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STEREOSELECTIVE PHOTOCYCLOADDITION OF EPOXYNAPHTHOQUINONES TO ALLYL ALCOHOLS

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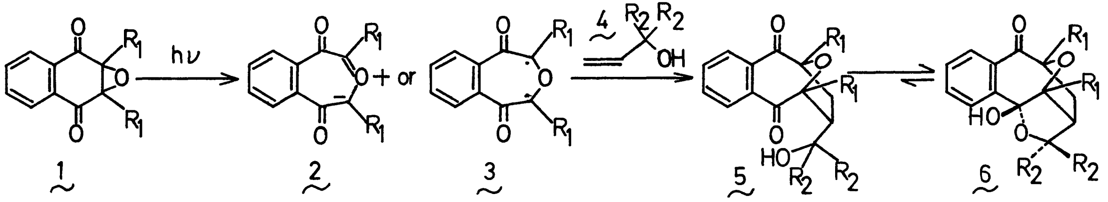
Irradiation of a benzene solution of 2,3-disubstituted epoxynaphthoquinones and allyl alcohols gave tetracyclic hemiketals 6.

Recently the photochemical generation of the carbonyl ylides 2 or 1,3-diradicals 3 from several epoxynaphthoquinones 1 has been reported.[1] These products are trapped by olefins, giving tricyclic tetrahydrofuran derivatives. However, isolation of these primary cycloadducts usually requires work-up at a low conversion, since they are photolabile and readily converted into alkylidene phthalides or spiro-[oxetanphthalide]s.[1] Now we have found the photo-induced cycloaddition of epoxynaphthoquinones to allyl alcohols gives tetracyclic compounds containing hemiketal linkage in good yields even at a high conversion of epoxynaphthoquinones.



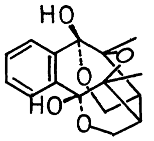
Typically, irradiation of 2,3-epoxy-2,3-dihydro-2,3-dimethyl-1,4-naphthoquinone (1a) (8.25 mM) and allyl alcohol (4a)(100 mM) in benzene with a 300W high-pressure Hg lamp through a Pyrex filter resulted in the stereoselective formation (84%) of tetracyclic compound (6a). The structure of 6a was determined by its elemental analysis and the following spectral data: IR(KBr) 3320(OH), 1700(C=O), and 1120 cm^{-1}; ^1H NMR ($CDCl_3$) 1.34(s, 3H), 1.50(s, 3H), 2.30(m, 2H), 2.63(m, 1H), 2.84(mobile, 1H), 3.75(d, J=10Hz, 1H), 4.04(dd, J=7 and 10Hz, 1H), and 7.36-7.70(m, 4H); ^{13}C NMR ($CDCl_3$) 203.2(s), 107.4(s), 94.4(s), 89.7(s), 71.3(t), 50.2(d), 44.1(t), 24.9(q), 19.5(q), and six sp^2 carbons; Mass (m/e) 260(M^+), 242(M^+-H_2O), 204, 186, and 184.

Similar cycloadducts 6b, 6c, and 6d were formed in moderate to high yields on irradiation of 1a and 1b with 4a or 2-methyl-3-butene-2-ol 4b (Table). The photocycloaddition of 1c showed a marked dependence on the olefins used; the cycloadduct 6e was obtained in 82% yield from the reaction with 4a but the intermediary ylide 2c (R_1=Ph) or 1,3-diradical 3c(R_1=Ph) was not trapped by 4b at all. In the hope of obtaining a cage compound 7, the photocycloaddition of 1a to *cis*-2-buten-1,4-diol was attempted, but mono-hemiketal 8 was formed in 84% yield.[2] In all runs examined, the corresponding exo-adducts were not found in the reaction mixture.

Table

1	R_1	4	R_2	Products(mp)	Yields(%)[a)]
1a	Me	4a	H	6a(183-184)	84
1a	Me	4b	Me	6b(198)	62
1b	Et	4a	H	6c(147-148)	69[b)]
1b	Et	4b	Me	6d(164-165)	64[b)]
1c	Ph	4a	H	6e(227-228)	82
1c	Ph	4b	Me	c)	-

a) Isolated yields based on the amount of 1 used. b) Type II photoelimination product, 2-ethyl-3-hydroxy-1,4-naphthoquinone, was formed in 4-5% yield. c) Photoisomerization to alkylidene phthalides was only observed. Ref. 1c.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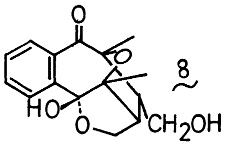
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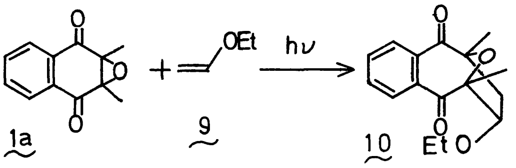
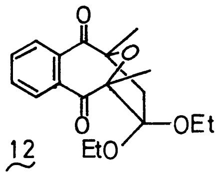
The lone pair electrons of allyl alcohols may play an important role in the stereoselective formation of 6 through the so-called secondary π-orbital overlap interaction with 1,3-dipole. Thus, we examined the photochemical reaction of 1a with ethyl vinyl ether 9, which yielded 10 (mp, 108-109°C) as the only primary adduct (in 75% yield at 30% conversion of 1a). The stereochemistry of 10 was determined by high field shift of methyl protons in ethoxy group(δ 0.74) due to the shielding effect of the benzene ring.[3] Intramolecular 1,4-hemiketal formation protects 6 against the secondary photoisomerization which may arise only from the diketo-form 5.

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The present results may provide an example that the photo-labile cycloadducts can be obtained by masking the photo-sensitive functionality with some groups of 1,3-dipolarophiles intramolecularly.

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. Spectral data of 8; mp 214-215°C; IR(KBr) 3400(OH), 1700(C=O), and 1250 cm^{-1}; ^1H NMR ($CDCl_3$) 1.33(s, 3H), 1.50(s, 3H), 2.60(m, 2H), 2.80(mobile, 1H), 3.80-4.00(m, 4H), 5.30(mobile, 1H), and 7.3-7.8(m, 4H).
3. To assure the structural proof on 10, the photochemical reaction of 1a with 1,1-diethoxyethylene 11 was examined. In the ^1H NMR spectrum of the corresponding primary adducts 12, methyl protons of two ethoxy groups appeared at 0.76 and 1.20, relating to endo- and exo-ethoxy group, respectively.
4. A referee suggested the groud-state interactions of 1 and 4 by hemi-ketal formation. The ^1H NMR and UV spectra of 1a in the presence of various amount of 4a, but no appreciable interaction was observed.

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