The Photochemical Reaction of 1,2-Naphthoquinone with Hydrogen Donors. An Explanation of the Coupling Sites of Alkyl and Acyl Radicals to 1,2-Naphthosemiquinone Radical

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The photoinduced addition reactions of toluene, diphenylmethane, phenylacetaldehyde, and diphenylacetaldehyde to 1,2-naphthoquinones have been investigated. Benzyl and diphenylmethyl radicals attack the 4-position of 1,2-naphthosemiquinone radical, whereas phenylacetyl radical attacks both the 3-position and the oxygen atoms of the semiquinone radical. The different attacking patterns of alkyl and acyl radicals to the semiquinone radical are successfully interpreted by taking into consideration the charge densities of the radicals concerned.

There is little question about the site of combination in reactions between simple radicals in which odd electrons are comparatively localized. However, since triphenylmethyl dimer was shown to be a cyclohexadiene derivative,[1] the coupling site and the factors governing it have become an issue in combination reactions in which radical centres are not straightforwardly evident.

Recently we reported that the photoinduced reductive addition reaction of 1,2-naphthoquinone with xanthene afforded 2-hydroxy-4-(xanthen-9-yl)naphthalen-1(4H)-one (1),[2] while the reaction with acetaldehyde gave 3-acetylnaphthalene-1,2-diol (2) and an isomeric mixture of naphthalene-1,2-diol mono-acetates (4).[3]. It is evident that these photoinduced reductive addition reactions proceed *via* similar reaction courses, *i.e.*, the photoexcited 1,2-naphthoquinone molecule in the triplet state abstracts hydrogen from xanthene or acetaldehyde to give a triplet radical pair consisting of 1,2-naphthosemiquinone radical and xanthenyl[2c] or acetyl[3c] radical in the solvent cage. The combination of these radicals in the cage yields adducts (1) or (2) and (4). Thus, the regiospecific additions of xanthenyl as well as acetyl radical to 1,2-napthosemiquinone radical are the subject of the present investigation.

We now report (i) additional examples of the different attacking pattern of alkyl and acyl radicals to 1,2-naphthosemiquinone radical and (ii) a rationale of the controlling factors on the radical coupling site.

Results and Discussion

After a benzene solution of 1,2-naphthoquinone and toluene was irradiated for 15 h, the product was separated on a silica gel column to give 4-benzylidene-2-hydroxynaphthalen-1(4H)-one (9a). Diphenylmethane similarly reacted with 1,2-naphthoquinone to yield quinone methide (9b).
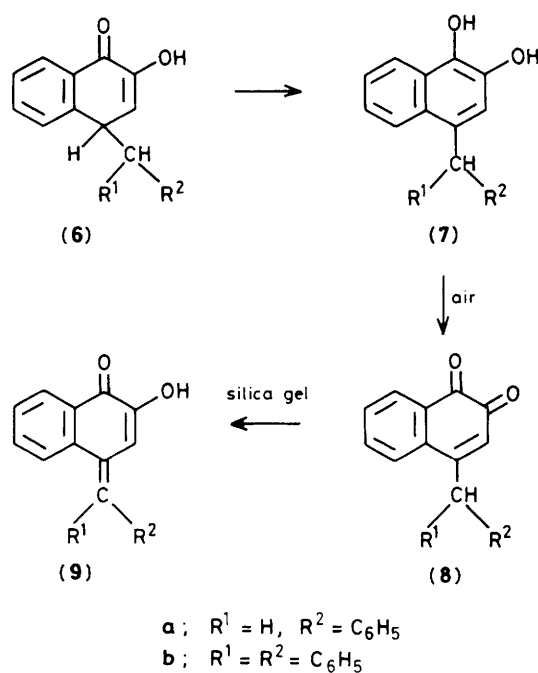
Supposedly the quinone methides (9a and b) are produced during the separating procedures because of the following evidence: (i) after irradiation of a benzene solution of 1,2-naphthoquinone and diphenylmethane, acetic anhydride–pyridine was added to the reaction mixture and the resulting solution was stirred overnight. After separation of the product, 4-diphenylmethylnaphthalene-1,2-diyl diacetate was obtained. This result indicates 4-diphenylmethylnaphthalene-1,2-diol is present in the reaction system. (ii) 4-Benzylnaphthalene-1,2-diol (7a) obtained by the reduction of 4-benzyl-1,2-naphthoquinone (8a) was easily air-oxidized to (8a). (iii) 4-Arylmethyl-1,2-naphthoquinones (8a and b) isomerized to the corresponding quinone methides on passing through a silica gel column.†

