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A PHOTOCHEMICAL REACTION OF 2-ALKOXY-3-BROMO-1,4-NAPHTHOQUINONE WITH 1,1-DIARYLETHYLENE —— A NOVEL SYNTHETIC METHOD OF 5-ARYL-7,12-BENZ(a)ANTHRAQUINONES

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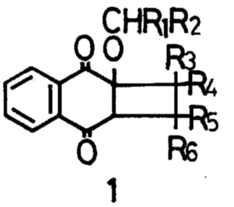
5-Aryl-7,12-benz[a]anthraquinone derivatives (**6**) was obtained in good yields in the photochemical reaction of 2-alkoxy-3-bromo-1,4-naphthoquinone with 1,1-diarylethylene.

Although the formation of the photo-addition compounds containing cyclobutane ring (**1**) and tetrahydropyran ring (**2**) has been confirmed in the photochemical reaction of 2-alkoxy-1,4-naphthoquinone with a variety of olefins,[1,2] we shall report here another novel type of the photochemical reaction of 2-alkoxy-3-bromo-1,4-naphthoquinone with 1,1-diarylethylene.



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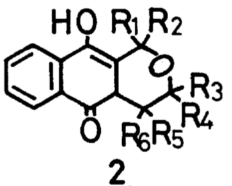

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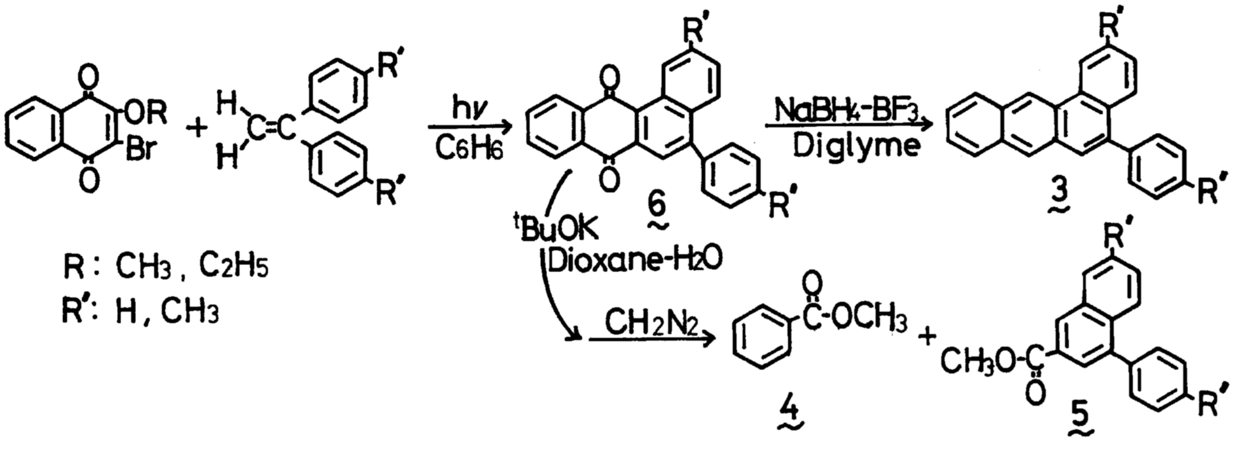
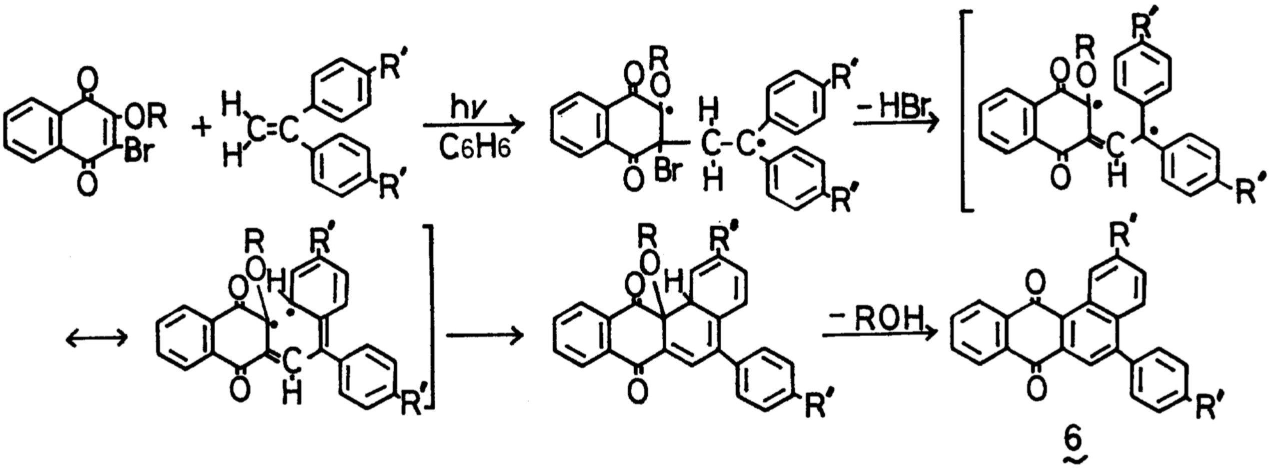
The photochemical reaction of 2-methoxy-3-bromo-1,4-naphthoquinone with 1,1-diphenylethylene is exemplified as a typical one. However, the reactions in several other combinations of quinones and olefins are found to proceed similarly(yields;ca 60%).

On irradiation of the benzene solution(20 ml) of 2-methoxy-3-bromo-1,4-naphthoquinone(0.5 mmol) and 1,1-diphenylethylene(2.0 mmol) by high pressure Hg arc lamp (300 W), photo-addition compound was isolated after the usual work-up. The photo-addition compound (yellow needles, mp 160.0-161.0°C after recrystallization from benzene, yield;61%) was subjected to the following examinations. Elemental analysis:Found;C,86.59;H,4.04%;Calcd.for $C_{24}H_{14}O_2$;C,86.20;H,4.19%. Mass:m/e=334(M^+, 100%), 306(M^+-CO,23%), 278(M^+-2CO,36%). IR(KBr disk):1665 cm^{-1}(C=O). UV max($CHCl_3$):419 nm(ε:3.88×10^3), 290(3.28×10^4). PMR($CDCl_3$):δ;7.48(5H,aromatic-H,broad singlet), 7.48-8.40(8H,aromatic-H,multiplet), 9.78 ppm(1H,aromatic-H,doublet, J=8.0 Hz). Reduction of the adduct by $NaBH_4$-BF_3 etherate in diglyme[3] gave 5-phenylbenz[a]anthracene (**3**)(nearly quantitative). On the other hand, when the adduct was subjected to the well-known cleavage reaction of 9,10-anthraquinones by treating with ^{t}BuOK in aqueous dioxane[4-6] and to the subsequent esterification with diazomethane, methyl benzoate



(4) and methyl 4-phenylnaphthalene-2-carboxylate (5) were isolated. The structures of these compounds (3), (4) and (5) were all confirmed through the inspection of their mass, IR and PMR spectra.

Taking into account of these results, the photo-addition compound is compatible with structure (6). The reaction pathway may be formularized tentatively as the followings:



This novel type of the photochemical reaction may lead to the simple and effective synthetic route of 5-aryl-7,12-benz[a]anthraquinone and 5-arylbenz[a]anthracene derivatives.

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