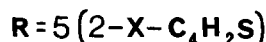
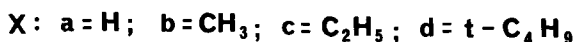
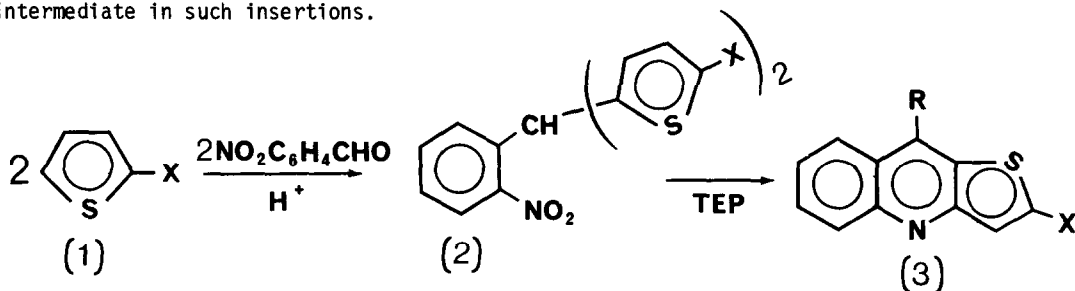


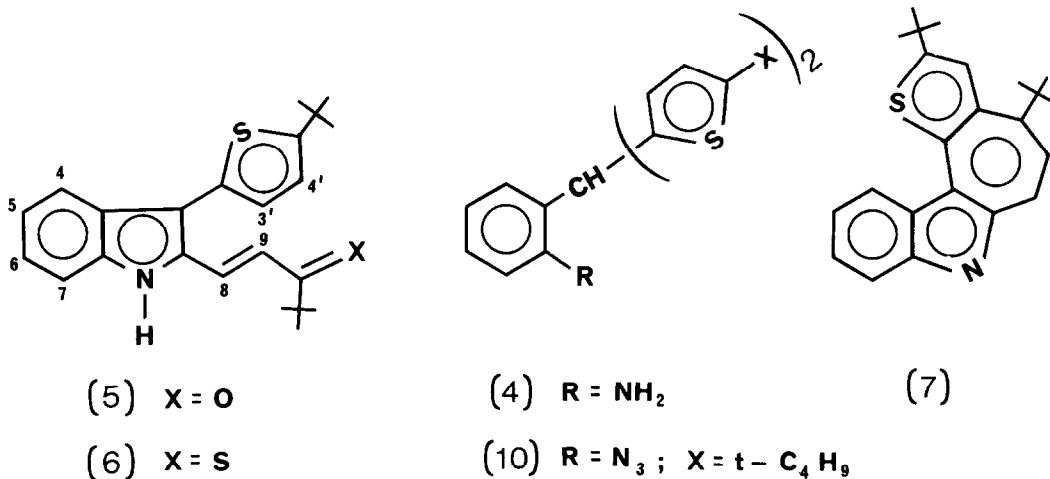
OPENING OF A THIOPHEN RING BY INTRAMOLECULAR NITRENE INSERTION

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Although there are several examples where nitrene insertion into furan rings leads to the isolation of imino-enones by ring opening^{1,2}, and although there is ample evidence for rearrangement of thiophen rings by nitrene insertion^{1,3,4}, there are no reports of the isolation of ring-opened products from reaction between thiophens and nitrenes. Recently it has been suggested that the rearrangement product from 2(*o*-nitrenobenzyl)-thiophen is formed via an unsaturated thio-aldehyde^{3,5}; we report here the isolation of unsaturated thione and the corresponding ketone from a nitrene attack on a thiophen ring, thus providing strong contributory evidence that such ring-opened products are intermediate in such insertions.



