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ONE-POT PHOTOCHEMICAL SYNTHESIS OF 4-ARYLNAPHTHO[2,3-d][1,3]DIOXEPIN-6,11-DIONE

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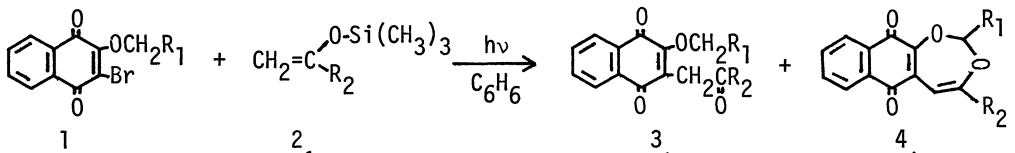
4-Arylnaphtho[2,3-d][1,3]dioxepin-6,11-dione was synthesized from 2-alkoxy-3-bromo-1,4-naphthoquinone and 1-aryl-1-trimethylsilyloxyethylene by a one-pot photochemical reaction.

In spite of the fascinating properties of [1,3]dioxepins as expected from those of diazepins, reports on [1,3]dioxepins have been rather sparse partly because of its synthetic difficulty.[1]

Here we wish to report a one-pot photochemical synthesis of naphtho[2,3-d]-[1,3]dioxepin derivatives. These [1,3]dioxepin derivatives have never been reported so far. Typically, 2-bromo-3-methoxy-1,4-naphthoquinone 1a (0.2 mmol) and 1-phenyl-1-trimethylsilyloxyethylene 2a (1.0 mmol) were dissolved in benzene (20 ml) and irradiated by a high pressure Hg lamp(300 W) for several hours.[2] After the complete consumption of 1a, chromatography of the reaction mixture gave two discrete photo-products, 3a and 4a, in a total yield of 40%(3a/4a=3/1)(see Scheme I).[3,4] One of them, 3a, was 2-benzoylmethyl-3-methoxy-1,4-naphthoquinone (yellow prisms, mp 146-148°C).[5] The other product, 4a, which was confirmed to be derived from 3a upon further irradiation,[6] was red needles, mp 168-169°C. ^{1}H-NMR($CDCl_3$):δ;5.75ppm(2H,s), 6.91(1H,s), 7.4-8.3(9H,m). ^{13}C-NMR($CDCl_3$):δ;94.0ppm, 95.0, 123.6, 125.6, 126.3, 126.7, 128.5, 130.0, 131.3, 131.6, 133.8, 134.3, 155.5, 163.1, 178.0, 183.5. IR(KBr):1660, 1580, 1560cm^{-1}. UVmax(EtOH):307nm(logε:4.36), 462(3.74).[7] These spectral data were all compatible with the [1,3]dioxepin, 4a, which was further confirmed by the following derivations(see Scheme 2).[8]

Other 2-alkoxy-3-bromo-1,4-naphthoquinone and 1-aryl-1-trimethylsilyloxyethylene can also serve as the starting materials for this photochemical reaction as illustrated in Scheme I (yields are shown in Table I). Thus, the photochemical reaction of 2-alkoxy-3-bromo-1,4-naphthoquinone with 1-aryl-1-trimethyl-



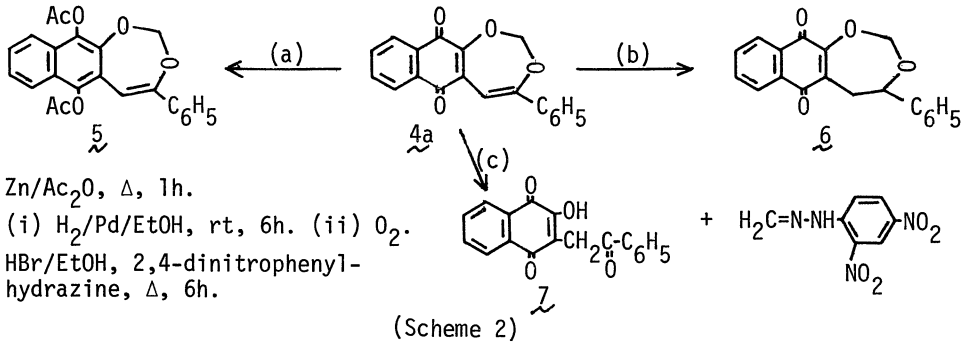
1
a:R_1=H
b:R_1=CH_3

2
a:R_2=phenyl
b:R_2=*p*-tolyl
c:R_2=2-thienyl

3
a:R_1=H, R_2=phenyl
b:R_1=H, R_2=*p*-tolyl
c:R_1=H, R_2=2-thienyl
d:R_1=CH_3, R_2=phenyl
e:R_1=CH_3, R_2=*p*-tolyl
f:R_1=CH_3, R_2=2-thienyl

4

(Scheme I)



(a) Zn/Ac_2O, Δ, 1h.
(b) (i) $H_2/Pd/EtOH$, rt, 6h. (ii) O_2.
(c) HBr/EtOH, 2,4-dinitrophenylhydrazine, Δ, 6h.

(Scheme 2)

Table 1. Yields of Photo-Products [a]

Starting Materials.		2-Alkoxy-3-(2-aryl-2-oxoethyl)-1,4-naphthoquinone (mp, °C)	4-Arylnaphtho[2,3-d][1,3]dioxepin-6,11-dione (mp, °C)
Quinone	Silyloxyethylene		
1a	2a	3a (146-148), 28%	4a (168-169), 12%
1a	2b	3b (133-134), 22%	4b (203-204), 16%
1a	2c	3c (90-93), 20%	4c (203-204), 12%
1b	2a	3d (105-106), 21%	4d (204-205), 20%
1b	2b	3e (127-128), 23%	4e (189-190), 21%
1b	2c	3f (98-100), 21%	4f (160-161), 17%

a) Yields were calculated on the basis of the quinone consumed after irradiation for 10 h.

silyloxyethylene provides us a new and feasible one-pot synthetic route to 4-arylnaphtho[2,3-d][1,3]dioxepin derivatives.

References and Notes.

1) J.F.Keana and R.H.Morse, Tetrahedron Lett., (1976) 2113.
2) Addition of pyridine (equimolar to 1a) was helpful to keep the reacting mixture clean.
3) The relative amounts of two products were dependent upon the reaction time. The maximum yield of 4a (24%) was achieved upon further irradiation at the expense of 3a (the yields in the text were calculated after irradiation for 10 h).
4) Purification of the products was best accomplished by column chromatography on silica gel using benzene-ether as solvent system. Lower yields of the isolated products were due to the formation of resinous matters.
5) The structure 3a was confirmed by the independent synthesis: by methylation[a] of 2-benzoylmethyl-3-hydroxy-1,4-naphthoquinone 7, which is derived from 2-hydroxy-1,4-naphthoquinone and phenylacetaldehyde.[b,c] a) M.G.Ettlinger, J.Am.Chem.Soc., 72, 3666 (1950). b) R.Hout and P.Brassard, Can.J.Chem., 52, 88 (1974). c) S.C.Hooker, J.Am.Chem.Soc., 58, 1163 (1936).
6) Upon irradiation, 3a-f gave the corresponding dioxepin derivatives 4a-f in yields of 40-80%.
7) The proposed structure is compatible with both MS and analysis data.
8) The structures of the reaction products, 5, 6, and 7, are compatible with NMR, IR, UV, MS, and analysis data.

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