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PHOTOCHEMICAL REDUCTION OF 9,10-*o*-BENZENO-4a,9,9a,10-TETRAHYDRO-1,4-ANTHRAQUINONE

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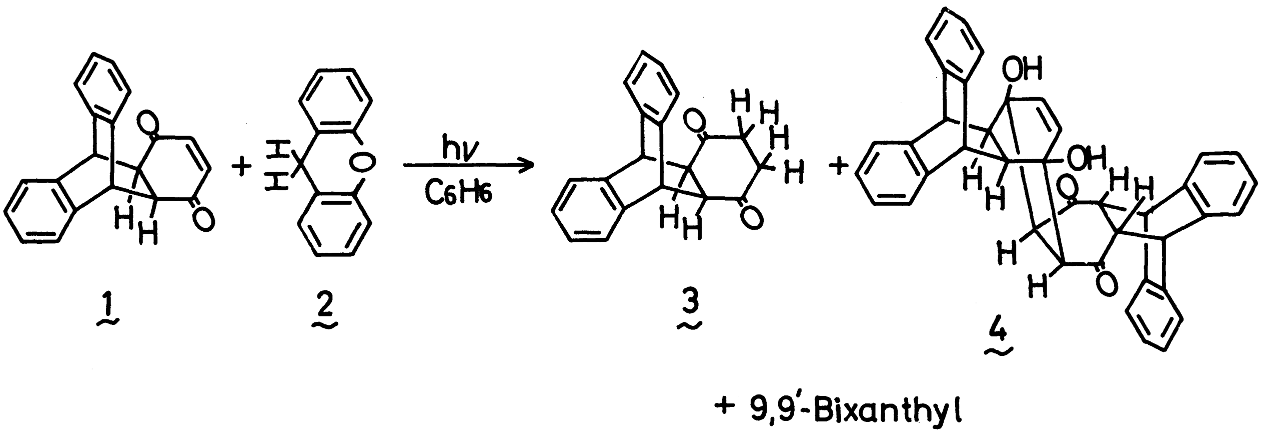
Irradiation of 9,10-*o*-benzeno-4a,9,9a,10-tetrahydro-1,4-anthraquinone **1** and xanthene **2** in benzene gave dihydro-monomer **3** and dihydro-dimer **4** of **1** as the final products. The course of the reaction and the structure of the unstable intermediates were investigated by means of ^{1}H-CIDNP technique.

Since the titled compound **1** has a *cis*-enedione group in the molecule resembling to *p*-benzoquinone, **1** is easily reduced photochemically to give good yields of the reduction products *via* the radical processes, and then one can observe the similar characteristic ^{1}H-CIDNP signals due to **1** or unstable intermediates during the course of the reaction.[1-3] However, the structures of the final products are quite different from those of the reaction of *p*-benzoquinone or of the derivatives. In the photochemical reduction of *p*-benzoquinone the product was solely hydroquinone. On the contrary, when a benzene solution of **1** and **2** (1:2,M/M) was irradiated by means of high pressure mercury arc lamp (300W), white needles **4** (>180°C,decomp., quite insoluble in benzene) were precipitated in a yield of 45 %. Another product was compound **3** (mp 210-212°C,yield;31%), whose structure was unambiguously deter-



