PREPARATION OF SOME NAPHTHO[2,3-*f*]ISOINDOLES[1]

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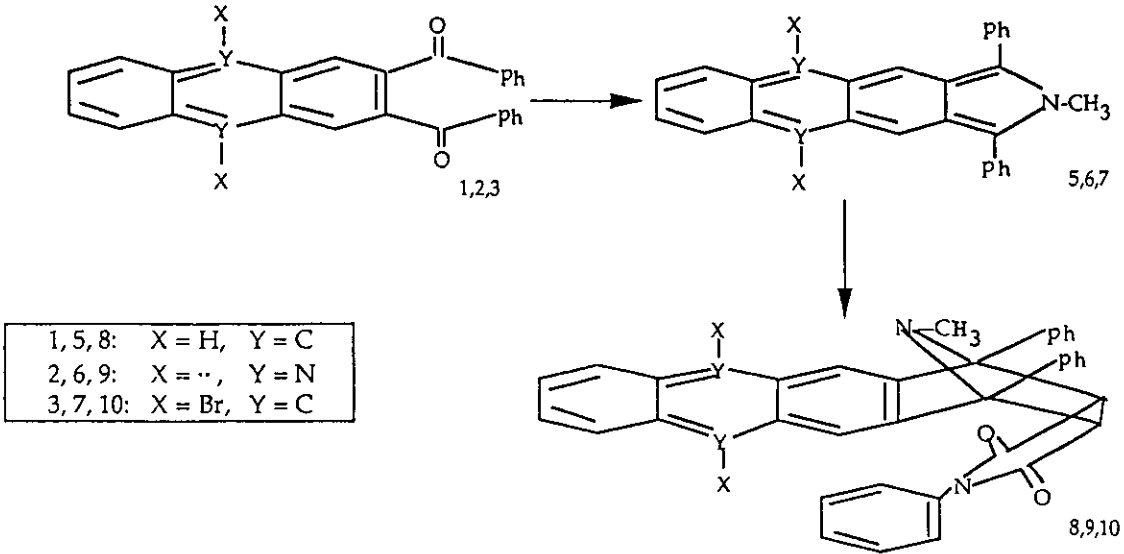
Abstract– The preparation of four derivatives of naphtho[2,3-*f*]isoindole is described. Three of these derivatives are highly reactive dienophiles.

The relative instability of isoindole and benz[*f*]isoindole is well established.[2] It would be expected that extensive linear conjugation of this *o*-quinoidal structure would increase its instability and therefore the isolation or transient detection of naphtho[2,3-*f*]isoindole has remained a challenge. Instead, introduction of electron withdrawing groups into the naphtho[2,3-*f*]isoindole system might stabilize it and hence render its isolation possible. In this communication, we report the preparation of four derivatives of naphtho[2,3-*f*]isoindole.

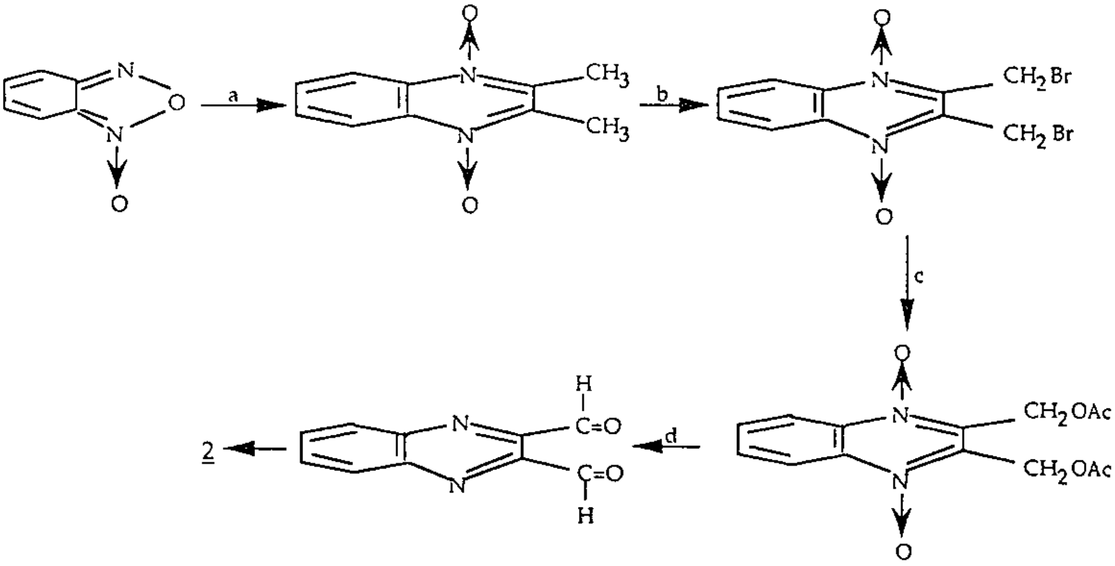
A starting point in these reactions was the preparation of 2,3-dibenzoylanthracene (1) and 2,3-dibenzoylphenazine (2). Condensation of 2,3-naphthalenedicarboxaldehyde[3] with 1,2-dibenzoylethane[4] in 5% methanolic KOH gave 1 as a bright yellow solid (80% yield, mp 180-181°C, lit.,[5], 180°C. Ir: 1665 cm^{-1}. Nmr (δ): s, 8.3 and 8.6 (2H each), m, 7.6 and 8.0 (14H)). This simple method is superior to that of the literature.[5] Bromination of 1 in acetic acid afforded 2,3-dibenzoyl-9,10-dibromoanthracene (3) (90% yield, mp 274-275°C. Ir: 1655, 1650 cm^{-1}. Nmr (δ): s, 9.0 (2H), m, 7.8 and 8.7 (12H)). Calcd for $C_{28}H_{16}O_2Br_2$: C, 61.77; H, 2.96; Br, 29.39. Found: C, 61.98; H, 3.05; Br, 29.80. Oxidation of 1 with $K_2Cr_2O_7$ in acetic acid gave 2,3-dibenzoyl-9,10-anthraquinone (4, 73% yield, mp 254-255°C. Ir: 1690, 1670 cm^{-1}. Nmr (δ): s, 8.7 (2H), m, 7.9 (14H). Calcd for $C_{28}H_{16}O_4$: C, 80.76; H, 3.87. Found: C, 80.51; H, 3.89. The synthesis of 2,3-dibenzoylphenazine (2, mp 205-206°C. Ir: 1680, 1660 cm^{-1}. Nmr (δ): s, 8.6 (2H), m, 7.9 (14H). Calcd for $C_{26}H_{16}N_2O_2$: C, 80.40; H, 4.15; N, 7.21. Found: C, 80.08; H, 4.17; N, 7.39) was affected by a series of reactions (Scheme I) that entailed the condensation of 2,3-quinoxalinedicarbaldehyde, generated in situ, with 1,2-dibenzoylethane in 5% methanolic KOH.

