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PHOTOCHEMICAL REACTION OF 1,2-NAPHTHOQUINONE WITH ARYLACETALDEHYDES. PRODUCTS AND THEIR INTRAMOLECULAR ISOMERIZATION

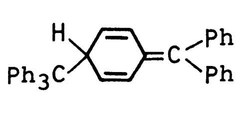
Kazuhiro MARUYAMA, Akio TAKUWA*, and Osamu SOGA*

Department of Chemistry, Faculty of Science, Kyoto University, Kyoto 606

**Department of Chemistry, Faculty of Science, Shimane University, Matsue 690*

Photochemical reaction of 1,2-naphthoquinone with phenylacetaldehyde in benzene afforded **5**, **6**, and **7**. The products, **5** and **6**, are combination products of 1,2-naphthosemiquinone radical with phenylacetyl radical, and the product **7** with benzyl radical. However, the reaction with diphenylacetaldehyde gave only **11** without accomanying any other expected acylation product. 4-Alkyl-1,2-naphthalenediols, **7** and **11**, were very sensitive to air and oxidized to quinones, **9** and **14**. The quinones isomerized intramolecularly to quinone methides, **10** and **15**, on silica gel during separating procedures.

Since the structure of "hexaphenylethane, *i.e.*, triphenylmethyl dimer" was elucidated as **1**,1) the problem of combining site and *dynamic* free spin distribution within the related radicals has become a top interest of free radical chemists. Our previous investigation on the photo-induced hydrogen abstraction reaction of 1,2-naphthoquinone from hydrogen donors indicated that xanthene gave 2-hydroxy-4-xanthene-9-ylnaphthalene*(4H)*-1-one **2**,2) while aliphatic aldehydes afforded 3-acyl-1,2-naphthalenediols **3** and an isomeric mixture of 1,2-naphthalenediol monoacylesters **4**,3) as stable products. These photo-induced reductive addition reactions proceed mainly *via* the combination of triplet radical pair consisted of 1,2-naphthosemiquinone radical and xanthenyl4) or acyl5) radicals. In this communication we wish to report on the different attacking positions by alkyl and acyl radicals to 1,2-naphthosemiquinone radical clarified in the photolyses of 1,2-naphthoquinone and arylacetaldehydes.



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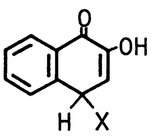

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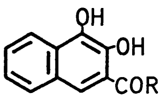

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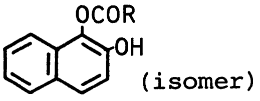

