[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF COLORADO]

# Mechanisms of Elimination Reactions. X. Deuterium Exchange in Base-Promoted Dehydrochlorination of β-Benzene Hexachloride[1]

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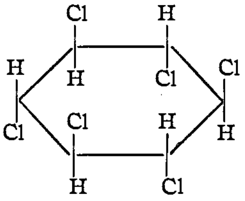
β-Benzene hexachloride was treated with sodium ethoxide in deuterated ethanol under conditions under which one-half of the material would be dehydrochlorinated. The remaining reactant was isolated and was found to contain a small amount of deuterated β-benzene hexachloride. This result has been interpreted as a demonstration of the existence of a carbanion intermediate in this elimination reaction.

It has been proposed[2,3] that β-benzene hexachloride undergoes elimination of the elements of hydrogen chloride under the influence of alkaline reagents *via* a carbanion intermediate. The β-isomer is the one[4] in which no members of a pair of hydrogen and chlorine atoms on adjacent carbon atoms are *trans* to each other (see structural formula).



β-Benzene hexachloride

One of the standard techniques for demonstrating the existence of a carbanion as an intermediate in an organic reaction is the test for deuterium exchange.[5] Skell and Hauser[6] have looked for deuterium exchange in the reaction of β-phenylethyl bromide with sodium hydroxide in deuterated aqueous ethanol by subjecting the unreacted bromide to deuterium analysis after 50–60% of the bromide had been converted to styrene. They found that deuterium did not accumulate in the unreacted bromide and assumed that there occurred in the elimination process a simultaneous loss of hydrogen and bromide as in equation (1), rather than initial loss of a proton yielding a carbanion, which might then revert to the initial halide by protium or deuterium exchange with solvent or else might lose a bromide ion giving olefin, as in equations (2) and (3)

$$HO^- + C_6H_5CH_2CH_2Br \xrightarrow{k_1} H_2O + C_6H_5CH{=}CH_2 + Br^- \quad (1)$$

$$HO^- + C_6H_5CH_2CH_2Br \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} H_2O + [C_6H_5CHCH_2Br]^- \quad (2)$$

$$[C_6H_5CHCH_2Br]^- \xrightarrow{k_3} C_6H_5CH{=}CH_2 + Br^- \quad (3)$$

However, the observed negative result suffers from two possible explanations—either the process is concerted, that is, equation (1) represents the correct mechanism, or equations (2) and (3) describe the process, but $k_3$ is much greater than $k_{-2}$.

Elimination from β-benzene hexachloride is complicated, although the system is somewhat simplified by the fact that loss of the first mole of hydrogen chloride is rate-determining.[2,3] If a carbanion intermediate is involved, then the elimination process in the presence of deuterated ethanol involves

$$\beta\text{-}C_6H_6Cl_6 + OEt^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} C_6H_5Cl_6^- + EtOH \quad (4)$$

$$C_6H_5Cl_6^- + EtOD \xrightarrow{k_5} C_6H_5DCl_6 + EtO^- \quad (5)$$

$$C_5H_5Cl_6^- \xrightarrow{k_6} C_6H_5Cl_5 + Cl^- \quad (6)$$

$$C_6H_5Cl_5 + 2EtO^- \xrightarrow{\text{fast}} C_6H_3Cl_3 + 2EtOH + 2Cl^- \quad (7)$$

$$C_6H_5Cl_6^- + EtOH \xrightarrow{k_8} \delta\text{-}C_6H_6Cl_6 + EtO^- \quad (8)$$

where equation (4) represents the removal of a proton from a molecule of β-benzene hexachloride, equation (5) represents the reverse of this reaction, which in the presence of deuterated ethanol labels the regenerated material, equation (6) represents an alternative fate of the carbanion, that is, decomposition to monoölefin and chloride ion, and equation (7) represents the summation of the fast steps[2,3] by which monoölefin is transformed to the product mixture of trichlorobenzenes. The system is somewhat complicated by the fact that the carbanion might not be expected to maintain its configuration,[7] and if this occurred and if the resulting carbanion reacted with solvent, δ-benzene hexachloride (labeled) would result. This isomer reacts with ethanolic alkali at least $10^4$ times more rapidly than does the β-isomer[2] and thus would not accumulate in solution but instead would dehydrochlorinate to trichlorobenzene, in effect instantaneously. This course of reaction is represented in equation (8).

