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Photoinduced Reactions. XXXIII. Photochemical Reaction of a *para*-Quinone Methide[1]

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The photochemistry of a quinone methide (Ia) was investigated. Ia was unchanged on photolysis of an alcoholic solution (0.0064 M) with a high-pressure mercury lamp (Pyrex filter). However irradiation of a highly dilute solution of Ia or a sensitized reaction (acetophenone) gave an alcohol adduct (IIe in methanol and IIf in isopropyl alcohol) which might be formed *via* triplet excited state(s) of Ia. The methanol adduct IIe was also formed by the irradiation of Ia in methanol with a low-pressure mercury lamp through quartz. In this case the formation of IIe appears to be initiated by photochemical decomposition of methanol.

Photolysis of quinone methides is of interest in connection with the photochemical discoloration of xanthene dyes and the photorearrangement of 2,5-cyclohexadienones. We investigated the photochemistry of a quinone methide (Ia). During the course of our study, two papers on the photochemical reaction of quinone methides have appeared. Becker[2] found the quinone methide Ia to convert a phenol (IIa) by the photolysis of a highly dilute solution in isopropyl alcohol or by the acetophenone-sensitized photolysis. Recently, Krull and Schuster[3] showed that a quinone methide (Ib) in ethyl ether or cyclohexadiene afforded photochemically the corresponding solvent-adduct IIb or IIc, respectively, together with a small amount of a reduction product (IId). These papers prompted us to report the results obtained in our investigation on photolysis of the quinone methide Ia.

On photolysis of a methanol solution (0.0064 M) with a high-pressure mercury lamp (Pyrex filter) Ia was entirely unchanged. However, a methanol adduct IIe and a reduction product IIa were formed in the presence of acetophenone in 74 and 7% yields,

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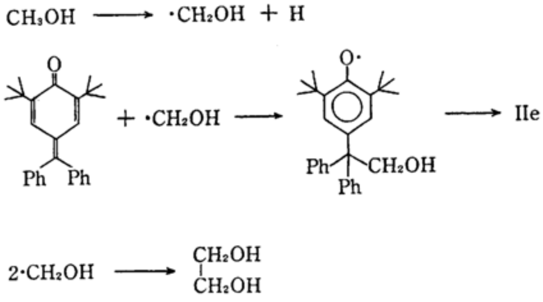
1) Part XXXII: T. Matsuura, K. Omura and A. Nishinaga, *Chem. Commun.*, **1969**, 366.

2) H.-D. Becker, *J. Org. Chem.*, **32** 2115 (1967).

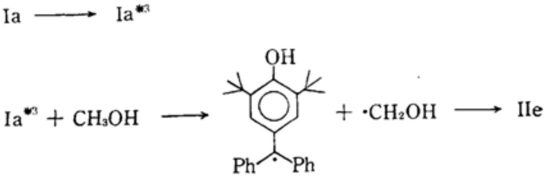
3) I. S. Krull and D. I. Schuster, *Tetrahedron Letters*, **1968**, 135.

respectively. The structure of the adduct IIe was assigned from the NMR spectra of the adduct and of its acetate (see Experimental Section). The methanol adduct IIe was also formed as a main product in 50% yield by irradiation of a dilute methanol solution of Ia. The formation of IIe in the photolysis of a highly dilute solution of Ia or a sensitized reaction was perfectly quenched by air-bubbling. Therefore, it should be reasonable to presume that the adduct IIe was formed *via* the triplet excited state(s) of Ia. On the other hand, photolysis of a highly dilute solution of Ia in isopropyl alcohol with a high-pressure mercury lamp afforded not only the reduction product IIa (63% yield), as reported by Becker,[2] but also an isopropyl alcohol adduct (IIf) in 11% yield. The structure of the isopropyl alcohol adduct IIf was also deduced from its NMR spectrum.