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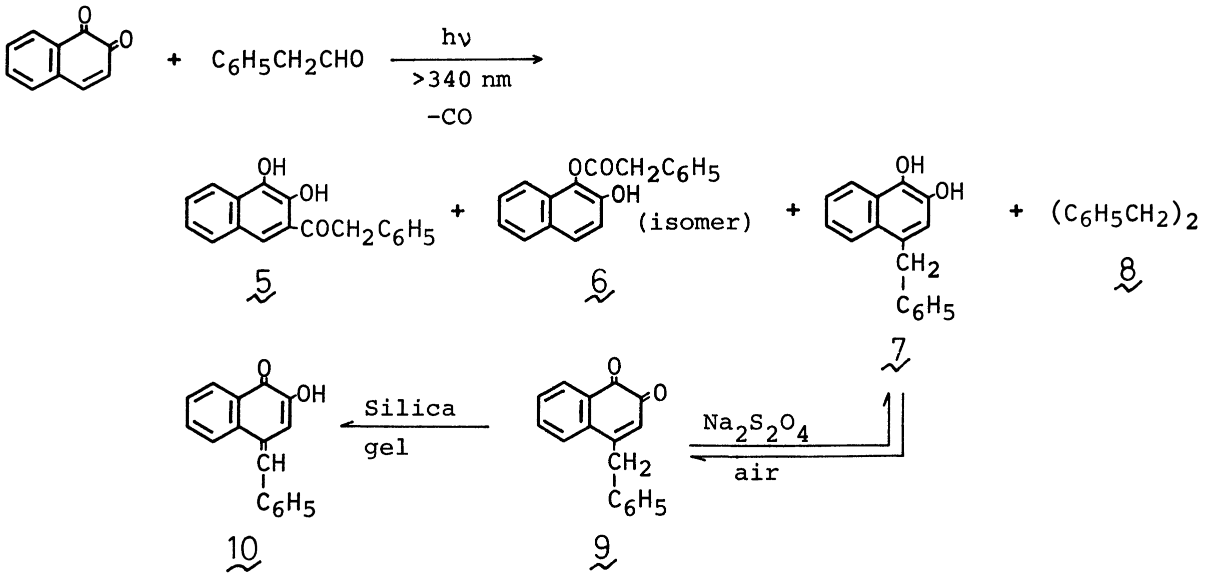
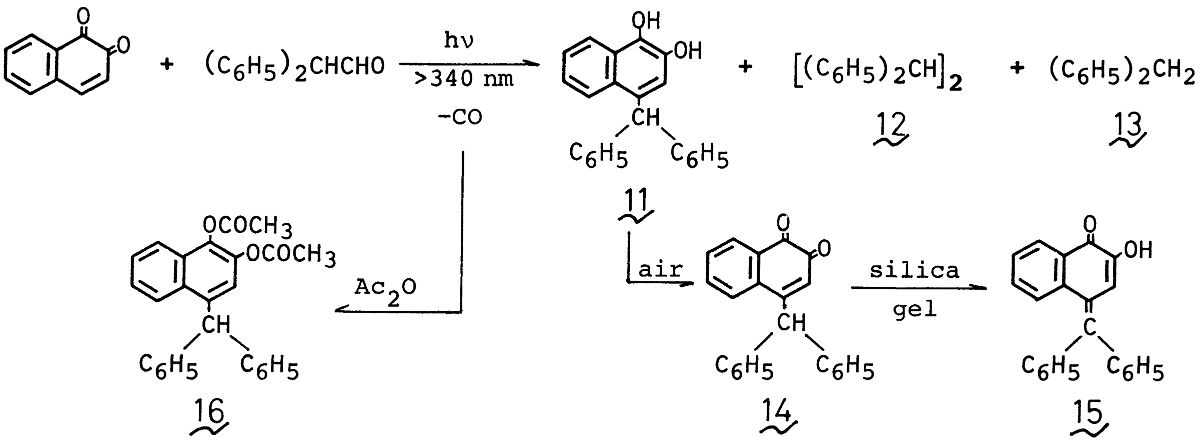
X : Xanthenyl
R : Acyl

After usual work-up, photolysis6) of a benzene solution of 1,2-naphthoquinone (1 mmol) and phenylacetaldehyde (2 mmol) gave 3-phenylacetyl-1,2-naphthalenediol **5**

(5%), 1,2-naphthalenediol monophenylacetates 6 (12%), 2-hydroxy-4-benzylidene-1,4-dihydronaphthalene-1-one (quinone methide) 10 (27%),7) and bibenzyl 8. When the products were separated by a silica gel plate, 4-benzyl-1,2-naphthoquinone 9 (4%)7) was obtained together with 5 (5.5%), 6 (10%), 10 (24%), and 8.



Photolysis6) of 1,2-naphthoquinone and diphenylacetaldehyde8) resulted in the formation of quinone methide 15 (60%),9) 1,1,2,2-tetraphenylethane 12, and diphenylmethane 13. On the other hand, separation of the products on a silica gel plate gave 4-diphenylmethyl-1,2-naphthoquinone 14 (62%)9) together with 15 (5%), 12, and 13.



