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PHOTOCHEMICAL REACTION OF EPOXYNAPHTHOQUINONES WITH ALCOHOLS. AN IONIC TRAPPING OF CARBONYL YLIDES

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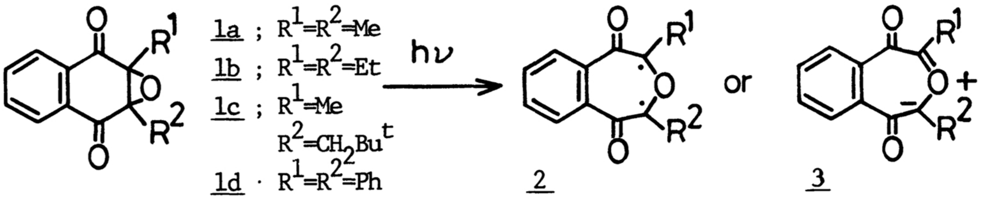
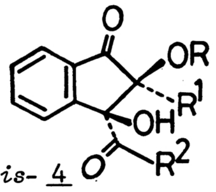
Irradiation of several 2,3-dialkyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinones in the presence of alcohol gave ring-contracted alcohol-adducts <u>via</u> nucleophilic addition of alcohol to carbonyl ylides.

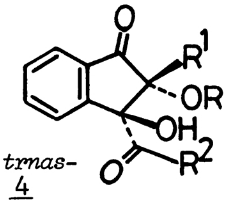
Recently, the photo-induced cycloadditions of epoxynaphthoquinones 1 to electron-rich and electron-deficient olefins,[1] aldehydes and ketones,[2] and singlet oxygen[3] were reported. The formation of the adducts has been interpreted by the photo-induced opening of the oxirane ring to form a carbonyl ylide 3 or 1,3-diradical 2 which is subsequently trapped by a suitable π-system.[4] The former has a zwitter-ionic structure and therefore is expected to be trapped by alcohol. In the present work, we have investigated the photochemical reaction of 1 in the presence of alcohol.


1a ; $R^1=R^2=Me$
1b ; $R^1=R^2=Et$
1c ; $R^1=Me$, $R^2=CH_2Bu^t$
1d ; $R^1=R^2=Ph$

Irradiation of a benzene solution (0.03M) of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone 1a in the presence of methanol (1.66M) with a 300-W high-pressure Hg lamp gave ring-contracted methanol-adducts, *cis*-4a (mp 87-88°C, 44%) and *trans*-4a (mp 62-64°C, 8%), 2,3-dimethyl-1,4-naphthoquinone 5a (7%), and 2,3-dimethyl-2-hydroxy-1,2,3,4-tetrahydronaphthalin-1,4-dione 6a (mp 86-88°C, 3%). The structures of the products were assigned on the basis of their spectral data and elemental analyses.[5] Similar irradiation of 1b[6] and 1c gave 4b (33%, *cis/trans*=2.2), 5b (12%), and 6b (3%),

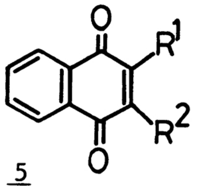


cis- 4



trnas- 4

4a ; $R^1=R^2=Me$, R=Me
4b ; $R^1=R^2=Et$, R=Me
4c ; $R^1=Me$, R=Me, $R^2=CH_2Bu^t$
4d ; $R^1=CH_2Bu^t$, R=Me, $R^2=Me$,
4e ; $R^1=R^2=Me$, R=Et



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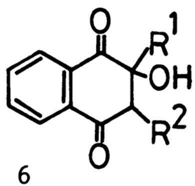

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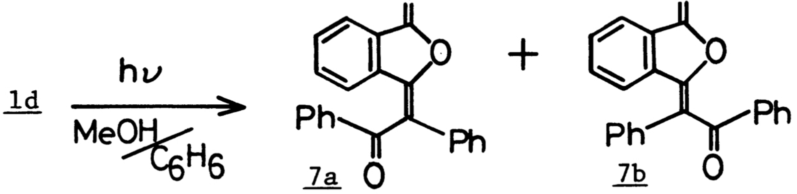
and 4c (30%, *cis/trans*=1.1), 4d (32%, *cis/trans*=1.4), and 5c (8%), respectively. However, irradiation of 1d under similar conditions led only to a slow photoisomerization to the alkylidene phthalides 7a and 7b[1b] and neither methanol-adduct nor photoreduction product was obtained.



