

PHOTOCHEMICAL CYCLIZATION OF ACYCLIC TRIENES

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THE formation of an acyclic hexatriene from a 1,3-cyclohexadiene system was first noted in the case of the light induced formation of calciferol via precalciferol from ergosterol.^{1,2} More recent investigations have shown that this ring cleavage reaction also takes place with a number of complex^{3,4,5,6} and simple 1,3-cyclohexadienes^{5,7,8} and may with some exceptions^{9,10} be a fairly general phenomenon.

Consideration of the reversible nature of the photo conversion of ergosterol to precalciferol² prompted us to investigate some simple acyclic trienes with a view toward demonstrating photochemical cyclization of such systems to 1,3-cyclohexadienes. Evidence for such cyclization has been found and thus demonstrates the reversible nature the 1,3-cyclohexadiene-acyclic triene conversion.

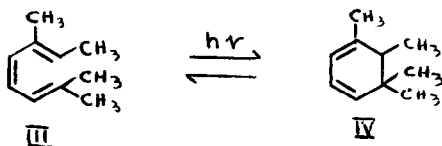
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- ¹ For a summary of this work see L.F. Fieser and M. Fieser, Steroids p. 124. Reinhold, New York (1959).
 - ² E. Havinga and J.L.M.A. Schlatmann, Tetrahedron **16**, 146 (1961).
 - ³ O. Jeger, J. Redel and R. Nowak, Helv. Chim. Acta **29**, 1241 (1946).
 - ⁴ L. Velluz, B. Goffinet and G. Amiand, Tetrahedron **4**, 241 (1958).
 - ⁵ D.H.R. Barton, Helv. Chim. Acta **42**, 2604 (1959).
 - ⁶ R.L. Autrey, D.H.R. Barton and W. Reusch, Proc. Chem. Soc. 55 (1959).
 - ⁷ R.J. DeBock, N.G. Minnard and E. Havinga, Rec. Trav. Chim. **79**, 922 (1960).
 - ⁸ R. Srinivasan, J. Amer. Chem. Soc. **82**, 5063 (1960).
 - ⁹ W.G. Dauben and G.J. Fonken, J. Amer. Chem. Soc. **81**, 4060 (1959).
 - ¹⁰ W.H. Schuller, R.N. Moore, J.E. Hawkins and R.V. Lawrence, J. Org. Chem. **27**, 1178 (1962).

The irradiation of 1,6-dimethyl-1,3,5-hexatriene I in ether solution with light from a high pressure mercury arc lamp gave rise to a mixture of polymer, recovered hexatriene I¹¹ and 1,2-dimethyl- $\Delta^{3,5}$ cyclohexadiene II. Under the conditions used it was found that the recovered monomeric product



mixture consisted of 90-95 per cent I and 5-10 per cent of II even with prolonged periods of irradiation, thus suggesting that a steady state of interconversion is reached. Prolonged irradiation, however, severely reduced the yield of monomeric products. Irradiation of II under similar conditions gave rise to a similar mixture of I and II. Hydrogenation of II gave largely trans-1,2-dimethyl cyclohexane (about 95 per cent by V.P.C. analysis), thus demonstrating the stereochemistry of II.

Similar irradiation of solutions of allo-ocimene III gave rise to a mixture which contained α -pyronene IV, recovered III and considerable polymer. As in the case of the interconversion of I and II the system was



observed to reach an apparent steady state at which the monomer composition¹¹ was about 20 per cent IV and 80 per cent III. Irradiation of IV gave rise to a similar mixture.

Irradiation of 1,3,5-hexatriene itself under the conditions used in the aforementioned examples gave a monomer and polymer mixture in which no

¹¹ The recovered trienes were mixtures of geometrical isomers, largely trans. The starting materials were essentially all trans isomer.

1,3-cyclohexadiene could be detected with certainty. We have no explanation for this difference in behavior at present.

Further work in this area of cyclization of conjugated polyenes is in progress and will be reported in detail at a later date.

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