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PHOTOCHEMICAL 2+2 CYCLOADDITION OF 2-CHLORO-1,4-NAPHTHOQUINONE TO ALKENES. A NOVEL SYNTHESIS OF 1,2-DIHYDROCYCLOBUTA[*b*]NAPHTHALENE-3,8-DIONES[1)]

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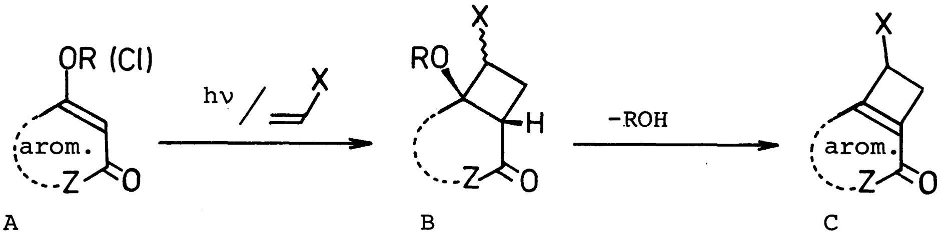
2-Chloro-1,4-naphthoquinone undergoes photochemical 2+2 addition at its 2- and 3-positions to alkenes. An elimination of hydrogen chloride from the adducts provides a facile and general synthetic method of 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones.

We have recently established a two-step synthetic method (Kaneko-Naito method) of a variety of cyclobutane-fused heteroaromatics.[2,3)] The first step in the method is a regioselective photochemical cycloaddition of heteroaromatics involving a β-alkoxy enone function in their ring system (A, *e.g.*, 4-alkoxy-2-pyridones, 4-alkoxy-2-quinolones, *etc.*) to alkenes giving the head-to-tail adducts (B). The second step is an elimination of an alcohol from the adducts either by base or acid to give the cyclobutane-fused heteroaromatics (C). Two important information concerning the second step have recently been obtained in our laboratories.[4,5)] These are i) the elimination of an alcohol from the adduct (B) is possible only if the double bond in the cyclobutene ring thus formed is involved in the aromatic ring system in the product (C) and ii) the corresponding adducts obtained from 6-chlorouracils and alkenes eliminate hydrogen chloride spontaneously under irradiation conditions (neutral solvent, room temp) to give 1,2-dihydrocyclobuta[e]uracils. These facts tell clearly that if this two-step method is applied to nonaromatic or weakly aromatic compounds, chlorine is much more attractive substituent than an alkoxyl group as the leaving group.



A   B   C

Taking these facts as well as the ready 2+2 photoadditions of 1,4-naphthoquinone derivatives to alkenes,[6)] we now have succeeded in the synthesis of

