An Unusual Acid-catalysed Rearrangement of 8-Methylenebicyclo[4.2.0]-octan-2-ones; *X*-Ray Crystal Structure of 4-Isopropyl-1,5-dimethylbicyclo[3.2.1]oct-3-ene-6,7-dione

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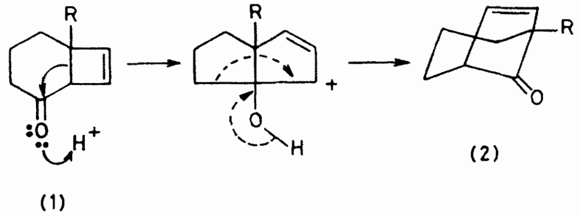
Summary The reactions of the 8-methylenebicyclo[4.2.0]-octan-2-ones (**5**) and (**6**) with toluene-*p*-sulphonic acid in boiling benzene lead to (**9**) and (**11**), respectively, by an unusual rearrangement; the structure of (**9**) was established by the *X*-ray diffraction analysis of the derived diketone (**10**).

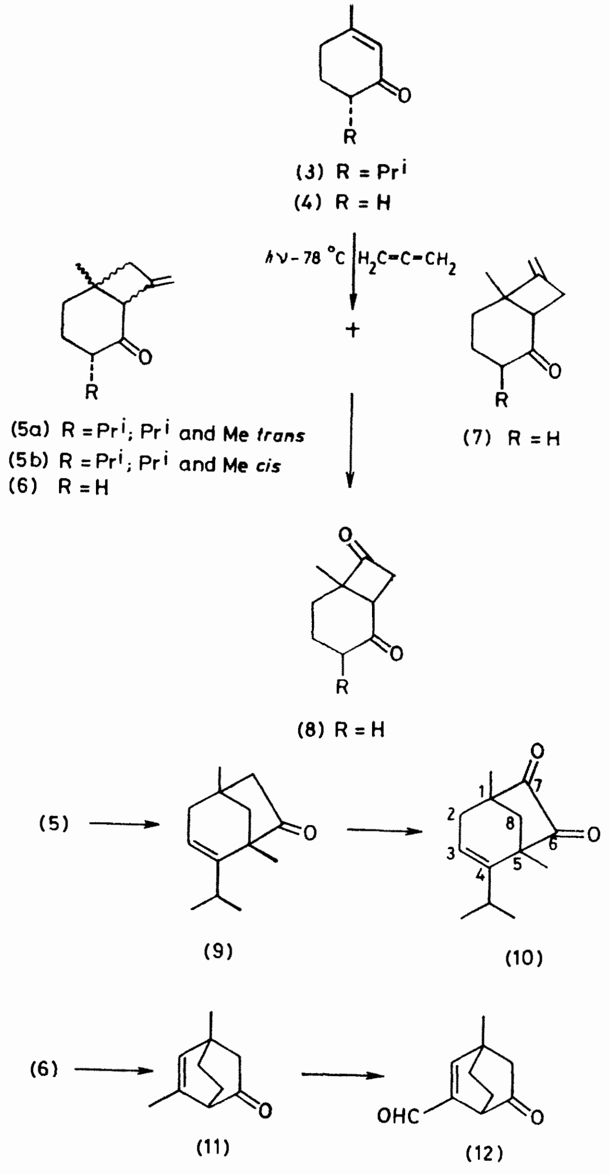
Bicyclo[4.2.0]oct-7-en-2-ones (**1**) undergo an acid-catalysed rearrangement to give bicyclo[3.2.1]oct-6-en-8-ones (**2**),[1] on treatment with either toluene-*p*-sulphonic acid in boiling benzene or boron trifluoride–ether in refluxing *o*-xylene.[2] The mechanism proposed is shown in Scheme 1.



Scheme 1.

The photochemical cycloaddition of allene to $\alpha\beta$-unsaturated ketones provides 8-methylenebicyclo[4.2.0]-octan-2-ones which have been used extensively in the synthesis of natural products.[3] Unlike compounds (**1**), these photoadducts do not undergo the rearrangement described above; the ring-opening mechanism and the final product depend on the acid catalyst. We report an unusual rearrangement of the 8-methylenebicyclo[4.2.0]octan-2-ones (**5**) and (**6**) with toluene-*p*-sulphonic acid in boiling benzene.

Irradiation of 1-piperitone (**3**) in the presence of allene at −78 °C provided a 3 : 1 mixture of the photoadducts (**5a**) and (**5b**)† (Scheme 2) which were separated by h.p.l.c. [column 25 cm × 7·9 mm i.d., packed with silica gel Lichrosorb Si 60, 5μm: (**5a**), retention time 8 min; $\Delta\epsilon$ $-0{\cdot}11$; λ_{max} 310 nm; (**5b**), retention time 10 min, $\Delta\epsilon$ $+0{\cdot}04$; λ_{max} 305 nm]. Under the same conditions, irradiation of 3-methylcyclohexenone (**4**) was not regiospecific and provided a 4 : 1 mixture of the photoadducts (**6**) and (**7**).[4] The structure of (**7**) was confirmed by OsO_4–$NaIO_4$ oxidative degradation to the stable diketone (**8**).



Scheme 2.

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† All new compounds gave satisfactory mass spectral analyses as well as supporting spectroscopic (i.r., 400 MHz ^1H n.m.r., and ^{13}C n.m.r.) data.

