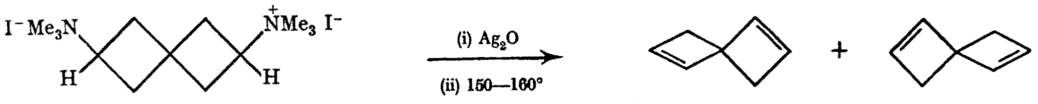
The Synthesis of Spiro[3,3]hepta-1,5-diene

By J. P. M. HOUBIERS, L. A. HULSHOF, and HANS WYNBERG*

(*Department of Organic Chemistry, The University, Bloemsingel* 10, *Groningen, The Netherlands*)

TREATMENT of 2,6-bisdimethylaminospiro[3,3]heptane dimethiodide (II) with an aqueous suspension of silver oxide, followed by pyrolysis of the product at 150—160°/50 mm. gave spiro[3,3]hepta-1,5-diene (I) (27% crude yield). (s, J 3·1 c./sec., 4H) and τ 7·30 p.p.m. (s 4H).[1] All new compounds had correct C and H values. The mass spectrum showed a parent peak at m/e 92 and a base peak at m/e 91. The spectrum was almost identical with the mass spectrum of toluene,[2] which would suggest a rearrangement under electron impact to the tropylium ion.[3]



(II)

(I)

The olefin condensed in a liquid nitrogen trap. The product was purified by g.l.c. (8 ft. × ½ in. column with 20% Silicon rubber GE-SE-30 on a Diatoport W 60—80 mesh in a F & M 700-0119 F gas chromatograph; oven temperature 60°). The diene (I) was a colourless, relatively stable liquid, b.p. 71·6°/762 mm. The i.r. spectrum showed absorptions at 3120m, 3050s, 2940s, 2850m, 1560w, 1320m, 1190w, 940w, 890m, and 720s cm.$^{-1}$. The u.v. spectrum was taken in the gas phase and showed a shoulder at 226 nm. and end absorption to shorter wavelengths. The ^{1}H n.m.r. spectrum (Varian A 60; CCl_4 solution with Me_4Si as an internal standard) showed signals at τ 3·94

Compound (I) represents a rigid dissymmetric 1,4-diene system and is therefore comparable to 5-methylenebicyclo[2,2,2]hept-2-ene,[4] which differs from this compound only in the completely orthogonal position of the p-orbitals at C-1 and C-5. The optical activity of (I) is the subject of further investigation. An attempt to prepare optically active (I) from optically active (II) was unsuccessful, only optically inactive (I) being recovered.† The methiodide (II) was prepared from 2,6-diaminospiro[3,3]heptane[5] by a Leuckart reaction followed by methiodation.[6]

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† Optically inactive diene (I) is to be expected if the pyrolysis proceeds *via* 6-trimethylammoniumspiro[3,3]hept-1-ene hydroxide, which has a plane of symmetry.

[1] See; S. Farid, W. Kothe and G. Pfundt, *Tetrahedron Letters*, 1968, **4151**, for a recent study of the n.m.r. spectra of cyclobutenes, and E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, 1967, **89**, 2047, as well as earlier work by Roberts on substituted cyclobutenes and long-range coupling effects. Our data is consistent with that of these authors. For instance the triplet may well be a collapsed AB quartet, while the singlet could represent a collapsed multiplet.

[2] P. N. Rylander, S. Meyerson, and H. M. Grubb, *J. Amer. Chem. Soc.*, 1957, **79**, 842.

[3] Different modes of fragmentation for the diradical of (I) have been suggested by R. Hoffmann, A. Imamura, and G. D. Zeiss, *J. Amer. Chem. Soc.*, 1967, **89**, 5215.

[4] L. S. Forster, A. Moscowitz, J. G. Berger, and K. Mislow, *J. Amer. Chem. Soc.*, 1962, **84**, 4353.

[5] S. E. Janson and W. J. Pope, *Proc. Roy. Soc.*, 1936, *A*, **154**, 53.

[6] The described reaction sequence is essentially the same as that of D. J. Cram and B. L. van Duuren, *J. Amer. Chem. Soc.*, 1955, **77**, 3576, used for the preparation of 1,6-spiro[4,4]nonadiene.