Some Novel Heterocycles from Deoxygenation of Indole *o*-Nitrophenyl Sulphides

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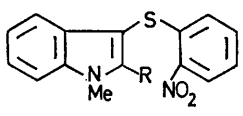
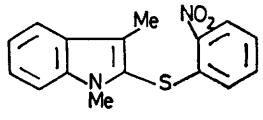
Summary With triethyl phosphite, the indolyl *o*-nitrophenyl sulphides (**1**), (**2**), and (**3**) gave, among other products, the dihydrobenzothiazepine (**4**), and the indolobenzothiazines (**7**) and (**9**), respectively, while the *o*-nitrophenylindoles (**10**) and (**11**) gave the isomeric indoloindoles (**12**) and (**13**); compound (**9**) changes rapidly into the spiro-oxindole (**8**).

IT has been known for some years that deoxygenation of aromatic nitro-compounds affords products formally derivable from nitrene intermediates.[1] In the phenyl *o*-nitrophenyl sulphide series, spirocyclic intermediates have been



(1) R = Me
(3) R = H



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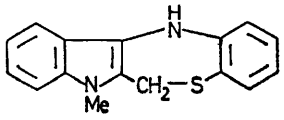

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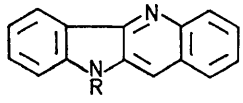
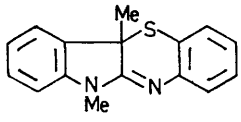


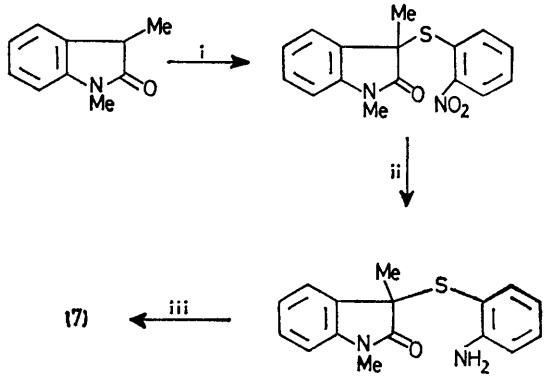
(5) R = Me
(6) R = H



(7)

implicated[2] in the formation of phenothiazines. No examples of nitrene cyclisations on to indole rings have so far been described although recently this has been attempted on the benzothiophen nucleus.[3] The high reactivity of indoles to electrophiles at the 3-position[4,5] and the possibility of synthesising new ring systems prompted an investigation of phosphite deoxygenation of *o*-nitrophenylsulphenylindole derivatives.

The indolyl *o*-nitrophenyl sulphides, (**1**)—(**3**), prepared from *o*-nitrobenzenesulphenyl chloride and the appropriate indole in ether–pyridine,[6] were heated under reflux for 3 h

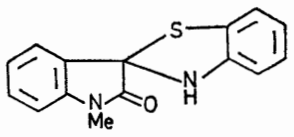


SCHEME 1. *Reagents:* i, *o*-$NO_2C_6H_4SCl$–tetrahydrofuran; ii, $Na_2S_2O_4$–EtOH–H_2O; iii, *p*-$MeC_6H_4SO_3H$–PhMe.

with $(EtO)_3P$ under nitrogen. The sulphide (**1**) gave, amongst other products, the dihydrobenzothiazepine (**4**) (34%), m.p. 186 °C, *m/e* 266 (M^+) and 232 ($M^+ - H_2S$), λ_{max} 251 and 331 nm which, on heating above its m.p., lost H_2S affording the indoloquinoline (**5**), m.p. 99 °C. Compound (**5**) was identical (i.r., mixed m.p., t.l.c.) with a sample prepared by methylation of the known[7] indolo-[3,2-*b*]quinoline (**6**).

The isomeric sulphide (**2**) on deoxygenation gave the indolobenzothiazine (**7**) (70%), m.p. 126—128 °C, *m/e* 266 (M^+) and 251 ($M^+ - Me$), λ_{max} 273, 298, and 333 nm, which was identical (i.r., mixed m.p., t.l.c.) with a sample synthesised as shown in Scheme 1.

Finally the sulphide (**3**) on deoxygenation under the above conditions gave, on work up in air, the spiro-oxindole (**8**) (15%), m.p. 167 °C, *m/e* 268 (M^+) and 240 ($M^+ - CO$), which was identical with a sample prepared from *N*-methylisatin and *o*-aminobenzenethiol. Other products, whose structures will be described more fully elsewhere, were also obtained in significant yields. Deoxygenation of (**3**) and rapid work-up afforded a solid, which was unstable in air, whose mass spectrum [*m/e* 268 (M^+) and 240 ($M^+ - CO$) (from **8**) and *m/e* 252 (M^+) and 237 ($M^+ - Me$)] and u.v.



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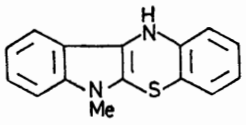

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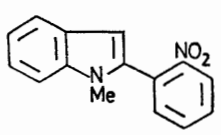

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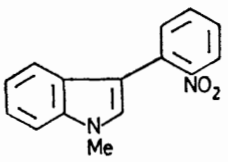

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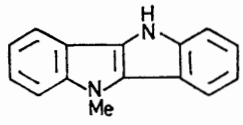

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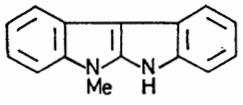
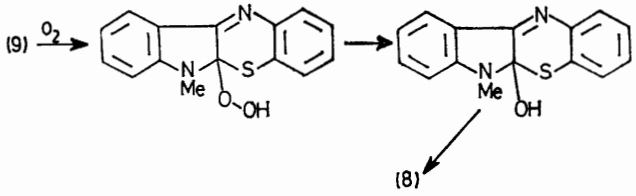


(13)

spectrum (λ_{max} 265 nm) were consistent with a mixture (*ca.* 1 : 4) of (**8**) and an indolobenzothiazine (**9**). Conversion of (**9**) into (**8**) in ethanol, in the presence of air, was rapid (half-life *ca.* 3 min) and could be followed spectroscopically in the u.v. cell (λ_{max} 265 → 256 and 310 nm). Instability to oxygen of 2,3-disubstituted indoles is well known;[8] the rapid conversion of (**9**) into (**8**) may also be rationalised as indicated in Scheme 2, attack of oxygen occurring at the 2- rather than the 3-position owing to activation by the 3-amino group.

Treatment of the *o*-nitrophenylindoles (**10**) and (**11**)[9] with $(EtO)_3P$ in cumene at 160 °C gave, respectively, (**12**), m.p. 212 °C, λ_{max} 260, 325, and 340 nm, and the novel indoloindole (**13**), m.p. 196 °C, λ_{max} 252 and 307 nm, in good yields, which were easily distinguishable by t.l.c. and h.p.l.c. Attempted desulphurisation of (**9**) with copper bronze[10] in 1,2,4-trichlorobenzene did not give (**13**) (h.p.l.c.) but gave only traces of (**12**).



SCHEME 2

In the cases of the indolyl sulphides (**1**) and (**2**), the results clearly indicate that deoxygenation is followed by the formation of a 5-membered spirocyclic intermediate which on sulphur migration leads to the stable products. The orientation of the indolobenzothiazine (**9**) follows by analogy.

The results show that phosphite deoxygenation of indolyl nitroaryl sulphides is a fruitful synthetic route to indolothiazepines and benzothiazines.

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