[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, UNIVERSITY OF WASHINGTON]

The Stereochemistry of the Debromination of Vicinal Dibromides by Metals[1]

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The debromination of *meso-* and *dl*-2,3-dibromobutane with sodium in liquid ammonia gave the same mixture of *cis-* and *trans*-2-butene, whereas *meso-* and 50% *meso*–50% *dl*-1,2-dibromo-1,2-dideuteroethane yielded slightly different mixtures of *cis-* and *trans*-1,2-dideuteroethylene. Magnesium in tetrahydrofuran, as well as zinc in water, yielded exclusively the "*trans*" debromination products with these dihalides. Both *meso-* and *dl-* forms of α,α'-dibromobibenzyl and sodium α,α'-dibromosuccinate gave essentially only the *trans*-olefin with magnesium or zinc. Conditions for debromination did not bring about isomerization of any of the olefin products. Debrominations with the divalent metals are discussed in terms of an ionic mechanism; those with sodium, in terms of a free radical mechanism.

It has been reported by Young, Jasaitis and Levanas[2] that the action of zinc on *meso*-4,5-dibromoöctane yields pure *trans*-4-octene, whereas *dl*-4,5-dibromoöctane yields *cis*-4-octene. In the present work, the results of which are summarized in Table I, it has been found that magnesium in tetrahydrofuran and zinc in water gives exclusively "*trans*" elimination of bromine from *meso-* and *dl*-2,3-dibromobutane and from 95% *meso*–5% *dl*-1,2-dibromo-1,2-dideuteroethane. On the other hand, with sodium in solution in liquid ammonia *meso-* and *dl*-2,3-dibromobutane gave a mixture of 2-butenes of essentially the same composition. Under the same conditions, a mixture of 95% *meso*–5% *dl*-1,2-dibromo-1,2-dideuteroethylene and a 50% *meso*–50% *dl*-mixture gave slightly different percentages of *cis-* and *trans*-1,2-dideuteroethylene (Table I).

TABLE I

SUMMARY OF DEBROMINATION RESULTS

Dibromide	*trans*-Olefin in product, % Mg in C_4H_8O	Zn in H_2O	Na in NH_3
95% *meso*–5% *dl*-CHDBrCHDBr[a]	96.0, 93.0	96.0, 94.0	56.5, 56.9, 56.4
50% *meso*–50% *dl*-CHDBrCHDBr[a]	....	....	50.3, 49.5, 49.2
meso-$CH_3CHBrCHCH_3Br$[a]	95.3, 94.8	95.2, 96.4	65.5, 65.5
dl-$CH_3CHBrCHCH_3Br$[a]	7.5, 4.6	3.5, 5.0, 3.0	68.5, 69.8
meso-$C_6H_5CHBrCHBrC_6H_5$	98, 100[b]	97, 100[b,c]	....
dl-$C_6H_5CHBrCHBrC_6H_5$	93, 88, 90[b]	88, 89[b]	....
meso-$(CHBrCOONa)_2$	....	88, 91[b]	....
dl-$(CHBrCOONa)_2$	....	94, 96[b]	....

[a] Estimated total experimental error of ±3%. [b] These figures are not very precise; see Experimental. [c] Ethanol as the solvent.

Although debromination of purely aliphatic dihalides with magnesium and zinc is stereospecifically "*trans*," the debromination with these divalent metals of α,α'-dibromobibenzyl and sodium α,α'-dibromosuccinate is not stereospecific. Both *meso-* and *dl*-α,α'-dibromobibenzyl gave close to 100% *trans*-stilbene with magnesium in tetrahydrofuran and zinc in ethanol. Parallel results were obtained by Otto and Stoffel[3] with zinc and hydrochloric acid in ethanol. The possibility existed that on debromination of *dl*-α,α'-dibromobibenzyl *trans*-stilbene might have arisen by isomerization of unstable *cis* products. For example, it has been reported[4] that the isomerization of *cis*-stilbene to *trans* by boron trifluoride occurs at 25°, although Downing and Wright[5] were unable to confirm this observation. However, it was shown in the present work that *cis*-stilbene remains unchanged under the conditions prevailing in the debrominations with magnesium or zinc.