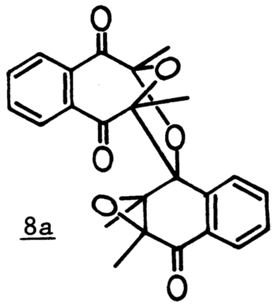
We have recently reported that allyl alcohols can efficiently trap 2 or 3 with double bond but not with hydroxyl group; the results indicate the nucleophilic addition of alcohols occurs more slowly than the 1,3-cycloaddition of olefins[7]. On the basis of this finding, the photoreactions of 1a with primary, secondary, and tertiary alcohols were studied. As shown in the Table, ethanol-adducts, *trans*-4e and *cis*-4e, were formed in 10 and 30% yields, respectively, in the irradiation of 1a in benzene at [EtOH]=1.66M, while 2-propanol and tert-butyl alcohol showed no ability of trapping 2 or 3. In the presence of 2-propanol, at [Pr^{i}OH]=1.66M, or in tert-butyl alcohol, the photoexcitation of 1a resulted only in the formation of dimers 8a and 8b *via* 2 or 3 (runs 8, 10, and 11). The photoreduction products, 5a and 6a, which may arise from the hydrogen abstraction of $^3(n, \pi^*)$ of 1a from alcohols were formed significantly at high concentration of methanol (runs 1, 2, and 5) and ethanol (runs 6 and 7) and predominantly in 2-propanol (run 9).

The formation of alcohol-adducts may most reasonably be explained in terms of either 1,3- or 1,5-nucleophilic addition of alcohol to the carbonyl ylide 2[8], followed by ring opening and intramolecular aldol condensation[9]. Observed steric effects for the formation of 4 is consistent with the mechanism involving the nucleophilic addition of alcohols. In the cases of 1a, 1b, and 1c, therefore, the photoexcitation seems likely to lead to intermediates with much ylide character. The relative rates of the nucleophilic addition of methanol and ethanol to that of the 1,3-cycloaddition

Table. Photochemical Reaction of 1a [a] in the Presence of Alcohols

Run	Solvent	Alcohol(M)	Conv.(%)	Product Distribution[b] 4	5	6	8 [c]
1	C_6H_6	MeOH (1.66)	80	52^d	7	3	-
2	C_6H_6	MeOH (1.66)	35	73^d	5	2	-
3	C_6H_6	MeOH (0.8)	40	65^d	3	1	2
4	C_6H_6	MeOH (0.2)	15	53^d	-	-	18
5	MeOH	-	82	43^d	12	4	-
6	C_6H_6	EtOH (1.66)	95	40^e	18	6	7
7	EtOH	-	60	28^e	40	11	-
8	C_6H_6	Pr^iOH (1.66)	20	-	2	5	78
9	Pr^iOH	-	25	-	55	28	-
10	C_6H_6	Bu^tOH (5.3)	60	-	-	-	85
11	Bu^tOH	-	65	-	-	-	82

a, Initial concentration; 30 mM. b, Determined by HPLC analysis of the reaction mixture; yields were based on the amount of reacted 1a . c, Sum of the yields of dimers 8a and 8b . d, Sum of the yields of *cis*- 4a and *trans*- 4a . e, Sum of the yields of *cis*- 4e and *trans*- 4e .



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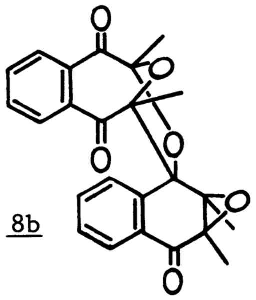

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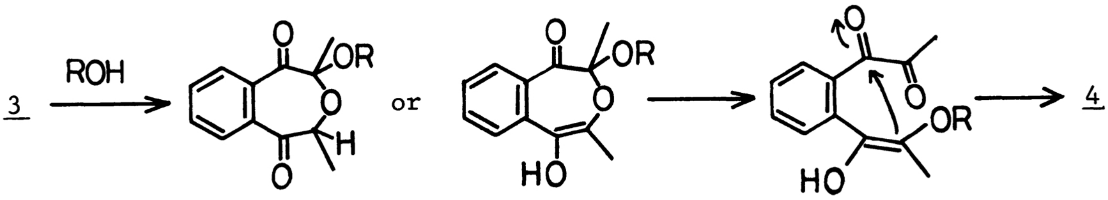

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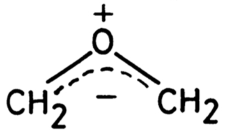
of the carbonyl group of 1a were calculated to be 0.44 and 0.10, respectively, on the basis of the product distributions observed in runs 4 and 6. As for 1d, one may envisage a 1,3-diradical character in the open form of oxirane ring. However, since it has been shown that the carbonyl ylide 3 or 1,3-diradical 2 largely cyclizes to reproduce 1,[10] the alternative possibility, that the cyclization is much faster than the nucleophilic addition of methanol to 2d, cannot be ruled out.

