

N-N distances. However, it is not possible to determine the direction of the covalent bonds, since the differences⁶ in the interatomic distances are not significant in most cases. This is so because the *x*-coordinates were not directly determined and also because the standard deviations of the remaining parameters are rather large. An accurate determination of bond distances will have to wait until three-dimensional neutron data can be obtained.

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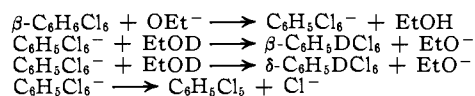
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The Mechanism of the Dehydrochlorination of β -Benzene Hexachloride¹

Sir:

Cristol proposed that the marked unreactivity of the β -isomer of benzene hexachloride (relative to that of the other isomers) is due to the absence, in that and only that isomer, of hydrogen and chlorine atoms *trans* to each other and on adjacent carbon atoms.² Although this proposal seems generally accepted, there is less agreement concerning the mechanism of the *cis*-dehydrochlorination of β -benzene hexachloride. Cristol and Fix³ pointed out that in a deuterated solvent the intermediate carbanion suggested for the reaction could either be deuterated with retention of configuration to yield labeled starting material, be deuterated with inversion of configuration to give labeled δ -benzene hexachloride, or lose a chloride ion to give a pentachlorocyclohexene. Either the δ -isomer or the pentachlorocyclohexene would then be rapidly dehydrochlorinated to a mixture of trichlorobenzenes.



As evidence for the intermediacy of a carbanion, Cristol and Fix reported 0.08% deuterium present in the β -benzene hexachloride isolated after about 50% dehydrohalogenation in 70% EtOD–30% EtOH.

Cram has stated that the most probable path of decomposition of the carbanion is *via* the formation of δ -benzene hexachloride, *cis* elimination from the carbanion being improbable, and that deuterated trichlorobenzenes should be produced in a deuterated solvent, since the deuterium atom of any intermediate δ -benzene hexachloride could be removed in a *trans* elimination only *via* a conformation with five axial chlorine atoms.⁴

In relation to our interest in the carbanion mechanism for β -elimination reactions,¹ we have examined the trichlorobenzene mixture produced in deuterated methanol.⁵ When 2.19 mmoles of β -benzene hexachloride was 70% dehydrohalogenated by 6.9 mmoles of sodium methoxide in 98% MeOD–2% MeOH, the trichlorobenzene mixture (containing 88% of the 1,2,4-isomer) produced had n.m.r. and infrared spectra almost identical with those of the trichlorobenzene mixture produced under very similar conditions in "light" methanol. From blank experiments we conclude that $3.1 \pm 1.0\%$ 1,2,4-trichlorobenzene-3-*d* and much less of any other deuterated trichlorobenzene were present in the products of reaction in MeOD. Determination of the rate constant for the dehydrochlorination of β -benzene hexachloride in methanol and comparison with that for the exchange of 1,2,4-trichlorobenzene-3-*d*^{1b} showed that between 1 and 5%⁶ of the 1,2,4-trichlorobenzene produced in the reaction in MeOD would have been transformed to 1,2,4-trichlorobenzene-3-*d*.

We therefore conclude that if the alkaline dehydrochlorination of β -benzene hexachloride is initiated to any major extent by carbanion formation, the intermediate carbanions almost always lose chloride ions and are only rarely reprotonated. The possibility that the reaction proceeds only to a minor extent *via* intermediate carbanions but consists largely of a concerted *cis* elimination from a conformation, like the boat form, in which the dihedral angle between the hydrogen and chlorine atoms being removed is quite small⁷ has not been ruled out. However, in view of the slow rate of such *cis* eliminations⁸ and the added energy that would be required in the present case to reach such a conformation, the dehydrohalogenation of β -benzene hexachloride seems surprisingly fast to be a reaction of this type.

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it seems that intermediate carbanions should be captured more efficiently in this solvent than in ethanol. If k_H/k_D is 5.0, 9% of the captured intermediates will escape deuteration in 98% MeOD but 68% will in 70% EtOD.

(6) Assuming that k_H/k_D is between 1 and 5.

(7) Cf. C. H. DePuy, R. D. Thurn, and G. F. Morris, *J. Am. Chem. Soc.*, **84**, 1314 (1962).

(8) Some of the data of Cristol and co-workers⁹ provide maximum values for the rates of such processes.

(9) S. J. Cristol and N. L. Hause, *J. Am. Chem. Soc.*, **74**, 2193 (1952); S. J. Cristol and E. F. Hoegger, *ibid.*, **79**, 3438 (1957).

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Photochemical and Thermal Rearrangement of α,β -Epoxyketones

Sir:

Investigations during the past decade have revealed the carbonyl group as an important and versatile chromophore in photochemical reactions.^{1,2} In view of the many acid- and base-catalyzed rearrangements exhibited by α,β -epoxyketones,³ it is surprising that the photochemical behavior of these substrates has not been widely studied.⁴ A recent investigation⁵ of the photolysis of some steroidal epoxyketones represents the only published case in which skeletal rearrangement occurs. We take this opportunity to report⁶

(1) P. de Mayo, *Advan. Org. Chem.*, **2**, 367 (1960).

(2) P. de Mayo and S. T. Reid, *Quart. Rev. (London)*, **15**, 393 (1961).

(3) R. Parker and N. Isaacs, *Chem. Rev.*, **59**, 737 (1959).

(4) The first of a few recent endeavors is that by H. E. Zimmerman, Abstracts of the Seventeenth National Organic Chemistry Symposium, June, 1961, Bloomington, Indiana, p. 31.

(5) C. Lehmann, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **45**, 1031 (1962).

(6) Part of this work was presented by W. Reusch and C. K. Johnson,

(1) (a) Part V in the series "The Carbanion Mechanism for β -Elimination Reactions"; (b) for part IV see J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962).

(2) S. J. Cristol, *J. Am. Chem. Soc.*, **69**, 338 (1947); cf. S. J. Cristol, N. L. Hause, and J. S. Meek, *ibid.*, **73**, 674 (1951).

(3) S. J. Cristol and D. D. Fix, *ibid.*, **75**, 2647 (1953).

(4) D. J. Cram in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 321.

(5) In view of the greater acidity and ion-solvating power of methanol