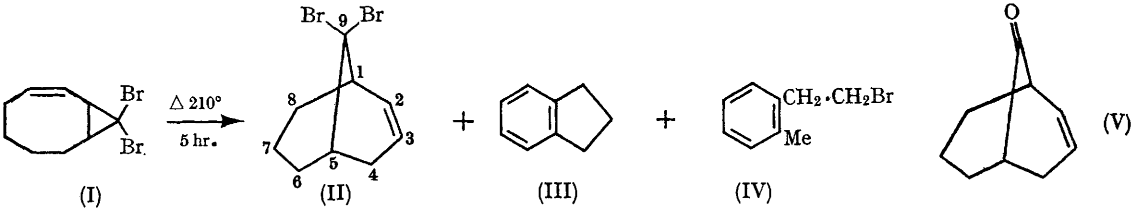
Thermal Rearrangements of 9,9-Dibromobicyclo[6,1,0]non-2-ene and Related Compounds

By M. S. BAIRD, D. G. LINDSAY, and C. B. REESE*
(*University Chemical Laboratory, Lensfield Road, Cambridge*)

WE report that when 9,9-dibromobicyclo[6,1,0]-non-2-ene (I) is heated at 210° for 5 hr., it undergoes a novel rearrangement to give a crystalline isomeric compound† (II) (30%), m.p. 154—155°. In addition, indane (III) and *o*-tolylethyl bromide (IV) are obtained, in yields of 43 and 15% respectively. On the basis, both of its spectroscopic and chemical properties, the crystalline rearrangement product (II) has been identified as 9,9-dibromobicyclo[3,3,1]non-2-ene.



The n.m.r. spectrum of (II) includes the following signals: τ 4·14 (1H), double-triplet, 3-H, 4·52 (1H, m, 2-H) 7·04 (1H, m, 1-H, 7·28—8·7 (9H, assigned to all other protons). Double irradiation at τ 7·04 causes the signal at τ 4·52 to collapse to a doublet (J 9·5 c./sec.); double irradiation in the region τ 7·84—8·12 causes the signal at τ 4·14 to collapse, but at no point is a simple doublet (J 9·5 c./sec.) obtained. This n.m.r. evidence is in accordance with (II) having the partial structure $>CH{-}CH{=}CH{-}CH_2{-}$, with the double-bond in a six-membered or larger ring.[1]

Treatment of (II) with silver acetate in ether–acetic acid solution for 18 hr. at 20° gives a ketone ($C_9H_{12}O$),† m.p. 98—99·5°, in quantitative yield. This material has ν_{max} (CCl_4) 1723 and 1730 cm.$^{-1}$ and shows negligible absorption in the u.v.; it forms a 2,4-dinitrophenylhydrazone, m.p. 196—197°, which appears from its u.v. absorption spectrum [λ_{max} (EtOH) 228 and 364 mμ (ϵ 17,800 and 23,000); λ_{min} 257 mμ (ϵ 11,300)] to be derived from an unconjugated ketone.[2] From a consideration of its n.m.r. spectrum and the above data,‡ it seemed likely that the ketone was bicyclo[3,3,1]non-2-en-9-one (V). This was confirmed by a direct comparison with authentic (V).§

As the low-field signals in the n.m.r. spectrum of the ketone (V) are virtually superposable upon those of its precursor (II), it may be assumed that no skeletal rearrangement occurs in the silver acetate reaction, and therefore that the crystalline rearrangement product (II) is 9,9-dibromobicyclo-[3,3,1]non-2-ene.

When a solution of (I) in excess quinoline is

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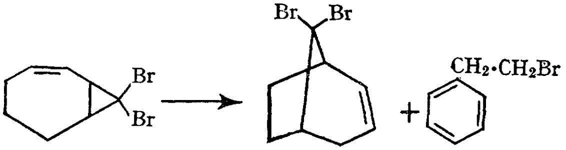
† Formulated as such on the basis of its mass spectrum and elemental analysis.

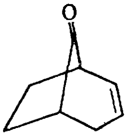
‡ C. S. Foote and R. B. Woodward, *Tetrahedron*, 1964, **20**, 687, report ν_{max} (CCl_4) 1733 cm.$^{-1}$ for (V), and 98—99°, 194·5—195·6° as the m.p.'s of (V) and its 2,4-dinitrophenylhydrazone, respectively. S. Brewis and P. R. Hughes, *Chem. Comm.*, 1966, 6, report the m.p.'s as 94—96° and 194—195·5°, respectively.

§ We thank Dr. P. R. Hughes for a generous gift of bicyclo[3,3,1]non-2-en-9-one (V).

heated under reflux (238°), and when (II) is heated alone at 205—215°, indane is the sole volatile organic product; however, when the latter compound (II) is heated in quinoline solution, there are no detectable volatile products. Thus the indane obtained by heating (I) in quinoline solution must be formed by a pathway which bypasses (II). Indane is the only volatile organic product obtained when 9,9-dichlorobicyclo[6,1,0]-non-2-ene, the chloro-analogue of (I), is heated alone under reflux (232—240°).



(VI) (VII) (VIII)



(IX)

The above rearrangement of the bicyclo[6,1,0]- to the bicyclo[3,3,1]nonene system finds a parallel in the conversion of 8,8-dibromobicyclo[5,1,0]oct-2-ene (VI) to 8,8-dibromobicyclo[3,2,1]oct-2-ene (VII). When (VI) is heated alone at 200° for 35 min., (VII) is obtained in 40% yield, together with 2-phenylethyl bromide (VIII) and other products. The structure of (VII) follows from its n.m.r. spectrum and from its conversion, by treatment with silver acetate in acetic acid for 3 hr. at 75°, into bicyclo[3,2,1]oct-2-en-8-one (IX) (70%).¶ When (VI) is heated in quinoline solution, under reflux (238°) for 20 min., styrene is obtained in 18% yield.

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[1] O. L. Chapman, *J. Amer. Chem. Soc.*, 1963, **85**, 2014.
[2] A. E. Gillam and E. S. Stern, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", Arnold, London, 1957, p. 120.