References and Notes

1. a) S. Arakawa, J. Org. Chem., 42, 3800(1977). b) H. Kato, H. Tezuka, K. Yamaguchi, K. Nowada, and Y. Nakamura, J. Chem. Soc., Perkin I, 1029(1978).
2. K. Maruyama and A. Osuka, Chem. Lett., 1979, 77.
3. K. Maruyama, A. Osuka, and H. Susuki, J. Chem. Soc., Chem. Comm., 723(1980).
4. A diradical character of the open form of 1 may depend on the substituents at 2- and 3-positions. According to the theoretical calculations on ethylene oxide, the carbonyl ylide C is predicted to possess a 38% diradical character. E. F. Hayes and A. K. Q. Siu, J. Am. Chem. Soc., 93, 2090(1971).



C

5. All new compounds gave satisfactory elemental analyses and spectral data. Selected spectral data follow. *cis*-4a; IR (KBr) 3460 (OH), 1720(conjugated five-membered ketone), 1603, 1459, and 1234 cm^{-1}; ^1H-NMR ($CDCl_3$) 1.26($-CH_3$), 2.35($-COCH_3$), 3.24 ($-OCH_3$), and 7.3-7.8(m, 4H); ^{13}C-NMR ($CDCl_3$) 201.7(C=O), 200.7(C=O), 91.0(s), 85.4 (s), 55.0(q), 21.0(q), and 19.4(q). *trans*-4a; IR (KBr) 3400(OH), 1725(conjugated five-membered ketone), 1600, 1455, and 1240 cm^{-1}; ^1H-NMR ($CDCl_3$) 1.40($-CH_3$), 1.80 ($-COCH_3$), 3.36($-OCH_3$), and 7.4-8.1(m, 4H). *cis*- and *trans*-4a were converted into acetates, *cis*-4a-acetate (mp 122-123°C, 78%, $HClO_4/Ac_2O$) and *trans*-4a-acetate (mp 99-101°C, 75%, $HClO_4/Ac_2O$). Stereochemistry of 4a was determined by comparison of each ^1H-NMR spectrum with that of each acetate, on the basis of the fact that the chemical shifts of methyl or methoxyl groups *cis* to hydroxyl group shift to lower field on acetylation. *cis*-4a-acetate; ^1H-NMR ($CDCl_3$) 1.22($-CH_3$), 2.06($-COCH_3$), 2.20($-OCOCH_3$), and 3.57($-OCH_3$). *trans*-4a-acetate; ^1H-NMR ($CDCl_3$) 1.57($-CH_3$), 2.02 ($-COCH_3$), 2.24($-OCOCH_3$), and 3,21($-OCH_3$). 6a; IR (KBr) 3500(OH), 1690(conjugated six-membered ketone), and 1270 cm^{-1}; ^1H-NMR ($CDCl_3$) 1.26(s, 3H), 1.42(d, J=6Hz, 3H), 3.16(q, J=6Hz, 1H), 4.00(mobile, 1H), 7.66-7.84(m, 2H), and 8.00-8.17(m, 2H); ^{13}C-($CDCl_3$) 201.3(C=O), 196.3(C=O), 78.4(C_2), 53.7(C_3), 22.1(q), and 7.6(q). The structure of 6a was confirmed by converting it into 5a (82%, $HClO_4/Ac_2O$).
6. Type II photoelimination product, 2-ethyl-3-hydroxy-1,4-naphthoquinone, was formed in 4-5% yield.
7. K. Maruyama, A. Osuka, and H. Suzuki, Chem.Lett., 1980, 919.
8. 1,5-Ethanol addition to carbonyl ylide was reported. E. F. Ullman and W. A. Henderson, J. Am. Chem. Soc., 88, 4942(1966).
9. Similar intramolecular aldol condensations have been considered in Hooker oxidation; the oxidative ring contraction of 2-hydroxy-1,4-naphthoquinones with hydrogen peroxide. P. Hodge, in " The Chemistry of Quinonoide Compounds", S. Patai, Ed., Wiley, New York, N. Y. , 1974, p. 592.
10. K. Maruyama and A. Osuka, J. Org. Chem., 45, 1898(1980).

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