acceleration in rate as the reaction proceeded. Passing a slow stream of dry nitrogen through the reaction flask reduced the extent of this acceleration, and a more rapid stream of nitrogen apparently removed this effect entirely and good first-order kinetics were obtained, giving a rate constant agreeing with that previously reported. The extent of this effect is shown in Fig. 1. Apparently, in this solvent the reaction is autocatalytic, with hydrogen chloride or sulfur dioxide acting as the catalyst.[10] In dioxane, toluene and ethylene chloride the rate was independent of nitrogen flow, and there was no evidence for autocatalysis in any of the other solvents either. No kinetic data could be obtained in any of the other solvents listed in Table I, because of side reactions, and the order in these solvents is therefore not known.

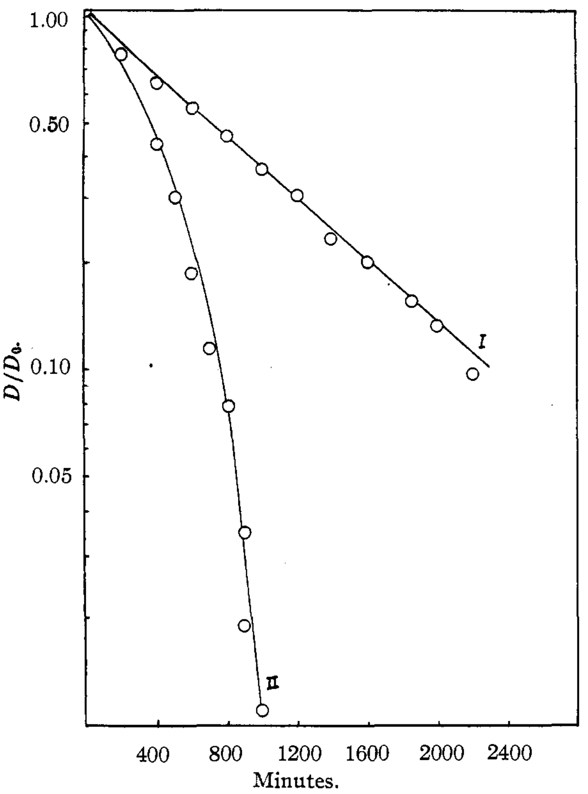


Fig. 1.—The course of decomposition of *s*-butyl chlorosulfite in isoöctane, as followed by optical density at 234 mμ: curve I, with nitrogen flow, curve II, with no gas flow.

TABLE III

RATES OF DECOMPOSITION OF CHLOROSULFITES IN VARIOUS SOLVENTS

| Chlorosulfite | Solvent | Temp., °C. | $k \times 10^4$ sec.$^{-1}$ |
|---|---|---|---|
| Butyl | Dioxane | 99 | 56 |
| Butyl | Dioxane | 77.5 | 9.8 |
| Butyl | Dioxane | 61.5 | 2.18 |
| Octyl | Dioxane | 76.5 | 10[a] |
| Pentyl | $(CH_2Cl)_2$ | 74 | 5.8 |
| Octyl | Tetrahydrofuran | 71 | 4.0 |
| Octyl | Dioxolane | 74 | 26 |
| Octyl | Acetal | 76.5 | 6.0 |
| Butyl | Isoöctane | 96 | 0.167 |
| Butyl | Toluene | 96 | 2.62 |
| Pentyl | Butyl ether | 99 | 1.0[b] |

[a] Polarimetric analyses used. [b] No 2-chloropentane could be isolated.

## Discussion

The variety of stereochemical results shows that at least two mechanisms must operate, one giving a

---

(6) R. L. Letsinger, L. G. Murray and R. L. Burwell, Jr., THIS JOURNAL, **73**, 2373 (1951).

(7) H. Braun, *Rec. trav. chim.*, **65**, 799 (1946).

(8) E. D. Hughes, C. K. Ingold and S. Masterman, *J. Chem. Soc.*, 1196 (1937).

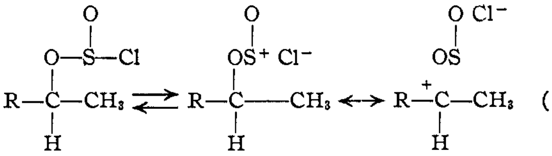
(9) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941.

