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PHOTOCHEMICAL REACTION OF EPOXYNAPHTHOQUINONE WITH AMINE. ITS DEPENDENCY ON SOLVENT STUDIED BY CIDNP TECHNIQUE

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The oxirane ring of epoxynaphthoquinones was reductively opened upon irradiation in the presence of triethylamine and, in addition, a cross adduct was obtained in the reaction with N,N-dimethylaniline in benzene. CIDNP signals observed in the reaction with N,N-dimethylaniline were interpreted as evidence for hydrogen atom abstraction in benzene and for electron transfer in acetone and acetonitrile.

Recently, the photophysical and photochemical behavior of triplet ketones in amine solutions has been extensively studied by means of a variety of techniques as an attractive subject.[1] Among these, CIDNP is an excellent tool by which to distinguish between a) neutral radical pairs and b) radical ion pairs which are responsible for the reproduction of the starting ketones and amines by degenerate process.[2] In this letter, the photochemical reaction of epoxynaphthoquinone (ENQ) with amine was investigated by product analysis as well as CIDNP technique.

Irradiation of a benzene solution of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone 1a (0.012M) in the presence of triethylamine (TEA) (0.1M) with a 300 W high-pressure Hg lamp through a Pyrex filter under a stream of nitrogen gave 2,3-dimethyl-2-hydroxy-1,2,3,4-tetrahydronaphthalen-1,4-dione 2a[3] (70%, trans/cis=1) and 2,3-dimethyl-1,4-naphthoquinone 3a (14%). The products 2a (86%, trans/cis=10) and 3a (6%) were also afforded upon irradiation of 1a and TEA in acetonitrile. Similarly, ENQ 1b-1f were reduced photochemically with TEA, resulting in the formation of the oxirane ring opened-reduced products 2 and 2' and substituted 1,4-naphthoquinones 3 (Table I). On the other hand, mixing of 1a and N,N-dimethylaniline (DMA) in benzene, acetone, or acetonitrile results in the formation of a yellow charge-transfer complex, whose absorption reaches to about 500 nm. Irradiation of a benzene solution of 1a (0.012M) and DMA (0.06M) gave a cross adduct 4a (mp 155-156°C, 32%), in addition to trans-2a (12%) and N-methylaniline (45%[4]). The structure of 4a was determined on the basis of its spectral data and elemental analysis.[5] When irradiated in acetonitrile, 1a and DMA gave a rather complex mixture from which low yields of trans-2a (8%) and N-methylaniline (12%) were isolated but the formation of 4a was not observed.

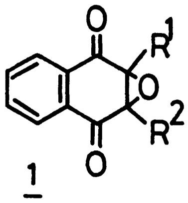
Typical CIDNP signals obtained on irradiation of a solution of 1a and DMA in benzene-d_6, acetone-d_6, or acetonitrile-d_3 are shown in Figure I.[6] In nonpolar solvents such as benzene-d_6, strong polarization was observed for the methyl protons of 1a

Table I Photoreduction of Epoxynaphthoquinones with Triethylamine in Benzene

	Epoxynaphthoquinone		Product Distribution (%)^a		
	R^1	R^2	2(t/c)	2'	3
1a	Me	Me	35/35	-	14
1b	Et	Et	33/31	-	19
1c	Me	H	-	44	14
1d	CH_2Ph	H	-	56	7
1e	Me	CH_2OPh	53/7	8	6
1f	Me	$CH_2C(CH_3)_3$	44/16	6	11

a, Isolated yields based on the consumed amount of ENQ.

b, Sum of the yields of trans-2' and cis-2'.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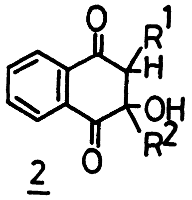
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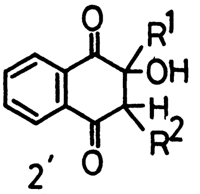
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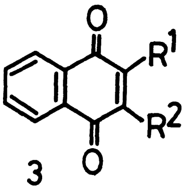
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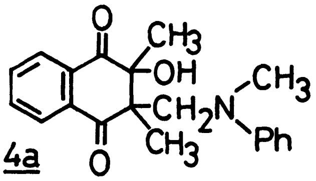
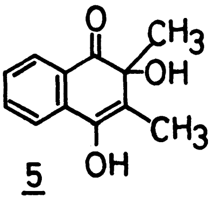

