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Oxosulfonium Salts. IV. Preparation and Reactions of Methylphenyloxosulfonium Methylide[1]

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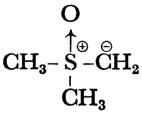
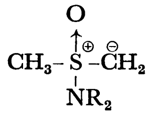
Synopsis. Methylphenyloxosulfonium methylide was synthesized, and its reactions with several substrates possessing C=C and C=O bonds were investigated.

Sulfur ylides have proved to be very versatile and useful synthetic intermediates.[2,3] However, the majority of the ylides investigated so far are tri-coordinated ylides, and dimethyloxosulfonium methylide[4] (**1**) and (dialkylamino)methyloxosulfonium methylide[5] (**2**) are the only examples of tetracoordinated sulfur ylides reported in the literature.



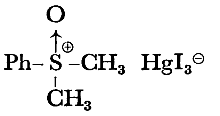
$CH_3-\overset{\overset{O}{\uparrow}}{\underset{CH_3}{\overset{\oplus}{S}}}-\overset{\ominus}{C}H_2$

1



$CH_3-\overset{\overset{O}{\uparrow}}{\underset{NR_2}{\overset{\oplus}{S}}}-\overset{\ominus}{C}H_2$

2



$Ph-\overset{\overset{O}{\uparrow}}{\underset{CH_3}{\overset{\oplus}{S}}}-CH_3\ HgI_3^{\ominus}$

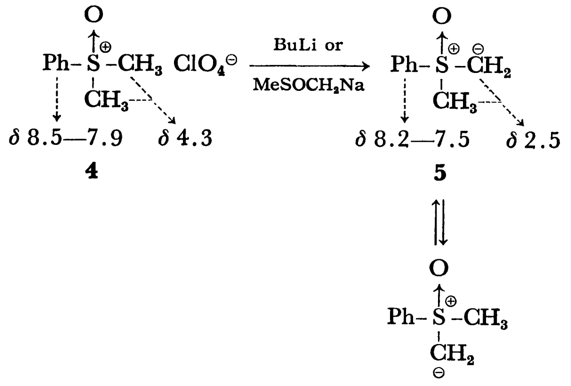
3

Since oxosulfonium ylides are expected to show reactivities differing from those of sulfonium ylides and are of interest especially for application to asymmetric syntheses, we have investigated the synthesis of new oxosulfonium ylides.

The reason why oxosulfonium ylides other than **1** have not been investigated is that the syntheses of oxosulfonium salts are very difficult. Alkylation of sulfoxides always results in *O*-alkylation with very little *S*-alkylation,[6] although as an exceptional case the *methylation* of *dimethyl* sulfoxide produces trimethyloxosulfonium ion in a good yield.[4] We have overcome this difficulty by using mercury(II) iodide as the catalyst, and obtained dimethylphenyloxosulfonium salt **3** from methyl phenyl sulfoxide and methyl iodide in a 49% yield.[6]

3 was converted into perchlorate **4** by use of silver perchlorate, and **4** was converted into methylphenyloxosulfonium methylide **5** by use of butyllithium or dimsylsodium.

When **4** was treated with NaH in DMSO-d_6, the NMR spectrum of the methylide obtained showed multiplets at δ 8.2—7.5 ppm (5H; C_6H_5) and δ 2.5 (5H; $-CH_3$, and $-\overset{-}{C}H_2$). This indicates that exchange of protons of $-CH_3$ and $-CH_2^-$ is rapid within the NMR time scale.

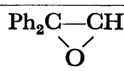
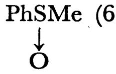
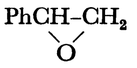
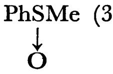
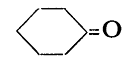
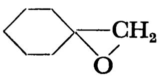
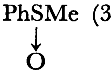
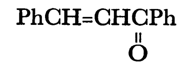
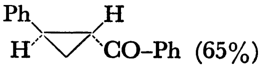
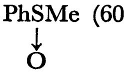
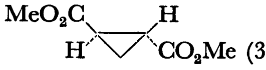
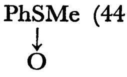
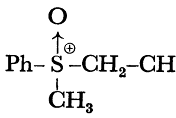
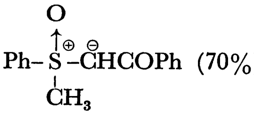


The aromatic hydrogens of **5** absorb in magnetic fields higher than those in **4**. This is reasonable since **5** has a negative charge next to the sulfonium sulfur atom.

