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PHOTOCYCLOADDITION OF BENZOPHENONE TO A CONJUGATED ENYNE

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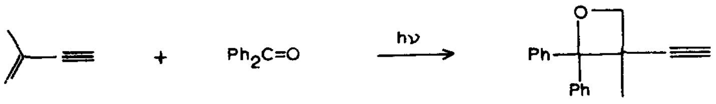
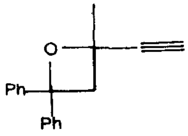
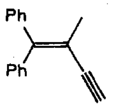
Whilst the photochemical reactions of olefins, acetylenes and conjugated dienes are well-established, the photoreactions of conjugated enynes have been little investigated. The benzophenone sensitised dimerisation of the enyne (1) has been studied,[1] but there have been no reports of the photocycloaddition of conjugated enynes to ketones. It is now reported that, in dilute solutions of the enyne (1), the major reaction occurring on photolysis in the presence of benzophenone is photocycloaddition to yield the oxetane (2).



(1) (2)



(3)



(4)

A solution of (1) (0.37 M) in benzene in the presence of benzophenone (0.40 M) as photosensitiser was photolysed[2] for 90 hr. Column chromatography gave, besides enyne dimers, unreacted benzophenone and benzpinacol (6%), the oxetane[3] (2) (58%); nmr (100 MHz, CCl_4) τ 2.3-2.9 (10H, m), 5.35 and 5.82 (each 1H, d, J = 5.5 Hz), 7.78 (1H, s), 8.65 (3H, s); ir (nujol) 3260 m (≡CH), 985 s (oxetane) cm^{-1}.

The nmr coupling constant and chemical shifts of the oxetane ring protons clearly indicate the assignment of structure (2) to the oxetane, rather than structure (3) resulting from the alternative orientation of cycloaddition to the double bond.[4] Interestingly, no products could be detected which had arisen from cycloaddition of the ketone to the triple bond[5] of the conjugated enyne.

Reaction of the oxetane with acid[6] (3×10^{-2} M perchloric acid in methanol, 3 days, 25°) resulted in cleavage of the oxetane ring, and the product (4) was isolated in 58% yield. Such ring cleavage provides further evidence for the oxetane structure as (2) rather than (3) .

By analogy with the mechanism for the photocycloaddition of benzophenone to conjugated dienes,[7] it is likely that reaction involves attack of triplet excited ketone on a ground state diene molecule; however, there are precedents for a mechanism involving attack of excited state olefin on ground state benzophenone.[8] Experiments designed to establish the photoreaction mechanism in the present instance are in progress.

References

1. (a) M. Herberhold and G.S. Hammond, Ber. Bunsenges. Phys. Chem., 1968, 72, 309; (b) G.T. Kwiatkowski and D.B. Selley, Tetrahedron Letters, 1968, 3471.
2. Pyrex reactor, 450 W medium-pressure mercury arc.
3. Satisfactory analyses were obtained for all new compounds.
4. Oxetane ring proton geminal coupling constants (and chemical shifts) are generally ~6 Hz (τ 4.9-6.2) at the α-CH_2, and ~11 Hz (τ 6.4-8.0) at the β-CH_2; J.A. Barltrop and H.A.J. Carless, J. Amer. Chem. Soc., in press.
5. For examples, see D.R. Arnold, Advan. Photochem., 1968, 6, 301.
6. S. Searles, in "Compounds with Three- and Four-Membered Rings", Part 2, ed. A. Weissberger, Interscience, New York, 1964, 983.
7. J.A. Barltrop and H.A.J. Carless, J. Amer. Chem. Soc., 1971, 93, 4794.
8. C. DeBoer, Tetrahedron Letters, 1971, 4977 and references therein.