

Photochemical Conversion of 7,7-Diphenyl-2,3-epoxybicyclo[3.2.0]heptan-6-ones into a 2-Oxabicyclo[2.1.1]hexan-3-one

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Photolysis of the epoxide (3) or (5) gave the strained lactone (4) in 40–50% yield; the bicyclic lactone (4) gave the functionalised cyclobutane (6) on treatment with acidic methanol, the structure of which was confirmed by X-ray analysis.

In view of the current interest in the photochemistry of epoxyketones,¹ and in particular the studies involving epoxybicycloheptanones,² we describe our results concerning the photolysis of some 2,3-epoxybicyclo[3.2.0]alkan-6-ones.

Treatment of 7,7-diphenylbicyclo[3.2.0]hept-2-en-6-one (1)³ with *N*-bromoacetamide in aqueous acetone gave the bromohydrin (2).⁴ Base-initiated dehydrobromination gave the epoxide (3) in good yield. Photolysis of this epoxide using a Hanovia medium-pressure mercury lamp through quartz, using benzene as solvent, gave one non-polar product. Chromatography over silica gave a crystalline solid (42%) with spectral characteristics in accord with the structure of the lactone (4): ν_{\max} 1800 cm⁻¹; δ (CDCl₃) 7.5–7.1 (10H, m, 2 × Ph), 6.12 (1H, d, *J* 9 Hz, CH=CPh₂), 4.73 (1H, dt, *J* 7.5, 1 Hz, H-1), 3.38 (1H, ddm, *J* 9, 2.5 Hz, H-5), 2.95 (1H, dt, *J* 7.5, 2.5 Hz, H-4), 2.35 (1H, dm, *J* 9 Hz, H-6 *exo*), and 2.21 (1H, ddm, *J* 9, 2.5 Hz, H-6 *endo*). The long-range coupling $J_{1,4} = 7.5$ Hz is typical for this ring system.⁵

Reaction of the ketone (1) with *m*-chloroperoxybenzoic acid gave the epoxide (3) (17%) and the stereoisomeric compound (5) (78%). Photolysis of the epoxide (5) under the above conditions gave the oxabicyclo[2.1.1]hexanone (4) (48%) as the only isolable product.

Treatment of the lactone (4) with methanol containing toluene-*p*-sulphonic acid gave the hydroxyester (6); the *cis* orientation of the three substituents on the cyclobutane ring

was confirmed by an X-ray analysis which also showed that the molecule adopts two conformations in the crystal.[†] The principal difference between these conformations is a 20° difference in the torsion angle about the bond linking the cyclobutane ring and the diphenyl side chain.

The photochemical conversion of the epoxides (3) and (5) into the lactone (4) presumably proceeds through a retro-[2 + 2] reaction to give a relatively stable alkenylketene;^{2,6} (8) and (9) are possible structures for the intermediates. Scission of the allylic C–O bond² followed by rapid addition across the cumulene moiety⁷ would lead to the observed product.

The epoxybicyclo[4.2.0]octan-7-one (7) did not behave in a similar manner; photolysis led to slow decomposition to a multitude of products.

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[†] Crystal data: C₂₀H₂₀O₃, monoclinic, $a = 8.929(1)$, $b = 24.951(3)$, $c = 15.638(2)$ Å, $\beta = 98.67(1)^\circ$, $U = 3444$ Å³, space group $P2_1/n$, $Z = 8$ (two crystallographically independent molecules in the asymmetric unit), $M_r = 300$, $D_c = 1.16$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 6$ cm⁻¹, $F(000) = 1312$. 4265 Independent observed reflections [$|F_o| > 3\sigma(|F_o|)$, $\theta \leq 58^\circ$] were measured on a Nicolet R3m diffractometer with Cu-K α radiation (graphite monochromator) and using ω -scans. The structure was solved by direct methods and refined anisotropically to give a current $R = 0.070$ and $R_w = 0.080$. 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.

