Tetrahedron Letters No.51, pp. 4483–4486, 1969. Pergamon Press. Printed in Great Britain.

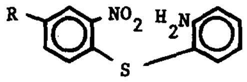
A NEW THERMAL REARRANGEMENT OF 2,2'-AMINONITRODIPHENYLSULFIDES

Franklin A. Davis and Ronald B. Wetzel (1)

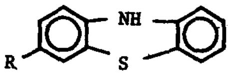
Department of Chemistry, Drexel Institute of Technology
Philadelphia, Pennsylvania 19104

(Received in USA 25 August 1969; received in UK for publication 3 October 1969)

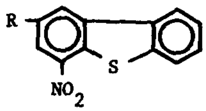
We wish to report a new thermal rearrangement of 2,2'-aminonitrodiphenylsulfides Ia-b to give phenothiazines IIa-b and 4-nitrodibenzothiophenes IIIa-b.



Ia, R=H
b, R=CH$_3$



IIa, R=H
b, R=CH$_3$



IIIa, R=H
b, R=CH$_3$

Heating 2-amino-2'-nitrodiphenylsulfide (Ia) (2) in a sealed tube with or without solvent at 190° for 15 hr., gave, after chromatography on Florisil, three identifiable fractions. The first, a white solid, m.p. 183° (lit. m.p.(3) 180°), was identified as phenothiazine (IIa) by comparison of its properties with an authentic sample. The second fraction gave yellow needles from ethanol, m.p. 160-1° (lit. m.p.(4) 161°), and was identified as 4-nitrodibenzothiophene (IIIa) by its infrared and mass spectra and by comparison of its ultraviolet spectrum with an authentic sample (4). The final fraction consisted of Ia.

Compound Ib, 2-amino-2'-nitro-4'methyldiphenylsulfide, was prepared in greater than 75 per cent yield by condensation of 2-mercaptoaniline with 3-nitro-4-chlorotoluene, m.p. 77-8°;

anal. calcd. for $C_{13}H_{12}N_2O_2S$: C, 59.98; H, 4.65; N, 10.76. Found: C, 59.79; H, 4.87; N, 10.59.

Diphenylsulfide Ib on heating gave results similar to Ia. 3-Methylphenothiazine (IIb), m.p. 167-8° (lit. m.p. (5) 168°), was identified by comparison of its properties with an authentic sample, and a yellow solid, m.p. 163-4° (needles from ethanol), was identified as 2-methyl-4-nitrodibenzothiophene (IIIb); anal. calcd. for $C_{13}H_9NO_2S$: C, 64.18; H, 3.73; N, 5.76; MW, 249. Found: C, 64.27; H, 3.78; N, 5.72; MW, 249 (mass spectrum). Structural proof of IIIb was based on its infrared and mass spectra and by independent synthesis.* The ultraviolet spectrum of IIIb was nearly identical to that of IIIa showing absorption at λ max 233 log ε 4.54; 267 log ε 4.15, 292 log ε 3.71, 302 log ε 3.88, and 382 log ε 3.71.

The yields of IIa-b and IIIa-b were appreciably better with solvent than without. These results are summarized in Table 1.

Table 1

Rearrangement of 2,2'-Aminonitrodiphenylsulfides at 190-5° for 15-16 hrs.

Diphenylsulfide	Solvent	Products (yields)
Ia	dimethylacetamide	IIa(31%), IIIa(20%), Ia(23%)
	-----	IIa(17%), IIIa(9%), Ia(60%)
Ib	dimethylacetamide	IIb(24%), IIIb(10%), Ib(50%)
	-----	IIb(18%), IIIb(6%), Ib(60%)

Phenothiazines IIa-b were apparently formed via a thermal Smiles rearrangement involving displacement and elimination of nitrous acid by the thiophenolate anion IV. A direct displacement of the nitro-group by the amine group would have resulted in 2-methylphenothiazine rather than the observed 3-methyl-phenothiazine (IIb).

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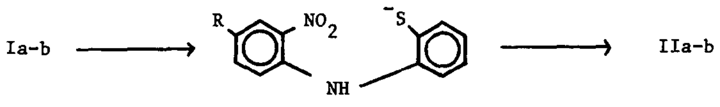
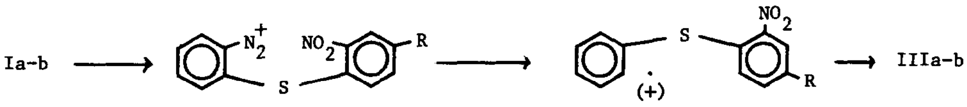
* Compound IIIb was prepared by thermal cyclization of the diazonium salt of Ib.



IV

Phenothiazines have been prepared by Smiles rearrangement of 2,2'-aminonitrodiphenylsulfides but invariably the reaction conditions required strong base and an acylamino group rather than the free amine (6). Furthermore Evans and Smiles reported that Ia does not undergo the Smiles rearrangement (7).

The 4-nitrodibenzothiophenes IIIa-b are undoubtedly formed via an intramolecular cyclization of intermediate V. Intermediate V may be formed either by homolytic cleavage of



VI V

the C-NH_2 bond or cleavage of the diazonium ion VI. The diazonium ion, VI, may be formed from Ia-b and nitrous acid produced in the rearrangement of Ia-b to IIa-b. Intramolecular cyclizations of similar diazonium salts are well known and have been extensively studied (8). We prefer the latter explanation since 2-aminodiphenylsulfide (9) gave no dibenzothiophene (10) under the reaction conditions.

Acknowledgement. We gratefully acknowledge support in part by a Frederick Gardner Cottrell grant-in-aid from the Research Corporation.

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