It has been assumed previously[2,3] that $k_4$ is the smallest in this series of reactions and that equation (4) represents the rate-determining step of the elimination process. If $k_5$ is much greater than $k_6 + k_8$, then this assumption would prove incorrect and substantially complete deuterium exchange would result. (This was not observed.) On the other hand, if the sum $k_6 + k_8$ is substantially greater than $k_5$, no measurable exchange would re-

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[1] Previous paper in series: S. J. Cristol and W. P. Norris, THIS JOURNAL, **75**, 2645 (1953). This work was reported in part at the Conference on Organic Reaction Mechanisms, Bryn Mawr, Pa., September 10, 1952.

[2] S. J. Cristol, THIS JOURNAL, **69**, 338 (1947).

[3] S. J. Cristol, N. L. Hause and J. S. Meek, *ibid.*, **73**, 674 (1951).

[4] S. B. Hendricks and C. Bilicke, *ibid.*, **48**, 3007 (1926); R. G. Dickinson and C. Bilicke, *ibid.*, **50**, 764 (1928).

[5] For leading references, see L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, Chapter VII.

[6] P. S. Skell and C. R. Hauser, THIS JOURNAL, **67**, 1661 (1945).

[7] Reference 5, p. 68.

sult, even if a carbanion were formed as in equation (4); only if $k_5$ is roughly comparable in magnitude with $k_6 + k_8$ will measurable amounts of deuterium exchange result.

In this work, β-benzene hexachloride was treated with sodium ethoxide in absolute ethanol containing about 70% ethanol-*d* and 30% ordinary ethanol for about one-half life of the elimination reaction. The reaction was then stopped, and the unreacted halide was recovered and purified. The product did not contain enough deuterium to be detected *via* infrared analysis. The material was analyzed mass-spectroscopically through the courtesy of Professors du Vigneaud and Rachele of Cornell University Medical College. Their duplicate results indicated that the sample contained 0.083 ± 0.002 excess atom % deuterium. As we feared that this small amount of deuterium might be the result of ethanol-*d* contaminant, the material was subjected to repurification, after which the sample contained 0.079 ± 0.002 excess atom % deuterium, and it is thus quite clear that the label was not due to ethanol-*d* contamination and that the fact of deuterium exchange has been established.

The quantitative result is somewhat obscured by the fact that the solvent contained about 30% ethanol-*d*. Thus, the theoretical excess atom % of 16.7, based upon the assumption that each molecule of benzene hexachloride had exchanged *one* hydrogen atom, must be reduced to $16.7 \times 0.7 = 11.7\%$ (assuming that the rate of deuteration of the carbanion is proportional to the proportion of ethanol-*d*). This means that $0.079/11.7 = 0.0068$ of the molecules of recovered benzene hexachloride contained the deuterium label. As the reaction was run for one-half life, the ratio $k_5/(k_6 + k_8)$ is also 0.0068 or 1/150, assuming that equations (4) to (8) represent the course of the reaction. Thus our results may be interpreted as indicating that a carbanion is involved in *this* elimination process, one molecule of the carbanion reverting to the deuterated β-benzene hexachloride for every 150 molecules which disappear by other fates.

These approximate calculations are based on deuterium exchange and the ratio $k_{-4}/(k_6 + k_8)$, which measures the reversion with ordinary ethanol, will probably differ due to the isotope effect.[8] However, the evidence seems to indicate without question the existence of a carbanion in the process of elimination.[9]

Leitch and Bernstein[10] observed that tetrachloroethane and trichloroethylene both gave trichloroethylene labeled in part[11] with deuterium when treated with calcium deuteroxide in heavy water. These authors did not consider the mechanism of these exchanges, but it is possible that a process involving the carbanion $CCl_2{=}CCl^-$ is involved here, which may revert to trichloroethylene (with a deuterium label) or decompose to dichloroacetylene and chloride ion.[12]