(1)

(2) R = CH₃ (4) R = CH₃
(3) R = CH₂C₆H₅ (5) R = CH₂C₆H₅
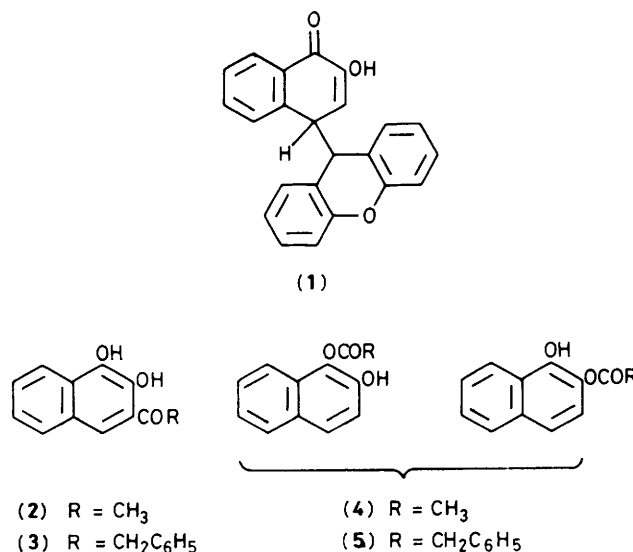
These results strongly indicate a sequence of structural changes from a primary product (6) to a final product (9) as illustrated in the Scheme. The primary product (6) enolizes to 4-arylmethylnaphthalene-1,2-diol (7), which is so air-sensititive that it is easily convertible into (8). The quinone (8) subsequently isomerized to quinone methide (9) during chromatographic separation.

In the photochemical reaction of 1,2-naphthoquinone with phenylacetaldehyde, phenylacetyl radical generated by the hydrogen abstraction by the photoexcited triplet state of 1,2-naphthoquinone undergoes an α-scission to yield benzyl radical and carbon monoxide.[5] Irradiation (λ > 340 nm) of a benzene solution of 1,2-naphthoquinone (1 equiv.) and phenylacetaldehyde (2 equiv.) afforded 3-phenylacetyl naphthalene-1,2-diol (3) (5%), naphthalene-1,2-diol mono(phenylacetate)s (5) (12%), and (9a) (27%). During the course of irradiation carbon monoxide evolved. Thus, phenylacetaldehyde afforded two combination products of both phenylacetyl radical and benzyl radical with 1,2-naphthosemiquinone radical. The products (3) and (5) are the combination products of phenylacetyl radical with 1,2-

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† Acid-catalysed isomerization of (8a) to (9a) was also reported by Fieser and Fieser.[4]

(6) → (7)

air ↓

(9) ← silica gel ← (8)

a ; $R^1 = H$, $R^2 = C_6H_5$
b ; $R^1 = R^2 = C_6H_5$

Scheme.

Figure 1. The coupling sites of alkyl and acyl radicals with 1,2-naphthosemiquinone radical

Figure 2. Charge densities of a, 1,2-naphthosemiquinone radical; b, benzyl radical; and c, acetyl radical

Volumes of carbon monoxide evolved in the photochemical reactions of 1,2-naphthoquinone with phenylacetaldehyde and diphenylacetaldehyde at 20 °C *

Irradiation time (h)	Volume of carbon monoxide (cm^3)	
	$C_6H_5CH_2CHO$	$(C_6H_5)_2CHCHO$
1	0.20	0.52
5	2.25	6.90
11	4.80	11.00
15	4.80	11.00

* A solution of the quinone (1 mmol) and aldehyde (1 mmol) in benzene (20 ml).

naphthosemiquinone radical, while the product (9a) is the combination product of benzyl radical.

On the other hand, irradiation ($\lambda > 340$ nm) of a benzene solution of 1,2-naphthoquinone and diphenylacetaldehyde resulted in the formation of (9b) (60%). No combination product of diphenylacetyl radical with 1,2-naphthosemiquinone radical was detected in this reaction. The Table shows that the decarbonylation of diphenylacetyl radical is more efficient than that of phenylacetyl radical probably because of the higher stability of diphenylmethyl radical than that of benzyl radical.[6] Therefore, the combination product of diphenylmethyl radical with 1,2-naphthosemiquinone radical is the exclusive product in the photochemical reaction of diphenylacetaldehyde with 1,2-naphthoquinone.

