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Reaction of Pummerer Rearrangement Intermediates with Sulphides and Thiols. Synthesis of Sulphonium Salts and Dithioacetals

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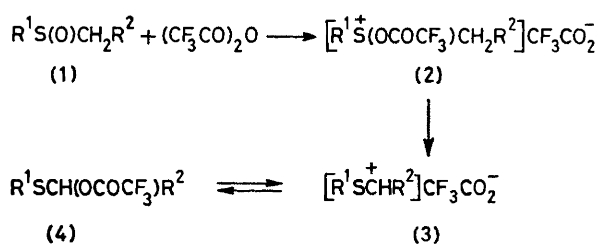
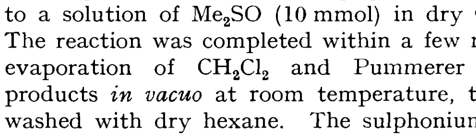
Summary Sulphides (**5**) and thiols (**6**) react instantly with the Pummerer rearrangement intermediates (**3**) at 0 °C to give sulphonium salts (**7**) and dithioacetals (**8**), respectively.

The Pummerer rearrangement has been suggested to proceed *via* a sulphonium ion and a sulphur-stabilized carbonium ion.[1] Although an intermediary sulphonium ion has been postulated in many reactions, only a sulphur-stabilized carbonium ion has been postulated in aromatic substitutions.[2] When sulphoxides (**1**) and $(CF_3CO)_2O$ are used, the Pummerer rearrangement is interpreted to proceed as shown in Scheme 1.[3]



Scheme 1

In previous papers[4] we have described the nucleophilic attack of the sulphur atom of sulphides (**5**) and thiols (**6**) on the sulphur cation of acyloxysulphonium salts (**2**) at −80 °C. We now report a different mode of reaction at 0 °C, *i.e.*, an attack of the sulphur atom of (**5**) and (**6**) on the carbon cation of intermediates (**3**), and the successful application of this reaction to the synthesis of sulphonium salts (**7**) and dithioacetals (**8**) (Scheme 2).



$$(\mathbf{3}) + \underset{\substack{(\mathbf{5})\\(\mathbf{6})\ (R^4 = H)}}{R^3SR^4} \rightarrow \underset{(\mathbf{7})}{[R^1SCHR^2\text{–}\overset{+}{S}R^3R^4]CF_3CO^-} \downarrow CF_3CO_2R^4 + \underset{(\mathbf{8})}{R^1SCHR^2SR^3}$$

Scheme 2

In a typical procedure, solutions of $(CF_3CO)_2O$ (13 mmol) and Me_2S (13 mmol) in dry CH_2Cl_2 were successively added to a solution of Me_2SO (10 mmol) in dry CH_2Cl_2 at 0 °C. The reaction was completed within a few minutes. After evaporation of CH_2Cl_2 and Pummerer rearrangement products *in vacuo* at room temperature, the residue was washed with dry hexane. The sulphonium salt (**7a**) was obtained as a colourless liquid in 64% yield [δ (CD_3CN) 2·42 (3H, s, MeS), 2·95 (6H, s, MeS^+), and 4·50 (2H, s)]; this n.m.r. spectrum was identical to that of the sulphonium salt prepared from $MeSCH_2SMe$ and $MeOSO_2F$.

The salt (**7a**) was also instantly obtained in 70% yield from Me_2S and the Pummerer rearrangement product (**4**, R^1 = Me, R^2 = H) in the presence of CF_3CO_2H, but without an acid Me_2S did not react with (**4**), *i.e.*, the CF_3CO_2H formed as a by-product in the Pummerer rearrangement plays an important role. Other sulphonium salts (**7b**—**g**) were similarly obtained (Table). On keeping at room temperature for a few days, (**7a**, **b**, **e**—**g**) were stable, but (**7c** and **d**) partially decomposed to $MeSCH_2SMe$. Treatment of (**3**)

TABLE

Reactant	R^1	R^2	R^3	R^4	Product	Isolated yield/%
(**5**)	Me	H	Me	Me	(**7a**)	64
(**5**)	Me	H	Me	Oct^n	(**7b**)	65
(**5**)	Me	H	Me	Bu^t	(**7c**)	54
(**5**)	Me	H	Me	$PhCH_2$	(**7d**)	67
(**5**)	Me	H	Et	Et	(**7e**)	70
(**5**)	Me	H	$-[CH_2]_4-$		(**7f**)	73
(**5**)	Ph	H	Me	Me	(**7g**)	40
(**6**)	Me	H	Ph	H	(**8h**)	94
(**6**)	Me	H	$PhCH_2$	H	(**8h**)	89
(**6**)	Ph	H	Ph	H	(**8j**)	69
(**6**)	Ph	Me	Ph	H	(**8k**)	76

with (**6**) gave (**8**) in the place of (**7**), probably because deprotonation from (**7**) was too rapid. Therefore, compounds (**8**) were isolated in high yields by distillation instead of washing with hexane in the above-mentioned procedure (Table).

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