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## Experimental

**Exchange Experiments.**—A solution of 100 mg. (0.36 mmole) of β-benzene hexachloride, m.p. 308–309° (dec.), and 1.50 ml. of 0.934 *M* ethanolic sodium ethoxide in 20 ml. of absolute ethanol containing about 75% ethanol-*d* was allowed to react for 28.5 hr. (slightly under one-half life) at 43.6°.[13]

The reaction was then stopped by cooling to −5°. Most of the ethanol was recovered by distillation under reduced pressure below 0°. Dilute nitric acid was then added, and the resulting mixture was evaporated to dryness. The solid residue was extracted twice with 5-ml. portions of water. The water-insoluble residue was dissolved in 30 ml. of ether; the ethereal solution was dried over magnesium sulfate and then evaporated to dryness. The residue was washed with three 3-ml. portions of cold *n*-heptane (to remove trichlorobenzenes). The residual solid was washed once with water and then redissolved in ether. After the solution had been dried over magnesium sulfate, it was evaporated to dryness. After two recrystallizations from toluene, 23.2 mg. of β-benzene hexachloride, m.p. 308–309° (dec.), was recovered. The samples were dried over phosphorus pentoxide. Several such runs were made.

The product was analyzed for deuterium content mass-spectrographically through the courtesy of Professors V. du Vigneaud and J. R. Rachele and duplicate results indicated that the sample contained 0.084 and 0.082 ± 0.002 excess atom % deuterium. This analyzed sample (34 mg.) was dissolved in 10 ml. of absolute ethanol and the solution was evaporated to dryness. The residual solid was then recrystallized from 16 ml. of 60% ethanol, and the resulting β-isomer was dried in an Abderhalden apparatus for 24 hours at 94° over phosphorus pentoxide. After this treatment the sample contained 0.077 and 0.081 ± 0.002 excess atom % deuterium.

**Preparation of Ethanol-*d*.**—The ethanol-*d* was prepared by heating a mixture of 5 g. (0.25 mole) of 99.9% deuterium oxide with 60 g. (0.375 mole) of aluminum ethoxide[15] for two hours at 50° after the initial heat of reaction had subsided. The alcohol was then removed by distillation through a fractionating column. The yields in three runs were 78, 85 and 93% of theoretical based upon deuterium oxide.

The resulting product had an infrared absorption maximum at 2.73–2.74 μ corresponding to that of an oxygen–hydrogen bond, as well as a more intense peak at 3.69 μ corresponding to an oxygen–deuterium bond. From the relative intensities of the 2.73 μ peak in the spectra of the ethanol-*d* sample and of ordinary ethanol, we calculated that our ethanol-*d* sample contained about 25% ethanol-*h*. This material was used as solvent for the deuterium-exchange experiments. We are unable to account for the extensive ethanol-*d* contamination.

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(8) W. F. K. Wynne-Jones, *J. Chem. Phys.*, **2**, 381 (1934).

(9) There remains the possibility that these results can be interpreted by the alternative assumption that only a small fraction (<1/150) of the β-benzene hexachloride molecules eliminate *via* a carbanion, and the major fraction *via* a concerted process. Arguments against this alternative explanation were given previously.[3]

(10) L. C. Leitch and H. J. Bernstein, *Can. J. Research*, **B28**, 35 (1950).

(11) Rough calculations (ours) based on their infrared spectral data indicate that 10–15% deuterium exchange occurred in their experiments.

(12) E. Ott, *Ber.*, **75**, 1517 (1942), has shown that trichloroethylene reacts with alkali to give dichloroacetylene.

(13) The rate constant for the alkaline dehydrochlorination of β-benzene hexachloride at 43.6° in absolute ethanol was found to be $12.0 \times 10^{-5}$ l./sec./mole. This is lower than that observed in 97.6% ethanol and is in agreement with the trend observed in work on the effects of solvent composition upon rates.[14]

(14) S. J. Cristol and W. Barasch, THIS JOURNAL, **74**, 1658 (1952).

(15) W. Chalmers in A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 599.