Photocycloaddition of Alkyl Ketones to Conjugated Dienes

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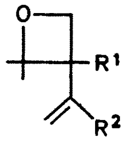
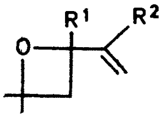
Summary U.v. irradiation of acetone and conjugated dienes gives vinyl-oxetans by a mechanism involving the singlet excited state of the ketone.

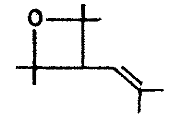
It is well-known that conjugated dienes act as efficient quenchers of the triplet state of alkyl ketones,[1] and it has generally been thought that the rapid transfer of triplet energy prevents other photochemical reactions (*e.g.* photocycloaddition) of the excited ketone with the diene.[2] In view of the observed photocycloaddition of benzophenone to conjugated dienes (where triplet reaction does compete with energy transfer),[3,4] and the establishment of a *singlet* mechanism for the photocycloaddition of alkyl ketones to certain substituted olefins,[5] we have investigated the photoreactions of acetone in the liquid phase with a series of conjugated dienes. We report that oxetans are generally formed by 1,2-photocycloaddition of the ketone to the conjugated diene, and present evidence to implicate the singlet excited state of the ketone in this reaction.†

Irradiation of a solution of butadiene in acetone with a medium-pressure mercury arc, in quartz or Pyrex apparatus, led to six products apparent on g.l.c. Four of these were the expected butadiene dimers, *cis*- and *trans*-1,2-divinylcyclobutane, 4-vinylcyclohexene, and cyclo-octa-1,5-diene.[7] The other two products (8 and 2%, based on converted diene) were the oxetans (I) and (II). Similarly, irradiation of acetone and isoprene led to the known photodimers of isoprene[7] plus two oxetans, (III) and (IV) (*ca.* 20% of the volatile photoproducts). Irradiation of acetone with 2,3-dimethylbuta-1,3-diene gave a single major oxetan product, (V), and with 2,5-dimethylhexa-2,4-diene gave (VI) in 28% yield.





(III) $R^1 = R^2 = H$



(VI)

(I) $R^1 = R^2 = H$
(II) $R^1 = Me, R^2 = H$
(IV) $R^1 = H\ R^2 = Me$
(V) $R^1 = R^2 = Me$

Similarly, butadiene (*ca.* 3M) in pentan-2-one gave the butadiene dimers, two oxetans (*ca.* 10% total yield) with structures analogous to (I) and (II), and also the products from photolysis of pentan-2-one (acetone and 1-methylcyclobutanol).[8]

Formation of the diene dimers is thought to proceed *via* attack of a triplet diene on another ground-state diene molecule.[7] Alkyl ketones are believed to have triplet

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† It has recently been suggested that penta-1,3-diene quenches the singlet excited state of an acyl nitrile, without forming oxetan.[6]

energies of 74—80 kcal mol^{-1}, and efficient diffusion-controlled transfer of triplet energy to the diene (triplet energy 54—60 kcal mol^{-1}) is expected: therefore, formation of oxetan in these systems is mechanistically interesting. Irradiations in Pyrex apparatus led to the same oxetans, and strongly suggest that the singlet excited state of the diene is not responsible for oxetan formation. Irradiation of a solution of acetone and butadiene containing benzophenone (triplet energy 69 kcal mol^{-1}) under conditions such that benzophenone absorbed virtually all the incident light, led only to the formation of butadiene dimers, and no oxetan. Reaction does not therefore involve attack of triplet diene on ground-state acetone.‡ Oxetan formation could proceed by attack of singlet or triplet excited ketone on ground-state diene, and the two possible pathways are outlined in kinetic Schemes 1 and 2.

