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PUMMERER REACTIONS OF N-ACETYLIMINODIALKYLSULFURANES[1]

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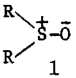
In the classical Pummerer reaction, sulfoxides are converted to α-substituted sulfides by acids, anhydrides and acyl halides.[2] The close formal resemblance in polarity between the S-O bond in sulfoxides (1) and the S-N bond in iminosulfuranes (sulfilimines) (2) suggested to us that iminosulfuranes might undergo Pummerer-type rearrangements. In this paper we describe the first examples of Pummerer rearrangements involving iminosulfuranes and electrophiles.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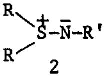
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N-Acetyliminodimethylsulfurane (3) was selected as the model compound for a study of the reactions with acetyl chloride, benzoyl chloride, and acetic anhydride, as this ylid is readily prepared in high purity.[3] The results obtained are shown in Table 1.

Table 1

REACTIONS OF N-ACETYLIMINODIMETHYLSULFURANE (3) WITH ACYL HALIDES AND ANHYDRIDES

Reactant	Solvent	Reaction Temp.,°C.	Products	Yields, %
CH_3COCl[a]	CH_2Cl_2	25-30	$HN(COCH_3)_2$	52
			CH_3SCH_2Cl	48
			HCl[c]	11
C_6H_5COCl[a]	CH_2Cl_2	25-30	$CH_3CONHCOC_6H_5$	40
			CH_3SCH_2Cl	39
			HCl[c]	16
$(CH_3CO)_2O$[b]	-	70-5	$NH(COCH_3)_2$	58
			$CH_3SCH_2OCOCH_3$	63

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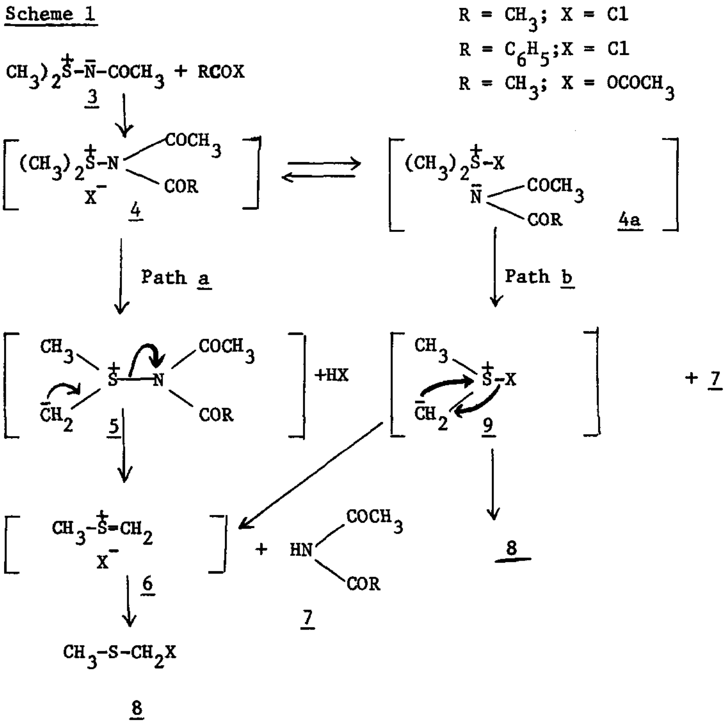
[a] Approximately equimolar (0.02 mole) proportions of 3 and the acid chloride in CH_2Cl_2 (50 ml.). Products were isolated by high vacuum distillation; the identity of the cold trap condensates and pot residues was established by comparison with authentic samples.[5,6]

[b] Approximately 0.02 mole of 3 in 25 ml (0.25 mole) of acetic anhydride. Products isolated and identified as above.[7]

[c] Trapped in the reaction mixture as N-acetyliminodimethylsulfonium chloride, and identified by comparison (ir) with an authentic sample, mp 132-3° (dec.).[3]

The mechanism of the Pummerer reaction involves initial nucleophilic attack of the highly polar oxygen atom in sulfoxides on the electrophilic carbonyl carbon atom of the acid chloride or anhydride to form an acyloxysulfonium salt, which then gives rise to an ylid. The ylid subsequently reacts via an intermolecular process.[2] We have rationalized the reactions of 3 in an analogous way (Scheme 1).

Scheme 1

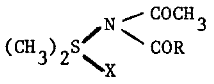


In the first step of Scheme 1, RCOX reacts with the iminosulfurane (3) to produce the intermediate (4) (not isolated), strictly analogous to the first step proposed in Pummerer rearrangements. Further reaction of 4 may proceed by two alternate pathways, Path a and/or Path b. At this time, no distinction can be made between these two alternatives.

In Path a, 4 eliminates the species HX to yield the ylid (5), a carbosulfurane. The species HX, in the cases where X=Cl, is a strong acid and converts some of the starting material (3) to the derived salt (N-acetyliminodimethylsulfonium chloride); this product is obtained in approximately 10-15% yield. The ylid (5) is cleaved to produce the ion-pair intermediate (6)(nonisolated) which can readily undergo intermolecular addition of X^- to yield α-chloromethylthiomethane (α-chloromethyl methyl thioether)(8, X = Cl) (39-48% yield) and the appropriate amide (7), diacetamide (52% yield) or N-benzoylacetamide (40% yield) (RCOX=CH_3COCl or PhCOCl respectively).When acetic anhydride is used, the final products are diacetamide (58% yield) and α-acetoxymethylthiomethane (8, X = $OCOCH_3$) (63% yield).

Path b must also be considered as it seems reasonable to assume that ion pairs 4 and 5 may coexist in equilibrium.[4] The anion in ion pair 4a should be highly stabilized as the nitrogen anion is attached to two strongly electron-withdrawing groups. This anion could readily abstract a proton from the $(CH_3)_2\overset{+}{S}-X$ entity to give the observed amides, and another ylid (9). A final rearrangement then yields the thioether product (8). On the other hand, 9 may decompose to ion pair 6 followed by recombination to 8.

An appealing alternative to ionic structures 4 and 4a is a neutral tetracovalent sulfur compound (10),[4] which could yield either ion pair 4 or 4a or proceed directly to products.



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A requirement of the pathways in Scheme 1 is that identical yields of amides and thioethers be obtained. Examination of Table 1 shows this to be the case.

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