In conclusion, as with xanthenyl radical, benzyl and diphenylmethyl radicals attack the 4-position of 1,2-naphthosemiquinone radical, while phenylacetyl radical attacks both the 3-position and the oxygen atoms of 1,2-naphthosemiquinone radical similarly to acetyl radical as illustrated in Figure 1.

To explain the differences in the coupling site of alkyl and acyl radicals to 1,2-naphthosemiquinone radical, the charge densities of 1,2-naphthosemiquinone radical* and benzyl
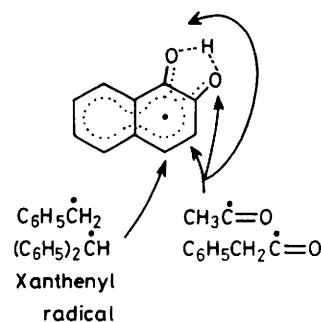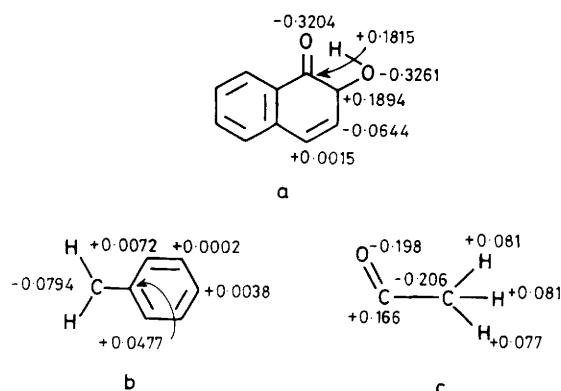
* We assumed that the hydrogen is attached to 2-O rather than 1-O in calculations of the charge densities of 1,2-naphthosemiquinone radical.

radical, as a typical alkyl radical, were calculated using the INDO SCF-MO method (Figures 2a and b),[7] and those of acetyl radical, as a typical acyl radical, were obtained by the STO-3G unrestricted Hartree–Fock method (Figure 2c).[7]

Figure 2a shows that the charge density on C-4 of 1,2-naphthosemiquinone radical is positive, while both C-3 and the oxygen atom have negative charges. The charge on the α-carbon atom of benzyl radical is negative as shown in Figure 2b. In contrast, Figure 2c shows that the carbonyl carbon of acetyl radical has a positive charge. Therefore, benzyl radical attacks the 4-position,† and acetyl radical attacks both the 3-position and the oxygen atoms of 1,2-naphthosemiquinone radical. These interpretations indicate that the charge densities of the radicals are the most important factor which determines the coupling site in combination reactions between 1,2-naphthosemiquinone radical and alkyl or acyl radicals.

Experimental

I.r. spectra were taken on a Hitachi 215 spectrometer. ^{1}H N.m.r. spectra were recorded on a JEOL MH-100 spectrometer, using tetramethylsilane as the internal standard. Mass spectra were measured with a Hitachi M-25 mass spectrometer. U.v. spectra were obtained on a Hitachi 200-20 spectrophotometer. Analytical g.l.c. was performed on a Hitachi 613 chromatograph, using

† Since the charge densities of C-1 and C-2 of 1,2-naphthosemiquinone radical are positive as for C-4, benzyl radical is also able to attack these carbons. However, the resulting 1,2-adduct is too unstable to isolate, and it may decompose to the original radical pair consisting of 1,2-naphthosemiquinone radical and benzyl radical. These phenomena were elucidated by the investigation of the 1,2-naphthoquinone with xanthene by means of the CIDNP technique.[2c]

a column packed with 5% SE-30 on Chromosorb W. Column chromatography was run on Merck silica gel 60 (70—230 mesh), eluted with benzene. 1,2-Naphthoquinone,[8] 4-benzyl-1,2-naphthoquinone,[9] and 4-diphenylmethyl-1,2-naphthoquinone[10] were prepared according to the methods described in the literature. Toluene, diphenylmethane, and phenylacetaldehyde were commercially available and were further purified by distillation. Diphenylacetaldehyde was prepared by the method of Daniloff and Danilova[11] Irradiation was carried out using a 300 W high-pressure mercury arc lamp. The solution to be irradiated was placed in a Pyrex tube and was, after deoxygenation with a stream of nitrogen, sealed with a serum cap. In the reaction with aldehyde, irradiation ($\lambda > 340$ nm) was performed through an aqueous solution (1 cm path length) of 2,7-dimethyl-3,6-diazacyclohepta-2,6-dienylium perchlorate[12] to prevent the excitation of the aldehyde itself.

