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REACTION OF PHENYL DITHIOBENZOATE AND N-BUTYLTHIOACETAMIDE WITH N-NITROSOACETANILIDES

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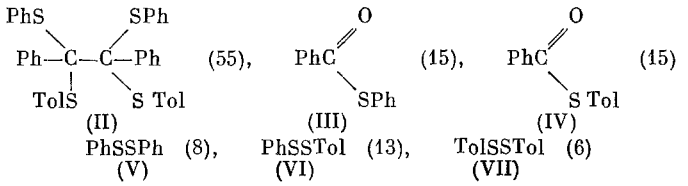
In our previous work [1, 2], we showed that the aryl radicals which arise in the radical arylation of compounds containing the C=S group such as thioureas, thioamides, and esters of thiocarboxylic acids always add at the S atom to form intermediate radical-adducts of the type $R-\dot{C}(X)SAr$ (X = NH_2, NHR, and OR). In many cases, these radicals may be detected by ESR spectroscopy by the use of spin traps and their subsequent chemical transformations may be followed by preparative methods.

In a continuation of this work, we studied the reaction of $p\text{-}MeC_6H_4^{\bullet}$ radicals ($Tol^{\bullet}$), generated by the decomposition of N-nitrosoaceto-p-toluidine (NAT), with the phenyl ester of dithiobenzoic acid PhC(S)SPh (I). This reaction proceeds at 20°C with virtually complete conversion of the starting dithioester; the products obtained and their yields (in % of theoretical yield) are given below



The high overall yield of products containing the $STol^{\bullet}$ group indicates that there is virtually complete addition of the tolyl radicals to the sulfur atom of the C=S group of the dithioester. The formation of 1,2-bisphenylthio-1,2-bistolylthio-1,2-diphenylethane (II) as the major product unequivocally indicates that the radical-adduct $PhC^{\bullet}(SPh)STol$ (A) is formed in the arylation of phenyl dithiobenzoate (I).

Dimerization as a pathway for the stabilization of radical-adduct A is noted for the first time in this reaction. In analogous reactions for thioamides and thioureas, the radical-adducts are stabilized by other pathways [1].

The formation of (III)-(VII) and the ratio of their yields may be explained assuming that the intermediate radical-adducts A not only dimerize but also undergo oxidation to radicals $PhC(\dot{O})(SPh)STol$ (B). The possibility of such a reaction has been established by an ESR spectroscopic study of analogous radicals formed in the thermolysis and photolysis of acetophenone diphenylmercaptol [3]. In the reaction studied, the products of the decomposition of the acylating reagent (the N-nitroso compound) may act as the oxidizing agent. The fragmentation

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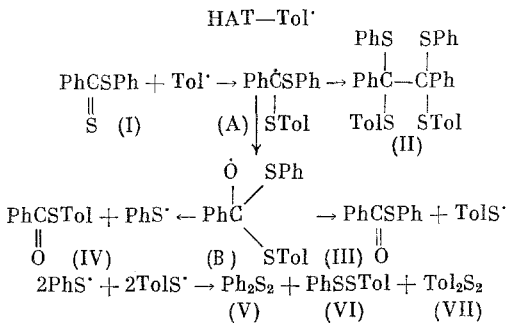
of B radicals due to β-elimination of the arylthio groups should clearly lead to the formation of the corresponding S-aryl thiolbenzoates and arylthio radicals, such that the entire process may be described by scheme 1.

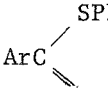
Scheme 1



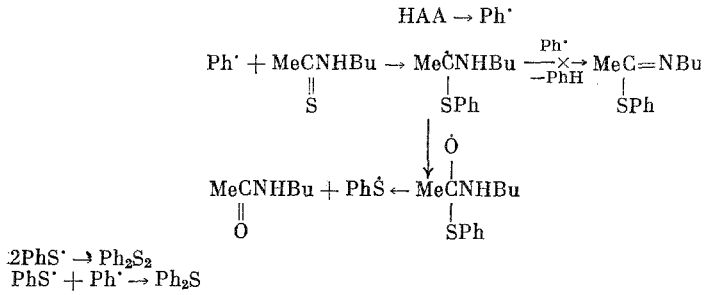
The absence of PhC(S)STol in the reaction products apparently indicates that the recombination of A radicals is more facile than fragmentation with breakage of an S—Ar bond observed in several other examples [2].