Thus, phenylacetaldehyde affords two combination products of both phenylacetyl radical and benzyl radical with 1,2-naphthosemiquinone radical (5 + 6 / 9 + 10 = 0.5), but diphenylacetaldehyde yields exclusively one combination product of diphenylmethyl radical with 1,2-naphthosemiquinone radical. During the photolyses it was recognized that decarbonylation of diphenylacetyl radical was much faster than that of phenylacetyl radical[10] resulting in the formation of alkylation product **14** or **15**, probably because of the higher stability of diphenylmethyl radical than that of benzyl radical.[11]

In separating the products on silica gel column unexpected products, **10** and **15** (quinone methide), were produced. Quick separation of the products on a silica gel plate, however, gave **9** or **14** accompanying with quinone methide and other products. This fact indicates that the methides, **10** and **15**, are isomerization products of **9** and **14**. Actually, TLC (developing solvent : benzene) of authentically synthesized pure **9** or **14**[12] gives two spots corresponding to **9** (*R_f 0.14*) and **10** (*R_f 0.33*) or **14** (*R_f 0.20*) and **15** (*R_f 0.30*). The relative facility of enolization of **9** and **14** (Q) to **10** and **15** (QM) on silica gel was shown in Figure 1, reflecting the almost linear migratory aptitude of hydrogen atom (**9** / **10** = 0.17 ; **14** / **15** = 14.7).[13]

Since **7** prepared by the reduction of **9** with sodium dithionite is easily oxidized to **9** with air, **7** and **11** should be initial products, but those easily air-oxidized to give **9** and **14** on silica gel, finally giving **10** and **15**. An additional support for this was obtained by acetylating the resulting mixture of the reaction of 1,2-naphthoquinone with diphenylacetaldehyde. The product was 1,2-diacetoxy-4-diphenylmethylnaphthalene **16** in the yield of 60%.[14]

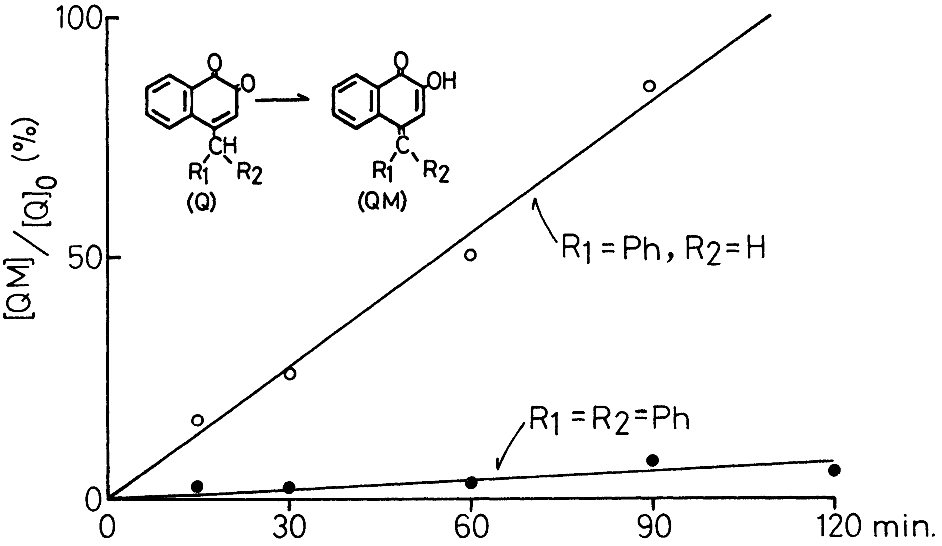


Fig. 1 Plots of isomerization rate of **9** to **10**, and of **14** to **15** on silica gel plate

Thus, alike to xanthenyl radical, benzyl and diphenylmethyl radicals attack at C_4-carbon of 1,2-naphthosemiquinone radical, while phenylacetyl radical attacks at oxygen atoms and C_3-carbon of 1,2-naphthosemiquinone radical similar to other aliphatic acyl radicals.

