CHEMISTRY LETTERS, pp. 323-324, 1978. Published by the Chemical Society of Japan

PHOTOCHEMICAL SYNTHESIS OF NEW NITROGEN-CONTAINING POLYCYCLIC AROMATIC COMPOUNDS —— NAPHTHO[2,3-c]CARBAZOLE AND ANTHRA[2,1-b]PYRROLE DERIVATIVES

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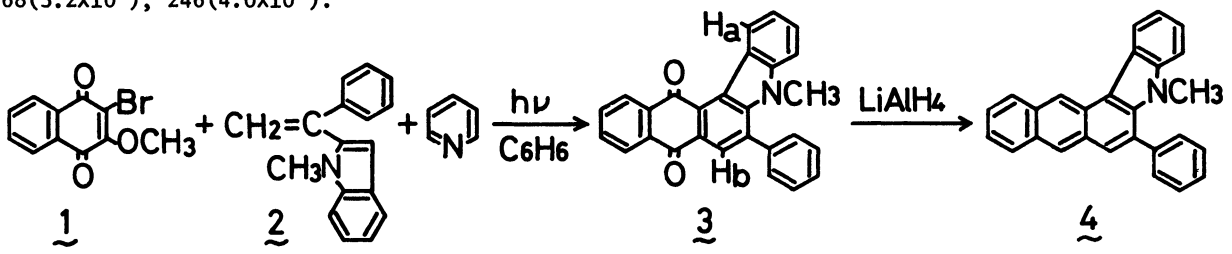
8,13-Naphtho[2,3-c]carbazoledione 3 and 6,11-anthra[2,1-b]pyrroledione 10 were synthesized in a good yield via photolysis of quinone and 1,1-diarylethylene. Reduction of 3 and 10 gave corresponding polycyclic aromatics 4 and 11.

Synthesis of polycyclic aromatics is of a recent active research in connection with their carcinogenic activity.[1] Polycyclic aromatics containing heteroatom in the molecule such as naphtho[2,3-c]carbazole has been synthesized previously.[2] However, the yield was poor. We wish herewith to report facile one-step synthesis of naphtho[2,3-c]carbazole and anthra[2,1-b]pyrrole derivatives in a good yield and in a highly regioselective manner.

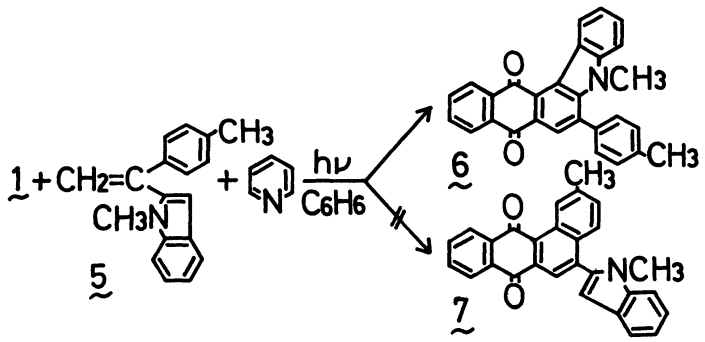
On irradiating a benzene solution(25 ml) of 2-bromo-3-methoxy-1,4-naphthoquinone 1 (0.5 mmol), 1-phenyl-1-(N-methylindol-2-yl)ethylene 2 (1 mmol) and pyridine (0.5 mmol) by a high pressure Hg arc lamp(300 W) for 8h, the quinone was found to be consumed completely. Subsequent purification of the reaction mixture by using chromatography on silica gel gave red-orange prisms, which were recrystallized from chloroform-hexane to give orange prisms; 5-methyl-6-phenylnaphtho[2,3-c]carbazole-8,13-dione 3, mp 256.0-257.5°C, yield: 61%, Anal. Found: C, 83.41; H, 4.63; N, 3.45%. Calcd for $C_{27}H_{17}NO_2$: C, 83.70; H, 4.42; N, 3.62%. Mass:m/e=387(M^+), IR(KBr):1675 and 1645cm^{-1}(CO), NMR($CDCl_3$):δ;3.31(3H, s,N-methyl), 6.90-7.75(5H,m), 7.42(5H,s,phenyl), 7.90-8.30(2H,m), 8.19(1H,s,H_b), 9.36(1H,d,J=8Hz, H_a), UV max($CHCl_3$):440nm(sh)(ε:5.7x10^3), 417(6.4x10^3), 344(2.7x10^4), 332(sh)(2.4x10^4), 303(1.7x10^4), 268(3.2x10^4), 246(4.0x10^4).



1 2 3 4

Reduction of the quinone 3 by $LiAlH_4$ in refluxing THF gave 4 in a yield of 47%; 5-methyl-6-phenylnaphtho[2,3-c]carbazole 4: pale green crystals, mp 189.5-191.0°C, Anal. Found: C, 90.43; H, 5.23; N, 3.82%. Calcd for $C_{27}H_{19}N$: C, 90.72; H, 5.36; N, 3.92%. Mass:m/e=357(M^+), IR(KBr): no absorption for ν_{CO}, NMR($CDCl_3$):δ;3.40(3H,s), 6.70-8.70(13H,m), 7.65(1H,s), 8.30(1H,s), 9.09(1H,s), UV max(EtOH):427nm(ε:4.4x10^3), 403(5.3x10^3), 377(1.2x10^4), 358(8.3x10^3), 341(4.9x10^3), 324(3.2x10^4), 310(3.3x10^4), 290(5.2x10^4), 265(4.8x10^4), 260(sh)(4.7x10^4), 251(sh)(4.2x10^4), 232(3.5x10^4), 219 (4.7x10^4), 205(5.1x10^4).

