Synthesis of 6-Methylbicyclo[4,2,0]octan-2-one by Photochemical Additions

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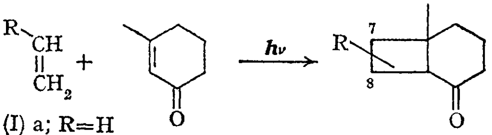
MANY examples of photo-cycloadditions of olefins to $\alpha\beta$-unsaturated ketones have been reported[1] but the use of ethylene itself has so far been very limited.[2] A direct addition of ethylene to cyclohexones would yield bicyclo[4,2,0]octanones having no substituents on the four-membered ring[3] which can be useful as synthetic intermediates.

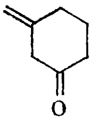
The photoaddition of ethylene (Ia) to 3-methylcyclohex-2-enone (II, 0·1 mole) was effected by bubbling ethylene into a benzene solution[4] for 80 hours at room temperature under u.v. irradiation.[5] Distillation and subsequent preparative g.l.c.[6] of the reaction mixture gave 40% of the desired bicyclic ketone (IIIa), i.r. (neat) 1690 cm.$^{-1}$, n.m.r. ($CDCl_3$) 1·20 p.p.m. (3H, singlet), and 10% of the unconjugated ketone (IV), leaving 50% of nondistillable crystals. The ketone (IV), i.r. (neat) 1715 and 890 cm.$^{-1}$, n.m.r. ($CDCl_3$) 4·74 p.p.m. (2H, broad doublet), is presumably produced through an intermediary enol form[7] of the conjugated ketone (II). The bicyclic ketone (IIIa) is a single product having the more stable *cis* ring juncture since it remained unchanged after passing through columns of alumina or after g.l.c., and readily gave a crystalline 2,4-dinitrophenylhydrazone, m.p. 135—136°.



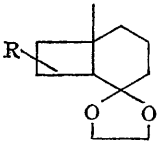
(I) a; R=H
b; R=OAc

(II)

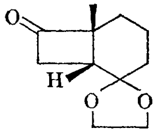
(III) a; R=H
b; R=AOc



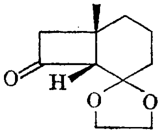
(IV)



(V) a; R=OAc
b; R=OH
c; R=O
d; R=H



(VI)



(VII)

The same bicyclic ketone (IIIa) could be formed on a preparative scale and in high yield by the following route. Irradiation of vinyl acetate[8] (Ib) (6·0 moles) and the cyclohexenone (II) (0·5 mole) in petroleum (700 ml.) for 24 hours at room temperature gave 68% of the bicyclic ketone (IIIb)[9] (b.p. 82—93°/0·005—0·008 mm. Hg).

Ketalization of the isomeric mixture (IIIb) gave the ketals (Va)[9] (95%, b.p. 84—97°/0·06 mm. Hg) which were hydrolyzed to the ketal alcohols (Vb) (98%, b.p. 91—98°/0·07 mm. Hg). Oxidation of (Vb) with chromic oxide and pyridine gave the ketone mixture (Vc) (92%, i.r. at 1780 cm.$^{-1}$) from which the isomers (VI) and (VII) could be separated by preparative g.l.c.[6] in a ratio of 4 to 1. The structure of (VI) is supported by its n.m.r. spectrum which shows an ABX pattern: H_A 2·86, H_B 3·20, and H_X 2·18 p.p.m.; J_{AB} 17·0, J_{AX} 8·8, and J_{BX} 9·0 c./sec. The predominant formation of the ketone (VI) indicates that the 7-acetoxy-compound is formed in preference to the 8-acetoxy-isomer in the photoadduct (IIIb). Finally, Wolff–Kishner reduction of the isomeric mixture (Vc) yielded the ketal (Vd), (90%) which was deketalized with 2N-HCl in ether to afford the bicyclic ketone (IIIa) in 91% yield; the ketone thus formed was identical in every respect (i.r., n.m.r., and g.l.c.)[6] to the ketone resulting from the direct addition of ethylene.

The photoaddition of vinyl acetate (Ib) to the ketone (II) was also carried out with a concave radiating monochromator (Japan Spectroscopic Company, model CRM-100). In this instrument, the light (200—700 mμ) from a 2 kw xenon source is separated by a concave grating, and the monochrome (*ca.* 15 mμ width) is led into 30 quartz sample cells aligned along a Rowland circle. After 16 hours of irradiating the above-mentioned petroleum solution of (Ib) and (II), a plot of the wavelength *versus* yield of product (measured by g.l.c.) indicated that (IIIb) was produced by the light ranging from 260 to 375 mμ; the maximum yield was obtained at 325 mμ, the wavelength corresponding to n—π^* transition bands of $\alpha\beta$-unsaturated ketones. The ratio of product (IIIb) to starting material (II) at 325 mμ was 24%.

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[1] E. J. Corey, J. D. Bass, R. LeMahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, 1964, **86**, 5570; and references cited therein.
[2] R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, 1966, **88**, 1330.
[3] *Cf.* H. O. House and T. H. Cronin, *J. Org. Chem.*, 1965, **30**, 1061.
[4] The photoaddition did not proceed in n-pentane or petroleum solutions.
[5] Taika 450 w high-pressure lamp, no filter.
[6] 20% SE-30 on Chromosorb W.
[7] W. A. Noyes, G. S. Hammond, and J. N. Pitts. *Adv. Photochem.*, 1963, **1**, 356.
[8] Kureha Kagaku Co., stabilized and not distilled before use.
[9] Eight isomers are theoretically conceivable for (IIIb) but the n.m.r. spectrum showed only six methyl singlets in the region 0·94—1·34 p.p.m. The number of isomers was reduced to four, as detected by n.m.r. methyl singlets, by passage through a g.l.c. column, by leaving the ethereal solution of mixture (IIIb) for 30 minutes on an alumina column, and by ketalization.