Photodecarboxylation of 2-Benzopyran-3-one Adducts and Photoreactions of the Derived *o*-Quinodimethanes

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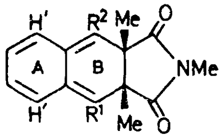
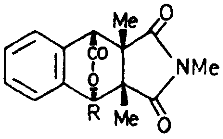
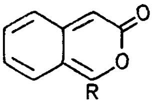
Summary Photodecarboxylation of the 2-benzopyran-3-one–trimethylmaleimide adducts (**6**) gives the *o*-quinodimethanes (**1**)–(**3**) which in subsequent photoreactions afford *inter alia* the benzobicyclohexenes (**7**), and cyclopropanes (**8**).



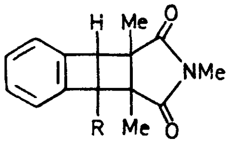
(1) R^1 = Ph, R^2 = H
(2) R^1 = Me, R^2 = H
(3) R^1 = R^2 = H
(5) R^1 = R^2 = Ph



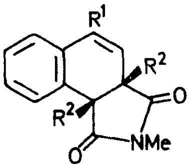
(4)



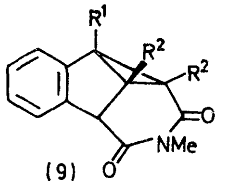
(6)



(7)



(8)



(9)

Unlike most esters those derived either from benzyl alcohol[1] or phenylacetic acid[2] undergo fairly efficient photodecarboxylation in solution. The method therefore seemed appropriate for preparation of the *o*-quinodimethanes (**1**)–(**3**) from the adducts (**4**). The properties of the *o*-quinonoids (**1**)–(**3**) were of interest in connection with the remarkable stability of (**5**).[3]

2-Benzopyran-3-one (**6**; R = H), generated by acetic anhydride dehydration of *o*-formylphenylacetic acid,[4] reacted smoothly with trimethylmaleimide to give the adduct (**4**; R = H). The adducts (**4**; R = Me) and (**4**; R = Ph) were prepared similarly. Photodecarboxylation of these adducts (degassed benzene solutions, medium pressure mercury lamp, ambient temperature) provided yellow solutions of the *o*-quinodimethanes (**1**)–(**3**). The long wavelength u.v. absorption shown by these solutions was similar in position and fine structure to the absorption of the isolable diphenyl derivative (**5**). The latter absorbs at only slightly longer wavelength ($\lambda_{\max}$ 415 nm) than the unsubstituted derivative (**3**) (400 nm), whilst both the monophenyl and monomethyl derivatives (**1**) and (**2**) absorb at *ca.* 410 nm. These results indicate that the phenyl substituents in (**5**) lie orthogonal to the *o*-quinonoid system† where they provide steric rather than conjugative stabilisation. In this conformation the *ortho*-hydrogens of each phenyl ring lie above and below the ring-B diene system and steric interference with the protons H′ and ring-B substituents is minimal. This explanation for the stability of (**5**) accords with the increased ring-B reactivity of (**1**)–(**3**). Whilst 2,3-diaza-1,4-naphthoquinone adds only to ring-A of (**5**), 1-phenyltriazoline-2,5-dione reacts with (**1**) to give two adducts derived by addition to the two faces of ring-B.

Attempts to isolate the *o*-quinonoids (**1**)–(**3**) failed, as, unlike (**5**), they are air-sensitive and readily undergo further photochemical reactions. Thus continued irradiation of a solution of (**1**) produced the *syn*-benzobicyclohexene (**7**; R = Ph) (28%), as well as the dihydronaphthalene (**8**; R^1 = Ph, R^2 = Me) (23%) and the cyclopropane (**9**; R^1 = Ph, R^2 = Me) (3·5%). Similar irradiation of (**2**) gave mainly (71%) the *syn*- and *anti*-isomers (**7**; R = Me) which showed NMe resonance at τ 7·68 and 6·9, respectively. Only a 10% yield of a mixture of the isomers (**7**; R = H) was formed on irradiation of (**3**); the major product (30%) is assigned structure (**9**; R^1 = H, R^2 =Me). In boiling xylene the bicyclohexenes (**7**) return to the corresponding *o*-quinoids (**1**)—(**3**), and photolysis of (**7**; R = Ph) and (**7**; R = Me) similarly gives (**1**) and (**2**), respectively.

The cyclopropanes (**9**) are derived by processes which must include a 1,2-shift of an imide carbonyl. The related 1,2-shift of keto-groups in $\beta\gamma$-unsaturated ketones is well known.[7]

Satisfactory analytical and spectroscopic data were obtained for all the pure compounds described.

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† Replacement of a 1-methyl group in (**6**) by phenyl produces a bathochromic shift of 11 nm (ref. 4) whilst introduction of a second phenyl group at C-4 produces a further shift of 20 nm (ref. 5). Phenyl substitution produces similar shifts in the u.v. spectra of isoquinolin-3-ones (ref. 6).

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[2] T. O. Meiggs and S. I. Miller, *J. Amer. Chem. Soc.*, 1972, **94**, 1989.

[3] D. W. Jones and G. Kneen, *Chem. Comm.*, 1971, 1356.

[4] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 536.

[5] J. M. Holland and D. W. Jones, *J. Chem. Soc.* (*C*), 1970, 530.

[6] D. W. Jones, *J. Chem. Soc.* (*C*), 1969, 1729.

[7] See R. C. Cookson and N. R. Rogers, *J. C. S. Chem. Comm.*, 1972, 809 for leading references.