Reactivity of Excited States of Thienyl, Pyrrolyl, and Furyl Ketones

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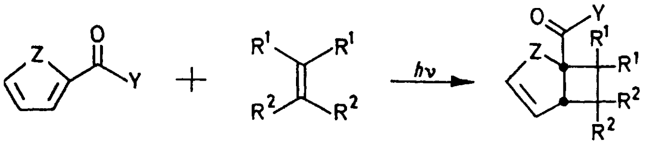
Summary Upon irradiation many 2-acyl-thiophenes, -furans, and -pyrroles undergo 2 + 2 cycloaddition to simple olefins at the $\alpha\beta$-positions of the ring, rather than oxetan formation across the carbonyl group, as in carbocyclic ketones; a $\pi \rightarrow \pi^*$ lowest triplet is implicated as the reactive excited state in these cases.

The photochemistry of aryl and aryl alkyl ketones has received much scrutiny during the past twelve years.[1] A fairly clear picture is now available of the factors governing the various transformations of excited states of these ketones, including reduction to pinacols,[2] oxetan formation,[3] and Norrish type II elimination.[4] One structure–reactivity correlation which has emerged is that in the case of those ketones whose lowest $n \rightarrow \pi^*$ triplet is of energy similar to or lower than that of the lowest $\pi \rightarrow \pi^*$ triplet, the former species, having odd-electron character on the carbonyl oxygen, readily undergoes the transformations mentioned above. Those ketones with a lowest $\pi \rightarrow \pi^*$ triplet are far less reactive photochemically.

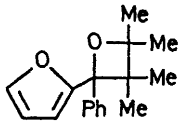
There appear to have been no studies of the photochemical behaviour of five-membered ring heterocyclic ketones. We report here our findings that several such ketones possess lowest $\pi \rightarrow \pi^*$ triplets and exhibit photochemical behaviour consistent with this electronic configuration. Irradiation[†] of 2-acetylthiophen [(1) 20 mmol] in the presence of excess of 2,3-dimethylbut-2-ene for 30 h gave, in addition to recovered (1), compound (6) (47%)[‡]. Use of isobutene as substrate resulted in a slower addition to produce the adducts (7) and (8) (40%)[‡] in a ratio of 41 : 59. These could be separated by g.l.c. and their identity was then apparent from their n.m.r. spectra. In the n.m.r. spectrum of the major isomer (8), the signal at τ 5·41 due to the allylic hydrogen at C-5 was a slightly broadened singlet, as was the signal due to the corresponding hydrogen of (6), whereas in the spectrum of (7) the C(5)-H signal (τ 6·02) was a slightly broadened pair of overlapping doublets (J 5·0, 5·2 Hz) from coupling to the two hydrogen on C-6 (verified by decoupling experiments).



(**1**) Z=S, Y=Me
(**2**) Z=O, Y=Me
(**3**) Z=NMe, Y=Me
(**4**) Z=S, Y=Ph
(**5**) Z=O, Y=Ph

(**6**) Z=S, Y=Me, $R^1=R^2=Me$
(**7**) Z=S, Y=Me, $R^1=Me$, $R^2=H$
(**8**) Z=S, Y=Me, $R^1=H$, $R^2=Me$
(**9**) Z=O, Y=Me, $R^1=Me$, $R^2=H$
(**10**) Z=O, Y=Me, $R^1=H$, $R^2=Me$
(**11**) Z=NMe, Y=Me, $R^1=R^2=Me$
(**12**) Z=S, Y=Ph, $R^1=H$, $R^2=Me$

Irradiation of 2-acetylfuran (2) in excess of isobutylene led very slowly to a complex mixture of products, the major one of which was the adduct (9) (36%).[‡] Of the three remaining components, which were unresolved by conventional g.l.c., one appeared to be the 2 + 2 cycloadduct of opposite orientation to (9), *i.e.* (10), from the similarity of their mass spectra. A second appears to be an oxetan, as the base peak is at m/e 136, or $M-30$ (loss of formaldehyde). The exact structure of the remaining adduct has not yet been elucidated.