The debromination with zinc and water of *meso-* and *dl*-sodium α,α'-dibromosuccinate gave results similar to those reported for the debromination of *meso-* and *dl*-ethyl α,α'-dibromosuccinate.[6] It was also found that sodium maleate is stable under the debromination conditions and hence could not have been an intermediate.

The conflicting facts concerning the debromination by metals can be resolved by assuming an ionic mechanism for debromination by the divalent metals, magnesium and zinc, and a free radical mechanism for debromination by the monovalent metal, sodium. The reaction with magnesium or zinc may proceed as shown in equation (1). This mechanism is the one proposed by Winstein, Young and Pressman[7] for dehalogenation by iodide ion, and was suggested by them to apply to other reducing agents such as zinc. Nucleophilic attack by the metal with its electron pair (or rather electrophilic attack by the bromo compound on the metal surface) could yield the ion Ia (or Ib). Backside attack by the electron pair with ejection of bromide ion and flattening of configuration at C_2 leads to product. The orbital picture of the reaction, more complicated to draw, gives the same conclusion. For reactants where there are only hydrogen and deuterium or alkyl

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[1] Part of this work was supported by the Office of Naval Research.

[2] W. G. Young, Z. Jasaitis and L. Levanas, THIS JOURNAL, **59**, 404 (1937).

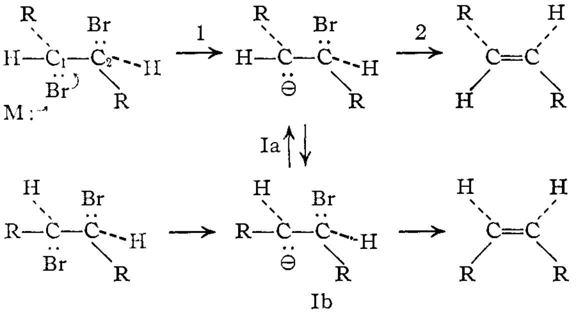
[3] R. Otto and F. Stoffel, *Ber.*, **30**, 1799 (1897).

[4] C. C. Price and M. Meister, THIS JOURNAL, **61**, 1595 (1939).

[5] D. C. Downing and G. F. Wright, *ibid.*, **68**, 141 (1946).

[6] A. Michael and O. Schultess, *J. prakt. Chem.*, **43**, 592 (1891).

[7] S. Winstein, W. G. Young and D. Pressman, THIS JOURNAL, **61**, 1645 (1939); see also S. J. Cristol, N. L. Hause and J. S. Meeks, *ibid.*, **73**, 674 (1951); and S. I. Miller and R. M. Noyes, *ibid.*, **74**, 629 (1952), for recent discussions of related mechanisms.



(1)

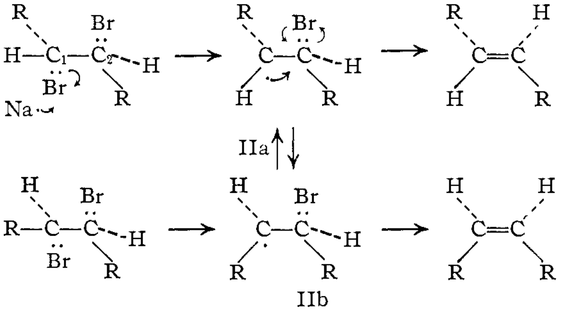
substituents (in addition to bromine) on C_1 and C_2, the second step takes place before loss of configuration at C_1; or, quite probably both steps occur simultaneously in a single process.

