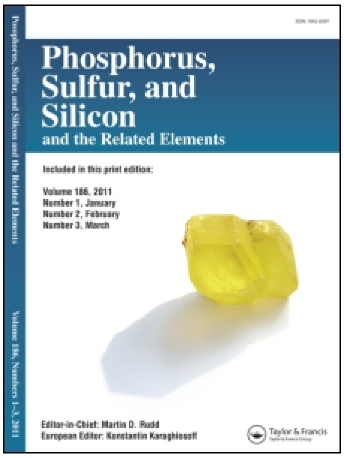

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SELENIUM DIOXIDE AND SELENIUM DISULFIDE AS GRIGNARD ELECTROPHILES

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Communication

SELENIUM DIOXIDE AND SELENIUM DISULFIDE AS GRIGNARD ELECTROPHILES

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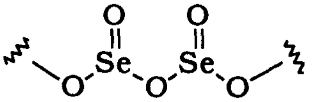
Selenium dioxide and a Grignard reagent give the 1-alkanol as the main product. The major products using selenium disulfide are the dialkylselenide and the dialkyl disulfide.

Key words: selenium dioxide; selenium disulfide; Grignard reaction.

Sulfur dioxide reacts on exposure to Grignard reagents[1] at the sulfur atom, giving salts of the corresponding sulfinic acids R—SO—OH which are often used as intermediates for sulfonic acid synthesis. In analogy, one might expect that selenium dioxide would react analogously, i.e., at the selenium atom. In fact there is an isolated report[2] to the effect that dialkyl selenides result, in 33–62% GC yields, from the action of Grignard reagents on selenium dioxide although there was no comment as to how the dialkyl selenide might have arisen. Alkyl lithiums were said to behave similarly. We have repeated some of these reactions and find that, in our hands, the major product from an alkyl Grignard is the corresponding alcohol, accompanied by a small amount of the dialkyl ether and the dialkyl selenide (Equation 1). Similarly, we do not get major amounts of dialkylselenides from the treatment of selenium dioxide with alkyllithiums. The alcohol presumably results from an attack of the carbanionic species to a SeO_2 oxygen, to give an ester of selenious acid which is then hydrolyzed on work-up.

$$n\text{-}C_9H_{19}MgBr + SeO_2 \rightarrow n\text{-}C_9H_{19}OH \text{ (86\% of isolated reaction product)} + (C_9H_{19})_2O \text{ (2\%)} + (C_9H_{19})_2Se \text{ (12\%)} \quad (1)$$

Both selenium dioxide and selenium disulfide apparently exist as polymeric chains such as



It was therefore of interest to see if selenium disulfide would react in an analogous manner with Grignard reagents, to give a useful synthesis of alkanethiols. It turned

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TABLE

Reaction of SeS_2 with Grignard reagents

Grignard RMgX	Products[a]					
	R_2Se	R_2S_2	RS-SeR	R_2Se_2	R_2S_3	R_2S_4
n-BuMgBr	33%	11%	2%	n.f.	4%	n.f.
sec-BuMgCl	49%	9%	0.5%	11%	0.6%	0.4%
t-BuMgBr	5%	n.f.	n.f.	n.f.	n.f.	n.f.
C_6H_5MgBr	23%	32%	0.6%	n.f.	1.2%	n.f.

[a] The percentages shown are GC yields, and are based on RMgX. GC peak identification is by MS and comparison with authentic samples (R_2Se, R_2S_2 and R_2Se_2) or by MS alone. n.f. = not found.

out however that this reaction is much more complex (Table), giving the dialkyl selenide and the dialkyl disulfide as main products but no thiol at all. Lithium, copper[3] or zinc based alkyl organometallics did not react any more cleanly. We thus conclude that at present, Grignard type reactions with selenium dioxide or disulfide have little to offer as far as synthetic utility is concerned.

A representative procedure follows: The Grignard reagent from *sec*-butylchloride (1 ml, 9.3 mmol) and Mg (0.27 g) in dry ether (10 ml) was injected with stirring into 1.4 g (9.8 mmol) of SeS_2 in ether (6 ml) under Ar at 0° (a lowering of the reaction temperature to −40° had no effect on the product distribution). After 20 h at ambient temperature the mixture was poured in water, acidified, and the ether extract dried and evaporated to give 1.22 g of product. This was analysed by GC (Micromat HRGC 412) using an SE54 column (25 m, inner ϕ 0.32 mm, 40°C, FID). The peaks eluted were identified by mass spectrometry (JEOL SX102, 70 eV), making use of the characteristic isotope patterns due to the presence of 0, 1 or 2 selenium atoms in a molecule, and of the 4% M + 2 ion increment for each sulfur atom present.

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