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HETEROGENEOUS REACTIONS

VIII *. THE HETEROGENEOUS GAS/SOLID REACTION OF 3-CHLOROPROPYLTRIMETHOXYSILANE WITH LITHIUM, SODIUM AND POTASSIUM METHOXIDES

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Summary

The heterogeneous gas/solid reaction of 3-chloropropyltrimethoxysilane with the solid alkoxide bases lithium, sodium and potassium methoxide has been studied at 150 and 190°C. The lithium compound yields solely 3-methoxypropyltrimethoxysilane in a convenient, high yield reaction. Reaction with sodium methoxide gave products resulting from substitution at silicon and carbon as well as elimination products. Potassium methoxide is the least reactive of the three bases studied and gave products similar to those of the sodium methoxide system. Under the conditions of heterogeneous reaction, some cleavage of the chloropropyl group is observed. It is suggested that this cleavage follows base-induced elimination to give allyltrimethoxysilane.

Introduction

Earlier studies in this series have investigated the heterogeneous gas/solid reactions of solid alkoxide bases and vaporized organosilane substrates [1—3]. This alternative to the more traditional solution phase reaction has been shown to have synthetic utility for the preparation of mono- and dialkoxyalkylsilanes [1] and chloromethyldimethylalkoxysilanes [2,3]. The principal advantages of these heterogeneous gas/solid reactions are short reaction times, generally good yields and greatly simplified work-up procedures. The reactions of the series of lithium, sodium and potassium methoxides with chloromethyldimethylchloro (and fluoro)-silane have been studied and some preliminary suggestions concerning relative reactivities and selectivities of these bases under

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* For part VII see ref. 3.

heterogeneous reaction conditions have been offered [3]. In the hope of learning more about the general trends and scope of reaction possibilities for this series of methoxide bases, their reactions with a new organosilicon substrate, 3-chloropropyltrimethoxysilane, have been examined. The reaction of 3-chloropropyltrimethoxysilane was of interest since, in principle, there is the possibility of competition between substitution at carbon and silicon as well as competition between substitution vs. elimination at carbon.

Results and discussion

Equation 1 summarizes the general reaction observed for the reaction of the

$$\underset{\text{vapor}}{R_3SiCH_2CH_2CH_2Cl} + \underset{\text{solid}}{MOMe} \xrightarrow[N_2\ \text{flow}]{150,190^\circ C} R_3SiOMe + R_3SiCH_2CH_2CH_2OMe + R_3SiCH_2CH{=}CH_2 + R_3SiCH{=}CHCH_3$$

$$R = OME \qquad M = Li, Na, K \qquad (1)$$

solid alkali metal methoxides with 3-chloropropyltrimethoxysilane. As observed earlier [3], the reaction with lithium methoxide was quite selective, giving solely 3-methoxypropyltrimethoxysilane. The high yields and excellent purity of the easily isolated products are obvious advantages of the heterogeneous reactions of lithium methoxide. While the product of this reaction surely could be obtained by more traditional methods, the lack of olefin contamination, lack of solvent to be separated and the short reaction times involved for the heterogeneous system are additional advantages. Lithium methoxide tends to be a weaker base than the sodium or potassium compounds as the solvent polarity decreases [4]. The lack of elimination products under heterogeneous conditions observed here may reflect this trend.

Also, as observed earlier, the reactions of the sodium base are more complicated than those of the lithium compound. Reaction with sodium methoxide gave all four of the products indicated in equation 1. Both substitution and elimination at carbon were observed and the balance between the two modes of reaction seems to be insensitive to temperature within the range of temperatures studied. This is in direct contrast to solution phase work where elimination products usually are favored at higher temperatures [5—8].

Earlier studies of the reactions of sodium methoxides have shown that traces of hydroxides can play a role in the observed chemistry [2,3]. It might be argued that the elimination in the present system, as well as the allyl—propenylsilane isomerization [9], are hydroxide-induced. Examination of the results presented in Table 1 as well as the results utilizing deliberately contaminated base argue to the contrary. With increasing hydroxide content the yield of olefinic products decreases while the distribution of the olefinic products remains roughly the same. As seen in Table 2 for sodium methoxide, the propenylsilane is favored at higher temperatures. Interestingly, the reverse trend is seen in the reactions utilizing potassium methoxide.

As evidenced by the observation of unreacted starting material even at the extreme of temperatures studied, potassium methoxide is the least reactive of

TABLE 1

REACTION OF 3-CHLOROPROPYLTRIMETHOXYSILANE WITH LITHIUM, SODIUM AND POTASSIUM METHOXIDE [a]

Run	Temp. (°C)	Base	Products	% Yield [b]
1	150	LiOMe	substitution [c]	93
2	190	LiOMe	substitution	95
3	150	NaOMe	$(MeO)_4Si$	8
			mixture of olefins [d]	16
			substitution	42
			starting material	5
4	190	NaOMe	$(MeO)_4Si$	16
			olefins	18
			substitution	42
5	190	NaOMe [e]	$(MeO)_4Si$	17
			olefins	11
			substitution	43
6	150	KOMe	$(MeO)_4Si$	20
			olefins	6
			substitution	25
			starting material	25
7	190	KOMe	$(MeO)_4Si$	27
			olefins	10
			substitution	28
			starting material	13

[a] Detailed experimental description given in Experimental. [b] As determined by internal standard yield analysis. [c] The substitution product is methoxypropyltrimethoxysilane. [d] The mixture of olefins is propenyl and allyltrimethoxysilane. The distribution of this mixture varies with temperature, see text. [e] This reaction utilized an older, presumably partially hydrolyzed, sample of base. See experimental and text for direct test of the role of hydroxide ion in the distribution of products.

the three methoxide bases studied. While Table 1 shows that the balance between elimination and substitution is relatively insensitive to temperature, the distribution of olefinic products is not, as shown by Table 2.

