

## Two Novel Tetracyclo-octanes

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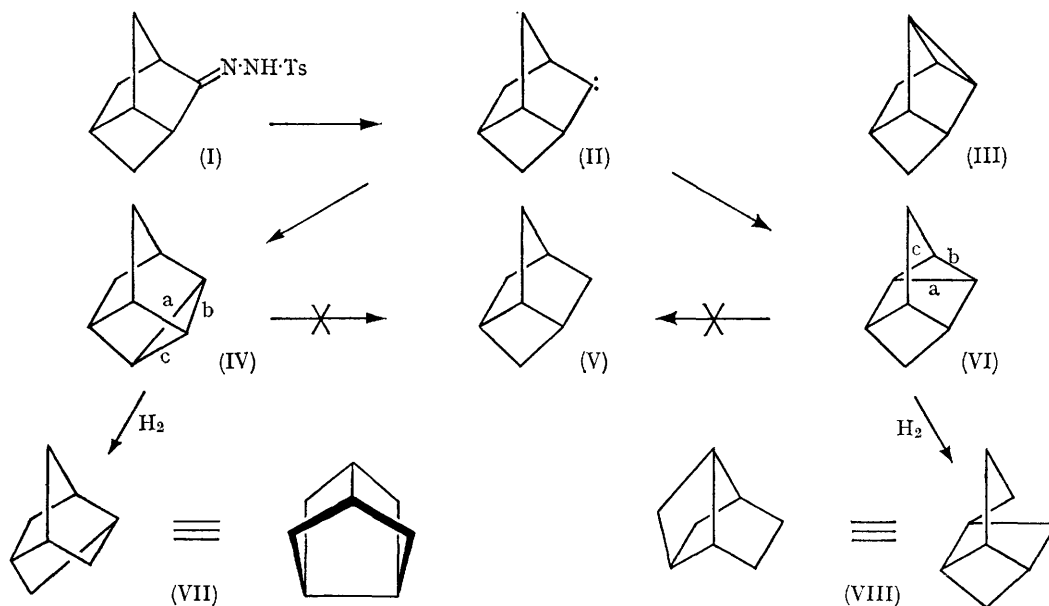
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As part of a programme devoted to small ring chemistry, we have recently become interested in syntheses<sup>1</sup> and reactions of bridged tetracyclo-octanes. One method among several likely approaches for synthesis is the generation of tetracyclo-octanes by way of appropriate tricyclic carbene intermediates.

Bivalent intermediate (II) is of particular interest since there are three possibilities for intramolecular carbenoid insertion, leading to tetracyclo-octanes (III), (IV), and (VI). Intermediate (II) was generated by carbenoid decomposition of the toluene-*p*-sulphonylhydrazone of tricyclo-[3,2,1,0<sup>3,6</sup>]octan-2-one (I)<sup>2</sup> in diglyme with an excess of sodium methoxide at 160°. Vapour-phase-chromatographic analysis of the volatile C<sub>8</sub>-hydrocarbon fraction (formed in 44% yield) on a 25 ft. Carbowax 20 M column showed the presence of only two components in a 35 : 65 ratio.

The 35% component is a solid at room temperature, m.p. 79.5—80.0° and must be tetracyclic since the infrared and n.m.r. spectra show no unsaturation. The n.m.r. spectrum (100 Mc.) exhibits four two-proton bands at  $\tau$  7.56—7.66, 7.95—8.07, 8.58—8.73, and 8.99—9.15 and two one-proton bands at  $\tau$  7.44—7.56 and 8.21—8.41. Spin decoupling experiments demonstrated that the four two-proton bands are due to four pairs of equivalent protons; the two one-proton absorption bands are due to two unique protons. Since structure (III) has no equivalent protons and (VI) possesses three pairs of equivalent protons and four unique protons, the correct structure for the 35% component must be the symmetrical structure (IV). Examination of (IV) reveals that it has the required two unique protons and four pairs of equivalent protons.

On catalytic hydrogenation over platinum in



<sup>1</sup> P. K. Freeman and D. G. Kuper, *Chem. and Ind.*, 1965, 424.

