

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

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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 $\begin{array}{c} \text{C} \\ | \\ \text{C}-\text{CH}_2\text{Br} \\ | \\ \text{C} \end{array}$ 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.

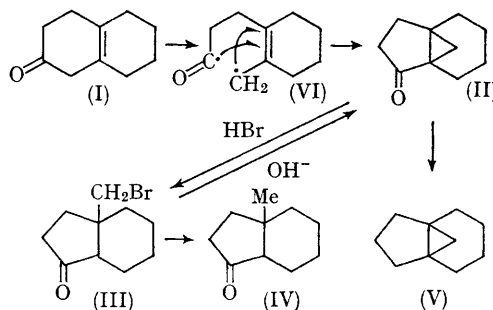
† The n.m.r. spectra were determined as solutions in CDCl₃ containing tetramethylsilane as an internal standard ($\delta = 0.0$ p.p.m.) using a Varian A-60.

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 -hydroxycœstr-5(10)-en-3-one indicate that it undergoes the same rearrangement.



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