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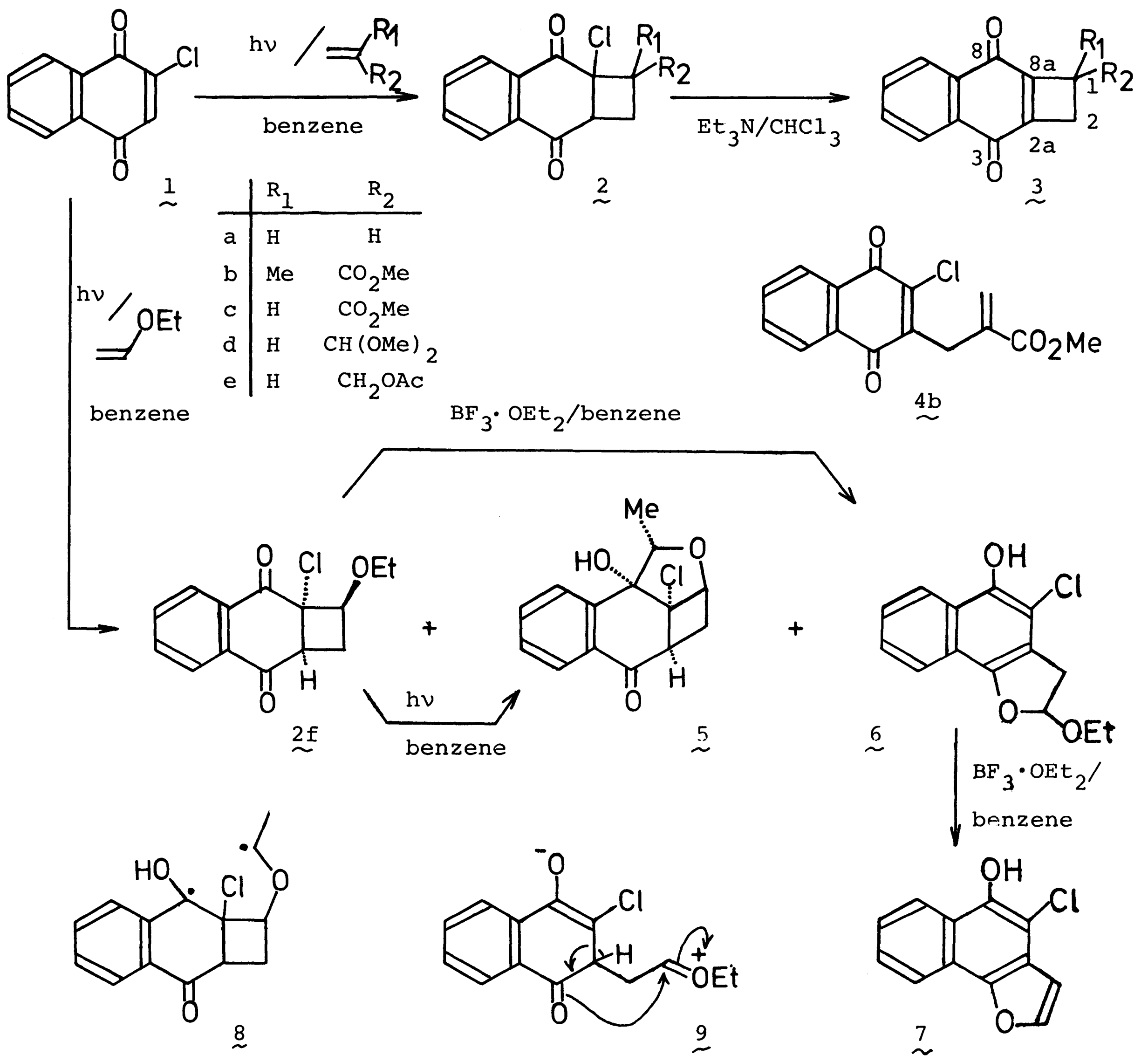
1,2-dihydrocyclobuta[*b*]naphthalene-3,8-diones from 2-chloro-1,4-naphthoquinone by an application of our two-step method.

Irradiation[7] of 2-chloro-1,4-naphthoquinone[8] (**1**) in benzene under bubbling of ethylene followed by silica gel column chromatography afforded 2a-chloro-1,2,2a,8a-tetrahydrocyclobuta[*b*]naphthalene-3,8-dione[9] [**2a**, mp 80-81 °C, δ ($CDCl_3$): 1.7-3.1 (m, 4H), 3.55-4.05 (m, 1H), 7.5-7.85 (m, 2H), 7.85-8.2 (m, 2H)] and 1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione[10,11] [**3a**, mp 195-200 °C (resolidified immediately and melted again at 259-264 °C),[12] δ ($CDCl_3$): 3.05 (s, 4H), 7.5-7.8 (m, 2H), 7.8-8.1 (m, 2H), ν_{max}^{KBr} cm^{-1}: 1670)] in the respective yields of 53 and 8%. Treatment of **2a** with triethylamine in chloroform at room temperature afforded **3a** in 90% yield. More conveniently, **3a** was synthesized from **1** in a higher overall yield by performing the above two-step without the isolation of **2a**. Thus, the whole product obtained by photoaddition of **1** to ethylene was treated directly with triethylamine as above gave **3a** as the sole product in 81% yield. Though **3a** was previously synthesized either from 2,3-*bis*-(bromomethyl)-naphthalene[10] or from dimethyl cyclobutane-1,2-dicarboxylate,[11] the present method is far more superior in its short step and high overall yield to those reported. Furthermore, various functional groups can be introduced into cyclobutene moiety of **3a** merely by using substituted ethylenes instead of ethylene in the photoaddition step.

