Evidence for a Bicyclo[3,1,0]hex-1-ene Intermediate in a Carbenoid Route to the 9,10-Di-isopropylidenetricyclo[4,2,1,$1^{2,5}$]decane System

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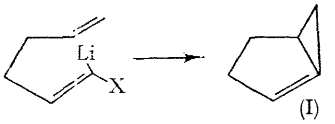
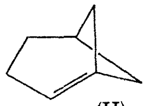
THE bicyclo[3,1,0]hex-1-ene system (I) is hitherto unknown. While outside the scope of Bredt's rule in its present interpretation,[1] because of its zero-bridge, molecular models indicate a total ring strain of (I) qualitatively and quantitatively comparable† to that of the bicyclo[3,1,1]-hept-1-ene system (II), which is certainly within the limits of Bredt's rule.[2] Thus, the species (II) might be thought capable of existing if the existence of the ring system (I) could be demonstrated. The latter ring system could result from an intramolecular version of the well known intermolecular methylenecyclopropane formation from alkylidenecarbenoids and olefins:[3]



(I)

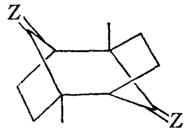


(II)

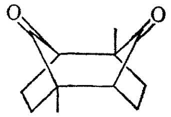
1-Chloro-2,5-dimethylhepta-1,5-diene (III),[4] on treatment with n-butyl-lithium in tetrahydrofuran, yielded, among other products, two hydrocarbons, "A" and "B", both with formula $C_{18}H_{28}$ (according to combustion analysis and mass spectra). "A", m.p. 82°, was the main solid product (yield 20—25%) from reactions performed below −50°, while "B", m.p. 164°, (yield 15—19%), predominated at −40°.‡

The structure of "A" is still not settled. According to its n.m.r. spectrum,§ which has three sharp signals at τ 8·83, 8·96, and 9·00 (6 : 6 : 6 H), the molecule has six methyl groups and a symmetry such that pairs of methyl groups are equivalent. The absence of absorptions in the double-bond region of its i.r. and Raman spectra, and its inertness toward $KMnO_4$, ozonolysis, and hydrogenation (Pd/C, 25°, 95 atm.), would fit a pentacyclic structure.

"B" is a 9,10-di-isopropylidenetricyclo[4,2,1,$1^{2,5}$]decane with two additional methyl groups at the bridgeheads, either in vicinal positions, or—more probably—as shown in formula (IV). It shows no double-bond signal in the i.r. spectrum but a strong Raman band at 1680 cm.$^{-1}$. The n.m.r. spectrum exhibits three singlets of equal intensity at τ 8·19, 8·29 (4 × $=$C–CH_3), and 8·77 (2× C–CH_3), and a multiplet centred around τ 7·67 (2× $=$C–CH). Ozonolysis of (IV) yielded acetone (identified by g.l.c.) and a diketone $C_{12}H_{16}O_2$, m.p. 196—197°, with an n.m.r. singlet at τ 9·03 (2× C–CH_3) and strong C=O absorptions at 1757 cm.$^{-1}$ (i.r., in CCl_4) and 1738 cm.$^{-1}$ (Raman signal, pure solid), supporting the five-ring structure (V). The dipole moment of the diketone (V) is almost zero (found 0·1 ± 0·3 D); this quickly eliminates the isomeric structure (VI).¶



(IV) Z=CMe₂
(V) Z=O



(VI)

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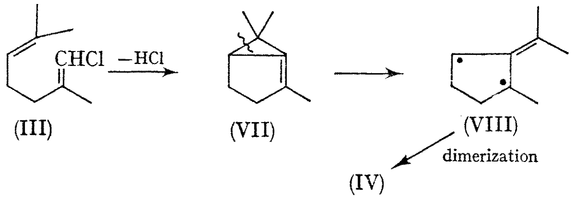
† As we will discuss in more detail in a subsequent paper.

‡ Reactions above −40° produced mixtures of "B" and a third isomer $C_{18}H_{28}$ ("C") of lower symmetry, which has not been isolated in a pure state so far.

§ Recorded in CCl_4, relative to internal Me_4Si.

¶ The parent molecule (V) without the bridgehead methyl groups, m.p. 194—196°, has recently been synthesized by another route: E. Baggiolini, E. G. Herzog, S. Iwasaki, R. Schorta, and K. Schaffner, *Helv. Chim. Acta*, 1967, **50**, 297. We thank Dr. Schaffner for a sample of his compound.

The formation of (IV) is rationalized by an α-elimination of HCl from the substrate (III) to give the strained bridgehead olefin (VII) [a trimethyl derivative of (I)]. Ring opening of (VII) yields the trimethylenemethane diradical (VIII), which dimerizes to form the product (IV).



The cleavage of methylenecyclopropanes without additional ring strain at elevated temperatures is well known,[5] as is the dimerization of trimethylenemethanes to give 1,4-dimethylenecyclohexanes. The latter process is ascribed to a triplet diradical,[6] which is the ground state of trimethylenemethane, as evidenced by both theoretical[7] and experimental[8] approaches.

A triplet diradical, formed by intersystem crossing from the singlet intermediate, might be involved, too, in the reaction under discussion. However, since the normal[9] ring-closure (or re-closure) of singlet trimethylenemethanes to methylenecyclopropanes is unlikely for (VIII), because of high ring-strain in the potential products, the dimer (IV) might result from the singlet diradical as well.

Our efforts to trap (VII), so far unsuccessful with several olefins, are continued and extended to related systems.

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