## 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  $\underline{2}$  or 1,3-diradicals  $\underline{3}$  from several epoxynaphthoquinones  $\underline{1}$  has been reported.<sup>1</sup> 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-[oxetan-phthalide]s.<sup>1</sup> Now we have found the photo-induced cycloaddition of epoxynaphtho-quinones 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 ( $\underline{4a}$ )(100 mM) in benzene with a 300W high-pressure Hg lamp through a Pyrex filter resulted in the stereoselective formation (84%) of tetracyclic compound ( $\underline{6a}$ ). The structure of  $\underline{6a}$  was determined by its elemental analysis and the following spectral data: IR(KBr) 3320(0H), 1700(C=0), and 1120 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 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); <sup>13</sup>C NMR (CDCl<sub>3</sub>) 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<sup>2</sup> carbons; Mass (m/e) 260(M<sup>+</sup>), 242(M<sup>+</sup>-H<sub>2</sub>0), 204, 186, and 184.

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

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<u>1</u>	<sup>R</sup> 1	<u>4</u>	<sup>R</sup> 2	Products(mp)	Yields(%) <sup>a)</sup>
<u>la</u>	Me	<u>4a</u>	Н	<u>6a</u> (183-184)	84
<u>la</u>	Me	<u>4b</u>	Me	<u>6b</u> (198)	62
<u>1b</u>	Et	<u>4a</u>	Н	<u>6c</u> (147-148)	69 <sup>b)</sup>
<u>1b</u>	Et	<u>4b</u>	Me	<u>6d</u> (164-165)	64 <sup>b)</sup>
<u>lc</u>	Ph	<u>4a</u>	Н	<u>6e</u> (227-228)	82
<u>lc</u>	Ph	<u>4b</u>	Me	c)	-

a) Isolated yields based on the amount of <u>1</u> 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. lc.

The lone pair electrons of allyl alcohols may play an important role in the stereoselective formation of <u>6</u> through the so-called secondary  $\pi$ -orbital overlap interaction with 1,3-dipole. Thus, we examined the photochemical reaction of <u>1a</u> with ethyl vinyl ether <u>9</u>, which yielded <u>10</u> (mp, 108-109°C) as the only primary adduct (in 75% yield at 30% conversion of <u>1a</u>). The stereochemistry of <u>10</u> was determined by high field shift of methyl protons in ethoxy group( $\delta$  0.74) due to the shielding effect of the benzene ring.<sup>3</sup> Intramolecular 1,4-hemiketal formation protects <u>6</u> against the secondary photoisomerization which may arise only from the diketo-form <u>5</u>.



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

- a) S. Arakawa, J. Org. Chem., <u>42</u>, 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 <u>8</u>; mp 214-215°C; IR(KBr) 3400(0H), 1700(C=0), and 1250 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) 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 <u>10</u>, the photochemical reaction of <u>la</u> with l,l-diethoxyethylene <u>11</u> was examined. In the <sup>1</sup>H NMR spectrum of the corresponding primary adducts <u>12</u>,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  $\underline{1}$  and  $\underline{4}$  by hemi-ketal formation. The <sup>1</sup>H NMR and UV spectra of  $\underline{1a}$  in the presence of various amount of  $\underline{4a}$ , but no appreciable interaction was observed.

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