References and Notes

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6) A benzene solution containing quinone and aldehyde was irradiated (> 340 nm) with a 300-W high-pressure Hg-lamp through a 1 cm of aqueous solution of 2,7-dimethyl-3,6-diazacyclohepta-2,6-diene perchlorate.[6a] 6a) S.L.Murov, "Handbook of Photochemistry", Marcel Dekker, New York, 1973, p. 99. The yields were based on quinone used.
7) **5** : Orange prism; mp 164-166°C; ^{1}H-NMR(CCl$_4$) δ 4.35(s, 2H), 5.88(s, OH), 7.21(s, 5H), 7.34-8.02(m, 5H), 11.36(s, OH); IR(KBr) 3450, 1650 cm^{-1}. **6** : White crystals; mp 108-109°C; ^{1}H-NMR(CDCl$_3$) δ 3.84(s, CH$_2$), 3.95(s, CH$_2$), 5.25(br, OH), 7.04-8.02(m, aromatic-H); IR(KBr) 3375, 1720 cm^{-1}. **9** : Orange prism; mp 178-180°C; ^{1}H-NMR(CCl$_4$) δ 4.02(s, 2H), 6.17(s, 1H), 7.27(s, 5H), 7.48-8.16(m, 4H); IR(KBr) 1690(w), 1650 cm^{-1}; UV(CHCl$_3$) $\lambda_{max}(\varepsilon)$ 404(2400), 340(2280), 271(3340) nm. **10** : Yellow needles; mp 180-182°C; ^{1}H-NMR(CCl$_4$) δ 6.82(s, OH), 7.49(s, 5H), 7.29-8.36(m, 6H); IR(KBr) 3340, 1620 cm^{-1}; UV(CHCl$_3$) $\lambda_{max}(\varepsilon)$ 311(12500), 395(29900) nm; MS, *m/e* 248(M^+).
8) S.Daniloff and E.V.Danilova, Chem. Ber., 59, 1032 (1932).
9) **14** : Orange yellow needles; mp 173.5-174.5°C; ^{1}H-NMR(CCl$_4$) δ 5.65(s, 1H), 5.88(s, 1H), 7.12-8.26(m, 14H); IR(KBr) 1695(w), 1665 cm^{-1}; UV(CHCl$_3$) $\lambda_{max}(\varepsilon)$ 405(2480), 328(3790) nm. **15** : Red crystals; mp 201-202°C; ^{1}H-NMR(CCl$_4$) δ 6.65(s, OH), 6.90 (s, 1H), 7.04-8.02(m, 14H); IR(KBr) 3350, 1615 cm^{-1}; UV(CHCl$_3$) $\lambda_{max}(\varepsilon)$ 428(22000) nm.
10) Volume of the evolution of carbon monoxide in these reactions was 0.2, 2.3, 3.1, and 4.8 ml for phenylacetaldehyde, and 2.1, 6.9, 8.0, and 11.0 ml for diphenylacetaldehyde, after irradiation for 2, 5, 8, and 11 h , respectively
11) E.M.Kosower, "An Introduction to Physical Organic Chemistry", John Wiley & Sons, New York, 1968, p. 86.
12) 4-Benzyl-1,2-naphthoquinone and 4-diphenylmethyl-1,2-naphthoquinone were prepared by the oxidation of 4-benzyl-1-naphthol and 4-diphenylmethyl-1-naphthol with Fremy's salts, respectively.
13) A known concentration (Q_0) of **9** and **14** was spotted on a silica gel plate, and those were developed with benzene after standing for 15, 30, 60, 90, and 120 min, and the spots corresponding to **10** and **15** were eluted with chloroform, and the amounts of QM were determined with electronic spectra.
14) **16** : White crystals; mp 170.5-171°C; IR(KBr) 1760 cm^{-1}; ^{1}H-NMR(CCl$_4$) δ 2.16(s, 3H), 2.36(s, 3H), 6.15(s, 1H), 7.00-7.85(m, 14H).

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