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ONE-POT PHOTOCHEMICAL SYNTHESIS OF NAPHTHO[1,2-g]QUINOLINE-7,12-DIONE DERIVATIVES ——— A NEW ROUTE TO AZA-ANALOGUE OF BENZ[a]ANTHRACENE-7,12-DIONES

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Substituted naphtho[1,2-g]quinoline-7,12-diones were synthesized regioselectively by one-pot photochemical reaction of 7-bromo-6-methoxyquinoline-5,8-dione with 1,1-diarylethylenes.

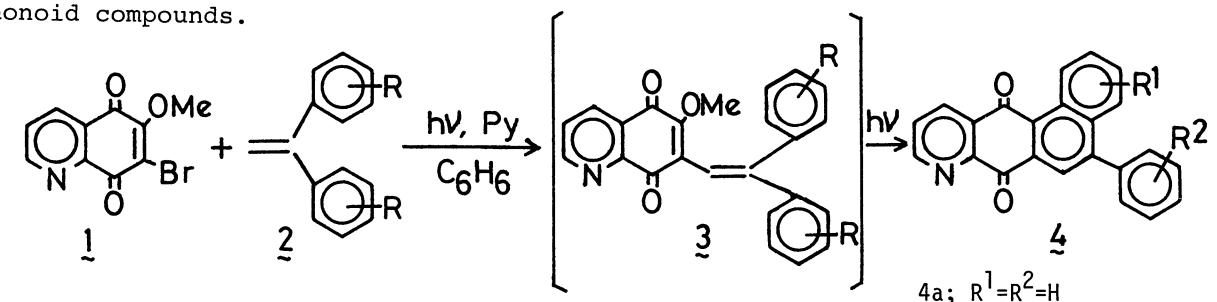
Although a variety of quinones derived from polycyclic aromatic compounds have been well investigated, quinone derivatives of naphthoquinolines containing a nitrogen atom in the D-ring of benz[a]anthracene skeleton have never been reported so far. Naphthoquinolines, an aza-analogue of benz[a]anthracenes, would be of potential interest because of their expected biochemical and physicochemical properties.[1] We wish to report here a facile one-pot regioselective photochemical synthesis of substituted naphtho[1,2-g]quinoline-7,12-diones from 7-bromo-6-methoxyquinoline-5,8-dione and 1,1-diarylethylenes.

As a typical example, a benzene solution (400ml) of 7-bromo-6-methoxyquinoline-5,8-dione 1 (1 mmol)[2] and 1,1-diphenylethylene 2a (2 mmol) was irradiated with a high pressure Hg arc lamp (300W) in the presence of pyridine (1 mmol) at room temperature for 1 h. After complete consumption of 1, purification of the reaction mixture by column chromatography on silica gel and subsequent recrystallization gave yellow needles; 5-phenylnaphtho[1,2-g]quinoline-7,12-dione 4a, mp: 242-3°C, yield 30%, Mass: m/e=335(M^+), IR(KBr): 1680, 1660, 1300cm^{-1}, NMR($CDCl_3$): δ; 9.80ppm (1H,d, J=8.5Hz), 9.09 (1H,dd,J=5,2Hz),8.64 (1H,dd,J=8,2Hz), 8.40 (1H,s), 8.00 (1H,dd,J=8, 1.5Hz), 7.5-7.9 (3H,m), 7.52 (5H,s), UV max($CHCl_3$): 246nm (logε=4.07), 310 (4.13), 373 (3.13), 427 (3.30).

The spectral data of 4a are all compatible with 5-phenylnaphtho[1,2-g]quinoline-7,12-dione. Similarly, other 1,1-diarylethylenes 2b-f gave successfully the corresponding naphtho[1,2-g]quinoline-7,12-dione derivatives 4b-f in a regioselective

manner in the photochemical reaction with 7-bromo-6-methoxyquinoline-5,8-dione 1 (see Scheme I and Table I). The structure of 4a was further confirmed by analyzing the ^{1}H-NMR chemical shift changes of the ring protons induced by addition of Eu(fod)$_3$. Although the intermediate 3 was not isolated in this work,[3] the regioselective condensation[4] to naphtho[1,2-g]quinoline-7,12-diones 4 would be understood in terms of the two-step reaction mechanism as shown in Scheme I.

Thus, the photochemical reaction of 7-bromo-6-methoxyquinoline-5,8-dione 1 with 1,1-diarylethylenes 2 provides us a facile regioselective one-pot synthetic route to naphtho[1,2-g]quinoline-7,12-dione derivatives 4 as a new member of quinonoid compounds.



1 2 3 4

Scheme I

4a; R^1=R^2=H
4b; R^1=2-OMe, R^2=p-OMe
4c; 3-OMe, m-OMe
4d; 4-OMe, o-OMe
4e; 2-Me, p-Me
4f; 3-Me, m-Me

Table I. Yields and Physical Properties of Naphtho[1,2-g]quinoline-7,12-diones

Starting Materials. Quinone	Ethylene	Irradiation Time (h)	Products	Yields %		mp(°C)
1	2a; R=H	1	4a; R^1=R^2=H	30	yellow needles	242-3
1	2b; p-OMe	10	4b; R^1=2-OMe, R^2=p-OMe	17	orange needles	256-7
1	2c; m-OMe	2.5	4c; 3-OMe, m-OMe	44	yellowish orange needles	244.5-5
1	2d; o-OMe	3	4d; 4-OMe, o-OMe	20	red needles	269-70
1	2e; p-Me	1.8	4e; 2-Me, p-Me	40	yellow needles	>300
1	2f; m-Me	1.3	4f; 3-Me, m-Me	24	yellow needles	243-4

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3)The formation of 3 was suggested at the earlier stage by inspection of the course of the reaction with TLC.
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