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PHOTO-INDUCED REACTION OF ALKYLATED 1,4-TOLUQUINONE CARRYING ESTER GROUP IN THE ALKYL SIDE CHAIN

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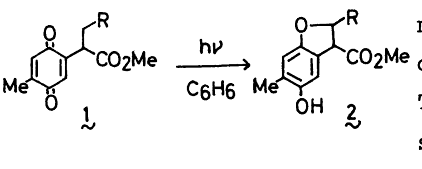
Irradiation of several 1,4-toluquinones **1a-d** having functionalized side chain rapidly gave bicyclic phenolic compounds **2a-d** in good yields via intramolecular hydrogen abstraction-proton transfer-cyclization. In the case of **1f**, however, it was found that intramolecular rearrangement occurred concomitantly.

Bruce and co-workers1) already reported that photoexited *p*-quinones abstracted hydrogen atom intramolecularly from the alkyl substituents. Orlando *et al.*2) also realized a rearrangement of the side chain during the photolysis of *t*-butyl-*p*-benzoquinone. In spite of these reports, the reported quinones react sluggishly to give a poor yield of dihydrobenzofuran derivatives.

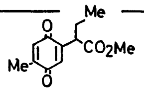
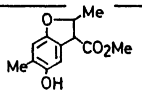
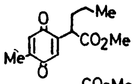
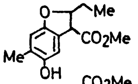
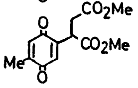
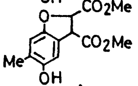
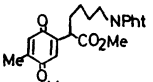
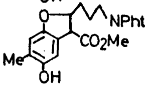
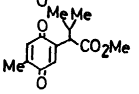
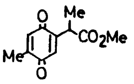
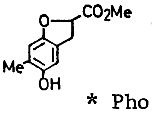
In view of the synthetic potentiality photo-induced intramolecular hydrogen abstraction reaction was extended to the following quinonoid compounds, *i.e.*, methyl 2-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)butyrate **1a** and other analogous **1b-f**.3),4) Photoreaction of quinones **1a-d** involving ester group at α-position of the alkyl side chain smoothly reacted and gave cyclized compounds **2a-d** in good yields.

Typically, a benzene solution (200ml) of quinone **1a**5) (2 mmoles) was externally irradiated at 0-10 °C for 30 min. with a 300 W high pressure Hg-lamp after bubbling nitrogen gas (conversion>90%). After removal of the solvent, chromatography of the residue on silica gel resulted in the isolation of a red syrup in a yield of 65%.6) Trituration of this syrup with petroleum ether-dichloromethane gave crystalline colorless needles; methyl 2,3-dihydro-2,6-dimethyl-5-hydroxybenzofuran-2-carboxylate **2a**, a cyclic product, mp 99-101 °C. The product **2a** showed the following spectral data; ^{1}H-NMR (CDCl$_3$) δ=1.40 (d, J=7.0 Hz, 3H), 2.18 (s, 3H), 3.42-3.68 (m, 1H), 3.79 (s, 3H), 4.63 (d, J=7.0 Hz, 1H), 4.71 (bs, 1H), 6.50 (s, 1H), and 6.63 (s, 1H)ppm; IR (KBr) 3440 and 1745 cm^{-1}; MS (m/e) 222 (M$^+$). The spectral data are all compatible with the structure of **2a**. Treatment of the photocyclic product **2a** with cerium(IV) ammonium nitrate in 70% aqueous acetonitrile at 0°C gave methyl 3-hydroxy-2-(4-methyl-3,6-dioxo-1,4-cyclohexadienyl)butyrate **3a** in a yield of 60%, mp 104,5-105.5 °C.7) The results of photolysis of some other quinones **1b-f** are summarized in Table.7)

