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PHOTOCHEMICAL ISOMERIZATION OF SIMPLE α,β-UNSATURATED KETONES

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IN our detailed study of photochemical behavior of simple acyclic α,β-unsaturated ketones (I), we have observed three different kinds of behavior of these ketones upon irradiation. One, the formation of cyclopropane derivatives when the carbon atom γ to the carbonyl group is a quarternary one (Ia, R=t-butyl, R'=R"=H; Ib, R=t-butyl, R'=CH_3, R"=H) has been reported (2). Other structurally similar ketones were found to undergo facile isomerization to the β,γ-unsaturated isomers, or were characterized by their unusual resistance to any photochemical change upon irradiation. Lack of reactivity was typical for simple homologs of I, 3-penten-2-one (Ic, R=CH_3, R'=R"=H), mesityl oxide (Id, R=R'=CH_3, R"=H) and 3,4-dimethyl-3-penten-2-one (Ie, R=R'=R"=CH_3) under a large variety of conditions. We have also observed this resistance in 4,5-dimethyl-3-hexen-2-one (If, R=$CH(CH_3)_2$, R'=CH_3, R"=H) (3). The lack of reactivity in this case was particularly surprising as its relative, 5-methyl-3-hexen-2-one (Ig, R=$CH(CH_3)_2$, R'=R"=H), was found to undergo a facile isomerization to the β,γ-isomer, 5-methyl-4-hexen-2-one (II) in very

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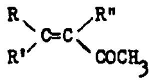
(1) Fellow of the Alfred P. Sloan Foundation.

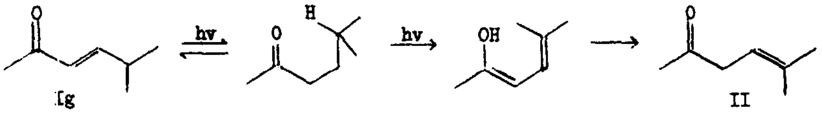
(2) M. J. Jorgenson and N. C. Yang, J. Am. Chem. Soc., 85, 1698 (1963).

(3) The cis-trans photostationary state (cis:trans, 95:5) of If was readily established. Upon prolonged irradiation a slow change to polymeric products took place.



I

good yield under the following conditions. The ketone (10 g.) was irradiated in 450 ml. of ether for 12 hours with a Hanovia 450 w. lamp employing a pyrex filter. At this time the complete conversion of the α,β-isomer to the β,γ-isomer was indicated by infrared and ultraviolet spectroscopy (4). Distillation afforded 7.5 g. (75%) of the pure β,γ-isomer as indicated by the usual characterizations and its n.m.r. spectrum, a one-proton triplet at 4.68τ (J = 7 cps), a two-proton doublet at 6.95τ (J = 7 cps) and three three-proton singlets at 7.94, 8.20 and 8.35τ. Facile isomerization of 3-hexen-2-one (Ih, R=C_2H_5, R'=R"=H) to its β,γ-isomer also occurred under similar conditions, but the isomerization was complicated by the formation of both cis and trans isomers of the product, 4-hexen-2-one.



Ig

II

The only report on the isomerization of simple acyclic α,β-unsaturated carbonyl compounds is by McDowell and Sifniades on the vapor phase isomerization of crotonaldehyde to 3-butenal (5, 6). We were unable to observe

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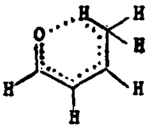
(4) This conversion was preceeded by a rapid cis-trans equilibration, achieved within one hour. Starting ketone and the β,γ-isomer had identical retention times in our gas chromatograph. Spectral analysis indicated that more than half of the starting ketone had reacted within two hours. Because of separation difficulties, the reaction was continued to completion.

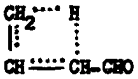
(5) C. A. McDowell and S. Sifniades, J. Am. Chem. Soc., 84, 4606 (1962).

