

Evidence for a Homolytic Transannular Reaction

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RECENTLY,¹ we reported a transannular reaction under homolytic conditions in the longifolene series. Since ionic hydrogen-transfers are well known in suitably disposed medium-sized rings,² the apparently free-radical nature of the observed reaction was of particular interest. Unfortunately, isolation of the transannular reaction product does not alone suffice to eliminate the possibility that hydrogen transfer occurred ionically in some subsequent reaction of the initially-formed normal adduct.³ We now wish to report a similar reaction in another system for which it has proved feasible to exclude the possibility of a secondary rearrangement.

Methylenecyclodecane (I),⁵ prepared from cyclodecanone⁶ by a Wittig reaction in benzene using sodium t-pentyloxide as base,⁷ was reacted with bromotrichloromethane by irradiating the solution with a 300-w incandescent lamp. The minor product (18%) lost hydrogen bromide during chromatography on silica, indicating a tertiary bromine. This adduct and its elimination product had infrared and n.m.r. spectra almost identical with those of the analogous substances (VI) and (VII) prepared in the same fashion from methylenecyclo-octane (V)^{8,9} (Equation 2). Hence the minor adduct and its elimination product are formulated as (II) and (IV) respectively (Equation 1).

¹(a) G. Ourisson, "Simonsen Lecture", *Proc. Chem. Soc.*, 1964, 274; (b) D. Helmlinger and G. Ourisson, *Annalen*, in press.

²(a) V. Prelog and J. G. Traynham in P. de Mayo, ed., "Molecular Rearrangements", Interscience, New York, 1963, p. 593; (b) J. Sicher, *Progr. Stereochem.*, 1962, 3, 202.

³ An unsuccessful search for the normal adduct has resulted in the isolation of another transannular product from the original reaction. The normal adduct, if formed at all, is certainly unstable (Ref. 4).

⁴ M. Fisch and G. Ourisson, unpublished.

⁵(a) J. G. Traynham and W. C. Baird, *J. Org. Chem.*, 1962, 27, 3189; (b) A. C. Cope, D. Ambros, E. Ciganek, C. G. Howell, and Z. Jacura, *J. Amer. Chem. Soc.*, 1960, 82, 1750.

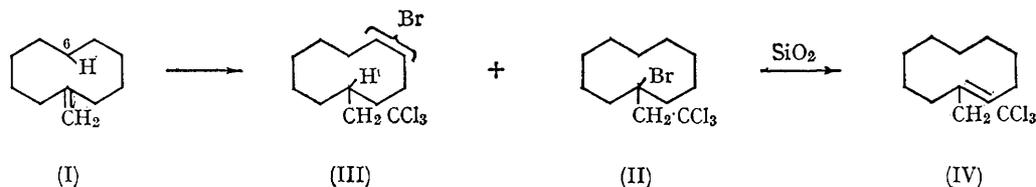
⁶ We wish to thank Prof. Eugen Müller for a generous gift of cyclodecanone.

⁷ J. C. Limasset and J. M. Conia, *Tetrahedron*, in press.

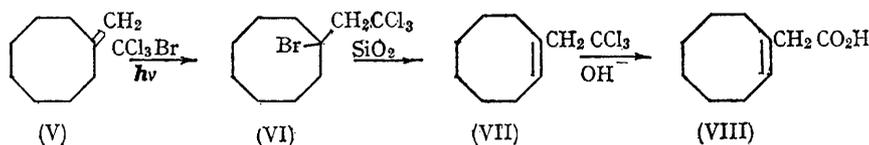
⁸ M. Vilkas and N. A. Abraham, *Bull. Soc. chim. France*, 1960, 1196.

⁹ Addition of bromotrichloromethane to methylenecyclo-octane yields only the normal adduct (Ref. 4).

The major product (III), (37%), was stable to chromatography, indicating the absence of tertiary bromine, and was clearly transannular in nature as shown by its n.m.r. spectrum. The exocyclic methylene was split by an adjacent proton



(Equation 1)



(Equation 2)

doublet at 2.58 p.p.m. ($J = 4.5$ c./sec.) and a $\cdot\text{CHBr}\cdot$ grouping was easily observable as a quintet at 4.35 p.p.m. ($J = 6.5$ c./sec.). Inspection of Dreiding models of (I) indicated C-6 as the most likely position of the bromine, but present evidence does not serve to exclude other isomers nor the possibility that the product obtained is a mixture. Structural work is in progress.

A priori, it is most unlikely that the product (II) could give rise to (III) ionically, since it is known that tertiary cations do not isomerize to secondary cations in the methylcyclodecane system.^{5a} This prediction was verified by the following experiment. A 1% solution of methylenecyclodecane in

bromotrichloromethane was irradiated in a sealed, degassed n.m.r. tube. Spectra were taken at frequent intervals until all the starting material was consumed (as shown by the complete disappearance of the exocyclic methylene absorption

at 4.87 p.p.m.). The relative proportions of the two products were ascertained by integrating the $\cdot\text{CHBr}\cdot$ quintet of (III) and the two-proton singlet of (II) at 3.35 p.p.m. ($\cdot\text{CBr}\cdot\text{CH}_2\cdot\text{CCl}_3$). The ratio of the adducts was found to be the same throughout the reaction, thus showing the transannular addition to be competitive with, and independent of the 1,2-addition. Since the normal Kharasch reaction is known to be of free-radical type,¹⁰ this evidence strongly suggests that the transannular reaction is also homolytic. The extension to longifolene is presumptive.

(Received, July 23rd, 1965; Com. 461.)

¹⁰ E. C. Kooyman, *Discuss. Faraday Soc.*, 1951, **10**, 163.