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THE CHEMISTRY OF O-SILYLATED KETENE ACETAL; PUMMERER REARRANGEMENT OF SULFOXIDES INTO α-SILOXYSULFIDES

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Summary: Treatment of sulfoxides with ketene silyl acetal in anhydrous acetonitrile in the presence of a catalytic amount of zinc iodide causes a Pummerer rearrangement to give α-siloxysulfides under extremely mild conditions.

The Pummerer rearrangement of sulfoxides is widely recognized as an important reaction because it provides a means for the facile introduction of α-substituted sulfides.1) Very recently, some silylating agents were found to be useful for the Pummerer type reaction of sulfoxides, but gave elimination products predominantly: The use of iodotrimethylsilane/diisopropylethylamine2) or chlorotrimethylsilane in the absence of added base3) gives α,β-unsaturated sulfides. We now report here a new methodology leading to α-siloxysulfides from the sulfoxides by a silicon induced Pummerer rearrangement.

We have reported that the use of ketene silyl acetals leads to rapid silylation of active hydrogen compounds, such as alcohols, carboxylic acids, mercaptans, enolizable ketones, and amides under neutral conditions.4,5) We now found that ketene methyl t-butyldimethylsilyl acetal (1)5) is quite useful for the Pummerer reaction of sulfoxides (2) leading to α-siloxysulfides (3) rather than α,β-unsaturated sulfides (4) under extremely mild conditions. This is the first case that ketene silyl acetal has been employed to effect Pummerer rearrangement.

The sulfoxides (2a-g) were treated with 1.2-2.4 eq. of 1 in anhydrous acetonitrile in the presence of 0.05 eq. of zinc iodide at ambient temperature to give the corresponding α-siloxysulfides (3a-g), in some cases, accompanied by the α,β-unsaturated sulfides (4c,g). The structures of 3 and 4 were proved by microanalyses and spectral data. The results are summarized in the Table.

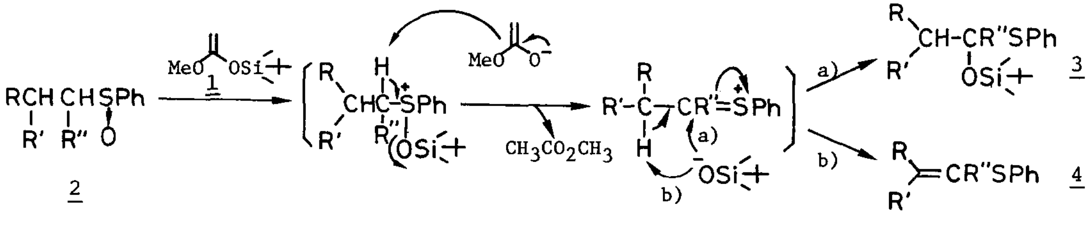
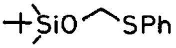
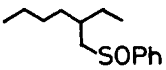
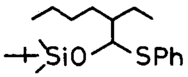
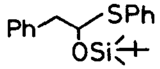
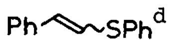
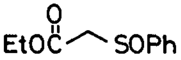
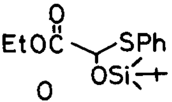
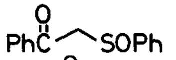
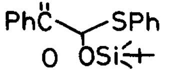
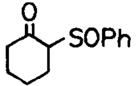
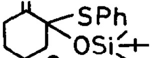
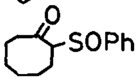
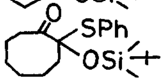
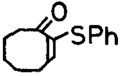


Table Pummerer Rearrangement of Sulfoxides (2a-g)

Sulfoxides (2)		Reaction Conditions	Products[a] (3 and 4)		Yield[b] (%)	M.p. (°C) (solvent) or B.p. (°C/mmHg)[c]
	2a	r.t. 12 h		3a	60	65-70/0.16
	2b	r.t. 24 h		3b	42	125-130/0.17
	2c	r.t. 20 h		3c	55	140-145/0.08
			 [d]	4c	16	140-145/0.65 (lit.[6] 154/0.8)
	2d	70°, 14 h[e]		3d	79	125-130/0.07
	2e	r.t. 1h → 70°, 14 h		3e	51	160-165/0.14
	2f	r.t. 1h → 70°, 14 h		3f	75	64.5-65 (MeOH-H_2O)
	2g	r.t. 1h → 70°, 14 h		3g	44	67-67.5 (MeOH)
				4g	48	110-115/0.15 (lit.[7] 110/0.3)

a) The microanalyses for all α-siloxysulfides (3a-g) were in satisfactory agreement with the calculated values. b) Distilled or chromatographed yields are given. c) Uncorrected melting and boiling points (bath temp.) are given. d) A mixture of Z and E-isomers (Z/E= ca.1/2) was obtained. e) The reaction was carried out in the absence of catalyst.

The rearrangement of β-ketosulfoxides (2d-g), readily obtained from ketones,[8] esters,[9] or α-haloketones[10] gave β-keto-α-siloxysulfides (3d-g) in a direct way, which may provide versatile routes to O-silylated α-ketols, glyoxals, α-ketoacids, glycols or α-hydroxy acids.

Referecnes

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