Stereoselective Trapping of a Photo-enol

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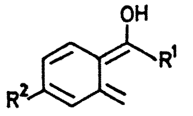
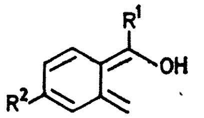
Summary Photolysis of *o*-tolualdehyde gives a photo-enol which can be trapped with maleic anhydride in a highly stereoselective manner.

Photo-enolisation, especially of *o*-alkylbenzophenones, is the subject of much current interest.[1] Recently Porter and Tchir have observed the formation of two isomeric enols from the flash photolysis of 2,4-dimethylbenzophenone.[2] These enols were assigned the structures (**1a**) and (**2a**) and appeared to form from a common triplet-state precursor. In non-polar solvents the photo-enol of longer lifetime was taken to be the (*E*)-isomer (**1a**), whilst the other, faster decaying, intermediate was assigned as the (*Z*)-isomer (**2a**). As a consequence of different lifetimes, Diels–Alder reaction would be expected to be favoured by the isomer of longer lifetime, *viz*. (**1a**). We have confirmed this expectation with *o*-tolualdehyde as starting material.

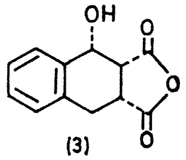
Photolysis† of the aldehyde with maleic anhydride in dry acetone gave one major adduct (**3**)‡, m.p. 118—135°, ν_{max} 3500, 1840, and 1760 cm^{-1}. The anhydride was unstable and on heating in tetrahydrofuran containing some dilute sulphuric acid gave an isomeric acid lactone (**4**), m.p. 160—164°, ν_{max} 3500, 2500, 1780, and 1720 cm^{-1}. Selective reduction of the free carboxyl group with diborane[3] gave a new lactone identified as the alcohol (**5**), m.p. 172—176°, ν_{max} 3450, 1760, and 1740 cm^{-1}. The lactone (**5**) was also obtained, together with an isomeric lactone (**6**) by direct reduction of the initial hydroxy anhydride (**3**) with sodium borohydride. Since, in both the bicyclic lactone (**4**) and the reduction product (**5**), the alcohol and carboxyl groups of the lactone functions must be *cis*, the initial adduct must have the relative stereochemistry



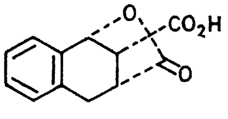
(1a) R^1 = Ph, R^2 = Me
(1b) R^1 = R^2 = H



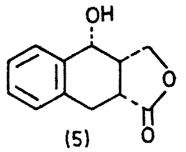
(2a) R^1 = Ph, R^2 = Me
(2b) R^1 = R^2 = H



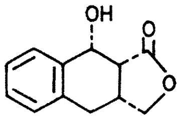
(3)



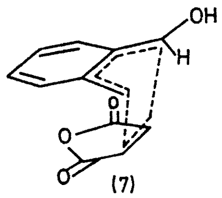
(4)



(5)



(6)



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† A Hanovia 125w medium-pressure mercury lamp was used in either Pyrex or quartz apparatus.

‡ No isomeric hydroxy-anhydrides could be isolated. All new compounds gave satisfactory micro-analyses.

depicted by (**3**).§ This adduct must therefore form from a Diels–Alder addition of the enol (**1b**) with the maleic anhydride by an *endo*-approach involving the maximum π-orbital overlap, *cf.* (**7**).[4]

Similar selectivity has been observed in the reaction between the photo-enol from *o*-methylbenzophenone and maleic anhydride and related dienophiles.[5] These reactions exemplify a potentially important synthetic process.

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§ Mass spectral and ^{1}H n.m.r. studies were consistent with these assignments and will be reported in detail in a full paper.

[1] N. C. Yang and C. Rivas, *J. Amer. Chem. Soc.*, 1961, **83**, 2213; N. D. Heindel, E. W. Sarver, and M. A. Pfau, *Tetrahedron Letters*, 1968, 3579; M. A. Pfau, N. D. Heindel, and T. F. Lemke, *Compt. rend.*, 1965, **261**, 1017; N. D. Heindel, J. Molnar, and M. A. Pfau, *Chem. Comm.*, 1970, 1373.

[2] G. Porter and M. F. Tchir, *Chem. Comm.*, 1970, 1372.

[3] *Cf.* G. Zweifel and H. C. Brown, *Org. Reactions*, 1963, **13**, 1.

[4] K. Alder and G. Stein, *Angew. Chem.*, 1937, **50**, 510; *cf.* "The Chemistry of Alkenes," ed. S. Patai, Interscience, New York, 1964, p. 910.

[5] F. Nerdel and W. Brodowski, *Chem. Ber.*, 1968, **101**, 1398.