(10) It has been observed that hydrogen chloride has an effect on stereochemical results of some reactions of thionyl chloride with alcohols: F. A. Abd Elhafez and D. J. Cram, THIS JOURNAL, **75**, 339 (1953).

chloride of retained configuration, and one giving an inverted product. An entirely distinct mechanism, going by way of a perfectly symmetrical intermediate, need not be considered, since even in aqueous solutions, where carbonium ion intermediates are possibly most favorable, secondary alkyl halides or sulfonates with a single asymmetric center do not yield totally racemic products on solvolysis.

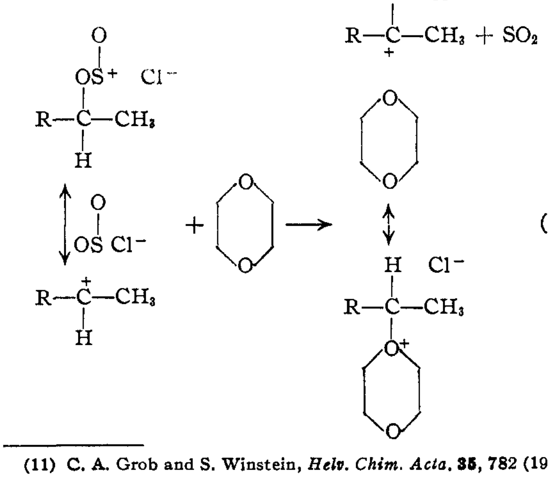
In dioxane and in toluene complete stereospecificity with opposite results is very nearly attained, but the rates of chlorosulfite decomposition differ only by a factor of about 20, and the rates in other solvents with intermediate results stereochemically are not markedly different. Thus, the rate determining step may well be similar or even identical in the different solvents, and we propose that this common step is the ionization of the sulfur–chlorine bond to give an undissociated ion pair. The slow reactions in the hydrocarbons may be ascribed partly to the low dielectric constant and partly to the very low ion solvating ability. The different stereochemical results in toluene, dioxane and acetonitrile, the base strengths of which increase in this order, suggest that basicity is not the only determining factor. The failure of the rates to follow accurately the dielectric constant of the solvent should not be used as evidence against ionization as the rate-controlling step. Thus an analogous reaction, the ionization of cholesterol dibromide and related substances to give the bromonium bromide ion-pair, also follows only very roughly the dielectric constant of the solvent.[11] On the basis of the stereochemical results and the solvent properties, three similar mechanisms are proposed for three apparently different cases. For the reaction giving retention of configuration, we can write the following three-step process.

First, ionization of the chlorine–sulfur bond, and consequent weakening of the carbon–oxygen bond.



$$\mathrm{R{-}\overset{\overset{\overset{O}{|}}{O{-}S{-}Cl}}{\underset{H}{C}}{-}CH_3 \rightleftarrows R{-}\overset{\overset{O}{OS^{+}\;Cl^{-}}}{\underset{H}{C}}{-}CH_3 \longleftrightarrow R{-}\overset{\overset{O\;Cl^{-}}{OS}}{\underset{H}{\overset{+}{C}}}{-}CH_3} \quad (1)$$

The dissociation of the ion-pairs in these solvents must be insignificant. The cation is written as the resonance hybrid to show its identity with a carbonium ion solvated with sulfur dioxide. The anion shown here is probably not different from the well-known ion resulting from solvation of chloride ion with sulfur dioxide.

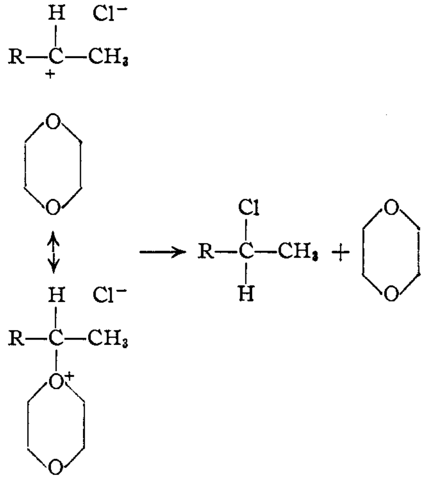


(2)

Second, the solvation of the resulting carbonium ion by the solvent, in this example dioxane, and the loss of the now unnecessary sulfur dioxide of solvation.

