region of "thermodynamic interpretation" of the FI is restricted by the low adsorbed quantities in which the effects characteristic of the saturated surface are not manifested.

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Reaction of sulfenamides with *N*,*N*-dimethylaniline in the presence of phosphorus(v) oxochloride

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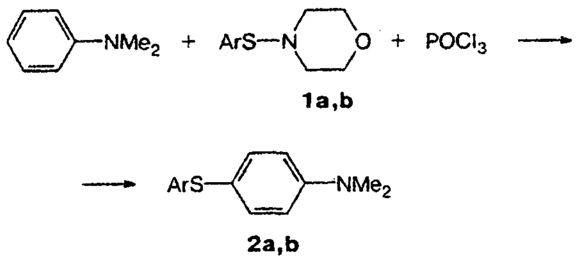
Reaction of arylsulfenamides with *N*,*N*-dimethylaniline in the presence of $POCl_3$ at room temperature affords unsymmetrical diaryl sulfide, only *para*-substituted *N*,*N*-dimethylanilines being formed.

Key words: sulfenamides, phosphorus(v) oxochloride, diaryl sulfides.

Sulfenylation of aromatic compounds with sulfenyl chlorides in the presence of Friedel—Crafts catalysts such as $AlCl_3$, $TiCl_4$, BF_3, and $FeCl_3$ was first described at the beginning of the 20th century and studied more extensively in the 1960s.[1—5] Later, sulfenamides activated with SO_3[6] and sulfenyl acetates activated with $AlBr_3$[6] were proposed as sulfenylating reagents. However, such reactions usually afford low yields, involving only reactive aromatic substrates. Recently, we found that arylsulfenamides in electrophilic sulfenylation of alkenes can be activated with phosphorus oxohalides.[7] It was promising to try this sulfenylating system in reactions with arenes.

We studied reactions of *p*-nitrophenylthiomorpholine (**1a**) and *o*-nitrophenylthiomorpholine (**1b**), both activated with $POCl_3$, with a number of aromatic substrates, *viz*., *N*,*N*-dimethylaniline, phenetole, anthracene, *p*-xylene, and toluene. The reaction with *N*,*N*-dimethylaniline (Scheme 1) yielded diphenyl sulfides monosubstituted at the *para*-position with respect to the dimethylamino group.

Scheme 1



Ar = 4-$NO_2C_6H_4$ (**a**), 2-$NO_2C_6H_4$ (**b**)

In the other cases, no substitution occurred; we recovered the starting aromatic compounds, yet disulfide, a product of sulfenamide decomposition, was formed. In all probability, the benzene ring activated with one or even two methyl groups still remains unreactive. The sulfenylation of phenetole seems to be hindered by the reaction of $POCl_3$ with the phenetole O atom rather than with the sulfenamide N atom.

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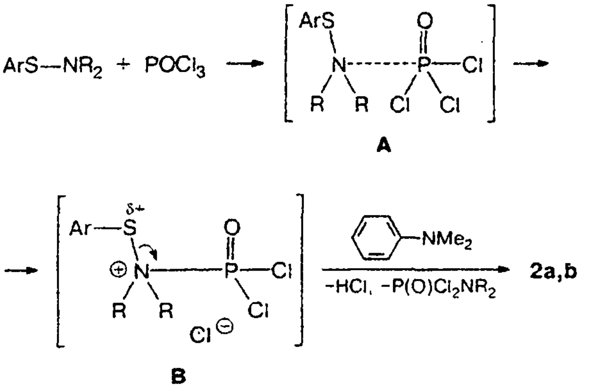
Apparently, the reaction of arylsulfenamide with phosphorus oxochloride, as in sulfenylation of alkenes, first gives a donor-acceptor complex **A** and then reagent **B**, in which the positive charge on the sulfur atom is higher than that in the starting sulfenamide (Scheme 2). As a result, the electrophilicity of the S^{II} atom becomes sufficient for sulfenylation of an aromatic substrate.

Scheme 2



Note that the sulfenylation of *N,N*-dimethylaniline occurs only at room temperature, as distinct from the sulfenylation of olefins with a sulfenamide—phosphorus oxochloride complex, which is completed at −40 °C within 10 min.[7] At lower temperatures, the reaction with *N,N*-dimethylaniline does not occur, while heating (refluxing in chloroform) predominantly favors the transformation of arylsulfenamide into the corresponding diaryl disulfide.

Experimental

^{1}H NMR spectra were recorded on a Varian VXR-400 instrument in $CDCl_3$.

Reactions of sulfenamides with *N,N*-dimethylaniline in the presence of phosphorus(v) oxochloride. A solution of $POCl_3$ (1 mmol) in anhydrous CH_2Cl_2 was slowly (~10 min) added with vigorous stirring at −20 °C to a solution of sulfenamide (1 mmol) in the same solvent. The reaction mixture was stirred for 10 min. Then a solution of *N,N*-dimethylaniline in anhydrous CH_2Cl_2 was added over 10 min, and stirring was continued for 6 h until reaction completion. The course of the reaction was monitored by TLC on a fixed layer of silica gel (Silufol). The reaction mixture was twice washed with water, and the organic layer was separated and dried over $CaCl_2$. Then, the organic fraction was passed through a thin layer of Al_2O_3, the solvent was removed *in vacuo*, and the residue was recrystallized from benzene.

4-Dimethylamino-4′-nitrodiphenyl sulfide (2a). Yield 43%. Yellowish brown crystals, m.p. 153—158 °C (from benzene). ^{1}H NMR, δ: 8.00, 7.06 (both d, each 2 H, 4-$NO_2C_6H_4$, J = 8.5 Hz); 7.38, 6.77 (both d, each 2 H, 4′-$Me_2NC_6\underline{H}_4$, J = 8.4 Hz); 3.05 (s, 6 H, NMe_2). Found (%): C, 60.85; H, 5.05; N, 9.88. $C_{14}H_{14}N_2O_2S$. Calculated (%): C, 61.29; H, 5.14; N, 10.22.

4-Dimethylamino-2′-nitrodiphenyl sulfide (2b). Yield 37%. Orange crystals, m.p. 188 °C. ^{1}H NMR, δ: 8.20, 6.82 (both d, each 1 H, 2-$NO_2C_6H_4$, J = 8.3 Hz); 7.29, 7.08 (both t, each 1 H, 2-$NO_2C_6H_4$, J = 8.3 Hz); 7.38, 6.77 (both d, each 2 H, 4′-$Me_2NC_6\underline{H}_4$, J = 8.4 Hz); 2.98 (s, 6 H, NMe_2). Found (%): C, 60.96; H, 4.78; N, 9.71. $C_{14}H_{14}N_2O_2S$. Calculated (%): C, 61.29; H, 5.14; N, 10.22.

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