Photoaddition of **1** to methyl methacrylate followed by the base treatment of the crude photoadduct (**2b**,[13] oil) afforded 1-methoxycarbonyl-1-methyl-1,2-dihydrocyclobuta[*b*]naphthalene-3,8-dione (**3b**, mp 89.5-90.5 °C) in 74% yield. In this case, a small amount (4%) of the ene product (**4b**, mp 76-77 °C) was obtained as the by-product. Though the photoadduct (**2c**, oil) between **1** and methyl acrylate was obtained in 76% yield, only 27% of **3c** (mp 158-159 °C) was obtained from **2c** by the above base treatment (the reaction period was *ca*. 10 min) and the dimer[12] of **3c** was obtained concomitantly in 34% yield. Actually, it was found that **3c** upon treatment with triethylamine in chloroform at room temperature gave the same dimer and the yield of the latter increased with an increment of the duration of base treatment.

Electron-rich olefins can also be used in these photoadditions, though the yields in the photoaddition step are low compared with those using electron-deficient olefins. Thus, by the two-step method (performed without the isolation of the adducts) using acrolein dimethylacetal and allyl acetate, **3d** (mp 100-101 °C) and **3e** (mp 109-109.5 °C) were obtained in the respective yields of 37 and 33%. Somewhat unexpected products were obtained by photoaddition of **1** to ethyl vinyl ether. Thus, irradiation of **1** in benzene in the presence of ethyl vinyl ether did not give the simple 2+2 adduct (**2f**) but gave two new-type products (**5**, mp 129.5-130 °C and **6**, mp 122-122.5 °C) in the respective yields of 21 and 38%. If the above photoaddition reaction was carried out in a basic solvent (1% pyridine/benzene), the adduct (**2f**, mp 99.5-100 °C) was obtained in 5% yield, together with **5** (32%) and **6** (4%). The following transformations of **2f** to **5** and **6** tell clearly that both of these products are the secondary products formed from the simple adduct (**2f**). Thus, irradiation of **2f** in benzene afforded **5** in 41% yield and the formation of **5** is best explained by assuming the biradical (**8**)



	R_1	R_2
a	H	H
b	Me	CO_2Me
c	H	CO_2Me
d	H	$CH(OMe)_2$
e	H	CH_2OAc

as an intermediate. In accordance with the proposed structure, treatment of 6[14] by BF_3-Et_2O in benzene afforded a furan derivative[15] (7, mp 82-83 °C) as expected. Almost quantitative formation of the same furan compound (7) from 2f by the same acid treatment indicates that the formation of 6 from 2f in the above photolyses proceeds *via* a zwitter ion (9) formed from 2f by HCl (generated *in situ* in these photolyses). This view is supported by an appreciable decrease of the yield of 6 in the photolysis performed in the basic medium as compared with that in benzene.

In summary, we have successfully applied our two-step procedure to carbocyclic series and elaborated a simple synthetic method of 1,2-dihydrocyclobuta[*b*]-naphthalene-3,8-dione (3a) and its 1-substituted derivatives (3b-3e). Utilizing these compounds (3a-3e), our attention is now focussed to develop a new synthetic method of anthraquinone derivatives by the application of so-called benzocyclobutene method.[16]

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