(6) We have shown two other reports [R. Ya. Levina, V. N. Kostin and P. A. Gembitskii, Zh. Obsch. Khim., 29, 2456 (1959)] of such isomerization could not be substantiated.

this isomerization in solution under a variety of conditions. Mousseron (7) and de Mayo (8) reported the isomerisation of ionones to unconjugated ketones. In both cases the dienones formed contained a conjugated diene system. Jeger (9) recently reported a similar isomerization in a cyclic ketone, 10-α-testosterone. In none of these cases were the mechanisms of these photochemical reactions defined, but transition states A and B were proposed for the isomerisation of crotonaldehyde (5).



A



B

In analogy with the observed photochemical enolization of o-substituted benzophenones (10), we have attempted to demonstrate that a similar mechanism may apply to the isomerization of α,β-unsaturated ketones. Irradiation of Ig in deuteromethanol (CH_3OD, 0.5 g. in 40 ml.) for 40 minutes led to 90% conversion of Ig to II. The n.m.r. spectrum of II thus obtained indicated that 95% of the hydrogen in the 3-position had been exchanged for deuterium demonstrating that the enol was an intermediate in this isomerisation (11). Deuterium incorporation occurred during ketonization. These experiments eliminate the

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(7) M. Mousseron-Canet, M. Mousseron and P. Legendre, Bull. Soc. Chim. France, 1509 (1961).

(8) P. de Mayo, J. B. Stothers and R. W. Yip, Can. J. Chem., 39, 2145 (1961).

(9) H. Wehrli, R. Wenge, K. Schaffner and O. Jeger, Helv. Chim. Acta, 46, 678 (1963).

(10) N. C. Yang and C. Rivas, J. Am. Chem. Soc., 83, 2213 (1961).

(11) Under identical conditions, irradiation of II in CH_3OD led to no exchange. Prolonged irradiation resulted in the exchange of all α-protons of II, and hence the short reaction time was chosen.

four-centered transition state B, as such a pathway would require the incorporation of a proton into the α-position in the deuterated medium.

The hydrogen transfer in the isomerization of α,β-unsaturated ketones is analogus to those observed in saturated ketones (12) and aromatic ketones (10), the reactive excited states of these ketones may well be n − π* in nature (13, 14, 15). Since crotonaldehyde photoisomerizes in the gas phase (5) but not in solution, it is reasonable to ascribe the difference to the large energy requirement for the abstraction of a primary hydrogen in the transition state A which will not be satisfied upon irradiation in solution. Similar explanation may apply to the photochemical stabilities of ketones Ic, Id and Ie. It seems then surprising that 4,5-dimethyl-3-hexen-2-one (If), although it has a readily abstractable tertiary hydrogen, shows no sign of isomerization under the usual condition. Platt (14) suggested that there may be major differences in photochemistry of molecules, depending whether n − π* or π − π* is the low lying triplet state. He also suggested that the sequence of triplet states may be reversed simply by methyl substitution in favorable cases. It is known that β-alkyl substituents have a very marked effect on the level of π − π* singlet excited states of α,β-unsaturated ketones (16). It would not be surprising that these substituents will also stablise the corresponding triplet states. Although 5-methyl-3-hexen-2-one (Ig) may possess a low lying n − π* triplet state, introduction of another β-methyl substituent to Ig will reverse the

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(12) N. C. Yang and D. H. Yang, J. Am. Chem. Soc., 80, 2913 (1958).

(13) G. S. Hammond and P. A. Leermaker, ibid., 84, 207 (1962).

(14) J. R. Platt, Ann. Rev. Phys. Chem., 10, 365 (1959).

(15) E. F. Zwicker, L. Grossweiner and N. C. Yang, J. Am. Chem. Soc., 85, 2671 (1963).

(16) R. B. Woodward, ibid., 63, 1123 (1941); 64, 76 (1942).

order of the triplet states that $\pi - \pi^*$ triplet becomes the low lying triplet for 4,5-dimethyl-3-hexen-2-one (If). Recently Hammond demonstrated that aromatic carbonyl compounds with low lying $\pi - \pi^*$ triplet states are resistant in light induced hydrogen transfer reactions (13). The difference in behavior between ketones If and Ig toward photochemical isomerization may be attributed to the possible difference in the nature of their low lying triplet states. The dependence of photochemical reactions on the nature of excited states may also apply to other ketones in this series. Demonstration of this hypothesis by physical measurements will be carried out in our laboratory.