In accord with scheme 1, the total yields of diphenyl, ditolyl, and phenyl tolyl disulfides, on one hand, and of aryl thiolbenzoate, on the other. Indeed, the data given above indicate that there is good agreement between these values. The finding that (III) and (IV) are formed in 1:1 ratio indicates that the PhS and TolS groups are eliminated to an equal extent.

The formation of equimolar amounts of phenyl benzoate and diphenyl disulfide in the radical phenylation of phenyl thionobenzoate PhC(S)OPh [2] is also apparently explained by oxidation of the radical-adduct and subsequent fragmentation.

In this regard, it is interesting to note that the radical arylation of thioamides in some cases may also proceed by an analogous scheme, i.e., through the oxidation of the radical-adduct. Thus, in our previous work [4], we showed that, in contrast to aromatic thioamides ArC(S)NHAr', which react with N-nitrosoacetanilide (NAA) to give **S-phenylisothioamides**  , **aliphatic thioamides AlkC(S)NHAlk** form only Ph_2S_2 and Ph_2S as virtually the only sulfur-containing products. In the present work, we showed that the reaction of N-butylacetamide with NAA gives N-butylacetamide in addition to Ph_2S_2 and Ph_2S. The yield of N-butylacetamide is close to the total yield of these sulfur-containing compounds. These results permit us to describe the reaction by scheme 2.

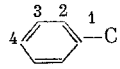
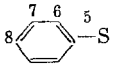
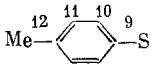
Scheme 2



Thus, in the case of aliphatic thioamides, the oxidation of radical-adducts is preferred over their cross-disproportionation with Ph· radicals to form N-butylisothioamide.

Scheme 2, in contrast to scheme 1, also involves the formation of Ph_2S due to the recombination of PhS· and Ph· radicals. This is explained by the presence of phenyl radicals in large excess during the reaction of N-butylthioacetamide with NAA since the conversion of the starting thioamide is only 50%.

TABLE 1. Chemical Shifts of the Aromatic Ring Carbon Atoms in the ^{13}C NMR Spectrum of PhC(SPh)(STol)—C(SPh)(STol)Ph

Aromatic ring	C atom number	$\delta^{13}C$, ppm from TMS
	1	139,76; 139,65
	2	128,68; 128,58
	3	127,35
	4	127,55
	5	133,27; 133,32
	6	135,22; 134,87
	7	127,73
	8	127,35; 127,73
	9	129,24; 128,94
	10	133,85
	11	128,58
	12	137,87; 137,62

We should stress that the alternative pathway for the formation of thiolic esters from dithioesters and, correspondingly, of amides from thioamides in these reactions, namely, hydrolysis by the action of the acid products of the decomposition of N-nitrosoacetanilides, may be excluded since a special experiment showed that phenyl dithiobenzoate does not undergo hydrolysis upon prolonged maintenance with acetic acid under the experimental conditions. Thioamides are known to undergo hydrolysis only in the presence of strong mineral acids [5].

All the compounds obtained in the present work, with the exception of (II), were identified relative to authentic samples by PMR spectroscopy, thin-layer chromatography R_f values, and gas–liquid chromatography retention times.

The structure of (II) was supported by ^1H and ^{13}C NMR spectroscopy and mass spectroscopy. The mass spectrum of this compound has peaks characteristic for fragments with m/z 321 (39%), PhC(SPh)STol, 178 (4.6%) PhCCPh, 123 (64%) STol, 109 (50%) SPh, 91 (47%) Tol, 77 (57%) Ph. PMR spectrum (δ, ppm): 2.21 s (6H, tolyl group CH_3), 6.9-7.7 m (28H, aromatic protons). The ^{13}C NMR spectrum has signals for the CH_3 group (δ, 21.20 ppm) and the tetrasubstituted carbon atom in addition to signals for the aromatic ring ^{13}C. The signal for the tetrasubstituted carbon atom is split (δ, 76.58 and 76.54 ppm) due to the existence of d, l- and meso forms.

Diastereomeric splitting is also found for several aromatic ring carbon atoms (Table 1).

EXPERIMENTAL

The ^1H and ^{13}C NMR spectra were taken on a Bruker WP-200 SY spectrometer in acetone-d_6 and CCl_4 from TMS as internal standard. The mass spectra were taken on an MS/DS-50 mass spectrometer with direct inlet. The sample inlet temperature was 20°C. The ionization chamber temperature was 150°C. The ionizing voltage was 70 eV. The gas–liquid chromatographic analysis was carried out on an LKhM-80 chromatograph with a katharometer detector on a 1 m × 3 mm column packed with 5% silicone SE-30 and 6% PEG (20,000) on Chromaton N-AW (0.16-0.20) in a helium stream. All the experiments were carried out in a nitrogen stream.