+ 9,9'-Bixanthyl

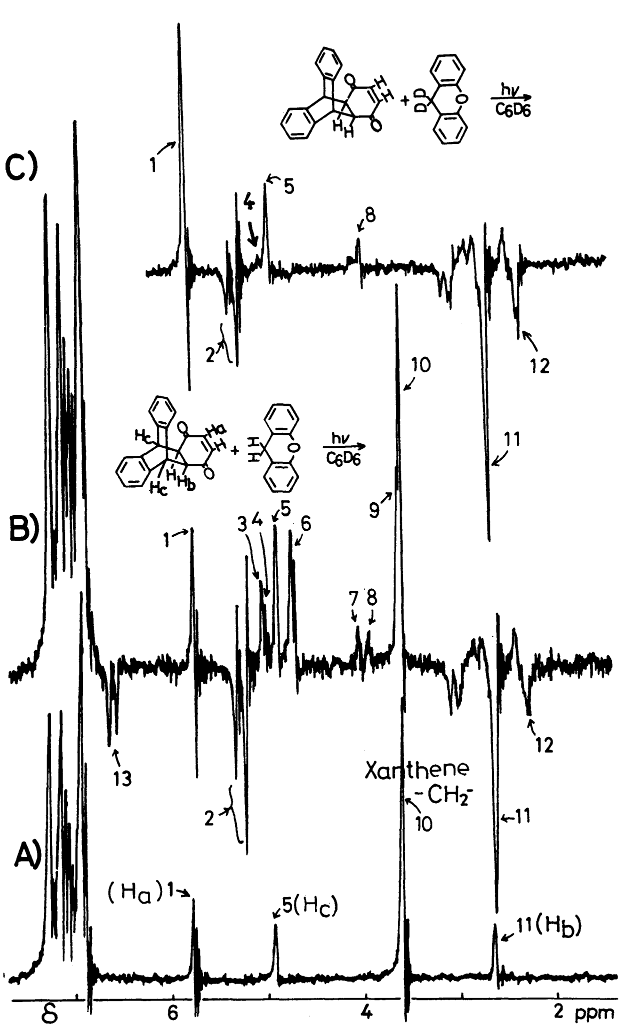


Fig. 1

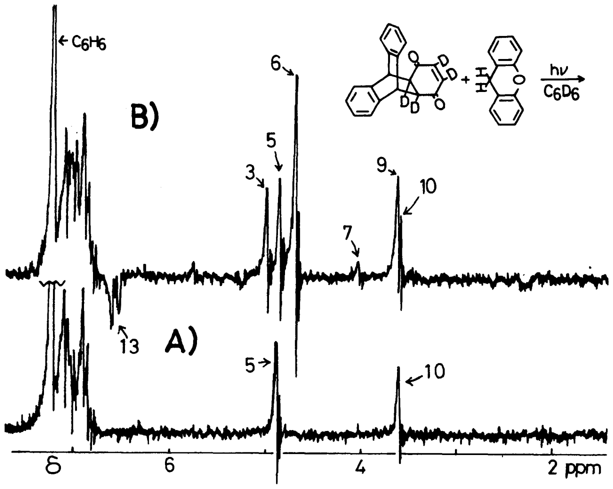


Fig. 2

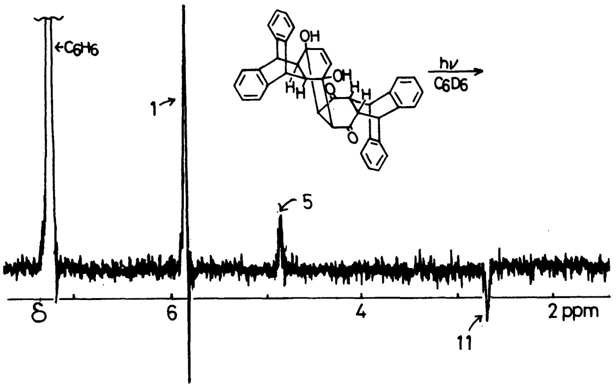


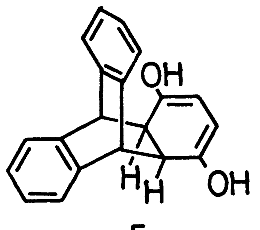
Fig. 3

Fig.1. ^{1}H-NMR spectra observed in the photochemical reaction of **1** and xanthene (1:2,M/M) (solvent:C_6D_6). A) Before irradiation. B) During irradiation. Signals 7 and 13 are due to methine and aromatic ring protons of accumulated 9,9'-bixanthyl. C) During irradiation (9,9-dideuterated xanthene was used).

Fig.2. ^{1}H-NMR spectra observed in the photochemical reaction of 2,3,4a,9a-tetradeuterated derivative of **1** and xanthene (1:2,M/M) (solvent:C_6D_6). A) Before irradiation. B) During irradiation.

Fig.3. ^{1}H-NMR spectrum observed in the photo-decomposition of **4** (solvent:C_6D_6).

mined by comparison with the authentic sample. The authentic sample was prepared by reduction of 1 with zinc and acetic acid. The ^{1}H-NMR, ^{13}C-NMR, IR spectra of 4 , and the molecular weight determined by vapor pressure method, 577 ± 20 (calculated, 574), are compatible with the given structure. Physical properties of 4 are the following; ^{1}H-NMR(CDCl$_3$);δ:2.08(2H,br s),2.16(2H,br s),2.84(2H,br s),4.10 (2H,OH,br s),4.50(2H,br s),4.69(2H,br s),4.92(2H,br s),7.0-7.6ppm(16H,aromatic-H,m). ^{13}C-NMR(CDCl$_3$);δ: 44.15, 46.75, 50.65, 53.89, 59.74, 67.37, 123.69, 124.67, 125.64, 125.96, 126.62, 128.40, 128.73, 210.69 ppm (chemical shifts are calibrated from TMS as an internal standard). IR(KBr disk);ν:1680 cm^{-1}(C=O), 3400 cm^{-1}(OH). UV max (CHCl$_3$); 295(sh), 269, 261, 241 nm. Diacetyl derivative of 4 ;white crystals, mp 112.6-118.2°C. Mass;m/e = 658(M^{+}). ^{1}H-NMR(CDCl$_3$);δ:2.24(6H,COCH$_3$,s), 2.92(2H, br s), 3.26(2H,br s), 3.38(2H,br s), 4.08(2H,br s), 4.70(2H,br s), 5.12(2H,s), 6.7-7.4 ppm(16H,aromatic-H,m). IR(KBr disk);ν: 1750 cm^{-1}(C=O,ester), 1690 cm^{-1}(C=O). These spectral data described above indicate the presence of the plane of symmetry in the molecule of 4 . Thermal decomposition of 4 dissolved in deaerated *o*-dichlorobenzene in a sealed tube at 140°C, 3hr, resulted the equimolar mixture of 1 and 3 . Mass analysis of dihydro-dimer, 4 , showed no molecular peak, but two strong peaks at m/e: 288 and 286. The dihydro-dimer, 4 , dissolved in CDCl$_3$ or C$_6$D$_6$ decomposed photochemically to give 3 and 1 showing CIDNP signals due to the resulted products (see Fig.3). Thus, 4 which has a structure of Diels-Alder adduct of 1 and 5 , is a sort of stable intermediates in the photochemical reaction of 1 . The concept was supported by the fact that from the photochemical reaction of 1 with 2 in the presence of an excess amount of N-phenylmaleimide was isolated the product 6 in a yield of ca. 70 %(>275°C, decomp.) without the formation of 3 and 4 . Spectral data(^{1}H-NMR and IR) were all compatible with the structure 6 . Xanthene 2 was oxidized to 9,9'-bixanthyl. Examination of the reaction by means of ^{1}H-CIDNP (see Figs. 1 and 2) suggests the formation of several kinds of unstable intermediates, judging from the absorption polarization signals(signal No. 1, 2, 3, 4, 5, 6, 8, 9, 11, 12, 13). The structures of the intermediates are not decisive yet, but from the comparison of the results with those of photo-reduction of *p*-benzoquinones or 1,4-naphthoquinones



