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PHOTO-INDUCED CYCLOADDITIONS OF EPOXYQUINONE TO ALDEHYDES AND KETONES

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Irradiation of a benzene solution of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (1) and an aldehyde gave 1,3-dioxolanes 3 and 4 in high yields. Photolysis of 1 in a ketone gave 1,3-dioxolane 5.

Photo-induced ring opening reactions at C-C bonds of oxiranes have attracted considerable synthetic interest and been a recent subject of mechanistic scrutiny[1). It is well known that carbonyl ylides generated thermally or photochemically from aryl oxiranes react with olefins to yield tetrahydrofuran derivatives. Houk suggested that the frontier orbital energies of carbonyl ylides are dominant factors for the reactivities toward various dipolarophiles[2). We have found that 2,3-dialkyl substituted epoxynaphthoquinones undergo photo-induced cycloadditions to electron-rich olefins as well as electron-deficient olefins, indicating the oxirane C-C bond cleavage leading to carbonyl ylides (or 1,3-diradicals)[3). We found, for the first time, that even aldehydes and ketones were able to trap the ylide.

We wish to report here the photo-induced cycloadditions of 2,3-dimethyl-2,3-epoxy-2,3-dihydro-1,4-naphthoquinone (1) to aldehydes and ketones. The cycloaddition of 1 to acetaldehyde represents the reactions. Irradiation of a benzene solution of 1 in the presence of acetaldehyde with light of wavelength above 300 nm for half an hour afforded two stereoisomeric 1,3-dioxolanes 3a and 4a in 58 and 34% yields, respectively. Consistent with the structure assignment, both 3a and 4a showed conjugated carbonyls at 1680 and 1685 cm^{-1} in their IR spectra, respectively, and the ^{1}H NMR spectra of 3a and 4a resembled well each other: 3a; (CCl_4) δ 1.18 (d, J=8Hz, 3H), 1.56 (s, 3H), 1.66 (s, 3H), 4.00 (q, J=8Hz, 1H), 7.60-7.75 (m, 2H), and 7.94-8.18 (m, 2H); 4a; (CCl_4) δ 1.30 (d, J=8Hz, 3H), 1.48 (s, 3H), 1.66 (s, 3H), 4.32 (q, J=8Hz, 1H), and 7.52-7.96 (m, 4H). Aldehydes 2b-e were found to react with 1 to give 1,3-dioxolanes 3b-e and 4b-e in mod-

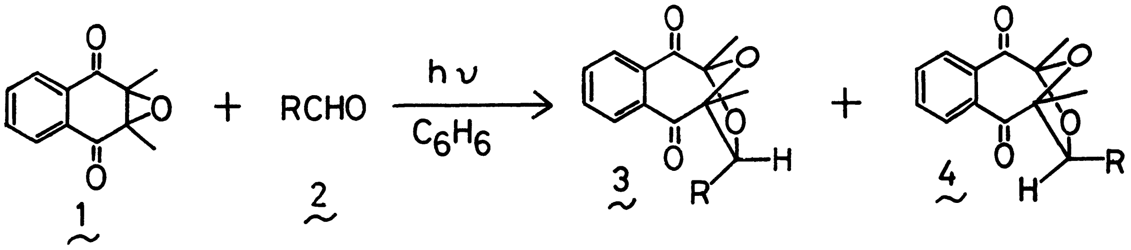
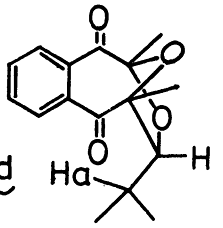
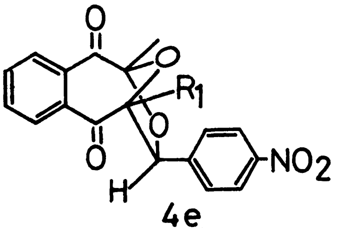


Table I Photocycloaddition of 1[a] to Aldehydes[b]

