Synthesis of Oxetans by Photocycloaddition of Aromatic Aldehydes to Hexamethyl(Dewar benzene)

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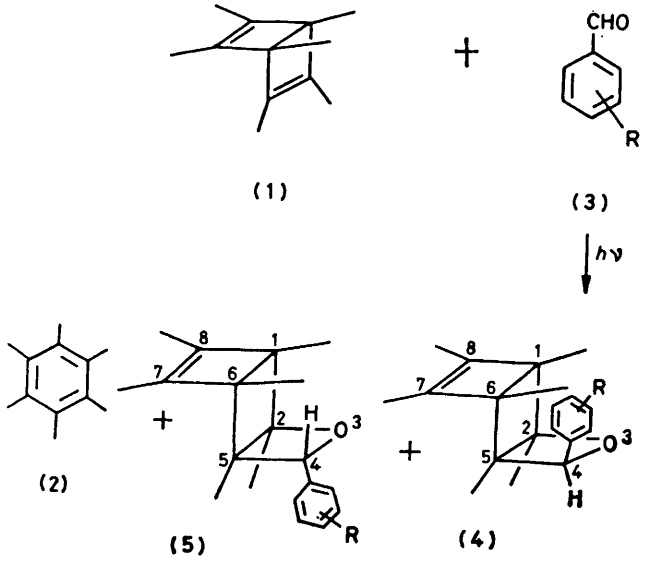
Summary U.v. irradiation of the aldehydes (**3**) in the presence of hexamethyl(Dewar benzene) yields the tricyclic oxetans (**4**) and (**5**) in competition with hexamethylbenzene formation.



a; R = H
b; R = 4-OMe
c: R = 2-Me

There is current interest in hexamethyl(Dewar benzene) (1,2,3,4,5,6-hexamethylbicyclo[2.2.0]hexa-2,5-diene) (**1**) in connection with the concept of adiabatic photoreactions.[1] It is known that (**1**) undergoes photosensitised isomerisation to hexamethylbenzene (**2**), *via* an exciplex.[2] The conversion of (**1**) into (**2**), sensitised by arenes or aromatic carbonyl compounds, is an efficient process and a chain reaction giving a quantum yield greater than unity has been observed.[3] We now report that aromatic aldehydes undergo an unexpected [2 + 2] photocycloaddition to (**1**) to yield tricyclic oxetans.

A solution of benzaldehyde (**3a**) and (**1**) in pentane was irradiated with u.v. light.† T.l.c. suggested the formation of two photoproducts, which were isolated following concentration and chromatography of the reaction product on silica gel. One component was easily identified as (**2**) (32%). The other component had a ^{1}H n.m.r. spectrum which suggested that it was a 1 : 1 mixture of two isomeric oxetans (**4a**) and (**5a**) (29%, based on consumed aldehyde), from the characteristic signals for the oxetan methine protons in the δ 5—6 region.[4] Careful rechromatography at low loadings on p.l.c. plates (eluting with ether–light petroleum, 1 : 12) separated the isomers (**4a**) and (**5a**). The slower-moving band showed in its ^{1}H n.m.r. spectrum six methyl singlets, including one at very high field (δ 0·26) and a benzylic proton as a singlet at δ 5·48. This compound was assigned the structure of the tricyclic oxetan (**4a**) in which the C-6 methyl group lies above the plane of the phenyl ring and is therefore most shielded. The corresponding upper band was assigned structure (**5a**), because of its high-field singlet at δ 0·48 due to the C-5 methyl group,‡ and

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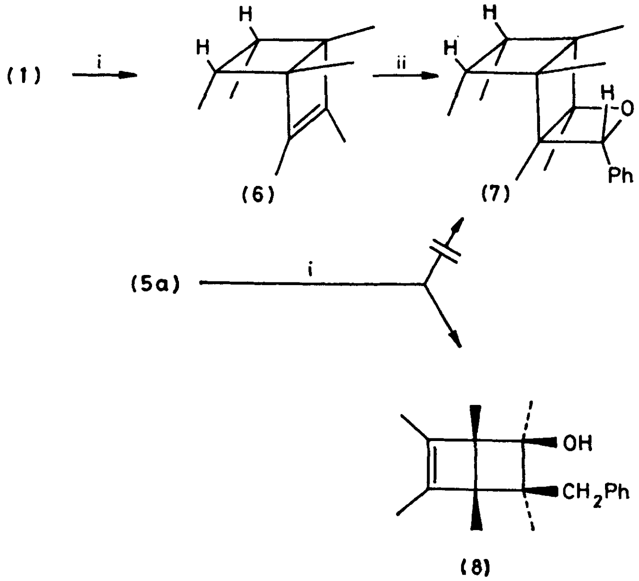
† A mixture of (**3a**) (10 mmol) and (**1**) (10 mmol) in pentane (130 ml) was used, with a medium-pressure mercury arc lamp and quartz apparatus. Irradiation was stopped after 3 h, when 70% of the aldehyde had reacted.

