The Directing Effect of Alkoxy-groups in the Photocycloaddition of Carbonyl Compounds to Olefins

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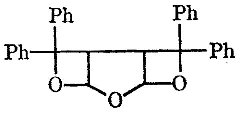
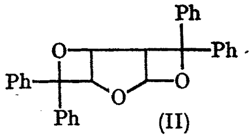
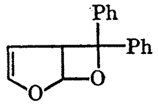
THE photocycloaddition of carbonyl compounds to olefins with electron-donating substituents generally involves attack of the ground-state olefin by the $^3(n\pi^*)$ excited carbonyl compound.[1] It has been suggested[2] that the major isomer(s) formed in the addition to unsymmetrically substituted olefins will be derived from the more stable of the two possible biradical intermediates formed by addition of the carbonyl oxygen to the carbon–carbon double-bond. This rule predicts, for example, the predominant isomers formed[1a,2,3] during addition of various ketones to isobutene and to 2-methylbut-2-ene. The only exception has been the direction of the second addition of benzophenone to furan. This reaction[4] yields more of (I) (28%) than of (II) (18%), a result not predictable on the basis of the stability of the intermediate radicals. It has been suggested[4a] that (I) might arise from the reaction of the radical, formed from triplet benzophenone and furan with another ground-state benzophenone, rather than *via* addition of triplet benzophenone to the enol-ether system of the mono-adduct (III).


(I)


(II)


(III)

Alkoxy-substituted olefins also show unexpectedly low directing-effects in the photocycloaddition reactions. In an extension of previous studies,[5] the photocycloaddition of carbonyl compounds to enol-ethers and to methylketen diethyl acetal has been investigated. These reactions† give high yields (60—85%) of isomeric oxetans, whose formulation are confirmed by v.p.c., n.m.r. analysis (100 Mc.), selective alcoholysis, hydrolysis, and lithium aluminium hydride reduction of the corresponding 2-alkoxy- and 2,2-dialkoxy-oxetans.[5] The results show that the direction of cycloaddition *cannot* be predicted on the basis of the stability[6] of the intermediate biradicals in these systems. A combination of factors such as radical stability, polarization of the reactants, and lack of selectivity due to enhanced reactivity of the olefin[7a] probably control the orientation in these additions. The photocycloaddition of ketones to methacrylonitrile has also been reported[8] to give oxetans not expected from considerations of the more stable biradical intermediate. Oxetan formation was shown to proceed *via* the singlet state of the ketones in these cases. In our systems, addition of penta-1,3-diene gave a large decrease in the rate of photocycloaddition, which indicated that the reactions must substantially occur *via* the triplet states of the carbonyl compounds.

Product compositions from the photocycloaddition of carbonyl compounds to alkoxy-substituted olefins

Carbonyl compound	Olefin	2-Isomer(s)* (%)
Acetone	$MeCH{=}CHOPr^n$	43
Cyclohexanone	,,	44
Benzophenone	,,	44
Acetone	$Me_2CH{=}CHOBu^n$	70
Acetone	$Me_2C{=}CHOPr^n$	70
Propanal	,,	$\geqslant 60$
Cyclohexanone	,,	64
Benzophenone	,,	80
Acetone	$Et_2C{=}CHOEt$	85
Cyclohexanone	,,	85
Acetone	$MeCH{=}C(OEt)_2$	45
Benzophenone	,,	45

* 2- and 3-Isomer = 100%; 2- and 3-alkoxyoxetans showed signals at τ 4·9—5·3 and 5·8—6·6 for their protons α and β to the ring oxygen, respectively. In most cases, isomers could be separated and were individually analysed. Satisfactory elemental, i.r. and n.m.r. analyses were obtained in all these cases.

Addition of ketones to allenes has recently been found[7a,b] to give surprisingly large amounts of 2-alkoxyoxetans (1,5-dioxaspiro[3,3]heptane derivatives) in the second addition. Our results indicate that this mode of addition may be due primarily to the low directing- effect of the alkoxy-groups in general, rather than to reduced stabilization of the alkoxy-radicals leading to the 2,5-dioxaspiro-[3,3]heptanes resulting from a decrease in the π-interaction in the small-ring systems.[7a]

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† Irradiations were carried out with a 450 W medium pressure mercury arc at 20° in water-cooled quartz reactors with Corex filters (acetonitrile solutions) or in Pyrex reactors (benzene solutions) at concentrations of 0·2—0·4 M in carbonyl compound and 0·4—0·8 M. in olefin.

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