

DATA TO THE CHEMISTRY OF PHENYL-ETHOXY SILANES

DETERMINATION OF PHENYL-ETHOXY SILANES BY PROGRAMMED TEMPERATURE GAS CHROMATOGRAPHY

By

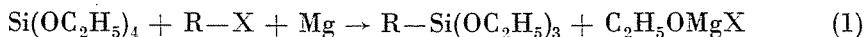
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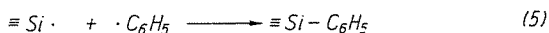
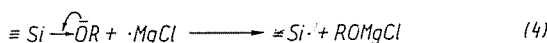
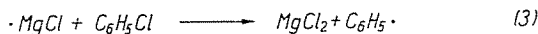
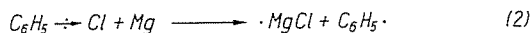
Presented by Doz. Dr. J. NAGY

Alkyl and aryl-alkoxy silanes are an important group of silicon organic compounds. The research workers of the Institute for Inorganic Chemistry have dealt with the method of preparation according to the Grignard reaction of the three basic methods found in the literature [1] that was used first for this purpose by KHOTINSKII and SEREZHENKOV [2, 3] in etheric medium according to the following reaction mechanism:

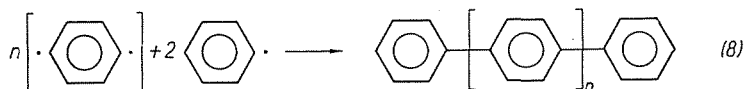
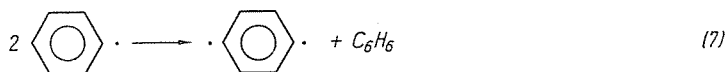
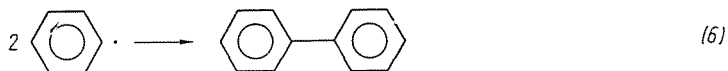


Instead of the etheric medium ANDRIANOV and GRIBANOVA used tetraethoxy silane [4]. This procedure was generalized and completed by PROSZT, LIPOVETZ and NAGY [5, 6]. The formation mechanism of the Grignard compound in tetraethoxy and alkoxy silane was studied by NAGY [7]. This work was spread to the field of allyl and phenyl-ethoxy silanes by NAGY and PÁLOSSY-BECKER [8], and NAGY and GÁBOR [9], respectively.

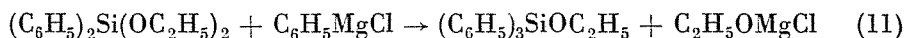
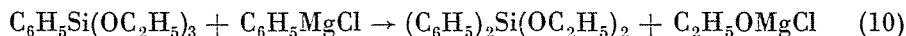
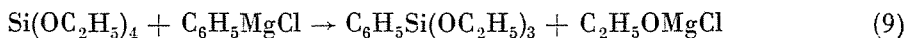
Before the description of the determination of phenyl-ethoxy silanes by means of programmed temperature gas chromatography let us see the main steps of its preparation.



Also side reactions take place besides the formation of Grignard compounds, in which the phenyl group formed in reactions (2) and (3) forms diphenyl and polyphenyl according to the following reaction equation:



Grignard reactions proceeding according to radical mechanism are as follows:



Summarizing the reaction mechanism it can be stated that the reaction product distilled off the Grignard salt may contain several contaminants, that are summarized in Table 1.

Table 1

Component	Formula	Boiling point (at 760 Hgmm)
1. Ethyl alcohol	$\text{C}_2\text{H}_5\text{OH}$	78.3
2. Benzene	C_6H_6	80.2
3. Chlorobenzene	$\text{C}_6\text{H}_5\text{Cl}$	132.0
4. Tetraethoxy silane	$\text{Si}(\text{OC}_2\text{H}_5)_4$	166.0
5. Phenyl triethoxy silane	$\text{C}_6\text{H}_5\text{Si}(\text{OC}_2\text{H}_5)_3$	235.0
6. Diphenyl	$\text{C}_6\text{H}_5\text{—C}_6\text{H}_5$	254.0
7. Diphenyl diethoxy silane	$(\text{C}_6\text{H}_5)_2\text{Si}(\text{OC}_2\text{H}_5)_2$	296.0
8. Triphenyl ethoxy silane	$(\text{C}_6\text{H}_5)_3\text{Si}(\text{OC}_2\text{H}_5)$	344.0
9. Polyphenyl		<360.0

Instead of the distillation method of analysis requiring great amounts of sample and being time consuming, a programmed temperature gas chromatographic method was elaborated for the analysis of the products.

In order to facilitate the calculation of the temperature program the optimal temperatures of analysis of the components of lower and higher boiling points were determined and found to be 160 and 300°C, respectively, under the given gas chromatographic conditions. On the basis of this the optimal gas chromatographic parameters of the analysis could be calculated for the programmed temperature technique (Table 2).

Table 2

Gas chromatograph: Carlo Erba Fractovap Model D
 Detector; thermal conductivity cell
 Bridge current: 130.0 mA
 Sensitivity: 1/64
 Sample introduction: 5.0 μ l, by a Hamilton syringe
 Temperature of evaporator: 450.0°C
 Temperature of detector: 400.0°C
 Temperature of annealing: 160.0 \pm 0.1°C
 After the temperature program: 310.0 \pm 0.1°C
 Temperature program: A heating program started in the second minute after the sample introduction, up to 310.0°C, at a heating rate 0.44°C/min
 Carrier gas: hydrogen
 Flow rate of carrier gas; 25.0 ml/min, at 23.2°C and 763 Hgmm
 Column: an aluminium spiral of 2.0 m length and 4 mm inner diameter
 Column filling: 60/80 mesh Chrom. W., wetted with 10% methyl silicon polymer (SE 30)
 Recorder: final amplitude 2.5 mV, 1.0 sec
 Chart speed: 0.5 inch/min

Fig. 1 shows one of the chromatograms obtained under optimal conditions.

The numbers of components in Fig. 1 are the same as those in Table 1. The qualitative and quantitative analysis was carried out by internal normalization.

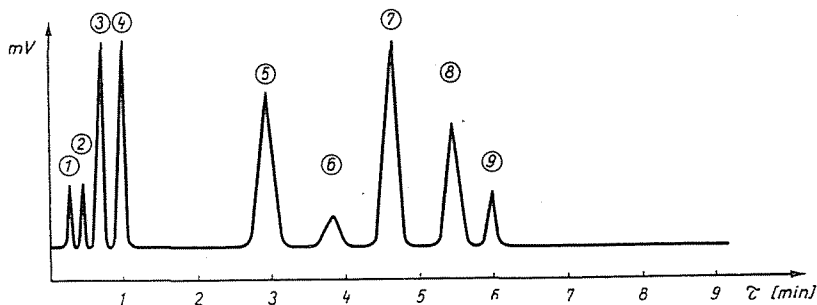


Fig. 1

Summary

After surveying the preparation methods for phenylethoxy silanes a programmed temperature gas chromatographic method is described for the qualitative and quantitative analysis of the products.

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