Photocycloaddition of *ortho*-Methyl Substituted Benzaldehydes to 2,3-Dimethylbut-2-ene

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Summary *ortho*-Methyl substituted benzaldehydes, (**4**)—(**6**), undergo unexpected photocycloaddition reactions with 2,3-dimethylbut-2-ene, producing the oxetans (**8**)—(**10**) in high chemical and quantum yields.

ortho-ALKYL substituted aromatic carbonyl compounds are known to undergo intramolecular hydrogen transfer on u.v. irradiation [*e.g.* (**1**)$\rightarrow$(**2**)],[1] yielding an unstable dienol which may be trapped in a Diels-Alder reaction by electron-deficient alkenes.[2] This ready photoreaction has precluded the observation of an oxetan product from the photocycloaddition of any *ortho*-alkyl substituted aromatic carbonyl to an alkene.[3] We now report that the methyl substituted benzaldehydes (**4**)—(**6**) undergo photochemically efficient cycloaddition reactions with 2,3-dimethylbut-2-ene, producing oxetans (**8**)—(**10**) in high yield.

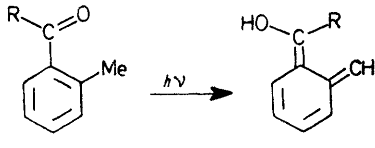
TABLE. Quantum and chemical yields of oxetans from photoreaction of aldehydes (**3**)—(**6**) with 2,3-dimethylbut-2-ene.

Oxetan	Quantum yield[a]	Chemical yield/%[b]
(**7**)	0·465[c]	90
(**8**)	0·53	94
(**9**)	0·47	93
(**10**)	0·32	76

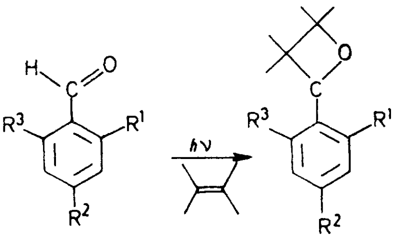
[a] Aldehyde (0·15 M), alkene (1·0 M) in benzene, Rayonet MGR-100 photochemical reactor, 300 nm lamps, 7—12% conversion, quantum yields ± 0·02. [b] Determined by g.l.c. on the above solutions at complete conversion of aldehyde. [c] N. C. Yang, R. Loeschen, and D. Mitchell, *J. Amer. Chem. Soc.*, 1967, **89**, 5465.

Typically, irradiation of the aldehyde (**4**) (3·6 g) and 2,3-dimethylbut-2-ene (2·5 g) in benzene (130 ml) under nitrogen in a quartz reactor for 5·5 h by a centrally positioned 450 W mercury arc gave the oxetan (**8**),† purified by column chromatography on alumina.

The quantum yields and chemical yields of oxetan formation are shown in the Table. It is surprising that the presence of *ortho*-methyl substituents on the aromatic ring does not hinder the efficiency of oxetan formation for aldehydes (**4**) and (**5**) compared with benzaldehyde (**3**). This points to a high rate of photocycloaddition in comparison with intramolecular hydrogen transfer[4] for these aromatic aldehydes.



(1) (2)



(3) R^1 = R^2 = R^3 = H (7)
(4) R^1 = Me, R^2 = R^3 = H (8)
(5) R^1 = R^2 = Me, R^3 = H (9)
(6) R^1 = R^2 = R^3 = Me (10)

Both cycloaddition and hydrogen abstraction are reactions expected of an (n, π^*) triplet excited state.[3] In a related system, Arnold has proposed that the photocycloaddition of two methyl substituted benzoylthiophens to 2-methylpropene (to give unisolated oxetans) occurs *via* a (π, π^*) excited state.[5] It may be worth reconsidering this assignment in view of the present results, where photocycloaddition can apparently compete successfully with intramolecular hydrogen abstraction for an (n, π^*) excited state.

(*Received*, 12*th May* 1975; *Com.* 548.)

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† New compounds were characterised by i.r., ^{1}H n.m.r. spectra, and elemental analysis or mass spectrometry.

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[2] E. Block and R. Stevenson, *J.C.S. Perkin I*, 1973, 308; B. J. Arnold, S. M. Mellows, and P. G. Sammes, *ibid.*, 1973, 1266.
[3] D. R. Arnold, *Adv. Photochem.*, 1968, **6**, 301.
[4] B. J. Arnold, S. M. Mellows, P. G. Sammes, and T. W. Wallace, *J.C.S. Perkin I*, 1974, 401; D. M. Findlay and M. F. Tchir, *J.C.S. Chem. Comm.*, 1974, 514.
[5] D. R. Arnold and B. M. Clarke, *Canad. J. Chem.*, 1975, **53**, 1.