Scheme 1: Singlet reaction

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}_1 \tag{1}$$

$$\mathrm{A}_1 \xrightarrow{k_2} \mathrm{A} \tag{2}$$

$$\mathrm{A}_1 \xrightarrow{k_3} \mathrm{A}_3 \tag{3}$$

$$\mathrm{A}_1 + \mathrm{D} \xrightarrow{k_4} \text{Oxetan} \tag{4}$$

Scheme 2: Triplet reaction

$$\mathrm{A} \xrightarrow{h\nu} \mathrm{A}_1 \tag{1}$$

$$\mathrm{A}_1 \xrightarrow{k_2} \mathrm{A} \tag{2}$$

$$\mathrm{A}_1 \xrightarrow{k_3} \mathrm{A}_3 \tag{3}$$

$$\mathrm{A}_3 + \mathrm{D} \xrightarrow{k_5} \mathrm{A} + \mathrm{D}_3 \tag{5}$$

$$\mathrm{A}_3 + \mathrm{D} \xrightarrow{k_6} \text{Oxetan} \tag{6}$$

$$\mathrm{A}_3 \xrightarrow{k_7} \mathrm{A} \tag{7}$$

In these Schemes, A and D refer to acetone and diene and the subscripts 1 and 3 designate the first excited singlet and triplet states. In Scheme 2, oxetan formation is in competition with triplet energy transfer and deactivation. Steady-state assumptions lead to the expressions:

Scheme 1 (Singlet reaction) $\Phi^{-1} = 1 + k_3/k_4[\mathrm{D}]$

Scheme 2 (Triplet reaction) $\Phi^{-1} = (k_5 + k_6)/k_6 + k_7/k_6[\mathrm{D}]$

where Φ = quantum yield of oxetan and [D] = diene concentration. It is assumed that $k_2 \ll k_3$, since the triplet quantum yield of alkyl ketones is near unity.[9]

The Figure is a plot of Φ^{-1} *vs.* $[\mathrm{D}]^{-1}$ for the formation of oxetan (VI) from acetone and 2,5-dimethylhexa-2,4-diene. Least-squares analysis, and consideration of the possible errors of measurement, gave an intercept of 2·3 (± 1·5) and a slope of 3·5 (±0·5). These results cannot be made to fit scheme 2. However, the plot is consistent with scheme 1, as the intercept could, within the experimental error, be 1. The slope (k_3/k_4) gives a value of 1—5 × 10^7 M^{-1} for the singlet rate constant of photocycloaddition, assuming that k_3 = 4—20 × 10^7 s^{-1}.[1] Our data do not preclude a triplet rate constant for cycloaddition of about the same magnitude, since this would give a quantum yield of 0·001—0·005 over the range of diene concentrations studied. Therefore, the suggestion that ketone singlet and triplet states can be comparably reactive to photocycloaddition may not be violated in our systems.[10] However, our data do call for caution in the use of conjugated dienes as quenchers of excited alkyl ketones, especially at high concentrations of diene.

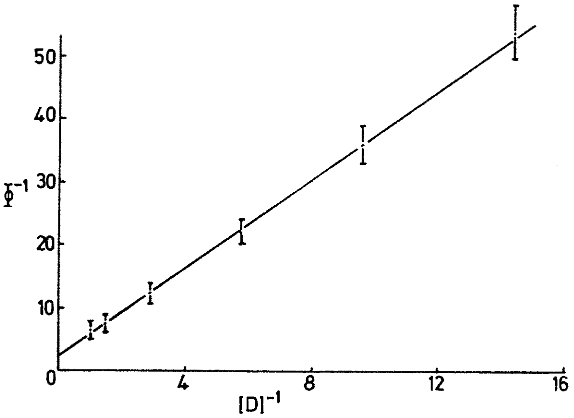

FIGURE. *Variation of reciprocal of* Φ, *the quantum yield of oxetan* (VI), *with reciprocal of* [D], *the molarity of* 2,5-*dimethylhexa*-2,4-*diene.*

We are investigating the effect of conjugated dienes on the fluorescence spectra of alkyl ketones, and observe sufficient fluorescence quenching to be compatible with our suggested singlet mechanism of reaction.

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‡ The photocycloaddition of benzophenone to butadiene is inefficient;[4] therefore, the triplet diene was not selectively attacking benzophenone rather than acetone.

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