These intermediates, while in many respects well described as carbonium ions "solvated" with sulfur dioxide or with dioxane, do not racemize. This results from the fact that the solvation introduces an asymmetry which is present even if the carbonium ion itself is planar.

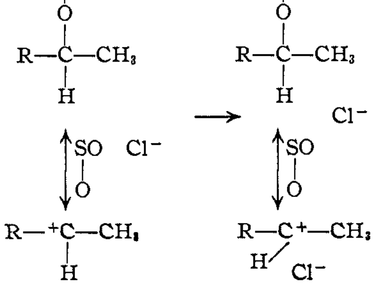
Third, the carbonium ion-pair collapses to give a neutral molecule.



(3)

This step may be regarded also as a displacement of dioxane from the oxonium ion, as well as a reaction of chloride ion with the solvated carbonium ion. Whatever words are used to describe the process, it is clear that the chlorine becomes attached to carbon on the same side of the plane of R, $CH_3$ and H from which $SO_2$ left. Thus these steps can explain the retention of configuration. The function of the solvent dioxane is seen to be exactly analogous to that of chlorine in the chlorobutanols[2] or phenyl in the phenylbutanols.[3]

In toluene a different mechanism must apply. However, the reversible reaction (1) can still occur, but since toluene is neither nucleophilic, nor a good solvating agent for carbonium ions for any other reason, (2) cannot take place. Thus the loss of sulfur dioxide from the carbonium ion cannot



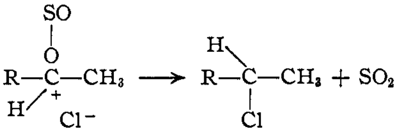
(4)

---

[11] C. A. Grob and S. Winstein, *Helv. Chim. Acta*, **35**, 782 (1952).

ordinarily occur, and attack on that side of the carbonium ion is difficult. Under these conditions a slower reaction can occur within the ion pair, consisting simply of a relative motion of the ions.

The rapid reaction analogous to (3) can now take place



$$\mathrm{R{-}\overset{\overset{SO}{|}}{\underset{H\diagup\ \ Cl^-}{\overset{O}{\underset{+}{C}}}}{-}CH_3 \longrightarrow R{-}\underset{\underset{Cl}{|}}{\overset{H\diagdown}{C}}{-}CH_3 + SO_2} \qquad (5)$$

to give the inverted chloride.

The distinction between these two mechanisms lies in the solvating power of the dioxane in the first case, which is able to displace sulfur dioxide from the carbonium ion. Toluene is clearly unable to compete for the carbonium ion with sulfur dioxide. Since chloride ion is able to displace both sulfur dioxide and dioxane, an order of solvating abilities can be constructed: $Cl^- >$ dioxane $> SO_2 >$ toluene. We believe that there is a continuous transition from the intermediates best described as having mostly covalent bonds and those which would ordinarily be described as solvated carbonium ions. These views are not intended to be fundamentally different from those of Swain.[12]

In the solvents acetonitrile, the ketones and most of the other solvents the stereochemical result is nearer to that in toluene than that in dioxane. In isoöctane the mechanism involving the previously mentioned autocatalytic reaction is present, so the stereochemical result of the first-order reaction alone is not known. It is clear, however, that in the case of the majority of the other solvents, no pertinent property is intermediate between that of dioxane and the other cyclic ethers and that of toluene. For this reason a combination of the mechanism proposed for toluene and that for dioxane is inadequate for these solvents. Nearly all of these solvents have appreciably higher dielectric constants than either dioxane or toluene, and the dissociation of ion-pairs is no longer prohibitively difficult. A new ionic chain reaction which would clearly give inversion is now possible (6).

$$\mathrm{Cl^- + ROSOCl \longrightarrow ClR + OSO + Cl^-} \qquad (6)$$

If ionization of the chlorosulfite provides this chloride ion, and the chains are broken by the reaction (7)

$$\mathrm{Cl^- + ROSO^+ \longrightarrow RCl + SO_2} \qquad (7)$$

then the reaction will be no longer kinetically first order, but can readily be shown to fall between first order and three-halves order, approaching the latter with long kinetic chains, that is, with reaction (6) accounting for most of the RCl produced. Experimentally we have no clear-cut case of one of these fairly high dielectric constant solvents which gives unmistakable first-order kinetics. These are not readily obtained in any of our solvents, both because the desired products account for only a small fraction of the total product, and because the solvents do not survive the strongly acid conditions, so that the solvent reacts extensively and becomes opaque in the region of analytical usefulness. The inversion of configuration in the presence of pyridine hydrochloride, shown in Table I, supports the idea of a reaction between chloride ion and chlorosulfite with inversion. Further support of this explanation is provided by the decomposition without solvent, which gives an extensively inverted product. This must be a fairly high dielectric constant medium with a fairly high concentration of chloride ion, by analogy with the high dielectric constant and significant self-ionization of the structurally similar thionyl chloride.[13]