When there are phenyl, carboxyl or other unsaturated groups on C_1, loss of configuration at C_1 may occur because increased conjugation of the electron pair of the ion Ia (or Ib) gives it a longer life and tends to "flatten" the configuration at C_1. If the backside mechanism is to apply, then time for rotation about the C_1–C_2 bond must also be available. In the equilibrium mixture containing Ia or Ib, Ia should predominate because of phenyl–phenyl (or carboxylate ion–carboxylate ion, etc.) repulsion. Phenyl–bromine repulsion is the same in both Ia and Ib. Actually, it is the properties of the transition states that determine the products and the over-all activation energy for the conversion of Ia to *trans*-olefin should be less than for the conversion to *cis*-olefin, because a shortening of the C_1–C_2 distance in the transition state of step 2 would lead to a relatively higher phenyl–phenyl repulsion in the latter case.

The debromination with sodium in liquid ammonia of the 2,3-dibromobutanes and 1,2-dibromo-1,2-dideuteroethanes cannot proceed *via* the intermediate carbanion (Ia or Ib), or by a single ionic process (*i.e.*, sum of steps 1 and 2) unless loss of configuration at C_1 occurred prior to formation of the carbanion. It seems likely that any step that would lead to "racemization" at C_1 would be a step in debromination. It is suggested that the sodium debrominations involve first the preliminary transfer of *one* electron by monovalent sodium to form the free radical intermediate IIa (or IIb). This intermediate loses its specific configuration at C_1 since it is unable to retain configuration.[8] Thus an equilibrium mixture of IIa and IIb and rotational isomers is formed. Attack by the single electron on C_2 and loss of a bromine atom would lead to the products. The most favorable orientation for the second step would be one in which the RC_1H plane is roughly perpendicular to the C_1C_2Br plane (*i.e.*, as in IIa and IIb). The best configuration for the second step would be a compromise between steric repulsion forces and the tendency for a maximum overlap of π-atomic orbitals to occur as the olefin is formed.

When R is methyl, steric repulsion forces favor an intermediate with configuration in the neighborhood of IIa. IIa should be converted to the *trans*-olefin more rapidly than IIb is converted to *cis* olefin because greater steric repulsion of methyls leads to an over-all higher transition state energy in the conversion of IIb to olefin. If an equilibrium between IIa and IIb is attained, it would be expected that the same mixture of *cis*- and *trans*-butene-2 be formed from either *meso*- or *dl*-2,3-dibromobutane, which, within experimental error, was found to be true.

In the case where R is deuterium, steric factors would not favor the preferential formation of either olefin.[9] The fact that *meso*-1,2-dibromo-1,2-dideuteroethylene gave 57% *trans*-1,2-deuteroethylene while 50% *meso*–50% *dl*-1,2-dibromo-1,2-dideuteroethylene gave 50% *trans*-olefin cannot be accounted for on the basis of experimental error. This result may be due to the intervention to a small extent of a stereospecific debromination (perhaps the ionic mechanism of equation (1)), or to an incomplete attainment of equilibrium between IIa and IIb before occurrence of the second step; *i.e.*, elimination of the second bromine atom may take place in a time less than the period of rotation. The intermediate radical (IIa $\rightleftarrows$ IIb) should have a slightly longer life in the case where R is methyl because of hyperconjugation, *i.e.*, $\mathrm{H{-}CH_2\dot{C}H{-}} \leftrightarrow \mathrm{H\cdot CH_2{=}CH{-}}$.



(2)

Inasmuch as the reaction $\cdot CH_2{-}CH_2Br \rightarrow C_2H_4 + Br$ is at least 7 kcal. endothermic, as calculated from standard thermochemical values, this explanation is speculative and dependent upon the details of the energetics of the first step.

As an alternative explanation of the steric course of the sodium debrominations, it may be that the single electron transfer forming the free radical IIa (which loses configuration) is followed by a second electron transfer from the solution to the free radical to form the mixture of ions, Ia $\rightleftarrows$ Ib. The loss of the second bromine then occurs by step 2 of equation (1).

