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PHOTOCHEMICAL SYNTHESIS OF NEW SULFUR-CONTAINING POLYCYCLIC AROMATIC COMPOUNDS — ANTHRA[2,1-b]THIOPHENE DERIVATIVES

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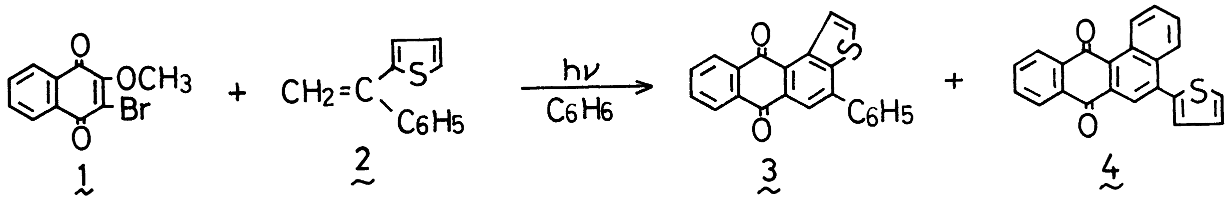
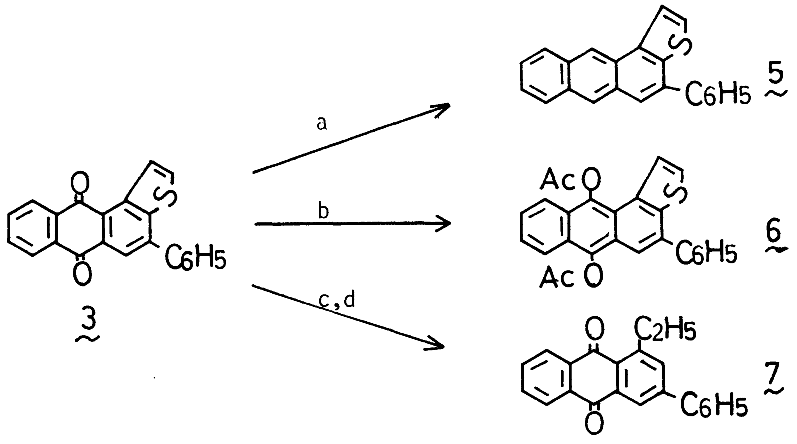
6,11-Anthra[2,1-b]thiophenedione 3 was yielded(62%) in the photochemical reaction of 2-bromo-3-methoxy-1,4-naphthoquinone 1 with 1-phenyl-1-(2-thienyl)ethylene 2. The reduction of 3 gave anthra[2,1-b]thiophenes.

Recently the present authors have reported on the photochemical synthesis of 7,12-benz[a]anthracenediones from 1,4-naphthoquinones and 1,1-diarylethylenes.1) The work was extended to the convenient synthesis of new sulfur-containing polycyclic aromatic compounds — anthra[2,1-b]thiophene derivatives, 3, 5, and 6.

On irradiating a benzene solution (25 ml) of 2-bromo-3-methoxy-1,4-naphthoquinone 1 (0.5 mmol) and 1-phenyl-1-(2-thienyl)ethylene 2 (1 mmol)2) by a high pressure Hg arc lamp for 4h, the quinone was found to be consumed completely. Addition of methanol(*ca.*1 ml) to the concentrated reaction mixture (*ca.* 5 ml) resulted in the precipitation of yellow crystals, which were recrystallized from $CHCl_3$-CH_3OH to give light yellow needles; 4-phenyl-6,11-anthra[2,1-b]thiophenedione 3, mp 221.0-221.5°C, yield:62%, Mass:m/e=340(M^+), IR(KBr):1670 cm^{-1}, NMR($CDCl_3$):δ;7.2-8.4(10H,m), 8.27(1H,s), 8.84(1H,d,J=6Hz), UV max($CHCl_3$):413nm(ε:4.7×10^3), 378(sh)(3.8×10^3), 303(sh)(3.8×10^4), 292(4.1×10^4), 252(2.6×10^4). 5-(2-Thienyl)-7,12-benz[a]anthracenedione 4 was also isolated as a minor product from the reaction mixture, yellow-orange needles, mp 182.0-183.5°C, yield: 8%, Mass:m/e=340(M^+), IR(KBr):1670 cm^{-1}, NMR($CDCl_3$):δ;7.1-8.5(10H,m), 8.34(1H,s), 9.65(1H,dd,J=9, 2Hz), UV max($CHCl_3$):429nm(ε:5.2×10^3), 345(sh)(6.2×10^3), 292(3.5×10^4), 248(2.9×10^4).