In the fairly high dielectric constant solvents, reaction (7) probably will not give the same stereochemical result as reaction (3) since the dissociation of the ion-pairs will allow the solvent to replace chloride ion in the ion-pair of reaction (3). The resulting carbonium ion is then symmetrically solvated and on reaction with chloride ion will give a racemic product. We cannot estimate the extent to which this process contributes to the loss of optical activity.

Several alternative steps can be suggested for these three mechanisms. As an alternative to the two steps (1) and (2) a single step displacement can be proposed to give the oxonium ion in one step. Since the reaction (1) takes place even in toluene, we have chosen to emphasize the carbonium ion character of the reaction, but believe that the nucleophilic character of the solvent is important, possibly because of the reversibility of reaction (1). An immediate ionization of the carbon–oxygen bond can also be written

$$\mathrm{ROSOCl \longrightarrow R^+ + OSOCl^-} \qquad (8)$$

The facile reaction of 3-chlorobutanol-2 with thionyl chloride[2] suggests that the ionization of the chlorosulfite is probably not much slower than that of 2-butyl chlorosulfite. It has been shown that a neighboring chlorine can be expected to retard ionization by the inductive effect by a factor of about $10^4$.[14] The apparent absence of this factor suggests that the initial ionization is more remote from the carbon–chlorine dipole, thus the ionization of the sulfur–chlorine bond is more attractive.

A factor which has not been considered is the possibility of further stereoisomerism due to an asymmetric sulfur. While this effect cannot be ruled out, there appears to be no evidence that the chlorosulfites are separable mixtures of isomers. Our samples had accurately reproducible ultraviolet spectra, and the rotation of one sample of the octyl compound was in rough agreement with that reported on an undistilled sample by Gerrard.[15] Since ionization of the sulfur–chlorine bond provides an easy route for interconversion of the isomers, we do not anticipate any considerable differences in reactivity.

A refinement may be of significance in reaction (1). The ionization may be assisted by the attack of a nucleophilic solvent on sulfur. This does not

---

[12] C. G. Swain and W. P. Langsdorf, Jr., THIS JOURNAL, **73**, 2813 (1951), and elsewhere.

[13] P. Walden, *Z. anorg. Chem.*, **25**, 209 (1900).

[14] S. Winstein, E. Grunwald and L. L. Ingraham, THIS JOURNAL, **70**, 821 (1948).

[15] W. Gerrard, *J. Chem. Soc.*, 85 (1944).

appear to be necessary in all solvents, and, if present, alters basically none of the arguments used before.

**Acknowledgment.**—We wish to thank the Research Corporation for a Frederick Gardner Cottrell grant which was of great assistance to this research.

HOUSTON, TEXAS

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, INSTITUTE OF POLYMER RESEARCH, POLYTECHNIC INSTITUTE OF BROOKLYN]

# The Reaction of Hydrogen Bromide with Cycloöctatetraene

BY C. G. OVERBERGER, MORTON A. KLOTZ[1] AND H. MARK

RECEIVED AUGUST 25, 1952

The reaction of cycloöctatetraene with two moles of hydrogen bromide in benzene solution and without solvent has been studied. Treatment of the unstable adduct with dimethylamine at room temperature gave largely a dimethylaminobromocycloöctadiene and a small amount of N,N',$\alpha$-trimethylbenzylamine. Hydrogenation of the dimethylaminobromocyclooctadiene gave dimethylaminocycloöctane identical in its properties and derivatives with the known compound. An attempt to demonstrate whether this was a radical or ionic reaction was inconclusive. The reaction of cycloöctatetraene with two moles of hydrogen bromide in glacial acetic acid gave largely $\alpha$-bromoethylbenzene as previously reported when one mole of hydrogen bromide was used and also a small amount of dimethylaminobromocycloöctadiene after treatment with dimethylamine at room temperature.