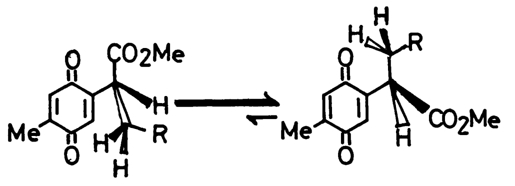


The photoreactions of these quinones **1a-d** proceeded rapidly to give dihydrobenzofuran derivatives **2a-d** in fairly good yields. These smooth reactions may be explained in terms of the following mechanism; β-methylene hydrogen atoms of alkyl side chain

Table

	Quinone **1**			Product **2**		Yield (%)
1a		bp 130-131°C/3Torr	**2a**		mp 90-91°C	65
1b		bp 143-145°C/3Torr	**2b**		mp 101-102°C	68
1c		mp 85-86°C	**2c**		mp 180-181°C	70
1d		oil	**2d**		mp 180-181°C	75
1e		bp 140-143°C/3Torr		mixture of several products		—
1f		mp 59-60°C	**2f**		* mp 153-154°C	41

* Photorearrangement product



are forced to occupy a favoring position for hydrogen abstraction by quinonoid carbonyl, because of the dipole-dipole repulsion between quinonoid carbonyl and ester carbonyl groups.

This photocyclization could provide a good synthetic method of coumaran derivatives **2**, which are easily transformed to quinones **3**.

However, in the photolysis of quinone **1e**, a complex mixture of several products was obtained in spite of its rapid consumption under similar conditions. Isolation and the structural determination of the photoproducts are still under investigation. Quinone **1f** was found to give another type of the dihydrobenzofuran with rearranged structure on irradiation under similar conditions.8) Now, the scope and the limitation of the photoreaction are being studied.

References and Notes

1) (a) J.M.Bruce, Quat. Rev., 21, 405 (1967) and papers cited theirin; (b) J.M.Bruce, D.Creed, and K.Dawes, J. Chem. Soc., (C), 3748 (1971). 2) C.M.Orland, H.Mark, A.K.Bose, and M.S.Manhs, J. Am. Chem. Soc., 89, 6527 (1967). 3) (a) E.C.Taylor. R.L.Robey, K.-T.Lin, B.Favre, H.T.Bozims, C.-S.Chiang, A. McKillop, and M.E.Ford., J. Am. Chem. Soc., 98, 3037 (1976); (b) K.Maruyama amd T.Kozuka, Bull. Chem. Soc. Jpn., 51, 3586 (1978). 4) P.Jacob,III., P.S.Callery, A.T.Shulgin, and N.Castagnoli,Jr., J. Org. Chem., 41, 3627 (1976). 5) All of the quinones **1** described were usually obtained from 4-methyl-2,5-dimethoxy-1-acylbenzene via two steps.3), 4) 6) Photocyclic products contain generally a small amount of the photorearranged isomeric product(<5%),but the latter can be removed by single recrystallization. 7) All products gave satisfactory elemental analyses and reasonable spectral data. 8) The product **2f** showed the following spectral data: Mp 153-154 °C; ^{1}H-NMR (CDCl$_3$) δ=2.20 (s, 3H), 3.14-3.62 (AB type, J=15, 10, and 7 Hz, 2H), 3.80 (s, 3H), 4.50 (s, 1H), 5.12 (dd, J=10 and 7 Hz, 1H), 6.60 (s, 1H), and 6.74 (s, 1H) ppm; IR (KBr) 3420 and 1740 cm^{-1}; MS (m/e) 208 (M$^+$). The structure of **2f** was established by comparing its ^{1}H-NMR spectra of other photocyclic products **2a-d** (in particular, the chemical shift of methine proton at α-position of ester group). Obviously, the chemical shift (dd, δ=5.12 ppm) due to the methine proton of **2f** appeared at a lower field than those (d, δ=4.40-4.76 ppm) of other photoproducts **2a-d**, indicating that the methine group is linked between the ether oxygen and the ester group.

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