

PHOTOADDITION OF ACETYLENIC KETONES TO OLEFINS

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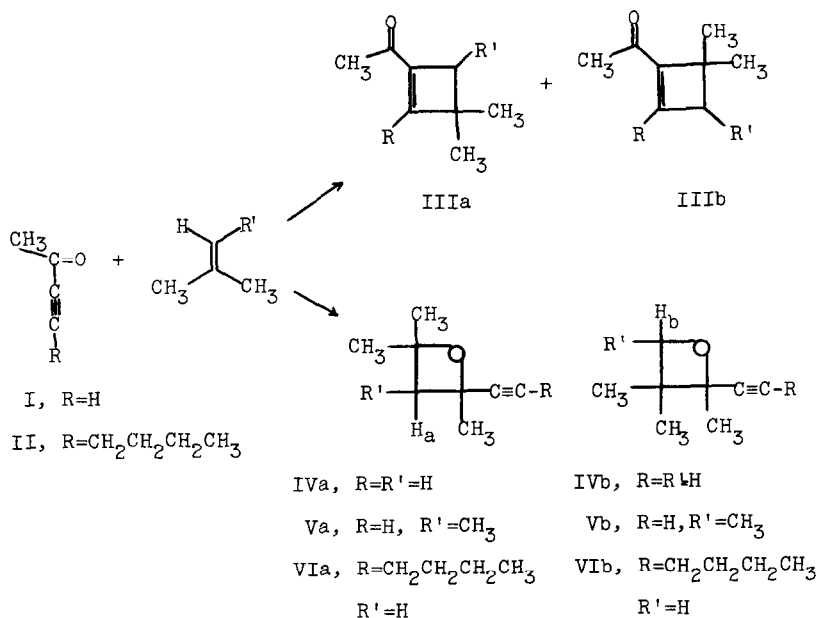
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(Received 18 August 1966)

The similarity of the ultraviolet absorption spectra of α,β -acetylenic ketones to those of α,β -ethylenic ketones raises the possibility that both α,β -unsaturated chromophores might exhibit parallel photochemical behavior. While the photochemistry of ethylenic ketones has been thoroughly explored,¹ that of acetylenic ketones has not been investigated. We wish to present here some preliminary findings on this subject.

While acetylenic ketones I ($\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 212 m μ , log ϵ 3.3) and II ($\lambda_{\text{max}}^{\text{C}_2\text{H}_5\text{OH}}$ 220 m μ , log ϵ 3.4) are very reactive photochemically, only intractable high molecular weight products are obtained upon irradiation in solution. In the presence of olefins, **however**, a clean addition reaction is observed. In analogy with the behavior of a large class of α,β -ethylenic ketones², addition of the acetylenic bond across the olefinic linkage would be expected to yield cyclobutenyl ketones IIIa and/or IIIb. However, this was not the reaction course followed. Addition

of the carbonyl to the double bond led to the exclusive formation of acetylenic oxetanes, instead. Such a reaction mode is characteristic of saturated ketones^{3,4} and typical of those aromatic ketones which possess a low lying $n \rightarrow \pi^*$ triplet state.^{5,6} The observed reaction course of acetylenic ketones suggests, therefore, that they too react via $n \rightarrow \pi^*$ excited state.



Irradiation* of 2.5 g of I in 50 ml of hexane and 100 ml of isobutylene led to 50% reaction after four hours. The adduct

* Hanovia 450 watt lamp with corex filter was employed. The reaction temperature was kept below -10° by means of a dry-ice bath.

was isolated in 46% yield* (b.p. 50-51° at 25 mm. Hg) and consisted of a ratio of isomers IVa (m.p. 45-46°) to IVb of 14:86. The structure of the products was adduced from elemental analysis and mass spectral molecular weight determination and from the infrared (no carbonyl absorption; strong acetylenic C-H stretching vibration at 3300 cm^{-1}) and n.m.r. spectra (three methyl singlets in 8.4-8.9 τ region; C=C-H singlet at 7.54 τ for IVa and 7.40 τ for IVb and methylene protons at 7.4 and 7.6 τ as AB quartet, $J=11$ c.p.s. for IVa and at 5.9 and 6.0 τ , $J=5$ c.p.s. for IVb).

Cycloaddition of I to 2-methyl-2-butene led to the formation of four adducts, consisting of the two expected geometrical isomers of both Va and Vb. By vapor phase chromatographic analysis the ratio of Va to Vb was found to be 30:70. The structure of Va and Vb was established by n.m.r. spectroscopy from the chemical shifts of protons H_a and H_b .**

The reaction of 3-octyne-2-one (II) with isobutylene proceeded in an analogous fashion to that of 3-butyne-2-one. Products VIa to VIb, formed in 82% yield (50% isolated yield b.p. 115° at 25 mm.), were produced in a ratio of 15:85.

It is noteworthy that the addition of the carbonyl in these acetylenic ketones proceeds quite stereoselectively, furnishing primarily that isomer whose diradical intermediate is more stable.⁴ The selectivity appears to be higher than that of

* The yield of product, evaluated by vapor phase chromatography employing an internal standard, was found to be 64%.

** Chemical shift of H_a proton is in the 7.5 τ region while that of proton H_b is 5.5-5.7 τ .

benzaldehydes and naphthaldehydes⁵, but somewhat less than that of saturated carbonyl compounds⁴, acetophenones and benzophenones.^{5,6} More of that isomer (Va), formed from the less stable diradical intermediate, is produced when 2-methyl-2-butene is employed instead isobutylene; this is consistent with the expected effect of the additional methyl group on the relative stabilities of the two diradical intermediates formed.⁴

References

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