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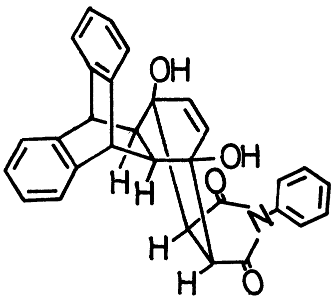

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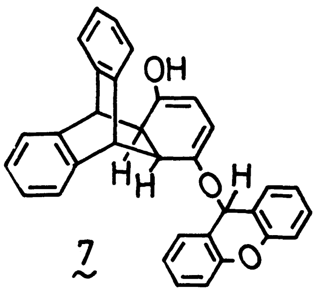
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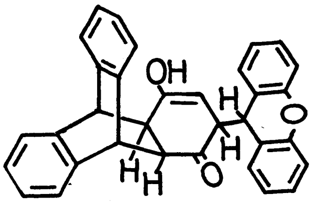
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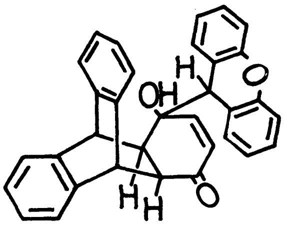
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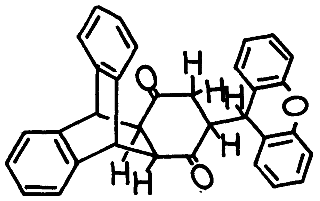
with xanthene, they may be assigned to **7** - **9** . Of these the formation of **8** was substantiated by the isolation of its keto-form **10** (yield,less than 5 %, >184°C,decomp.) under very cautious work-up of reaction mixture. Product **10** is so unstable in solution as to decompose easily by treating it with silica gel, but once purified, it is stable. The structure of **10** was determined spectroscopically.[4] Another outstanding feature of the reaction is the appearence of strong polarization signals due to **1** during irradiation (see Fig. 1 , that is; signal 1: absorption polarized, and signal 11: emission polarized). No polarization signals as such can be observed in the absence of xanthene. This is, therefore, a clear indication of reproduction of **1** from a free radical intermediate; presumably from **11** . Taking into account of the possible disproportionation reaction of **11** , one will be convincible of the formation of **5** and the reproduction of **1** *via* radical process. As soon as the compound **5** is formed this may be trapped by **1** to give **4** , which is crystallized out from the benzene solution because of its poor solubility in benzene. We can observe no detectable polarization signals due to **3** nor **4** .[5]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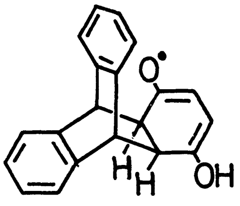
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2) K.Maruyama, T.Otsuki, S.Arakawa,and A.Takuwa; Bull.Chem.Soc.Japan,46,2470(1973).

3) K.Maruyama, and S.Arakawa; ibid., 47, 1960(1974).

4) Mass;m/e=468(M^+). IR(KBr disk);ν:1707 cm^{-1}(C=O). ^{1}H-NMR(C_6D_6);δ:1.92-2.40(3H,m), 2.40-2.80(2H,m), 4.72(1H,d,J=3.9Hz), 4.90(1H,br s), 5.06(1H,d,J=2.5Hz), 6.5-7.8 ppm(16H,aromatic-H,m).

5) The fact might be indicative of the presence of something affecting the fast relaxation of nuclear spin polarization.

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