<sup>2</sup> R. R. Sauers and R. A. Parent, *J. Org. Chem.*, 1963, **28**, 605, have reported the synthesis of tricyclo[3,2,1,0<sup>3,6</sup>]octan-2-one.

methanol, (IV) gave only one product, m.p. 105.0—105.5° which must be tricyclic, since infrared and n.m.r. spectra show no unsaturation. Hydrogenolysis of equivalent bonds (a) or (b) in (IV) does not occur, since the spectral data of the product clearly do not fit tricyclo[3,2,1,0<sup>3,6</sup>]octane (V), synthesized by Wolff-Kishner reduction of tricyclo[3,2,1,0<sup>3,6</sup>]octan-2-one and by hydrogenolysis of 2-chlorotricyclo[3,2,1,0<sup>3,6</sup>]octane. No cyclopropane absorption is apparent in the infrared or n.m.r. spectra, and thus bond (c) must undergo hydrogenolysis to yield tricyclo[3,3,0,0<sup>3,7</sup>]octane (VII). The n.m.r. spectrum (60 Mc.) shows singlets at  $\tau$  7.72 (4H) and 8.68 (8H) and thus is consistent with structure (VII), which possesses only two kinds of hydrogen. Formation of (VII) reinforces the assignment of structure (IV) to the 35% component since (VII) cannot be formed by reductive bond fission of either (III) or (VI).

Tricyclic (VII) appears to be of considerable interest since it possesses a symmetrical arrangement of four fused cyclopentane rings and its relationship to adamantane may be illustrated by noting that conversion of two oppositely situated one-carbon bridges of adamantane into zero-carbon bridges produces hydrocarbon (VII). The only known derivative of this hitherto unsynthesized hydrocarbon appears to be tricyclo[3,3,0,0<sup>3,7</sup>]octane-1,3-dicarboxylic acid.<sup>3</sup>

The 65% component, a liquid at room temperature, is isomeric with the 35% component. A

nortricyclene skeleton is suggested by infrared absorption at 3050 (m), 1022 (w), and 785 (s) cm.<sup>-1</sup>.<sup>4</sup> Lack of carbon-carbon double-bond stretching absorption in the infrared spectrum and of olefinic hydrogen in the n.m.r. spectrum demonstrates that the major component is tetracyclic. The n.m.r. spectrum (100 Mc.) shows five bands at  $\tau$  7.68—7.80 (2H), 7.90—8.06 (2H), 8.21—8.35 (2H), 8.47—8.57 (2H), and 8.60—8.66 (2H). Subsequent spin decoupling demonstrated that the absorption bands at  $\tau$  7.68—7.80, 8.47—8.57, and 8.60—8.66 are due to pairs of equivalent protons, with the remaining two bands due to pairs of non-equivalent protons. Thus the spectral data are consistent only with structure (VI) for the 65% component.

On catalytic hydrogenation over platinum in methanol, (VI) absorbed hydrogen rapidly and gave a single product which exhibits no unsaturation in its infrared or n.m.r. spectra. The product, therefore, must be tricyclic, but is not (V) [cleavage at bond (a)] as demonstrated by spectral comparison. Since no cyclopropane absorption is evident above 3000 or near 1020 cm.<sup>-1</sup> in the infrared, cleavage at one of the equivalent bonds (b) or (c) must have occurred, producing tricyclo[3,3,0,0<sup>2,7</sup>]octane (VIII). The n.m.r. spectrum (60 Mc.) of (VIII) shows complex absorption bands at  $\tau$  7.62—7.95 (4H) and 8.12—8.93 (8H).

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<sup>3</sup> O. W. Webster and L. H. Sommer, *J. Org. Chem.*, 1964, **29**, 3103.

<sup>4</sup> E. R. Lippincott, *J. Amer. Chem. Soc.*, 1951, **73**, 2001; K. Alder, H. K. Schäfer, H. Esser, H. Krieger, and R. Reubke, *Annalen*, 1955, **593**, 23; J. D. Roberts, E. R. Trumbull, W. Bennett, and R. Armstrong, *J. Amer. Chem. Soc.*, 1950, **72**, 3116.