(13)

Irradiation of 1-methyl-2-acetylpyrrole (3) in excess of 2,3-dimethylbut-2-ene (80 h; Corex filter) gave a 15% conversion into the adduct (11).[‡]

Irradiation of mixtures of 2-benzoylthiophen (4) and isobutene gave a 25% conversion into adduct (**12**) as shown by spectral examination of the reaction mixtures. The instability of the product in contact with the usual absorbants prevented its isolation by chromatography. Besides absorption obviously due to (4) the i.r., n.m.r., and mass spectra were in accord with structure (**12**).

Irradiation of 2-benzoylfuran (5) in 2,3-dimethylbut-2-ene gave oxetan (13) as the sole primary product,[‡] in contrast to the behaviour of (1)—(4).

The photolysis of mixtures of (1) and 2,3-dimethylbut-2-ene, in the presence of sufficient xanthone or triphenylene to absorb > 98% of the incident light, gave (6) at a rate comparable to that observed in the direct irradiation, implicating triplets as intermediates in the present cycloadditions.[§]

These 2 + 2 cycloadditions to the aromatic rings of ketones (1)—(4) are in distinct contrast to the ready additions of the carbonyl group of phenyl ketones to olefins, suggesting that the reactive excited state of (1)—(4) may be predominantly $\pi \rightarrow \pi^*$, rather than $n \rightarrow \pi^*$, in nature. This hypothesis is supported by the observation of long-lived phosphorescence from ketones (1), (2), and (4). In EPA glass

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[†] Irradiations were performed with a 450-W medium-pressure mercury arc using a Pyrex filter, unless otherwise noted.

[‡] Satisfactory i.r. n.m.r., and mass spectral data were obtained for these compounds.

[§] Experiments involving dienes as quenching agents were inconclusive owing to the consumption of diene, *via* dimerization, much more rapidly than the ketone–olefin addition.

at 77 K, these ketones show emission with a moderate degree of fine structure, of lifetimes 0·105, 0·152, and 0·178 s, respectively. Such relatively long lifetimes are characteristic of $\pi \rightarrow \pi^*$ triplets; furthermore, the fine structure in each of the spectra is irregular and the spacings do not correspond to the C=O stretching frequency, as is the case with $n \rightarrow \pi^*$ triplets.[5] Ketone (**5**) on the other hand, shows phosphorescence with τ 0·003 s, a value similar to those of known $n \rightarrow \pi^*$ triplets[5] and in keeping with the chemical behaviour of (**5**) observed here.

A case analogous to those of (**1**)—(**4**) involving a benzene derivative is the addition of benzonitrile to 2-methylbut-2-ene to yield a bicyclo[4,2,0]octadiene;[6] the lowest triplet of benzonitrile has been assigned the $\pi \rightarrow \pi^*$ configuration.[7] The lowest triplets of naphthyl ketones, also $\pi \rightarrow \pi^*$ in nature, are similarly unreactive to olefins at the carbonyl group, but react at the ring positions.[8,9]

It has thus been shown that numerous simple 2-thienyl-, -furyl-, and -pyrrolyl-ketones possess a lowest triplet state of predominantly $\pi \rightarrow \pi^*$ character and that these states react at the ring positions with olefins.

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[1] For reviews see (a) P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 1968, **5**, 323; (b) R. O. Kan, "Organic Photochemistry", McGraw-Hill, New York, 1966.

[2] N. J. Turro, "Molecular Photochemistry", Benjamin, New York, 1966, ch. 6.

[3] D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.

[4] P. J. Wagner, *Accounts Chem. Res.*, 1971, **4**, 168.

[5] R. S. Becker, "Theory and Interpretation of Fluorescence and Phosphorescence", Wiley-Interscience, New York, 1969, pp. 147—155.

[6] J. G. Atkinson, D. E. Ayer, G. Buchi, and E. W. Robb, *J. Amer. Chem. Soc.*, 1963, **85**, 2257.

[7] K. Takei and Y. Kanda, *Spectrochem. Acta*, 1962, **18**, 1201.

[8] T. R. Chamberlain, J. D. Green, and J. J. McCullough, Abstracts 161st National ACS Meeting, Spring, 1971, No. 123.

[9] N. C. Yang and A. Shani, *Chem. Comm.*, 1971, 815.