Treatment of a methanolic solution of either 1, 2, or 3 with aqueous methylamine under reflux conditions for one hour, followed by cooling to room temperature and subsequent reduction with aqueous sodium borohydride yielded 1,3-diphenyl-2-methylnaphtho[2,3-*f*]isoindoles (5, 6, or 7) respectively as greenish blue solids which were collected by suction filtration but could not be purified by crystallization due to their relative instability especially in solution. Isoindole (5) was least stable followed by 6. Isoindole (7) could be kept in the solid form for six months at room temperature without significant decomposition. The identity of these naphtho[2,3-*f*]isoindoles was established by mass spectrometry, ir spectroscopy and their high reactivity as dienophiles towards *N*-phenylmaleimide at room temperature to give endo adducts (8, 9, or 10). Assignment of endo structures was based on the presence of two aromatic protons as a multiplet at a relatively high field (δ 6.1) attributed to shielding of the ortho protons of the *N*-phenyl group by the benzo ring situated almost above these protons.[6] The structures of adducts (8) (mp 212-214°C), (9) (mp 204-205°C), and (10) (mp 215-218°C) were confirmed by ir, nmr, mass spectrometry and elemental analysis. Some difficulty was encountered in their recrystallization as they tend to decompose upon heating either in solution or in the solid form (blue coloration of presumably 1, 2, or 3). Furthermore, the mass spectra of 8, 9, and 10 showed their parent peaks in addition to stronger peaks due to M^+ of isoindoles (5, 6, and 7). The reaction of 4 with methylamine and reduction with $NaBH_4$ gave a bright red solid (11, 80% yield, mp 320-323°C. Ir: 1665 cm^{-1}. Nmr (δ): s, 8.7 (2H), m, 8.4 (2H), m, 7.6 (11H), and s, 3.9 (3H). Calcd for $C_{29}H_{19}NO_2$: C, 84.24; H, 4.63; N, 3.39. Found: C, 84.09; H, 4.81; N, 3.15. Isoindole (11) did not react with *N*-phenylmaleimide, and upon heating a solution of these, 11 decomposed and no adduct could be isolated. Compound (11) is quite stable in the solid form but decomposes slowly in solution at room temperature. Apparently, the electron withdrawing effect of the 9,10-diketo groups and the disruption of the extended linear conjugation of the *o*-quinoidal system rendered 11 ineffective as a dienophile. Furthermore, addition of excess $NaBH_4$ in the preparation of 11 lead to a lower yield of 11 presumably due to reduction of this product.



1, 5, 8:	X = H,	Y = C
2, 6, 9:	X = ··,	Y = N
3, 7, 10:	X = Br,	Y = C

Scheme I

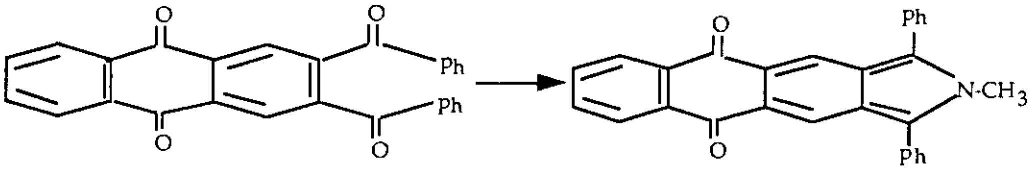


a) butanone, pyrrolidine in acetonitrile, warming, 65% yield.

b) Br_2 in $CH_3COOC_2H_5$, heat, 85% yield.

c) KOAc in DMSO, heat, 78% yield.

d) 1,2-dibenzoylethane in 5% methanolic KOH, 72% yield.



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ACKNOWLEDGEMENT

We thank Dr. Adnan Atfah of Yarmouk University, Jordan, for some of the mass spectral data.

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Received, 2nd December, 1991