Experimental

Preparation of Materials.—Pure *dl*-2,3-dibromobutane was prepared by addition of bromine to *cis*-2-butene (Phillip Research Grade, 99.7% pure) by the method of Young, Dillon and Lucas.[10] The dihalide was distilled through a 23-in. twisted wire gauze column under 52 mm. pressure; b.p. 78.5–79.0° (52–53 mm.), n^{25}_{D} 1.5125.

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[8] For a recent discussion of the configuration of free radicals see G. W. Wheland "Advanced Organic Chemistry," Ed. II, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 713.

[9] In unpublished work in these laboratories, the *cis–trans* equilibrium of 1,2-dideuteroethylene has been found to correspond within 1% to a 50–50 mixture.

[10] W. G. Young, R. Dillon and H. Lucas, THIS JOURNAL, **51**, 2534 (1929).

Pure *meso*-2,3-dibromobutane was prepared by the same method from *trans*-2-butene (Phillip Research Grade, 99.32% pure); b.p. 72.6–72.8° (50 mm.), n^{25}D 1.5090.

Mixtures of 95% *meso*- and 5% *dl*-1,2-dibromo-1,2-dideuteroethane and of 50% *meso*- and 50% *dl*-1,2-dibromo-1,2-dideuteroethane were prepared by methods used earlier.[11]

meso-α,α'-Dibromobibenzyl, m.p. 232–234°, was prepared by addition of bromine to *trans*-stilbene.[12] *dl*-α,α'-Dibromobibenzyl, m.p. 111.5–113°, was made by addition of bromine to *cis*-stilbene.[13]

meso-α,α'-Dibromosuccinic acid, m.p. 255–257°, was prepared by the method of Rhinesmith,[14] and the *dl* isomer, m.p. 165–167°, by the method of McKenzie.[16] The corresponding sodium salt of each acid was prepared by neutralization of an alcohol solution with an equivalent of sodium ethoxide.

Debromination of the Dibromobutanes and Dibromoethanes.—The elimination reactions were run in an all-glass vacuum apparatus which consisted of a 50-ml. round bottom flask attached through a Dry Ice condenser to several traps. Magnesium turnings (approx. 0.1 g.) and purified tetrahydrofuran (15 ml.), freshly distilled from butylmagnesium bromide, were introduced into the flask. The contents of the flask were frozen, pumped on and melted several times in order to remove dissolved air. Purified nitrogen was introduced into the system and was allowed to escape through a side-arm as the dibromobutane or dibromoethane (about 0.03 ml.) was added to the frozen contents. The side-arm was sealed and the nitrogen pumped off. The flask contents were allowed to melt in the dark and the reaction proceeded at room temperature. The material collected in the liquid nitrogen traps was distilled from trap to trap a few times to ensure complete removal of solvent, and was then analyzed to determine the *cis*- and *trans*-olefin percentages.

Debrominations with zinc dust (approx. 0.4 g.) in water (6 cc.) were run in the same way. Debrominations with sodium (0.06 g.) and liquid ammonia (about 20 ml.) also were run in the same way except that the first trap contained dilute sulfuric acid to remove entrained ammonia.

Blank runs were made on *trans*-1,2-dideuteroethylene and on *cis*- and *trans*-butene-2 under the elimination reaction conditions in the presence of metal and metal halide. No isomerization of the olefins took place.

Analysis of Ethylenes from 1,2-Dibromo-1,2-dideuteroethanes.—The per cent. of *cis*- and *trans*-olefin in the 1,2-dideuteroethylene reaction product was obtained from the infrared absorption[16] at 987 cm.$^{-1}$ (*trans*) and 842 cm.$^{-1}$ (*cis*). Known mixtures of *trans* and *cis* isomers were used to obtain an empirical calibration of composition of mixture *versus* transmission at the two frequencies. A Beckman IR-2 instrument was used. The results are summarized in Table I.