Reduction of 3 by $LiAlH_4$ in THF gave 5 in a yield of 32% ; 4-phenylanthra[2,1-b]thiophene 5 : pale yellow crystals, mp 155.5-157.0°C, Mass: m/e=310(M^+), IR(KBr): neither OH nor CO, NMR($CDCl_3$):



a) $LiAlH_4$,THF, reflux, 5h

b) Zn-Ac_2O, reflux, 1h

c) Raney-Ni(W-7), C_6H_6-C_2H_5OH, reflux, 4h

d) [O]

δ;7.1-8.3(12H,m), 8.42(1H,br,s), 8.77(1H,br,s), UV max($CDCl_3$): 388nm(ε:8.8x10^3), 368(1.2x10^4), 350(8.8x10^3), 337(sh)(5.5x10^3), 293(6.8x10^4), 284(sh)(5.9x10^4), 256(sh)(4.2x10^4), 248(sh)(3.8x 10^4). Moreover, 6,11-diacetoxy-4-phenylanthra[2,1-b]thiophene 6 was also yielded by reductive acetylation of 3 ; 6 : slightly yellow crystals, mp 263-265°C, yield:60%, Mass:m/e=426(M^+), IR(KBr):1755 cm^{-1}, NMR($CDCl_3$): δ; 2.61(3H,s), 2.69(3H,s), 7.1-8.0(11H,m), 8.24(1H,d,J=6Hz), UV max($CHCl_3$):402nm(ε:1.2x10^4), 380(1.4x10^4), 362(1.1x10^4), 345(sh)(7.1x10^3), 297(6.8x10^4), 275(5.9x10^4), 257(sh)(4.0x10^4), 246(3.5x10^4).

On the other hand, desulfurization of 3 by Raney-Ni(W-7) in C_6H_6-C_2H_5OH resulted in the formation of 1-ethyl-3-phenyl-9,10-anthracenedione 7(yield:13%), yellow needles, mp 133.0-134.5°C, Mass: m/e=312(M^+), IR(KBr):1650 cm^{-1}, NMR($CDCl_3$): δ ;1.38(3H,t,J=8Hz), 2.88(2H,q,J=8Hz), 7.1-8.6(11H,m), UV max($CHCl_3$): 435nm (sh)(ε:7.3x10), 315(3.3x10^3), 263(3.9x10^4).

Although as a synthetic alternative we found that the thermal Diels-Alder reaction[3] of 1,4-naphthoquinone with 2 in acetic acid(100h, 5h) gave 3(yield: 6%), the yield of the present photochemical reaction was better than that.

References and Notes

1) K. Maruyama and T. Otsuki, Chem. Lett., (1975) 87.
K. Maruyama and T. Otsuki, and K. Mitsui, Bull. Chem. Soc. Jpn., 49 , 3361 (1976) .

2) The compound 2 was synthesized via Grignard reaction of methyl magnesium bromide with phenyl 2-thienyl ketone and the subsequent dehydration of the resulting alcohol (overall yield:77%).

3) A similar Diels-Alder reaction of 1,4-benzoquinone with 2-vinyl thiophene was reported to yield 6,9-naphtho[2,1-b]thiophenedione. *Cf.* W.Davies and Q. N. Porter, J. Chem. Soc., (1957) 4957.

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