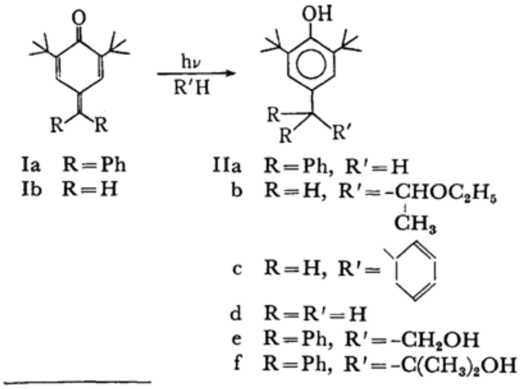
It should be noted that the adduct IIe (44% yield) was also formed by the irradiation of Ia in methanol with a low-pressure mercury lamp (quartz filter) under bubbling nitrogen. On the other hand, in isopropyl alcohol the reduction product IIa was formed in 54% yield in addition to the adduct IIf (11%). In contrast to the photolysis of Ia with a high-pressure mercury lamp, the adduct IIe was also obtained in the presence of air, although in a low yield (14%), and 2,6-di-*t*-butyl-*p*-benzoquinone was obtained in 16% yield. When a low-pressure lamp with a Vycor filter was used for the photolysis of Ia in methanol, the formation of the adduct IIe was completely depressed. This is obviously due to the fact that a Vycor filter cuts off the 185-mμ line responsible for the photodecomposition of methanol to the hydroxymethyl radical as reported by Yang *et al.*[4] In fact, methanol was photochemically decomposed to afford ethylene glycol (80 mg per hour) with the low-pressure mercury lamp (quartz filer). These facts confirm that the formation of the adduct IIe in the photolysis of Ia with a low-pressure mercury lamp using a quartz filter resulted from the addition of the hydroxymethyl radicals, formed by the photochemical decomposition of methanol, to the quinone methide Ia as shown in Scheme I, rather than the excitation of Ia. The formation of IIe at high dilution or in the acetophenone-sensitized photolysis may be initiated by hydrogen abstraction of the triplet state(s) of Ia as described in Scheme II.



Scheme I



Scheme II



Ia R=Ph
Ib R=H

IIa R=Ph, R'=H
b R=H, R'=-CHOC$_2$H$_5$ (CH$_3$)
c R=H, R'=
d R=R'=H
e R=Ph, R'=-CH$_2$OH
f R=Ph, R'=-C(CH$_3$)$_2$OH

Experimental

Photolysis of Ia in Methanol. (*a*) *With a Low-pressure Mercury Arc Lamp.* A solution containing 1.00 g of the quinone methide Ia in 720 m*l* of methanol was irradiated for 15.5 hr with a 40 W low-pressure mercury arc lamp surrounded by a quartz filter under bubbling nitrogen. After removal of the solvent under reduced pressure, the residue was chromatographed on 40 g of silica gel. Elution with 75 m*l* of benzene yielded 120 mg of a yellow oil which was shown by a tlc analysis to contain a small amount of IIa. Further elution with 160 m*l* of benzene gave 482 mg of pale yellow crystals which were recrystallized from petroleum ether to afford the adduct IIe as colorless crystals, mp 119—120°C. NMR (in $CDCl_3$); τ 2.78 (10H, singlet, $2C_6H_5$), 3.08 (2H, singlet, two aromatic protons), 4.88 (1H, singlet, a phenolic OH), 5.42 (2H, singlet, CH_2O-), 8.41 (1H, singlet, OH), and 8.66 (18H, singlet, two *t*-butyl groups).

Found: C, 83.30; H, 8.58%. Calcd for $C_{28}H_{34}O_2$: C, 83.54; H, 8.51%.

The acetate of the adduct IIe was prepared as usual (acetic anhydride and pyridine). Recrystallization from methanol gave colorless crystals, mp 124—126°C. NMR (in $CDCl_3$): τ 2.78 (10 H, a difused singlet, two phenyl). 3.11 (2H, singlet, two aromatic protons), 4.88 (1H, singlet, a phenolic OH), 4.92 (2H, singlet, CH_2O-), 8.12 (3H, singlet, CH_3COO), and 8.67 (18H, singlet, two *t*-butyl groups).

Found: C, 81.22; H, 8.32%. Calcd for $C_{30}H_{36}O_3$: C, 81.04; H, 8.16%.

(*b*) *With a Low-pressure Mercury Arc Lamp under Air.* A solution containing 500 mg of Ia in 250 m*l* of meth-

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[4] N. C. Yang, D. P. C. Tang, D. Thap S. and J. Sallo, *J. Am. Chem. Soc.*, **88**, 2851 (1966).

anol was irradiated for 16.5 hr with a 40 W low-pressure mercury arc lamp (quartz filter) under bubbling air. After removal of the solvent under reduced pressure, the residue was chromatographed on 40 g of silica gel. Elution with 200 m*l* of petroleum ether-benzene (1 : 1) gave 31 mg of a yellow oil which was shown by a vpc analysis to contain a trace of benzophenone. Further elution with 170 m*l* of the same solvent yielded 46 mg of yellow crystals, mp 59—60°C, which were identified as 2,6-di-*t*-butyl-*p*-benzoquinone (by infrared spectrum and mixture mp). Elution with 200 m*l* of benzene afforded 11mg of yellow oil which was not further investigated. Elution with 100 m*l* of benzene gave 84 mg of yellow crystals which were identified as the adduct IIe (by infrared spectrum).