Analysis of Butenes from 2,3-Dibromobutanes.—The per cent. of *cis*- and *trans*-2-butene in the product of each debromination was obtained from the infrared absorption at 699 cm.$^{-1}$ at various total pressures with the Beckman IR-2. At 699 cm.$^{-1}$ there is very little absorption by *cis*-2-butene.[17] The extinction coefficients of the *cis* and *trans* compounds were measured with pure olefins and the analytical procedure confirmed with known mixtures. The results are summarized in Table I.

Debromination of Stilbene Dibromide.—*dl*-α,β-Dibromodibenzyl (3.4 g., 0.01 mole) was stirred with magnesium turnings (2.0 g.) and purified tetrahydrofuran (70 ml., freshly distilled from butylmagnesium bromide) in the dark for 12 hours. The solvent was removed under reduced pressure and the residue was extracted with hot petroleum ether. The petroleum ether solution on being concentrated and cooled yielded 1.80 g. (100%) of crude *trans*-stilbene, m.p. 102–116°. Recrystallization from petroleum ether gave 0.76 g., m.p. 121–123°. On another occasion the residue, after removal of solvent, was extracted with anhydrous ether and percentages of *cis*- and *trans*-stilbene determined on dilute aliquot samples from values of the optical density at 276 and 294 mμ. The readings were made in a Beckman DU ultraviolet spectrophotometer. The results are summarized in Table I.

The debromination under the above conditions (a crystal of iodine was needed to initiate the reaction in this case) of *meso*-α,α'-dibromobibenzyl in several runs yielded stilbene which spectral analysis showed to be 100% *trans* (Table I). The *trans*-stilbene, m.p. 120–123°, was also isolated in 100% yield. When *cis*-stilbene was treated for 15 hours under the conditions of the elimination in the presence of magnesium, magnesium bromide and a crystal of iodine, spectral analysis showed 99.1% *cis*-stilbene to be still present. After an additional three hours at reflux temperature, the analysis showed 93.4% *cis* still present.

Other duplicate runs were made with the dibromides (0.02 mole) and zinc (0.06 g. atom) in absolute ethanol (100 ml.) at reflux temperatures for two hours in an atmosphere of nitrogen. The stilbene formed from the *dl*-dibromide was at least 88% *trans* (by isolation and from spectral analysis, see Table I). The stilbene obtained from the *meso*-dibromide was essentially 100% *trans*. Blank runs were made on *cis*-stilbene under the reaction conditions (four hours reflux in the presence of zinc and anhydrous zinc bromide). Spectral analysis showed 97% *cis*-stilbene remaining.

Debromination of Sodium α,α'-Dibromosuccinate.—A mixture of *dl*-α,α'-dibromosuccinate (0.06 mole), 20 mesh zinc (0.2 g. atom) and water (50 ml.) was stirred in the dark for three hours as the temperature rose to about 50°. The mixture then was cooled in an ice-bath and 10% hydrochloric acid (40 ml.) was added. The white crystals of fumaric acid were recovered by suction filtration and dried; yield 4.4 g., 75%, m.p. 255–262° dec. The amount of maleic acid in the filtrate was determined by boiling for several hours to isomerize maleic acid to fumaric. The precipitate that formed was collected. The yield of this impure residue was 1.2 g., m.p. 170–192°. Recrystallization from water gave 0.2 g. of fumaric acid, m.p. 240–255°. The per cent. of pure fumaric acid formed directly in the debromination reaction, based on total pure fumaric acid isolated, was 96%. In a duplicate run the per cent. fumaric acid was 94% (Table I).

In similar duplicate runs with *meso*-α,α'-dibromosuccinate the yield of pure fumaric acid isolated was 74 and 69%, respectively, and represented 91 and 88% of total pure product isolated (Table I). A spectral method of analysis proved useless in this case because of failure to follow Beer's law. Blank runs made on sodium maleate under the debromination reaction and isolation conditions indicated no isomerization to acid; *i.e.*, no fumaric acid precipitated upon acidification of the reaction mixture, and a 94% yield of pure fumaric acid was recovered after isomerization in hot acid.

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