Irradiation of 1,2-Naphthoquinone with Toluene.—A benzene solution (20 ml) of 1,2-naphthoquinone (158 mg, 1 mmol) and toluene (5 ml) was irradiated for 15 h. After evaporation of the solvent, the residue was chromatographed on a silica gel column to give (**9a**) (13 mg, 5%) as yellow needles, m.p. 180—182 °C (lit.,[4] 181—182 °C); $\nu_{max.}$(KBr) 3 340 (OH), 1 620 (C=O), 1 598, 1 415, and 1 208 cm^{-1}; δ(CCl$_4$) 6.82 (1 H, s, OH), 7.49 (5 H, s, Ph), and 7.29—8.36 (6 H, m, quinonoid H, benzylidene H, and ArH); m/z (%) 248 (M^+, 100), 230 (26), 219 (14), and 202 (47).

Irradiation of 1,2-Naphthoquinone with Diphenylmethane.—(a) A benzene solution (25 ml) of the quinone (1 mmol) and diphenylmethane (1 g, 6 mmol) was irradiated for 48 h. Work-up and chromatography gave 4-diphenylmethylene-2-hydroxynaphthalen-1(4*H*)-one (**9b**) (97 mg, 30%) as red crystals, m.p. 200—202 °C (Found: C, 85.1; H, 5.1. C$_{23}$H$_{16}$O$_2$ requires C, 85.2; H, 5.0%); $\nu_{max.}$(KBr) 3 350 (OH), 1 616 (C=O), 1 590, 1 408, 1 300, and 1 212 cm^{-1}; δ(CCl$_4$) 6.65 (1 H, s, OH), 6.90 (1 H, s, quinonoid H), and 7.40—8.02 (14 H, m, 2 × Ph and ArH).

(b) After irradiation as in (a), acetic anhydride (2 ml) and pyridine (6 ml) were added into the irradiating mixture, and the resulting solution was stirred overnight. The usual work-up and chromatography yielded 4-*diphenylmethylnaphthalene*-1,2-*diyl diacetate* as crystals, m.p. 170—171 °C (Found: C, 78.9; H, 5.4. C$_{27}$H$_{22}$O$_4$ requires C, 79.0; H, 5.4%); $\nu_{max.}$(KBr) 1 770 (ester C=O), 1 605, and 1 200 cm^{-1}; δ(CCl$_4$) 2.16 (3 H, s, OCOCH$_3$), 2.36 (3 H, s, OCOCH$_3$), 6.15 (1 H, s, CH), 6.65 (1 H, s, 3-H), and 7.00—7.85 (14 H, 2 × Ph and ArH).

4-Benzylnaphthalene-1,2-diol and its Oxidation.—4-Benzyl-1,2-naphthoquinone[9] (**8a**) (0.5 mmol) was reduced with sodium dithionite (0.8 g) by the modified method of Fieser and Fieser[4] to yield 4-benzylnaphthalene-1,2-diol (**7a**) (60 mg, 48%) as pale yellow crystals, m.p. 48 °C; $\nu_{max.}$(KBr) 3 350 (OH), 1 605, and 1 100 cm^{-1}. The diol (**7a**) was so air-sensitive that it was oxidized by air to afford the original quinone (**8a**).

Isomerization of (**8a**) *and* (**8b**).—A benzene solution of (**8a**) (0.5 mmol) or (**8b**) (0.5 mmol) was chromatographed on silica gel (10 g) with benzene as eluant to yield the quinone methide (**9a**) (90 mg, 73%) or (**9b**) (129 mg, 80%), respectively.