‡ Methyl groups similarly situated *cis* to an adjacent phenyl group have chemical shifts of this order in the examples of the *exo*-oxetans from (**3a**) with 1,2-dimethylcyclobutene (δ 0·60), 1,2-dimethylcyclohexene (δ 0·59), and 1,2-dimethylcyclohexa-1,4-diene (δ 0·64); H. A. J. Carless and H. S. Trivedi, unpublished results.

a benzylic proton at δ 5·36 which is more shielded than that of (**4a**).

It is believed that the oxetans (**4a**) and (**5a**) are the result of *exo*-attack on the diene (**1**), as in the comparable reactions of hydrogenation,[5] cyclopropanation,[6] epoxidation,[7] and attack by singlet oxygen on (**1**).[8] However, *endo* attack of chlorosulphonyl isocyanate on (**1**), leading to rearrangement, has been reported.[9]

A similar irradiation involving 4-methoxybenzaldehyde (**3b**) and (**1**) in benzene solution allowed the isolation of (**2**) (26%) and the analogous adducts (**4b**) and (**5b**) (1 : 1 ratio, 20%) which were separated by p.l.c. on silica gel.§ Irradiation of 2-methylbenzaldehyde (**3c**) and (**1**) yielded, apart from (**2**), a 1 : 1 mixture (29%) of the oxetans (**4c**) and (**5c**) which were similarly separated.



SCHEME. *Reagents:* i, PtO$_2$, H$_2$; ii, PhCHO, $h\nu$.

Hydrogenation of (**5a**) using platinum oxide in methanol gave, instead of the hoped-for oxetan (**7**), a compound assigned the structure of the alcohol (**8**) (Scheme).[10] However, irradiation of benzaldehyde (**3a**) in the presence of the dihydro-derivative (**6**)[5] did give the reduced oxetan (**7**), as a single isomer assigned the stereochemistry shown on the basis of the methyl singlet at δ 0·64 in its ^{1}H n.m.r. spectrum.

An irradiation of benzophenone with (**1**) in benzene solution indicated only the steady formation of (**2**) and no change in the amount of benzophenone. A similar irradiation of acetophenone and (**1**) showed no acceptable evidence for oxetan formation. The lack of oxetan formation in these cases shows that triplet energy transfer is not the dominant feature which prevents cycloaddition, since benzaldehyde has a triplet energy which lies between those of acetophenone and benzophenone.[11] Thus, the formation of oxetans from irradiation of aromatic aldehydes (**3**) in the presence of (**1**) must indicate their relatively high reactivity towards photocycloaddition. This idea is further emphasised by the isolation of the oxetans (**4c**) and (**5c**) from the *ortho*-methyl substituted aldehyde (**3c**), where cycloaddition is able to compete favourably with the normal enolisation of the excited state.[12] It is interesting that (**1**) has recently been reported to be unreactive towards radicals which normally add to double bonds.[13]

Thermolysis of the oxetan (**5c**) in a sealed glass ampoule at 230 °C followed by g.l.c. showed the exclusive formation of (**2**) and (**3c**). Under these conditions it was not possible to tell if (**1**) was an initial thermolysis product because it is rapidly converted into (**2**) at temperatures above 80 °C.[14] A photocycloaddition–thermolysis sequence in related systems could provide a means of solar energy storage, particularly since recent studies have shown that highly substituted aromatic compounds can be converted photochemically[15] or thermally[16] into their corresponding Dewar isomers.

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§ Satisfactory i.r. and n.m.r. spectral data, and elemental analysis, were obtained for new compounds.

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