4a

(a; designated in Figure I, E) and DMA (d, A), in addition to enhanced absorption siganls (b,c, and e, A), of which b and c disappeared in the reaction of 1a-d_6 (R^1=R^2=CD_3). In acetone-d_6, however, the polarized direction for the methyl protons of DMA was inverted. In contrast, irradiation of 1a and DMA in polar solvents such as acetonitrile-d_3 caused selective line broadening for the methyl protons (g) and the ortho protons (h) of DMA. The line broadening indicated rapid and degenerate electron exchange between $DMA^{+\cdot}$ and DMA, since it was observed only during irradiation.[7] Light-induced polarizations and broadening were almost completely suppressed in the presence of piperylene (0.1M), indicating the triplet reaction. By analyzing the polarization with the aid of Kaptein's rules[8], the triplet neutral radical pair (between 7 and 8) is suggested to be involved in benzene-d_6, which can explain the formation of 4a and trans-2a as well, while the triplet radical ion pair (between 9 and 10) is suggested in acetone-d_6. The polarized signals b,c, and e suggested the formation of unstable intermediates, whose structures were not decisive yet, but they could be assigned to 5 and 6, respectively, on the basis of their chemical shifts and the results starting with 1a-d_6 . In acetonitrile, the radical pair seems to diffuse apart into the solvent rather than regenerate 1a and DMA by reverse electron transfer. The similar CIDNP effects and solvent dependency were observed when 1a was subjected into the light-induced reaction with a variety of aromatic amines: N,N-diethylaniline, N,N-dibenzylaniline[9], N-benzyl-N-methylaniline[9], N,N-dimethyltoluidine, and N,N-dimethl-1-naphthylamine. The solvent effects observed in 1a and DMA system are quite parallel to the results on the primary reaction of the triplet benzophenone with N,N-diethylaniline studied by Arimitsu et al.[10], where they measured the yields of product ions and ketyl radicals in various solvents and revealed that the course of the reaction was solvent-dependent; in polar solvents such as acetonitrile ionic dissociation took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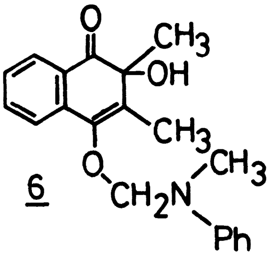
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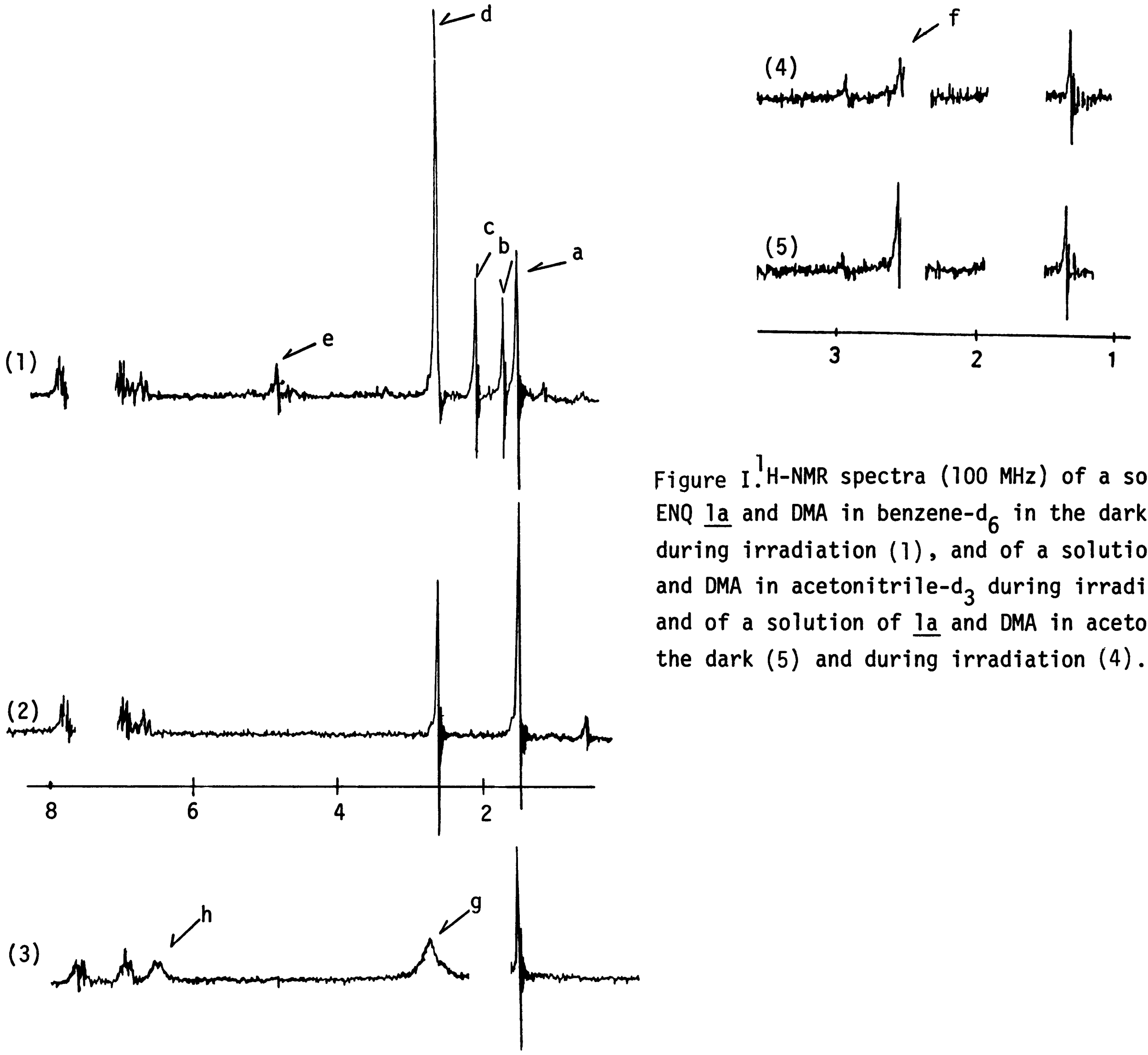
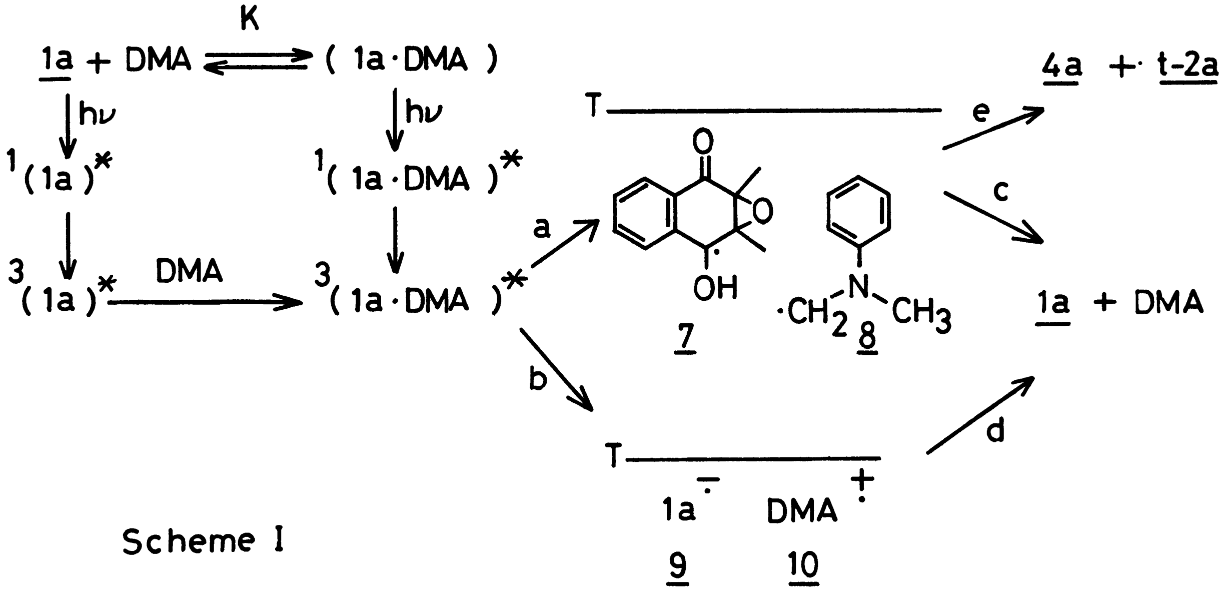


