

PHOTOCYCLOADDITION OF ACETONE TO ACYCLIC OLEFINS

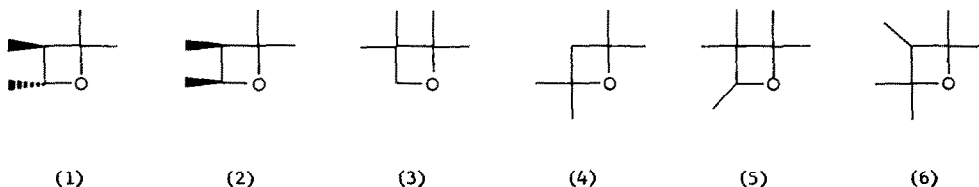
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(Received in UK 19 June 1973; accepted for publication 6 July 1973)

The isomerisation of olefins photosensitised by aliphatic ketones has been studied,¹ but it has not been widely appreciated that photocycloaddition of aliphatic ketones to alkyl substituted acyclic olefins is a commonly competing process. Recently, however, acetone was found to react photochemically with 2,3-dimethylbut-2-ene to give an oxetane cycloaddition product, amongst others.^{2,3} It is now shown that ultraviolet irradiation of acetone in solution in the presence of olefins (2-methylpropene, 2-methylbut-2-ene or but-2-ene) leads in each case to oxetanes as the major photoproducts.

In a typical experiment, irradiation of a solution of cis-but-2-ene (23g) in acetone (84g) under nitrogen in quartz apparatus, using a 450W medium-pressure mercury arc for 13h, led to the formation of 1 and 2 as the major products⁴ observed by g.l.c. analysis. The oxetanes were isolated by distillation and preparative g.l.c., and characterised from i.r. and n.m.r. spectra, and mass spectra or elemental analysis. Similarly, 2-methylpropene gave 3 and 4 (ratio 4.5 : 1), whilst 2-methylbut-2-ene gave 5 and 6 (ratio 1.6 : 1).



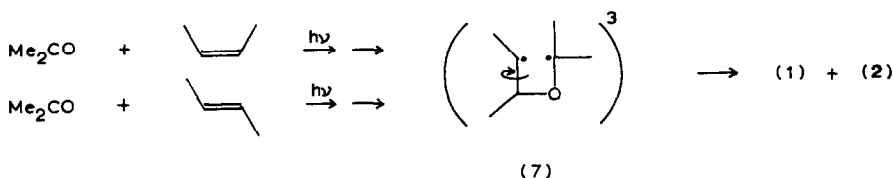
Irradiation of acetone in the presence of either cis- or trans-but-2-ene led to cis-trans isomerisation in competition with oxetane formation. The stereochemistry of

oxetane formation was investigated under conditions in which olefin isomerisation was small (Pyrex tubes, Rayonet reactor, 290-330 nm photolysis, <4% but-2-ene isomerisation). The results showed that memory of the original olefin stereochemistry was largely lost during oxetane formation, since either cis- or trans-but-2-ene gave similar oxetane mixtures:

Starting Olefin	Oxetane Ratio (<u>1</u> : <u>2</u>)
<u>cis</u> -but-2-ene	1.61 ± 0.06
<u>trans</u> -but-2-ene	2.02 ± 0.10

Experiments using 2,3-dimethylbuta-1,3-diene as a triplet quencher showed that 0.1 M diene quenched at least 98% of the photocycloaddition between acetone and cis-but-2-ene. Thus, addition appears to proceed via a triplet mechanism, in complete contrast with the photoaddition of acetaldehyde to cis-but-2-ene, which is a stereoselective, singlet reaction.⁵ This difference in reactivity between two closely related carbonyl compounds deserves further investigation.

The above results support the intermediacy of a triplet 1,4-biradical, (7), in the formation of oxetane. The biradical must have sufficient lifetime for bond rotations to compete with ring closure.



References

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