R	Total Yields[c]	3/4[d]	Products 3 (mp °C)	4 (mp °C)
Me	71 (92)[e]	1.7	3a (98)	4a (89)
Et	75	1.9	3b (92)	4b (80)
n-Pr	65	1.8	3c (oil)	4c (82)
i-Pr	60	1.0	3d (94)	4d (90-91)
Ar[f]	78	0.33	3e (165)	4e (187)

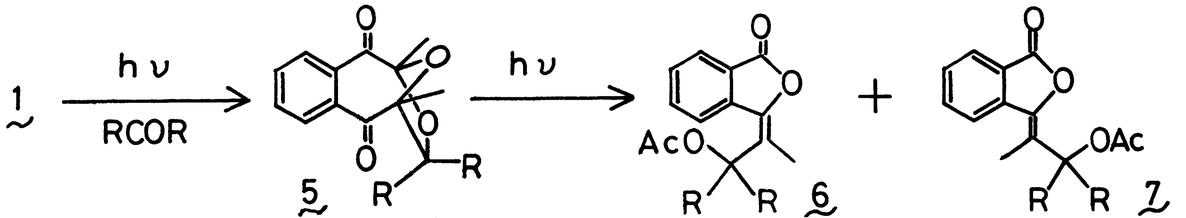
a, Epoxyquinone ; 10 mM. b, Degassed benzene solutions were added 10 eq. of aldehydes. c, Isolated yields. d, Isomer ratios determined by HPLC. e, ^1H NMR yield. f, Ar=p-nitrophenyl.


3d


4e

erate to high yields (Table I). In the ^1H NMR spectra of 4a-e, the methine protons are deshielded by the carbonyl group occupied cis to these protons. The H_a proton of 3d is considerably shielded (δ 1.50) by the benzene ring presumably because of somewhat restricted free rotation of isopropyl group (compare, the H_a of 4d; δ 1.96). The marked upfield shift in 4e for R_1 methyl (δ 1.15) resulting from shielding by the aromatic ring provides strong support for the structure determination.

On the other hand, photolysis of a highly diluted acetone solution of 1 (8.25 mM) gave 5a in 85% yield. 5a; colorless crystals, mp 86.5°C; IR (KBr) 2990, 1680 (a conjugated ketone), 1592, and 1150 cm^{-1}; ^1H NMR (CCl_4) δ 1.18 (s, 3H), 1.40 (s, 3H), 1.50 (s, 3H), 1.70 (s, 3H), 7.65-7.76 (m, 2H), and 7.98-8.20 (m, 2H). These spectral data



5a, R=Me; 5b, R=Et;
5c, R-R=$(CH_2)_4$; 5d, R-R=$(CH_2)_5$

6a, R=Me;
6d, R-R=$(CH_2)_5$

7a, R=Me;
7d, R-R=$(CH_2)_5$

Table II Photocycloaddition of 1 to Ketones

Ketone	Conc.(mM)	Product Distribution(%)[a]			
		5	6	7	Dimers[b]
Acetone	82.5	23	-	-	39
Acetone	8.25	85	4	3	-
3-Pentanone	40	12	c	c	12
Cyclopentanone	8.25	69	-	-	18
Cyclohexanone	82.5	57	-	-	21
Cyclohexanone	8.25	78	12	7	-

a, Isolated yields. b, See note 4). c, Not isolated, but observed by ^{1}H NMR.

