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THE REACTION OF DICHLORODIETHOXYSILANE WITH ISOPRENE IN THE PRESENCE OF MAGNESIUM

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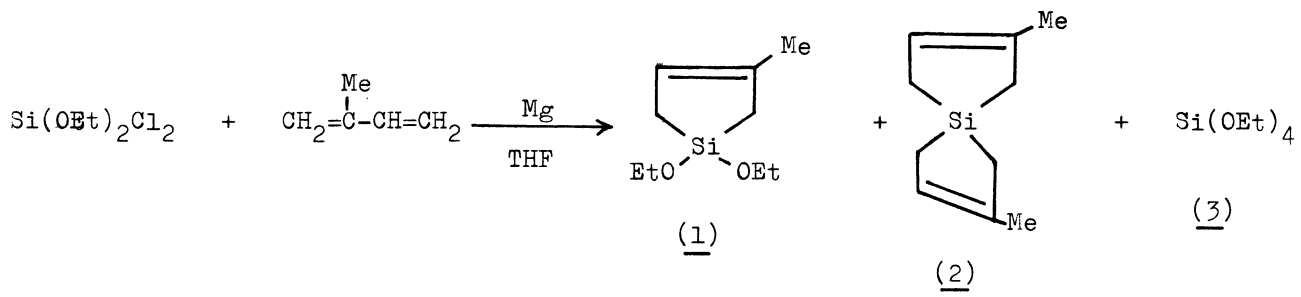
Dichlorodiethoxysilane was treated with isoprene in the presence of magnesium in THF. It was found that new silacyclopentene derivatives i.e., 1,1-diethoxy-3-methyl-1-silacyclopentene-3(1), and 2,7-dimethyl-5-silaspiro[4.4]nonadiene-2,7(2), were produced in good yields, while sodium was used instead of magnesium in the reaction 2 was obtained in a low yield.

In the course of our studies on the synthesis of silacyclic compounds,[1] we have interested in the synthesis of silaspiro compounds. Relatively little work has been reported on the synthesis of silaspiro compounds.[2]
We now wish to report in this communication a new convenient method for the preparation of silacyclopentene derivatives; 1,1-diethoxy-1-silacyclopentene-3(1), and 2,7-dimethyl-5-silaspiro[4.4]nonadiene-2,7(2).

In a preliminary experiment, attempt to prepare 2 by treating the mixture of tetrachlorosilane (or tetraethoxysilane) and isoprene with magnesium in THF[3] was unsuccessful. Therefore we have undertaken to use dichlorodiethoxysilane as starting material in place of tetrachlorosilane by considering the difference of the reactivity between silicon-alkoxy and silicon-halogen bond for Grinard reagent.[4]

In a typical experiment, a tetrahydrofuran(THF) solution(160ml) of 14g(0.074mol) of dichlorodiethoxysilane[5] and 12.6g(0.185mol) of isoprene was refluxed in the presence of 3.8g(0.15mol) of magnesium under nitrogen atmosphere. After stirring for about 30 hr, tetrahydrofuran was removed and n-hexane was added. The resulting magnesium salts were separated from the solution by filtration. Distillation gave 2 in 79.4% yield(10.0g).

In this reaction, when equimolar amounts(0.15mol) of dichlorodiethoxysilane and magnesium were employed in order to obtain 1, it was found by glc analysis of the reaction mixture(5% SE-52, Chromosorb W, 3m, 165°C) that compounds 1, 2, and tetraethoxysilane(3) were produced in 32.5, 23.2, and 23.1% yield respectively.



When the reaction was carried out with sodium in place of magnesium, 2 and 3 were obtained in low yields.

Table. The Reaction of Dichlorodiethoxysilane with Isoprene

$Si(OEt)_2Cl_2$ g(mol)	isoprene g(mol)	Mg g(mol)	product g(%)		
			(1)(bp 190°C)	(2)(bp 143°C/150mmHg)	(3)(bp 167°C)
14(0.074)	12.6(0.185)	3.8(0.156)	trace	10.0(79.4)	
25(0.13)	16.5(0.24)	3.2(0.13)	(32.5)*	(23.2)*	(23.1)*
13.3(0.07)	9.5(0.14)	1.7(0.07)	(29.8)*	(23.0)*	(26.3)*
25(0.13)	9.0(0.13)	6.7(0.3)(Na)	trace	2.3(10.6)	

* The yields were estimated by glc.

The structural assignments were accomplished by the analysis of IR and NMR spectra [1. IR; $\nu_{C=C}$ 1640cm^{-1}, silicon-containing five membered ring[6] 1030cm^{-1}, 1010cm^{-1}: NMR;(CCl_4) δ 0.9-1.0(4H, Si-CH_2), 1.1(t., 6H, C-CH_3), 1.5-1.7(3H, =C-CH_3), 3.5(q., 4H, O-CH_2), 5.0-5.2(1H, =C-H): 2. IR; $\nu_{C=C}$ 1640cm^{-1}, silicon-containing five membered ring 1025cm^{-1}, 1010cm^{-1}: NMR(CCl_4) δ 1.1-1.5(8H, Si-CH_2), 1.5-1.7(6H, =C-CH_3), 4.9-5.2(2H, =C-H)].

It may be considered that 3 resulted from the reaction of magnesium diethoxide and dichlorodiethoxysilane as follows.

$$1 \xrightarrow[\text{isoprene}]{Mg} 2 + Mg(OEt)_2$$

$$Mg(OEt)_2 \xrightarrow{Si(OEt)_2Cl_2} Si(OEt)_4 + MgCl_2$$

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