When the thiophens (1a)-(1d) were condensed with *o*-nitrobenzaldehyde using P₂O₅ in chloroform and ether solutions, all gave *o*-nitrophenyl-di-(5-X-thien-2-yl)methanes (2a)-(2d). Deoxygenation of these nitrocompounds with triethylphosphite (TEP) in boiling cumene gave in all cases as principal product the corresponding 9-(5-X-thien-2-yl)-2-X-thieno[3,2-b]quinoline (3a)-(3d). All had similar spectral properties exemplified by compound (3d)⁶ (Found: C, 72.7; H, 6.55; N, 3.25. C₂₃H₂₅NS₂ requires C, 72.75; H, 6.65; N, 3.65%); m/e 379 (M⁺), 364, 226, 149, 131, 119; δ(CDC1₃) 1.38 (18H, s), 6.83 (1H, d, J 4Hz, H3'), 7.12 (1H, d, J 4Hz, H4'), 7.3 (1H, s, H3), 7.3-7.7 (2H, overlapping tr of d, H6 and H7), 8.13 p.p.m. (2H, d, H5 and H8). Addition of Eu(fod)₃ simplified the spectrum, revealing 2 doublets at low field for H5 and H8. The only other products common to all deoxygenations were the corresponding amines (4a)-(4f).