Irradiation of 1,2-Naphthoquinone with Phenylacetaldehyde.—A benzene solution (80 ml) of 1,2-naphthoquinone (2 mmol) and phenylacetaldehyde (480 mg, 4 mmol) was irradiated for 36 h. During the course of irradiation carbon monoxide evolved. The usual work-up and chromatography yielded 3-*phenylacetylnaphthalene*-1,2-*diol* (**3**) (28 mg, 5%) as orange prisms, m.p. 164—166 °C (Found: C, 77.7; H, 4.9. C$_{18}$H$_{14}$O$_3$ requires C, 77.7; H, 5.1%); $\nu_{max.}$(KBr) 3 450 (OH), 1 650 (C=O), 1 445, 1 340, 1 325, 1 290, 1 180, 950, and 715 cm^{-1}; δ(CCl$_4$) 4.35 (2 H, s, CH$_2$), 5.88 (1 H, s, 1-OH), 7.21 (5 H, s, Ph), 7.34—8.02 (5 H, m, ArH), and 11.36 (1 H, s, 2-OH), *naphthalene*-1,2-*diol mono*(*phenylacetate*)*s* (**5**) (67 mg, 12%), a mixture of isomers (isomer ratio 2:3), as crystals, m.p. 108—110 °C (Found: C, 77.6; H, 5.0. C$_{18}$H$_{14}$O$_3$ requires C, 77.7; H, 5.1%); $\nu_{max.}$(KBr) 3 350 (OH), 1 720 (ester C=O), 1 595, 1 245, and 1 115 cm^{-1}; δ(CDCl$_3$) 3.84 (s, CH$_2$), 3.95 (s, CH$_2$), 5.25 br (OH), and 7.04—8.01 (m, Ph and ArH), (**9a**) (134 mg, 27%), and a small amount of bibenzyl (g.l.c. analysis).

Irradiation of 1,2-Naphthoquinone with Diphenylacetaldehyde.—A solution of 1,2-naphthoquinone (1 mmol) and diphenylacetaldehyde (745 mg, 3.8 mmol) in benzene (25 ml) was irradiated for 15 h. During the course of irradiation carbon monoxide evolved. The usual work-up and chromatography gave (**9b**) (194 mg, 60%) and small amounts of diphenylmethane and 1,1,2,2-tetraphenylethane (g.l.c. analysis).

Measurement of Carbon Monoxide.—The volumes of carbon monoxide, respectively, evolved in the photochemical reactions of 1,2-naphthoquinone (1 mmol) with phenylacetaldehyde (1 mmol) and diphenylacetaldehyde (1 mmol) in benzene (20 ml) at 20 °C were measured periodically by means of an azotometer. The results are summarized in the Table.

References

1 H. Lankamp, W. H. Nauta, and C. MacLean, *Tetrahedron Lett.*, 1968, 249.
2 (a) K. Maruyama and A. Takuwa, *Chem. Lett.*, 1972, 135; (b) K. Maruyama and A. Takuwa, *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1529; (c) K. Maruyama, A. Takuwa, and O. Soga, *J. Chem. Soc., Perkin Trans. 2*, 1979, 255.
3 (a) K. Maruyama and A. Takuwa, *Chem. Lett.*, 1974, 471; (b) A. Takuwa, *Bull. Chem. Soc. Jpn.*, 1976, **49**, 2790; (c) K. Maruyama, A. Takuwa, S. Matsukiyo, and O. Soga, *J. Chem. Soc., Perkin Trans. 1*, 1980, 1414.
4 L. F. Fieser and M. Fieser, *J. Am. Chem. Soc.*, 1939, **61**, 596.
5 K. U. Ingold, in 'Organic Free Radicals,' ed. W. A. Pryor, American Chemical Society, Washington, 1978, p. 190.
6 E. M. Kosower, 'An Introduction to Physical Organic Chemistry,' Wiley, New York, 1968, p. 86.
7 T. Kawamura, unpublished results.
8 A. H. Blatt, 'Organic Syntheses,' Wiley, New York, 1948, Coll. Vol. II, p. 430.
9 L. F. Fieser and C. K. Bradsher, *J. Am. Chem. Soc.*, 1939, **61**, 417.
10 L. F. Fieser and J. L. Hartwell, *J. Am. Chem. Soc.*, 1935, **57**, 1484.
11 S. Daniloff and E. Venus-Danilova, *Chem. Ber.*, 1926, **59**, 1032.
12 S. L. Morov, 'Handbook of Photochemistry,' Marcel Dekker, New York, 1973, p. 99.