The reactions between **5** and several substrates were investigated, and the results are summarized in the Table.

Other substrates examined were CO_2, $PhCH_2Br$, Me_3SiCl, PhNCO and $PhN_2^+BF_4^-$, but it was not

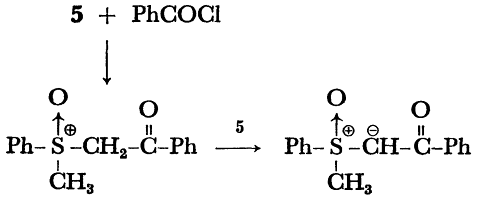
Table 1. Products of the reactions between **5** and several substrates

Substrate	mol/mol **5**	Products (mol % yield)[a]
Ph_2CO	1.02	 (73%)  (63%)
PhCHO	1.02	 (41%)  (32%)
	1.07	 (26%)  (39%)
trans-Stilbene	1.09	*trans*-Stilbene (88%)
 $PhCH{=}CH\underset{\overset{\|}{O}}{C}Ph$	1.00	 (65%)  (60%)
Dimethyl maleate	1.00	 (32%)  (44%) Dimethyl fumarate (4%)
$Me_3O^{\oplus}\ BF_4^{\ominus}$	1.35	 (42%)
PhCOCl	0.51	 (70%)[b]

a) Based on the mol of **5** used. b) Based on half the mol of **5** used.

possible to isolate characterizable products.

As shown in the Table, the reaction between **5** and benzoyl chloride produced a stable oxosulfonium phenacylide. This can be explained by assuming the deprotonation of methylphenacylphenyloxosulfonium ion with **5**.



In the reaction with methyl maleate, the product of addition was not methyl cyclopropane-*cis*-dicarboxylate, but methyl cyclopropane-*trans*-dicarboxylate. One should note that methyl fumarate was produced in a 4% yield. These facts suggest that after **5** was added to methyl maleate the C=C bond in the adduct rotated, and the products were formed from the more stable conformation.

In the reaction with benzylideneacetophenone, **5** transfers the methylene to its C=C bond, whereas sulfonium ylide $PhMe\overset{+}{S}–\overset{-}{C}H_2$ transfers the methylene to the C=O bond.[7]

If optically-active $ArAr'\overset{+}{S}(\to O)\overset{-}{C}H_2$ could be synthesized, their reactions with various substrates would be of great interest.

Experimental

Conversion of 3 to 4. A saturated solution of $AgClO_4$ (25 g, 120.5 mmol) in acetone was added drop by drop to a stirred solution of **3** (25.5 g, 34.6 mmol) in acetone (400 ml), and the HgI_2 and AgI formed were filtered off. After the filtrate was evaporated in a vacuum, the residue was washed with ether and recrystallized three times from ethanol; the yield of **4**, 4.4 g (50%).

Conversion of 4 to 5. The following two methods were used. a) After **4** (0.8 g, 3.14 mmol) was dissolved in THF (30 ml; dried by refluxing with $LiAlH_4$ overnight) under a nitrogen atmosphere, the solution was cooled to −60 °C, and a hexane solution of butyllithium (1.6 M, 2.2 ml; 3.45 mmol) was added. The mixture was stirred for 1 h at −60 °C.

b) A slightly excess NaH (0.1 M mineral oil dispersion) was washed several times with petroleum ether in a three-necked flask under nitrogen, and then some DMSO (dried over CaH_2 for 3 h) was added. The mixture was heated to and kept at 70 °C until evolution of hydrogen ceased (about 1 h). After it was cooled to room temperature, a DMSO solution of **4** was slowly added.

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