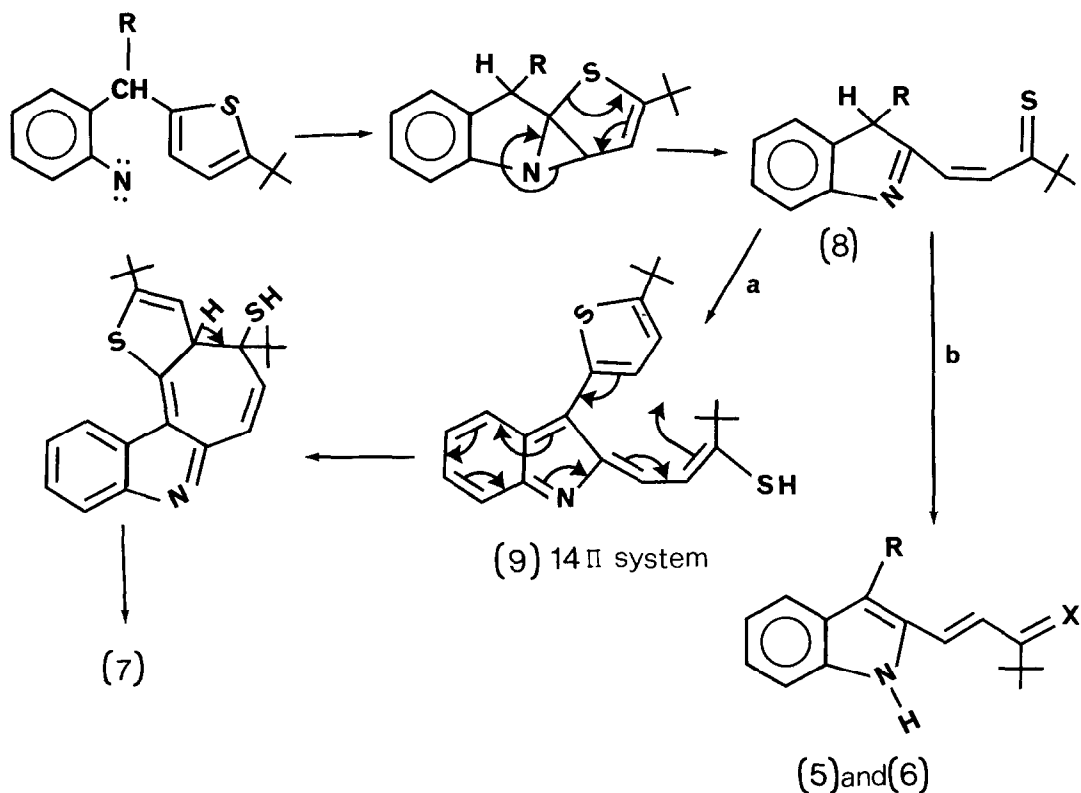


From the deoxygenation of compound (2d) three additional products were obtained. The first eluted from the alumina column during purification was deep blue in colour, the second yellow; after the amine (4d) (10% yield) and the thienoquinoline (3d) (~ 30% yield), a second yellow compound was obtained. All the coloured products were unstable, and have been characterised by exact mass determinations of the molecular ions, and by n.m.r. spectroscopy. The first yellow compound (~ 1.5%) had the formula $C_{23}H_{22}NOS$ (M^+ found 365.1809, required 365.1813; $M-57$ found 308.1120, required 308.1109; $M-(57 + 56)$ 252.0482, required 252.0483). The 1H n.m.r. spectrum leaves no doubt that this is the unsaturated ketone (5); $\delta(CDCl_3)$ 1.1 (9H, s), 1.3 (9H, s), 6.2 (1H, d, J 12.7 Hz, H9) 6.75 (1H, d, J 3.7 Hz, H3'), 6.82 (1H, d, J 3.7 Hz, H4'), 7.03 (1H, tr of d, J 7 and 1.6 Hz, H5 or H6), 7.24 (1H, d, J 12.7 Hz, H8), 7.26 (1H, tr of d, J 5.7 and 1.3 Hz, H6 or H5), 7.37 (1H, br d, H4), 7.65 (1H, br d, H7), and 12.4 p.p.m. (1H, br s, exch. D_2O , indole H). The other yellow band was the least stable of the three compounds being rapidly changed in air to give a mixture containing a compound of R_F identical with the ketone (5); this was the thione (6) (M^+ 381; $C_{23}H_{27}NS_2$ requires 381). $\delta(CDCl_3)$ 1.2 (9H, s), 1.4 (9H, s), 6.83 (1H, d, J 3.7 Hz, H3'), 6.94 (1H, d, J 3.7 Hz, H4'), 6.97 (1H, d, J 15.6 Hz, H9), 7.0-7.34 (3H, m, H5-7), 7.88 (1H, br d, H5 J 7 Hz, H5), 8.06 (1H, d, J 15.6 Hz, H8), and 8.72 p.p.m. (1H, br s, exch. D_2O , indole NH). In both of these spectra the most notable feature is a pair of widely spaced doublets with large J values derived from the AB system in the unsaturated side chain. The blue compound (6-8%) is thought to be the non-alternant polycycle (7). M^+ 347.1707; $C_{23}H_{25}NS$, requires 347.1708. λ_{max} 610 nm ($\epsilon > 10,000$); ^{13}C n.m.r. multiplicity in off-resonance spectrum shown as s, d, q, $\delta(CDCl_3)$ 29.14(q), 31.96(s), 32.55(q), 34.65(s), 110.18(s), 112.32(d), 112.86(d), 120.31(d), 121.24(d), 121.68(d), 123.53(s on d), 126.8(d), 132.1(s), 132.64(s), 133.86(s), 139.66(s), 151.26(s), and 157.54 p.p.m.(s), a total of 7 CH absorptions and 8 quaternary absorptions in the aromatic region. The 1H n.m.r. was relatively uninformative, showing peaks at δ 1.33 and 1.45 (both 9H, s), 5.64 (1H, s), 6.80 (1H, d, J 4 Hz), 6.85-7.17 (3H, m), and 7.55 (2H, overlapping d) p.p.m. In the scheme it can be seen that

the intermediate (8) can give by alternative hydrogen shifts either the compounds (5) and (6) by path (b), or the intermediate 14π system (9) by path (a). Cyclisation of the intermediate (9) and elimination of H_2S can lead to structure (7), whose non-alternant structure could account for the intense colour. Efforts are under way to synthesise the parent polycyclic system contained in structure (7) for a comparison of spectral properties. That all compounds are true nitrene products was confirmed by preparing the amine (4), m.p. 102-104° (petrol), (Found: C, 71.95; H, 7.65; N, 3.7. $C_{23}H_{29}NS_2$ requires C, 72.0; H, 7.60; N, 3.65%), and hence the azide (10), m.p. 91-93° (petrol), (Found: C, 67.15; H, 6.55; N, 10.2. $C_{23}H_{27}N_3S_2$ requires C, 67.45; H, 6.65; N, 10.25%), and decomposing the latter at 190° in trichlorobenzene. All five products were obtained in approximately the same proportions as in the deoxygenation.

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SCHEME



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