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PHOTOCYCLOADDITION OF ALKYL KETONES TO α,β-UNSATURATED NITRILES.

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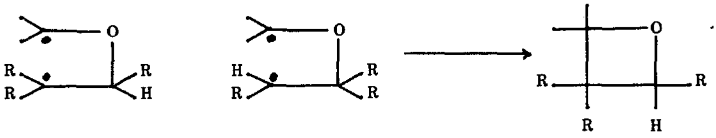
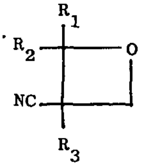
The photocycloaddition of ketones to olefins substituted with electron-donating groups seems to involve(1) attack by the electrophilic oxygen atom of a $^3(n\pi^*)$ state of the ketone to give the more stable of the two possible biradical intermediates (I) which subsequently cyclises to the oxetane (II).

Our studies on the photochemical additions of alkyl ketones to the electron-deficient double bond of α,β-unsaturated nitriles indicate that this reaction proceeds *via* a *singlet* $(n\pi^*)$ state of the ketone and that the orientation of the resulting oxetane is not that expected from consideration of the more stable biradical intermediate. We are prompted to publish this work because of a recent report(2) on the photocycloaddition of ketones to maleic anhydride and trans-1,2-dicyanoethylene.

Irradiation(3) of acetone, 3-pentanone, cyclopentanone and cyclohexanone in the presence of methacrylonitrile (V, R_3= Me) gives (VI, R_3= Me) as the only detected oxetane product, together with the two geometrically isomeric head-to-head dimers of methacrylonitrile (VII, R_3 =Me)(4).



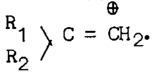
(I) (II)



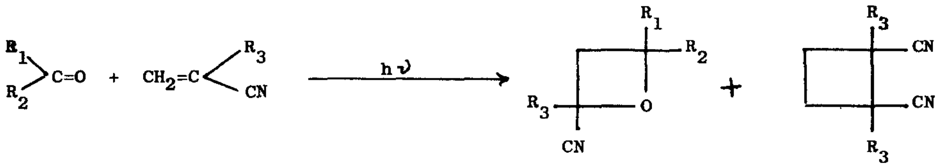
.(III)

Yields, determined by g.l.c., and based on methacrylonitrile consumed, were (VIa, R_3= Me) (42%) and (VII, R_3= Me) (25%).

The n.m.r. spectra show that the oxetanes have structures (VI, R_3= Me) rather than (III, R_3= Me) for the CH_2 group has the position (τ = 7.19-7.66) and coupling constant (J = 11.5 c/s) typical of the position β to the oxygen atom. Confirmation is derived from the mass spectrographic fragmentation into



$$\begin{matrix} R_1 \\ R_2 \end{matrix}\!\!\!>\overset{\oplus}{C} = CH_2.$$



(IV, a-d) (V) (VI, a-d) (VII)

(a), $R_1 = R_2 =$ Me; (b), $R_1 = R_2 =$ Et; (c), $R_1R_2 = -(CH_2)_4-$; (d), $R_1R_2 = -(CH_2)_5-$

Irradiation of acetone with acrylonitrile (V, $R_3 =$ H) gives analogously an oxetane of similar orientation, the two known head-to-head dimers of acrylonitrile(5) and polymer. Crotonitrile (cis-trans mixture) gives the appropriate cis- and trans-oxetanes as the main products.

We believe that the oxetanes arise from the $^1(n\pi^*)$ state of the ketones, and the dimers from a triplet state of the α,β-unsaturated nitrile, on the following evidence:

(i) Irradiation conducted in pyrex apparatus, in which only the ketone $n \rightarrow \pi^*$ transition is excited, lead to the same products. This argues strongly against a singlet excited state of the α,β-unsaturated nitrile being involved in either oxetane formation or dimerisation.

(ii) Triplet quenchers (1,3-pentadiene; 2,5-dimethyl-2,4-hexadiene), at concentrations which are known to deactivate ketone triplets efficiently, do not reduce the rate of formation of the oxetane. This suggests that the oxetane arises from the $^1(n\pi^*)$ state of the ketone, the only singlet state energetically accessible.

The implication of the $^1(n\pi^*)$ state of the ketones in oxetane formation is supported by the observation that the fluorescence of acetone and cyclopentanone is partially quenched by added methacrylonitrile.

(iii) The same triplet quenchers do inhibit the rate of formation of methacrylonitrile dimers, giving a linear Stern-Volmer plot of [relative quantum yield]$^{-1}$ against quencher concentration. This is good evidence for the dimers being formed exclusively by a triplet mechanism.

(iv) Sensitisation of the reaction mixture with a variety of sensitisers (E_T = 74-62 kcals/mole) using 366 mμ light, absorbed only by the sensitiser, gives methacrylonitrile dimers but no oxetane. This confirms that triplet excited methacrylonitrile is responsible for the production of dimers, but cannot be involved in oxetane formation. The use of sensitisers with triplet energies less than 61 kcals/mole led to no reaction: this parallels the results of Hosaka and Wakamatsu(5) for the photodimerisation of acrylonitrile.

The following scheme explains the observed results:-

$$\begin{tikzcd}
K \arrow[r, "h\nu"] & {}^1K \arrow[r, "i.s.c."] \arrow[d, "M"] & {}^3K \arrow[r, "M"] & {}^3M \arrow[d, "M"] \\
 & \text{K-M (oxetane)} & & \text{M-M (dimer)}
\end{tikzcd}$$

Formation of oxetane from singlet excited ketone (^1K) competes with intersystem crossing to the ketone triplet (^3K). The ketone triplet transfers triplet energy to ground state methacrylonitrile (M) to give triplet methacrylonitrile (^3M) from which the cyclobutanes are derived.

The irradiation of acetophenone or benzophenone with α,β-unsaturated nitriles gave dimers but no oxetanes. This may be because the very rapid intersystem crossing rate in aromatic ketones ($\sim 10^{10}$ sec^{-1}, cf. acetone, 4×10^7 sec^{-1}.(6)) blocks the production of oxetane (the singlet product) and leads only to triplet products.

The orientational specificity of these cycloadditions which seems to be a function of the excited state of the ketone (no evidence was found in the u.v. spectra for ground state complexes between the nitrile and ketone) will be discussed in the full paper.

References

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2. N.J.Turro, P.Wriede, J.C.Dalton, D.Arnold & A.Glick, *J. Am. Chem. Soc.*, **89**, 3950 (1967).
3. Typical irradiation conditions were 0.1M nitrile in ketone, irradiated with deoxygenation in a quartz reactor, with a Hanovia 450 w. med. pressure mercury arc.
4. Compounds were characterised by infrared, n.m.r. and mass spectra, and satisfactory analyses were obtained for all new compounds.
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