Figure I. ^{1}H-NMR spectra (100 MHz) of a solution of ENQ 1a and DMA in benzene-d_6 in the dark (2) and during irradiation (1), and of a solution of 1a and DMA in acetonitrile-d_3 during irradiation (3), and of a solution of 1a and DMA in acetone-d_6 in the dark (5) and during irradiation (4).



Scheme I

place completely, while the hydrogen atom abstraction proceeded exclusively in non-polar solvents such as benzene.

No detectable CIDNP signal was observed in 1a and TEA system in benzene-d_6, presumably because of practical lack of the back process in the neutral radical pair, but distinct CIDNP effects, which can be interpreted as evidence for the disproportionation in the triplet neutral radical pair, were observed in more polar solvents such as acetone-d_6 and acetonitrile-d_3.

References

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2. a) H. D. Roth and A. A. Lamola, J. Am. Chem. Soc., 96, 6270(1974). b) H. D. Roth and M. L. Manion, ibid., 97, 6886(1975). c) B. M. P. Hendriks, R. I. Walter, and H. Fisher, ibid., 101, 2378(1979).
3. trans-2a; A. Osuka, H. Suzuki, K. Maruyama, Chem. Lett., 1981, 201. Spectral data of cis-2a are as follows; IR(CCl_4) 3460(OH), 1695(C=O), 1600, and 1250 cm^{-1}; ^1H-NMR ($CDCl_3$) δ 1.19(d, J=6Hz, 3H), 1.43(s, 3H), 3.22(q, J=6Hz, 1H), 4.00(mobile, 1H), 7.7-7.9(m, 2H), and 8.0-8.2(m, 2H).
4. Based on the consumed amount of 1a.
5. Spectral data of 4a are as follows; IR(KBr) 3460(OH), 1680(C=O), 1600, 1500, 1350, 1280, and 1140 cm^{-1}; ^1H-NMR ($CDCl_3$)δ 1.24(s, 3H), 1.38(s, 3H), 2.66(N-CH_3), 3.40 and 3.64(ABq, J=15Hz, N-CH_2), 6.1-6.3(m, 2H), 6.4-6.6(m, 1H), 6.7-6.9(m, 2H), 7.3-7.5(m, 2H), 7.7-7.9(m, 2H); ^{13}C-NMR($CDCl_3$) 200.3(C=O), 197.3(C=O), 77.1(s), 62.9(s), 58.7(t), 43.6(q), 26.4(q), 24.8(q), and ten aromatic carbons. Anal. Calcd. for $C_{20}H_{21}O_3$: C, 74.28; H, 6.55; N, 4.33%. Found: C, 74.24; H, 6.53; N, 4.12%. Stereochemistry of 4a was not determined yet.
6. The device used for measurement of CIDNP during irradiation was described elsewhere; K. Maruyama, T. Otsuki, A. Takuwa, and S. Arakawa, Bull. Chem. Soc. Jpn., 46, 2460 (1973). Irradiation of charge-transfer complex of 1a-DMA ($\lambda > 400$ nm) gave rise to the similar CIDNP effects but their intensities were rather weak, presumably because of poor light intensity. Thus, light of wavelength longer than 300 nm was used for the CIDNP examination.
7. M. L. M. Schilling, R. S. Hutton, and H. D. Roth, J. Am. Chem. Soc., 99, 7792(1977)
8. R. Kaptein, J. Chem. Soc., Chem. Comm., 1971, 732. Available data permit a reasonable estimate for the radical parameter: g(7), g(9)$\gtrsim$2.0035, ref. 2c); g(8)=2.0030, ref. 2b); g(10)$\simeq$2.0028, ref. 2c); $a_H(\overset{+\cdot}{N}CH_3) > 0$, and $a_H(\overset{\cdot}{N}CH_2) < 0$.
9. In these cases, strong polarized absorption was observed for the formyl proton of resulting benzaldehyde in benzene-d_6.
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