A Novel Thermal Rearrangement of 2-Nitrobenzenesulphenanilides

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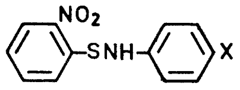
Summary 2-Nitrobenzenesulphenanilides (Ia,b) undergo an unusual thermal rearrangement to give phenothiazines (IIIa,b), aminonitrodiphenyl sulphides (IIa,c), and 2-aminobenzenesulphonanilides (IVa,b).

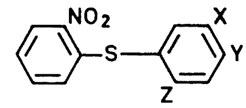
RECENT interest in nucleophilic participation by *o*-nitro-groups[1] prompts us to communicate some unusual thermal reactions of 2-nitrobenzenesulphenanilides. Previously, 2-nitrobenzenesulphenanilide (Ia) and 2-nitrobenzenesulphen-*p*-toluidine (Ib) have been reported to rearrange on heating to give only aminonitrodiphenyl sulphides (IIa) and (IIb), respectively.[2] In a reinvestigation of this rearrangement we have observed quite different results.

Heating sulphenamide (Ia) in a sealed tube with an excess of aniline for 15 hr., gave (IIIa),[3] (IIc),[4] (IIa),[5] and (IVa).[6] Sulphenamide (Ib) with *p*-toluidine gave (IIIb),[7] (IIb),† m.p. 87—88°, and (IVb).[8] 3-Nitrobenzenesulphenanilide (V), m.p. 92—93°, when heated in aniline gave only *o*- and *p*-aminodiphenyl sulphides (IVa), m.p. 63—64°, and (IVb), m.p. 130—131°. Products were separated by chromatography and identified by comparison with authentic samples. These results are summarized in the Table.

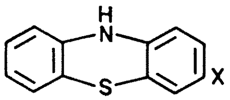
The major products isolated from the thermal reactions of sulphenamides (Ia, b) were the 2-aminobenzenesulphonamides (IVa, b). Compounds (IVa, b) were undoubtedly formed *via* an intramolecular transfer of oxygen from the nitro-group to the sulphur. This was supported by the lack of sulphonamide formation for sulphenamide (V) in which the nitro-group is not in the *o*-position, and by the fact that the absence or presence of oxygen has no effect on the yields of (IVa, b). Intramolecular transfer of oxygens has recently been demonstrated in the base-catalysed rearrangement of(Ia) to 2-azobenzenesulphenate.[1b]



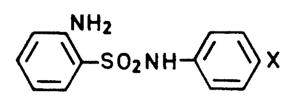
(I)a;X = H
b;X = Me



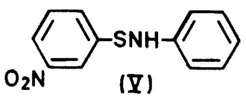
(II)a;X = Z = H,Y = NH$_2$
b;X = Me,Y = H,Z = NH$_2$
c;X = Y = H,Z = NH$_2$



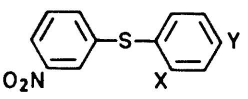
(III)a;X = H
b;X = Me



(IV)a;X = H
b;X = Me



(V)



(VI)a;X = NH$_2$,Y = H
b;X = H,Y = NH$_2$

Phenothiazines (IIIa, b) were apparently formed *via* a

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† Satisfactory elemental analysis, i.r. spectra, and ^{1}H n.m.r. spectra, were obtained for all new compounds.

Thermal reactions of nitrobenzenesulphenanilides at 195 ± 2° *for* 15 *hr.*

Sulphenamide	Solvent	Products (% yield)
(Ia)	Aniline	(Ia) 34%; (IIa) 12%; (IIc) 5%; (IIIa) 3%; (IVa) 37%
(Ib)	*p*-Toluidine	(IIb) 18%; (IIIb) 14%; (IVb) 55%
(V)	Aniline	(VIa) 22%; (VIb) 60%

thermal Smiles rearrangement of 2,2'-aminonitrodiphenyl sulphides (IIc) and (IIb), respectively.[9]

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