of 5a are consistent with the 1,3-dioxolane structure. Upon further irradiation, 5a underwent photochemical isomerization to give alkylidene phthalides 6a and 7a in 45 and 20% yields, respectively. 6a; colorless crystals, mp 111-113°C; IR (KBr) 2990, 1763 (a strained five-membered lactone), and 1743 (ester) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.74 (s, 6H), 1.90 (s, 3H), 2.24 (s, 3H), and 7.24-8.37 (m, 4H): 7a; colorless oil; IR (CCl$_4$) 2990, 1768 (a strained five-membered lactone), and 1740 (ester) cm^{-1}; ^{1}H NMR (CCl$_4$) δ 1.74 (s, 6H), 2.02 (s, 3H), 2.14 (s, 3H), and 7.40-7.92 (m, 4H). The allylic methyl protons of 7a are deshielded (δ 2.02), since the allylic methyl group is Z to the benzene ring in 7a. The alkylidene phthalide structure of 6a and 7a was definitely substantiated by the ozonolysis of 6a and 7a, which yielded phthalic anhydride and keto ester 8. 1,3-Dioxolanes 5b-d were obtained upon irradiation of 1 in various ketone solutions (Table II). Since photochemical dimerization of 1 occurred competitively$^{4)}$, highly diluted solutions of 1 in ketones should be employed to accomplish high yields of 5a-d.

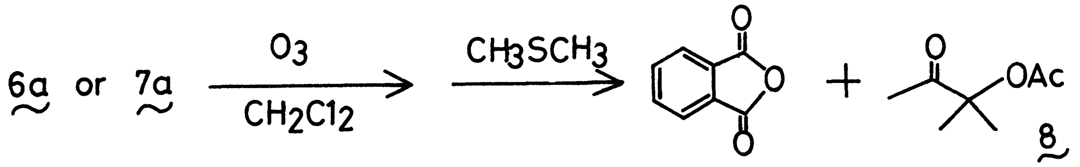
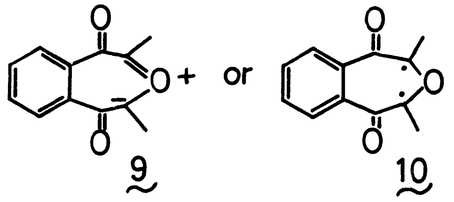
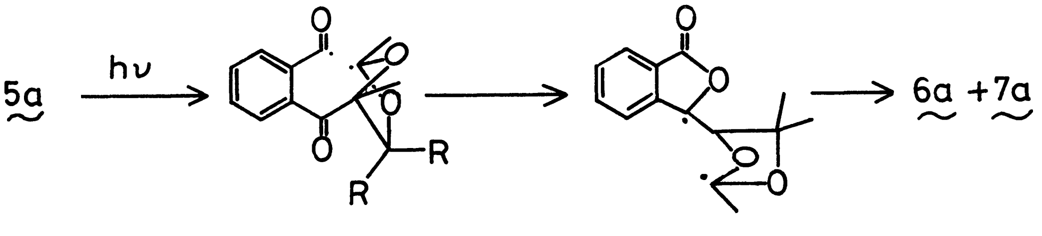


Photo-induced cycloadditions of 1 to aliphatic aldehydes and ketones were undertaken with light of wavelength above 350 nm, under which conditions aliphatic aldehydes and ketones are transparent. Formation of 3, 4, and 5 can be explained in terms of the trapping of the carbonyl ylide 9 or 1,3-diradical 10 with carbonyl groups of aldehydes and ketones in ground





states. Observed photochemical isomerization of 5a to 6a and 7a may involve the initial α-cleavage (Norrish Type I) and subsequent free radical rearrangement.

While a few examples of 1,3-dioxolanes resulted from the reaction of thermally generated carbonyl ylides (>145°C) with less volatile carbonyl compounds can be found in literature5),6), no cycloaddition of photogenerated carbonyl ylides to carbonyl compounds has been reported so far. To our knowledge, simple ketones are hard to react with the carbonyl ylides. In fact, acetone was once used as an effective sensitizer for the generation of carbonyl ylides from cis- and trans-stilbene oxide7). Although rather extremely diluted conditions are required to obtain the high yields of 5a-d, this reaction is quite interesting from the theoretical standpoint of the reactivity of carbonyl ylides.

References and Notes

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