Reaction of Phenyl Dithiobenzoate (I) with NAT. A sample of (I) was obtained according to Perdersen et al. [6]. A solution of 2.3 g (10 mmoles) (I) and 2 g (11 mmoles) NAT in 40 ml acetone was stirred for 20 h at 20°C. The solvent was distilled off. The residue was subjected to chromatography on a column packed with L100/160 silica gel. Elution with 9:1 hexane–benzene gave 0.3 g of a mixture of disulfides Ph_2S_2 (V), TolSSPh (VI), and Tol_2S_2 in 1.4:2.2:1.0 ratio (as indicated by gas–liquid chromatography). Elution with 3:1 hexane–benzene gave 1.8 g (55%) 1,2-bisphenylthio-1,2-bistolylthio-1,2-diphenylethane (II) as a noncrystallizing oil. Elution with 1:1 hexane–benzene gave 0.7 g of a mixture of S-phenyl thiolbenzoate (III) and S-tolyl thiolbenzoate (IV) in 1:1 ratio (as indicated by gas–liquid chromatography and PMR spectroscopy).

Action of Acetic Acid on (I). A solution of 0.5 g (I) and 0.15 g acetic acid in 10 ml acetone was stirred for 20 h at 20°C. Gas–liquid chromatography indicated that the reaction mixture did not contain (III). After distilling off the solvent, the dry residue had mp 61°. A mixed sample with (I) did not give a depressed melting point. The yield 0.48 g (96%) (I).

Reaction of N-Butylthioacetamide with NAA. A solution of 1.5 g (11.5 mmoles) thioamide and 2.0 g (12 mmoles) NAA in 25 ml acetone was stirred for 20 h at 20°C. The acetone was distilled off and the residue was subjected to chromatography on a column packed with L100/160 silica gel using 10:1 benzene–ethanol as eluent to yield (in order of elution): 0.7 g of a 70:30 mixture of Ph_2S_2 and Ph_2S (the ratio was found by gas–liquid chromatography), 0.7 g starting thioamide, and 0.4 g MeCONHBu.

CONCLUSIONS

1. The reaction of phenyl dithiobenzoate with N-nitroso-p-toluidine proceeds with complete capture of the tolyl radicals formed in the decomposition of NAT by the thione group. The major reaction product is 1,2-bisphenylthio-1,2-bistolylthio-1,2-diphenylethane, which indicates the intermediate formation of the radical-adduct $PhC^{\bullet}(SPh)STol$ (A).

2. A side-reaction leading to the formation of S-tolyl and S-phenyl thiolbenzoates and diaryl disulfides is explained by the oxidation of radical-adduct A and subsequent fragmentation due to loss of an $ArS^{\bullet}$ radical.

3. The reaction of N-butylthioacetamide with N-nitrosoacetanilide involves oxidation of radical-adduct $MeC^{\bullet}(SPh)NHBu$ and subsequent fragmentation, which is the major pathway of the reaction leading to the formation of N-butylacetamide, diphenyl disulfide, and diphenyl sulfide.

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STABILITY OF 2-HYDROXYALKYL ESTERS OF THIO- AND SELENOPHOSPHORIC ACIDS WITH TWO 1,1-DIMETHYL-2,2,2-TRICHLOROETHOXY SUBSTITUENTS AT THE PHOSPHORUS ATOM

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The introduction of two bulky t-BuO groups at the phosphorus atom in 2-hydroxyalkyl esters of dialkylthiophosphoric acids prevents the hydroxy–thiol rearrangement [1].

The introduction of one 1,1-dimethyl-2,2,2-trichloroethoxy (DMTCE) group, which is more resistant to decomposition than the t-BuO group, at the phosphorus atom does not prevent the hydroxy–Thiol rearrangement of such 2-hydroxyalkyl esters but only hinders it [2].

In the present work, we showed that the introduction of two DMTCE groups stabilizes not only 2-hydroxyalkyl esters of thiophosphoric acids but also their selenium analogs. S- or Se-2-Hydroxyalkyl esters with two bulky DMTCE substituents at the phosphorus atom were obtained as a result of the reaction of oxiranes with the corresponding thio- or selenoacids as follows

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