In the reaction of 1 with 2, 5, or 9 containing N-methylpyrrole ring in the molecule, only one of two possible isomers[3] was obtained in every reaction. The adducts were assigned to structures, 3, 6, and 10 respectively on the basis of their physical and spectral data. A characteristic low field signal[4](δ;9.4-10) attributable to the other type of adduct(e.g. 7) could not be observed in



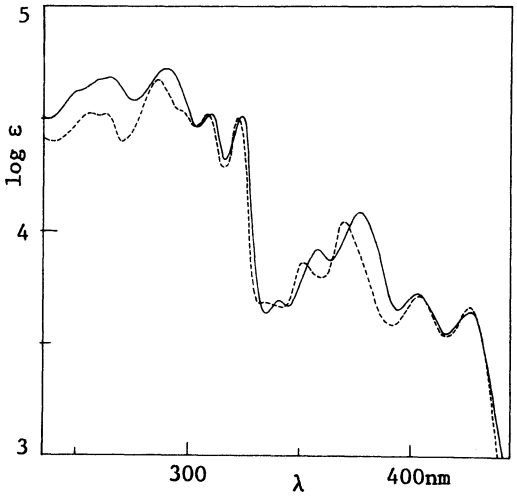
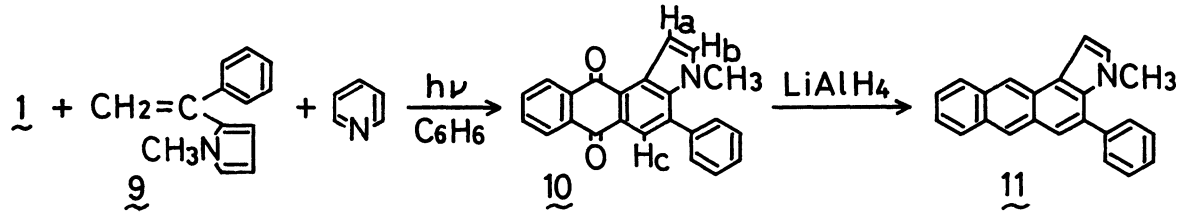


Fig. 1. UV absorption spectra in EtOH ——, 5-methyl-6-phenylnaphtho[2,3-c]-carbazole 4; ----, 5-methylnaphtho[2,3-c]carbazole 8[2)]

their NMR spectra.[5)] Furthermore, this structure was also confirmed by the presence of strong resemblance between the UV spectrum of 4 and that of 5-methylnaphtho[2,3-c]carbazole 8.[2a)] (Fig. 1)

Using 1-phenyl-1-(N-methylpyrrol-2-yl)ethylene 9 as olefin in the reaction, we obtained 3-methyl-4-phenylanthra[2,1-b]pyrrole-6,11-dione 10 in a yield of 50%; 10: orange-yellow prisms, mp 240°C, Anal. Found: C,81.67; H, 4.37; N, 4.18%. Calcd for $C_{23}H_{15}NO_2$: C, 81.88; H, 4.48; N, 4.15%. Mass:m/e=337 (M^+), IR(KBr):1665cm^{-1}(CO), NMR($CDCl_3$):δ;3.32(3H,s,N-methyl), 7.20(1H,d,J=1.5Hz,H_b), 7.41(5H,s, phenyl), 7.55-7.85(2H,m), 7.71(1H,d,J=1.5Hz,H_a), 7.93(1H,s,H_c), 8.05-8.35(2H,m), UV max($CHCl_3$): 440nm(sh)(ε:4.1x10^3), 420(sh)(4.4x10^3), 392(5.0x10^3), 306(sh)(2.7x10^4), 291(3.2x10^4), 250(3.0x10^4), 247(sh)(2.9x10^4). Reduction of 10 by $LiAlH_4$ gave 3-methyl-4-phenylanthra[2,1-b]pyrrole 11, pale



yellow crystals, mp 146.5-147.0°C, yield 52%, Anal. Found: C, 89.98; H, 5.50; N, 4.61%. Calcd for $C_{23}H_{17}N$: C, 89.86; H, 5.58; N, 4.56%. Mass:m/e=307(M^+), IR(KBr): no absorption for ν_{CO}, NMR($CDCl_3$): δ;3.19(3H,s), 6.79(1H,d,J=2Hz), 6.70-7.95(9H,m), 7.05(1H,d,J=2Hz), 7.83(1H,s), 8.16(1H,s), 8.53(1H, s), UV max(EtOH):396nm(ε:6.3x10^3), 376(8.1x10^3), 360(sh)(6.2x10^3), 302(sh)(3.0x10^4), 288(4.9x10^4), 271(5.6x10^4), 237(4.3x10^4), 223(sh)(3.2x10^4), 207(2.9x10^4).

References and Notes

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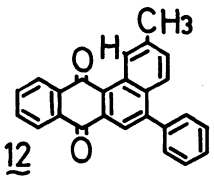
c)K. Maruyama, K. Mitsui and T. Otsuki, Chem. Lett., 853 (1977).

4) For example, the aromatic proton at C-1 of 2-methyl-5-phenylbenz[a]-anthracene-7,12-dione 12 showed a characteristic low field singlet signal(δ;9.52)(see ref. 3b).



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5) Adduct 6 :NMR($CDCl_3$):δ;2.46(3H,s), 3.36(3H,s), 7.15-7.80(9H,m), 8.05-8.35(2H,m), 8.21(1H,s), 9.38(1H,d,J=8Hz).

(Received February 4, 1978)