Upon treatment with a large amount of toluene-*p*-sulphonic acid (1 : 1, w/w) in boiling benzene for 2 h, the mixture (**5a**) and (**5b**) rearranged to (**9**) [ν_{max} 3040, 1735, and 810 cm^{-1}; δ 0·93 and 1·03 (2d, 6H, J 7·5 Hz), 1·15 (s, 3H), 1·27 (s, 3H), and 5·46 (t, 1H); m/z 192 (M^+)]; the structure was confirmed by the selenium dioxide oxidation of (**9**) to give (**10**) [m.p. 57—60 °C; ν_{max} 1765 and 1745 cm^{-1}, δ 0·85 and 1·03 (2d, 6H, J 7·5 Hz), 1·16 (s, 3H), 1·42 (s, 3H), and 5·63 (t, 1H); m/z 206 (M^+)], the structure of which was determined by X-ray crystal structure analysis. Monoclinic crystals of (**10**) were obtained from pentane solution (0·2 × 0·3 × 0·5 mm). *Crystal data*: $C_{13}H_{18}O_2$, space group $P2_1/n$, a = 14·864(4); b = 10·102(3); c = 17·134(4) Å; β = 109°5(1), U = 2425·2 Å^3, Z = 8. 1918 independent reflexions were measured with $I > 2\sigma(I)$ on a four-circle PW 1100 automatic diffractometer using Cu-K_α radiation. The structure was solved by direct methods with the aid of a multisolution technique,[5] and anisotropically refined to a final conventional R factor of 8·6% (all hydrogen atoms were located on difference Fourier syntheses and their co-ordinates, as well as their isotropic thermal factors, were not refined). The Figure shows one of the two independent molecules in the unit cell.‡

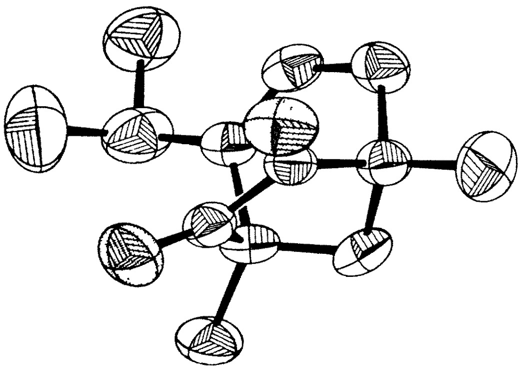
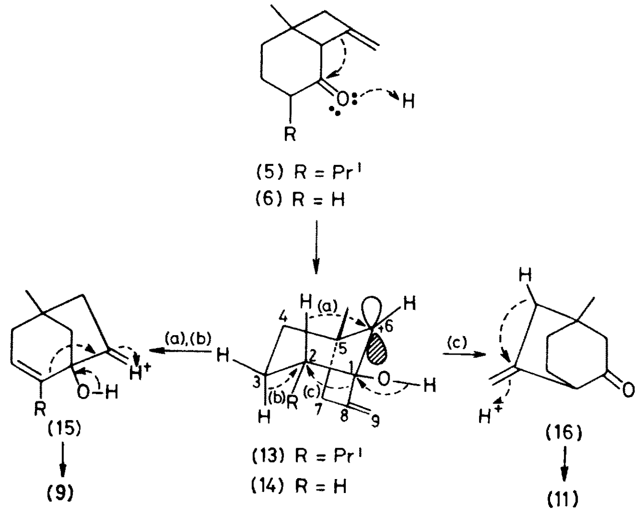


FIGURE. Molecular structure of (**10**) (shaded ellipsoids represent oxygen atoms).

Unlike (**5**), which rearranges to a bicyclo[3.2.1]octanone system, the photoadduct (**6**) gave, under the same conditions, the bicyclo[2.2.2]octanone (**11**) [ν_{max} 3020, 1720, 1645, and 820 cm^{-1}; δ 1·22 (s, 3H), 1·80 (d, 3H, J 1·5 Hz), 1·88 (s, 2H), 2·93 (m, 1H), and 5·79 (m, 1H)]. Oxidation of (**11**) with selenium dioxide provided the aldehyde (**12**) [ν_{max} 2810, 2720, 1725, 1680, and 1610 cm^{-1}; λ_{max} 281 nm (ϵ 8780); δ 1·43 (s, 3H), 2·03 (s, 2H), 3·83 (m, 1H), 7·23 (m, 1H), and 9·56 (s, 1H)].



SCHEME 3.

The rearrangement of (**5**) and (**6**) to (**9**) and (**11**), respectively, probably proceeds as indicated in Scheme 3. Models show that in the conformation of the cations (**13**) and (**14**), the vacant orbital at C-6 and the C-2–H bond are parallel. The 1,3 hydride shift from C-2 to C-6 (sense a) is therefore readily understood. When R = Pr^i, *i.e.* (**13**), the elimination of the proton at C-3 (sense b) stabilizes the carbocation and leads to the trisubstituted double bond compound (**15**) which rearranges to (**9**). When R = H, compound (**14**), elimination (sense b) would be disfavoured; the bond C-1–C-8 is favourably disposed for migration (sense c) leading to (**16**).

It is interesting to note that products like (**2**), which could be formed by the mechanism shown in Scheme 1, were not observed.

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‡ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

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[2] S. Ayral-Kaloustian and W. C. Agosta, *J. Am. Chem. Soc.*, 1980, **102**, 314.
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