

A New Photochemical Rearrangement of $\beta\gamma$ -Unsaturated Cyclic Ketones

By J. R. WILLIAMS and HERMAN ZIFFER

(National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland 20014)

WHILE the photochemistry of saturated conjugated cyclic ketones has been extensively explored,¹ comparatively little is known of the photolytic reactions of $\beta\gamma$ -unsaturated cyclic ketones.² We now report a novel photochemical rearrangement of the $\beta\gamma$ -unsaturated ketone (I) to the conjugated cyclopropyl ketone (II).

Irradiation of a *t*-butyl alcohol solution of 3,4,5,6,7,8-hexahydronaphthalen-2(1*H*)-one (I) (λ_{\max} 281 $m\mu$, ϵ 38),³ under nitrogen with a high-pressure mercury arc (Hanovia) using a Pyrex filter, yielded the photo-product (II) in greater than 60% conversion.* Compound (II) had the same molecular formula as the starting material and its n.m.r. spectrum† showed absence of vinyl protons. Further spectral data [$\lambda_{\max}(\text{MeOH})$ 208 $m\mu$, ϵ 5200; 277 $m\mu$, ϵ 138] and [$\nu_{\max}(\text{film})$ 3065, 1715 cm^{-1}] indicated the presence of a cyclopropane ring conjugated with a five-membered ring ketone.⁴

On treatment of (II) with hydrobromic acid in glacial acetic acid, it was converted in good yield into (III), whose n.m.r. spectrum showed an AB quartet

centred at 3.62 p.p.m. ($\Delta\nu$ 5.4 c./sec., $J = 10.3$

c./sec.) characteristic of a $\begin{array}{c} \text{C} \\ | \\ \text{C}-\text{C}-\text{CH}_2\text{Br} \\ | \\ \text{C} \end{array}$ grouping.⁵

Regeneration of (II) was effected by treatment of the bromo-compound with alkali, showing that no rearrangement had occurred during the acid treatment and agreeing with its formulation as a γ -bromo-ketone. Hydrogenolysis of (III) using Pd-CaCO₃ yielded (IV), whose n.m.r. spectrum now showed the presence of a methyl group on a quaternary carbon: 1.18 p.p.m. (3H, singlet). The i.r. spectra of (III) and (IV) [$\nu_{\max}(\text{film})$ 1742 cm^{-1} and 1740 cm^{-1} , respectively] showed the presence of a cyclopentanone system. The above results require (II) to contain a five-membered ring ketone conjugated with a cyclopropane ring, the β -carbon of which is quaternary.

Confirmation of the presence and position of the cyclopropane ring was established by conversion of (II), by Wolff-Kishner reduction, into the known hydrocarbon (V).⁶ A comparison of its i.r. and

* The remaining 40% was a mixture of starting material plus several other photo-products each present in low yield.

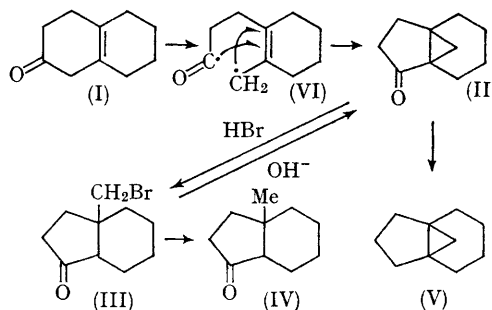
† The n.m.r. spectra were determined as solutions in CDCl₃ containing tetramethylsilane as an internal standard ($\delta = 0.0$ p.p.m.) using a Varian A-60.

n.m.r. spectra with those obtained from an authentic sample of (V) (tricyclo[4,3,1,0^{1,6}]decane) showed them to be identical. The nonequivalent protons of the cyclopropyl methylene group in (V) gave rise to an AB quartet centred at 0.24 p.p.m. ($\Delta\nu$ 12.9 c./sec., $J = 4.5$ c./sec.) in the n.m.r. spectrum. The absence of the cyclopropyl protons in (II) appears to be the result of conjugation of the cyclopropane ring with the carbonyl group resulting in a downfield shift of the cyclopropyl protons.⁷

Although we have no evidence at present which would indicate a preference for either radical or ionic type intermediates, one can formulate the reaction as proceeding *via* (VI) in the sequence shown opposite.

The generality and stereochemical course of this photochemical reaction is now under study.

Experiments with 17 β -hydroxyoestr-5(10)-en-3-one indicate that it undergoes the same rearrangement.



(Received, January 9th, 1967; Com. 024.)

¹ K. Schaffner, *Adv. in Photochem.*, 1966, **4**, 81, and references cited therein.

² G. Buchi and E. M. Burgess, *J. Amer. Chem. Soc.*, 1960, **82**, 4333; P. D. Gardner and H. F. Hamil, *ibid.*, 1961, **83**, 3531; G. O. Schenck and R. Steinmetz, *Chem. Ber.*, 1963, **96**, 520; P. E. Eaton, *Tetrahedron Letters*, 1964, 3695; R. Criegee and H. Furrer, *Chem. Ber.*, 1964, **97**, 2949; R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, and G. Freund, *ibid.*, p. 2942; R. L. Cargill, M. E. Beckham, A. E. Siebert, and J. Dorn, *J. Org. Chem.*, 1965, **30**, 3647; R. L. Cargill, J. R. Damewood, and M. M. Cooper, *J. Amer. Chem. Soc.*, 1966, **88**, 1330.

³ A. J. Birch, A. R. Murray, and H. Smith, *J. Chem. Soc.*, 1951, 1945.

⁴ T. Norin, *Acta Chem. Scand.*, 1961, **15**, 1676.

⁵ R. Ginsig and A. D. Cross, *J. Amer. Chem. Soc.*, 1965, **87**, 4629.

⁶ W. G. Dauben and P. Lang, *Tetrahedron Letters*, 1962, 453; E. Vogel, W. Wiedemann, H. Kiefer, and W. F. Harrison, *ibid.*, 1963, 673.

⁷ G. Stork and J. Ficini, *J. Amer. Chem. Soc.*, 1961, **83**, 4678.