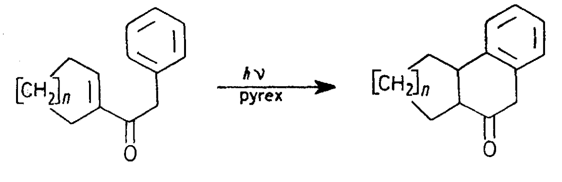
Photocyclisation of Benzyl Cycloalk-1-enyl Ketones

By Masaru Tada,* Hiroshi Saiki, Kyo Miura, and Hiraku Shinozaki
(*Department of Chemistry, School of Science and Engineering, Waseda University, Shinjuku, Tokyo* 160, *Japan*)

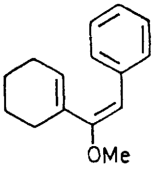
Summary The benzyl cycloalk-1-enyl ketones (I)—(III) cyclise photochemically *via* singlet and triplet excited states to give the products (V)—(VII) in MeOH with and without CF_3CO_2H, in benzene with BF_3–Et_2O or CF_3CO_2H, and in MeCN with and without CF_3CO_2H.

An attempted cyclisation of benzyl cyclohex-1-enyl ketone (II) with Lewis acid led to recovery of starting material.[1] We report here the photochemical cyclisation of benzyl cycloalk-1-enyl ketones (I)—(III) under various conditions.

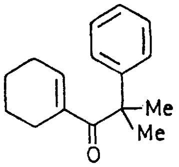


(I) n = 1 (III) n = 3
(II) n = 2 (IV) n = 4
(V) n = 1 (VII) n = 3
(VI) n = 2

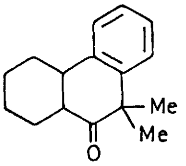
Irradiation of the ketones (I)—(III) in benzene containing 0·05 M BF_3–Et_2O through Pyrex glass gave the products (V), b.p. 72 °C at 0·1 mmHg, (VI), b.p. 90 °C at 0·1 mmHg, and (VII), b.p. 145 °C at 0·2 mmHg in 79, 87, and 90% yields, respectively.† With the ketone (IV), however, starting material was recovered under similar conditions. The products (V) and (VII) were homogeneous by g.l.c. analyses but the product (VI) consisted of the *cis*- and *trans*-ring fusion isomers (VIa) and (VIb).‡ The *cis*-ring fusion in (VIa) was confirmed by its conversion into *cis*-1,2,3,4,4a,9,10,10a-octahydrophenanthrene,[2] followed by thioacetalisation and desulphurisation using Raney-Ni; (VIb) was deduced to be the *trans* isomer. The formation of (VIa) and (VIb) is not due to isomerisation of the product under the reaction conditions. Treatment of the product (VI) with acid or base, with varying ratios of both isomers did not change the original ratio.



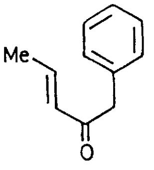
(VIII)



(IX)



(X)



(XI)

The ketone (II) was examined under a wide variety of conditions to investigate the nature of the reaction. CF_3CO_2H is as effective a catalyst as BF_3–Et_2O for the photocyclisation of (II), and polar solvents such as MeOH and MeCN provide a good system for the cyclisation even without acid catalyst. The reactivity decreases as follows, as judged by the time required for completion of the reaction; 0·05 M-CF_3CO_2H–MeOH§ $>$ MeOH $>$ 0·05 M CF_3CO_2H–C_6H_6 $\approx$ 0·05 M BF_3–Et_2O–C_6H_6 $>$ 0·05 M CF_3CO_2H–MeCN $>$ MeCN $\gg C_6H_6$. The fact that the cyclisation in MeOH is faster than in MeCN suggests the importance of the acid function rather than the polarity.

---

† All new compounds gave satisfactory elemental analyses, and mass, i.r., and n.m.r. spectra.

‡ The ratio of (VIa) to (VIb) is dependent on the solvent; (VIa) : (VIb) = *ca.* 1 : 1 for BF_3–Et_2O–C_6H_6, 4 : 1 for MeOH and 5 : 1 for MeCN.

§ Enol ethers of (VIa) and VIb) were isolated using CF_3CO_2H–MeOH as the reaction system.

One possible mechanism of the cyclisation, a Cope-type rearrangement of the formal triene system in the enol form of the ketone (II), was eliminated by the following observations; the enol ether (VIII) underwent only geometrical isomerisation upon irradiation, and the dimethyl derivative (IX) gave the cyclised product (X), b.p. 100 °C at 0·2 mmHg, which was difficult to isolate in practical yield owing to its photo-lability.

The failure of the photocyclisation of the ketone (IV) must be due to a rapid relaxation of the excited state by isomerisation to the *trans*-cyclo-octene system.[3] This was further supported by irradiation of benzyl propenyl ketone (XI) which caused geometrical isomerisation rather than cyclisation.

In MeOH, the ketone (I) was converted smoothly into (V) and (II) was converted more slowly into (VI). The ketone (III), however, was not cyclised into (VII) in MeOH. The cyclisation of (I) in MeOH was quenched efficiently by pent-1,3-diene to give a linear Stern–Volmer plot, $k_Q\tau = 16$. In contrast to the reaction in MeOH, compounds (I)–(III) all readily cyclised to give (V)—(VII), respectively, in C_6H_6 containing 0·05 M BF_3–Et_2O. Stern–Volmer plots for the quenching experiments in the latter systems showed curved lines. Inflections and plateaus at $\Phi_0/\quad = 1\cdot8$ for *(I) and* $\Phi_0/\Phi = 1\cdot3$ *for (II) show that the both singlet and* triplet processes are involved in the reaction of (I) and (II): 56% singlet for (I) and 77% singlet for (II).[4] The reaction of (III) essentially was not quenched by penta-1,3-diene, indicating that the cyclisation of (III) in benzene containing 0·05 M BF_3–Et_2O involves only a singlet process.

Carbonyl compounds form complexes with BF_3–Et_2O,[5] and the u.v. absorption of the ketone (II) in hexane containing 0·05 M BF_3-Et_2O shows a new strong absorption around 270 nm with a concomitant decrease in the intensity of the π–π^* absorption at 224 nm; the pattern of absorption in C_6H_6 containing BF_3–Et_2O (the same system as in the photoreaction) is quite different from the absorption in the absence of acid in the n–π^* region. This spectroscopic behaviour, in conjunction with the quenching experiments, suggests that charge-transfer excitation of the complex between the carbonyl compound and BF_3 is most probably responsible for the photochemical cyclisation, *via* a singlet process.

Financial support by the Matsunaga Science Foundation is acknowledged.

(*Received*, 1st *October* 1974; *Com.* 1230.)

---

[1] J. W. Cook and C. L. Hawett, *J. Chem. Soc.*, 1933, 1098; W. S. Johnson and C. D. Gutsche, *J. Amer. Chem. Soc.*, 1946, **68**, 2239.

[2] J. W. Cook, N. A. McGinnis, and S. Mitchel, *J. Chem. Soc.*, 1944, 286.

[3] R. Noyori, H. Inoue, and M. Kato, *J. Amer. Chem. Soc.*, 1970, **92**, 6699.

[4] N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, 1968, **90**, 6863.

[5] A. Pagliardini, G. Elegant, and M. Azzaro, *Tetrahedron Letters*, 1972, 4241.