(c) A Sensitized Reaction. A solution containing 500 mg of Ia and 6.67 g of acetophenone in 90 m*l* of methanol was irradiated for 17 hr with 100-W a high-pressure mercury arc lamp (Ushio UM 102) surrounded by a Pyrex cooling jacket under bubbling nitrogen. After the solvent had been removed under reduced pressure, the residue was chromatographed on 200 g of silica gel. Elution with 5 m*l* of benzene yielded 33 mg of yellow crystals. Recrystallization from methanol afforded 14 mg of pale yellow crystals which were identified as IIa (by infrared spectrum). Further elution with 20 m*l* of benzene gave 60 mg of a yellow oil which was not further investigated. Elution with 110 m*l* of benzene yielded 400 mg of yellow crystals. Recrystallization from petroleum ether gave 206 mg of colorless crystals, mp 118—120°C, which were identified as IIe (by infrared spectrum and mixture mp).

(d) With High Dilution. A solution containing *ca.* 15 mg of Ia in 1000 m*l* of methanol was irradiated with a 450-W high-pressure mercury arc lamp (Ushio UM 450) surrounded by a Pyrex cooling jacket under bubbling nitrogen until the yellow color discolored (50 min). Further *ca.* 15 mg of Ia was added and irradiated. This operation was repeated eight times and the total amount of the quinone methide Ia irradiated was 125 mg. After removal of the solvent under reduced pressure, the residue was chromatographed on 5 g of silica gel. Elution with 10 m*l* of benzene yielded 45 mg of a yellow oil which was shown by a tlc analysis to contain Ia and IIa. Further elution with 40 m*l* of benzene gave 68 mg of pale yellow crystals. Recrystallization from petroleum ether afforded pale yellow crystals, mp 119—120°C, which were identified as the adduct IIe (by infrared spectrum and mixture mp).

Photolysis of Ia in Isopropyl Alcohol. *(a) With a Low-pressure Mercury Arc Lamp.* A solution containing 500 mg of Ia in 200 m*l* of isopropanol was irradiated for 6 hr with a 40-W low-pressure mercury arc lamp surrounded a quartz filter under bubbling nitrogen. After removal of the solvent under reduced pressure, the residue was crystallized from petroleum ether to give 87 mg of pale yellow crystals, which were identified as IIa (by infrared spectrum). The mother liquor was chromatographed on 20 g of silica gel. Elution with 25 m*l* of petroleum ether - benzene (1 : 1) afforded 184 mg of pale yellow crystals, which were identified as IIa (by infrared spectrum). Further elution with 165 m*l* of petroleum ether - benzene (1 : 1) yielded 44 mg of a yellow oil which was not further investigated. Elution with 150 m*l* of petroleum ether - benzene (1 : 1) gave 66 mg of pale yellow crystals, which, on recrystallization from petroleum ether, afforded the adduct as chloroless crystals, mp 155.5—156.5°C. NMR (in $CDCl_3$); τ 2.81 (12H, a difiused singlet, two phenyl and two aromatic protons), 4.93 (1H, singlet, a phenolic OH), 8.44 (1H, singlet, OH), and 8.52 (6H, difused singlet, 2 CH_3), and 8.69 (18 H, singlet, two *t*-butyl groups).

Found: C, 83.71; H, 9.19%. Calcd for $C_{30}H_{38}O_2$: C, 83.67; H, 8.90%.

(b) With High Dilution. The procedure analogous to that performed in the photolysis of Ia in methanol was used. The total amount of the quinone methide Ia which was irradiated in a period of 28 hr was 330 mg. After removal of the solvent under reduced pressure, the residue was chromatographed on 15 g of silica gel. Elution with 100 m*l* of petroleum ether-benzene (1 : 1) gave 207 mg of yellow crystals which were identified as IIa (by infrared spectrum). Further elution with 50 m*l* of petroleum ether - benzene (1 : 1) afforded 13 mg of a yellow oil which was not investigated. Elution with 250 m*l* of 32 mg of yellow crystals, which were identified as IIf (by infrared spectrum).

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