Temperature Dependence of Orientation in the Photosensitised Addition of Maleic Anhydride to Methylbenzenes

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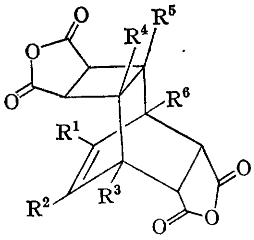
THE benzophenone-photosensitised addition of maleic anhydride to mono- and di-substituted benzene derivatives has been reported by several groups of workers.[1–4] N.m.r. spectra of the 2 : 1 adducts[3,4] seemed to confirm the earlier evidence[2] that 1,2-addition of maleic anhydride to substituted benzenes occurs specifically at the positions most remote from the substituents.

We now report that the benzophenone-photosensitised additions of maleic anhydride to toluene, *o*-xylene, and *p*-xylene give two thermally stable structural isomers† the ratios of which are dependent upon the temperature of the irradiated solution. This unusual effect is most strongly marked in the addition to *p*-xylene, where each isomer can be formed almost free of the other merely by varying the temperature over a range of 80°.

The mixture of isomers formed from maleic anhydride and toluene was resolved by fractional crystallisation from acetone into two 2:1 maleic anhydride–toluene adducts of structures (I) and (II) [m.p. 290—297° (decomp.) and 240—243° respectively; tetramethyl esters, m.p. 106—107° and 155—157°, respectively].



(I) R^1 = Me, $R^2 = R^3 = R^4 = R^5 = R^6$ = H

(II) R^3 = Me, $R^1 = R^2 = R^4 = R^5 = R^6$ = H

(III) $R^1 = R^2$ = Me, $R^3 = R^4 = R^5 = R^6$ = H

(IV) $R^1 = R^6$ = Me, $R^2 = R^3 = R^4 = R^5$ = H

(V) $R^3 = R^6$ = Me, $R^1 = R^2 = R^4 = R^5$ = H

(VI) $R^1 = R^4$ = Me, $R^2 = R^3 = R^5 = R^6$ = H

(VII) $R^1 = R^3 = R^5$ = Me, $R^2 = R^4 = R^6$ = H

(VIII) $R^1 = R^2 = R^3 = R^4 = R^5 = R^6$ = H

At 20° the ratio of isomers (I) and (II) was 1:1, whereas at 100° it was 3:2. The corresponding relative quantum yields were as follows: 20°, 1·0, 1·0; 100°, 1·35, 0·9. Absolute quantum yields have not been measured exactly, but are approximately 0·02 of these values. In contrast, the unsensitised photoaddition of maleic anhydride to toluene at 20° gave adducts (I) and (II) in the ratio 4:1. This difference from the sensitised addition adds weight to the previous evidence for mechanistic differences between sensitised and unsensitised additions to aromatic rings.[5]

The photosensitised addition of maleic anhydride to *o*-xylene gave a mixture of isomers (III) and (IV) [m.p. 300—310° (decomp.) and 235—240° respectively; tetramethyl esters, m.p. 162—164° and 140—141°, respectively] in the ratio 1:1 at 20° and 2:1 at 100°.

The photosensitised addition of maleic anhydride to *p*-xylene gave the isomeric 2:1 adducts (V) (m.p. 255—257°; tetramethyl ester, m.p. 181—182°) and (VI) (m.p. > 330°; tetramethyl ester; m.p. 143—145°) in the ratio 20 : 1 at 20° and 1 : 10 at 100°. The corresponding ratios of quantum yields at 20° and 100° were approximately 1·0 : 0·05 and 0·025 : 0·25 respectively: absolute values have not yet been measured. Maleic anhydride and mesitylene gave only a single 2 : 1 adduct (VII) (m.p. 254—256°; tetramethyl ester, m.p. 131·5—133°) at 20° and 100°.

All the compounds now reported have elemental analyses and n.m.r. spectra consistent with the structures assigned. The infrared spectra of adducts (I)—(IV), (VI), and (VII) were almost superimposable on that of the benzene–maleic anhydride adduct (VIII): the stereochemistry of adduct (VIII) has been previously established.[6] Oxidation of each toluene adduct (I) and (II) with fuming nitric acid gave *cis*-*anti*-*cis*-cyclobutanetetracarboxylic dianhydride, thereby further supporting the indicated stereochemistry and providing evidence (not clearly available from the n.m.r. spectra) that the methyl group in adduct (II) is at R(3) rather than R(4), *i.e.*, that 2,3- rather than 1,2-addition to toluene had occurred. Adducts formed by 1,2-addition, *viz.*, (VI) and (VII), gave no trace of the above dianhydride on oxidation.

We do however have reservations about the stereochemistry of one of the *p*-xylene adducts written provisionally as (V), following reference 3. The n.m.r. spectrum [$(CD_3)_2CO$] showed two vinyl protons as a sharp singlet, τ 3·82, as required, but the infrared spectrum differed somewhat from those of the other adducts, especially in the 850—1300 cm.$^{-1}$ region. Oxidation with a 1:1 mixture of concentrated nitric and sulphuric acids gave, after treatment of the product with diazomethane, the oxidation-resistant hexamethyl ester (IX) in high yield. The peracid oxidation sequence used[6b] to establish the stereochemistry of the benzene adduct (VIII) proved inconclusive with the adduct (V) although it confirmed structure (VI) for the second

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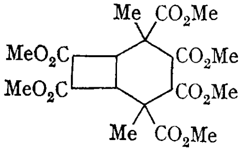
† Adducts (I), (II), (IV), (VI), and (VII) have two optical isomers.

(new) *p*-xylene adduct. Although the stereochemistry of adduct (V) remains undecided (the 'cyclobutane' anhydride ring may be *endo*), it is clear that 2,3-addition of maleic anhydride is favoured at 20°, and 1,2-addition at 100°.

A brief survey has indicated that reaction temperatures are unspecified in over 80% of recent publications in the field of organic photochemistry. Temperature effects such as those now described may well be more common than appears currently to be believed. They can be taken to imply the presence of a thermal activation step in the reaction of a photochemically-generated intermediate species, or they may result from the effects of temperature on equilibria involving precursor complexes in solution. Preliminary spectroscopic studies have given some evidence that the latter factor is important in the *p*-xylene–maleic anhydride system.



(IX)

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