In connection with current work designed to elucidate the structure of several cycloöctatetraene dimers, it became of interest to study the peroxide-catalyzed addition of hydrogen bromide to cyclooctatetraene in order to obtain information as to whether a radical such as a bromine atom would isomerize the ring. It soon became apparent that the reaction with hydrogen bromide could not be mechanistically categorized as easily as hoped. This paper will describe the addition of two moles of hydrogen bromide to cycloöctatetraene in benzene and without solvent, the course of the reaction when benzoyl peroxide is added, and the effect of radical inhibitors on the products of the reaction.

In addition, the work of Reppe and co-workers,[2] who added hydrogen bromide to cycloöctatetraene in glacial acetic acid, was repeated and an additional product was isolated and characterized when two moles of hydrogen bromide was employed.

Two moles of hydrogen bromide was added to cycloöctatetraene and, after treatment of the adduct with dimethylamine, the product, unstable in air, was either treated with picric acid to give a stable picrate, or, if the amine was to be used immediately, was distilled to give I in 68.4% yield based on cycloöctatetraene and a 5.5% yield of N,N',$\alpha$-trimethylbenzylamine (II). I was obtained from its picrate by chromatography on activated alumina in 85–94% yield. On the addition of one mole of hydrogen bromide, only I could be obtained in lower yield.[3]

The ultraviolet absorption spectrum, $\lambda_{max}$ 222 m$\mu$, log $\epsilon$ 3.78 (Fig. 1), indicates that a conjugated system of double bonds is present and demonstrates that this product is probably an eight-membered ring and not a bicycloöctene derivative. Cope and Overberger[4a] reported $\lambda_{max}$ 220, log $\epsilon$ 3.9 for $\alpha$-desdimethylgranatanine. Quantitative reduction over platinum at atmospheric pressure (97%, calculated for 3 moles of hydrogen) gave dimethylaminocyclooctane identical in its physical properties with that reported in references 7 and 13. The infrared spectrum[5] of the methiodide of dimethylaminocycloöctane prepared in this way was identical with the spectra of the methiodides prepared as described by 4a and 4b. The melting point of the picrate derivative is also identical with that reported in references 4b and 13.

The N,N',$\alpha$-trimethylbenzylamine (II) was identical with a known sample prepared from $\alpha$-bromoethylbenzene. A mixed melting point with a known sample of its picrate was not depressed.

When the reaction was carried out in the presence of benzoyl peroxide, a similar result was obtained: the average yield of I was 42.3%, and of N,N',$\alpha$-trimethylbenzylamine, 8.1%. When the reaction was carried out in the presence of different concentrations of radical inhibitors, such as *p*-thiocresol, *sym*-trinitrobenzene and *p*-*t*-butylcatechol, the reaction gave about the same proportion of products.

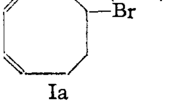
When hydrogen bromide was added to cyclooctatetraene in glacial acetic acid according to the procedure of Reppe, *et al.*, $\alpha$-bromoethylbenzene was obtained as reported. The physical constants of the product were shown to be identical with a known sample. The infrared spectrum was identical with the spectrum of a known sample. When the reaction was carried out with two moles of hy-

---

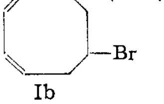
[1] This paper comprises a portion of a thesis presented by Morton A. Klotz in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the Graduate School of the Polytechnic Institute of Brooklyn.

[2] W. Reppe, O. Schlichting, K. Klager and T. Toepel, *Ann.*, **560**, 1 (1948).

[3] The most probable structures for the dimethylaminobromocyclooctadiene are Ia and Ib. Evidence for the position of the bromine and



Ia



Ib

dimethylamino groups is not reviewed in this paper. Evidence accumulated thus far has revealed that the bromine is not in an allylic or vinyl position and that a vinyl amine is not present. It is always possible that the intermediate dibromo compound is a bicyclic derivative but it is unlikely.

[4] (a) A. C. Cope and C. G. Overberger, THIS JOURNAL, **70**, 1433 (1948); (b) A. C. Cope and L. L. Estes, Jr., *ibid.*, **72**, 1128 (1950).

[5] We are indebted to Professors A. C. Cope and R. C. Lord of the Massachusetts Institute of Technology for the samples of methiodides and the infrared spectra, respectively.