For the reactions of sodium and potassium methoxide, the formation of tetramethoxysilane as well as the elimination products merit some comment. It

TABLE 2

DISTRIBUTION OF OLEFINIC PRODUCTS IN THE REACTIONS OF 3-CHLOROPROPYLTRIMETHOXYSILANE WITH POTASSIUM AND SODIUM METHOXIDES [a]

Temp. (°C)	propenyltrimethoxysilane/allyltrimethoxysilane [c]	
	KOMe [b]	NaOMe
150	1.64	1.31
160	1.43	1.21
170	1.34	1.20
180	1.18	2.90
190	1.14	2.21

[a] As determined by integration of the allyl hydrogen region of the NMR spectrum corrected for three versus two allyl hydrogens. [b] Throughout the range of temperatures studied the overall yield of olefins based on starting silane was 8.5 ± 2.5% for KOMe and 15 ± 4% for NaOMe. [c] The furthest downfield allyl resonance is tentatively assigned to propenyltrimethoxysilane. (see Experimental).

is possible that the tetramethoxysilane is formed by a direct displacement of the chloropropyl group under heterogeneous conditions. However, by analogy to solution phase work with various bases, the initial formation of allyltrimethoxysilane is a more likely source for the resultant displacement of the chloropropyl group. The isomerization and/or cleavage of allyl and propenylsilicon bonds by strong bases in solution has been shown to be particularly facile and it has been estimated that such cleavages occur at a rate too fast to be solely electrophilically assisted [8].

An earlier study of the reaction of sodium methoxide and 3-bromotricyclo-$[2.2.1.0.^{2,6}]$heptane (which as a result of geometrical constraints imposed by its carbon framework is precluded from reaction via β elimination) was rationalized in terms of a radical anion-free radical process [10]. It is unlikely that the present study involves similar chemistry. A β elimination to give the observed olefinic products seems more probable in analogy to the interaction of secondary alkyl bromides with potassium t-butoxide [11]. The present study represents the first situation where there is a competition between elimination and substitution reactions at carbon centers under heterogeneous conditions. With sodium methoxide the principal component of the products is that resulting from substitution at the carbon center. In contrast, the potassium methoxide reactions have a higher percentage of products derived from elimination among the products formed. Other work in these laboratories has shown that sodium methoxide is more reactive toward substitution at silicon centers than is potassium methoxide [3,12]. The contrasts between the product distributions for these two bases in this work may result from a similar trend for substitution at carbon centers. Alternatively, but much more difficult to quantify, potassium methoxide may be more basic than sodium methoxide under heterogeneous conditions.

In summary, lithium methoxide shows high reactivity and selectivity in its reactions with organosilicon substrates. Thus far, for the systems studied, lithium methoxide reacts to give solely substitution at the silicon—halogen bond [3] or, in this study, a primary carbon—chlorine bond. Interestingly lithium methoxide fails to react with a primary carbon—bromine bond [12]. Reaction with the sodium compound is usually complicated, giving several products and often favoring those resulting from substitution reactions. Potassium methoxide appears to be the least reactive methoxide base under heterogeneous conditions, and, in some regards, its chemistry is different from either the sodium or lithium methoxides [3].

Experimental

Mass spectra were obtained using a Varian EM 600 mass spectrometer operating at 70 eV. A Varian T-60 NMR spectrometer was used to obtain NMR spectra which were recorded with samples in CCl_4 solution with chloroform as an internal standard. An F&M model 700 gas chromatograph equipped with a 6 ft 15% SE-30 column was used for preparative and analytical work. Elemental analyses were obtained from Scandinavian Microanalytical Laboratories, Herlev, Denmark. 3-Chloropropyltrimethoxysilane was a generous gift from Dow Corning Corporation, Midland, Michigan. The starting silane was of excellent purity and was used without further purification. The bases were obtained from Ventron.

All of the reactions reported in this work utilized the same experimental procedure. A detailed description of one reaction with each base is given in example.

Reaction of 3-chloropropyltrimethoxysilane with lithium methoxide

The basic apparatus for heterogeneous gas/solid reactions has been previously described [2,13,14]. The furnace tube was charged with 3.80 g (0.1 mol) of freshly opened lithium methoxide. The tube was fitted with the addition apparatus and the assembled apparatus was connected to a nitrogen line. The tube and its contents were "baked out" under a nitrogen flow at 190°C for 30 minutes. The exit of the furnace tube was equipped with a cylindrical trap immersed in Dry Ice/acetone. The nitrogen flow was adjusted to 60 ml/min and the addition apparatus was wrapped with a four foot heating tape. The latter was connected to a Variac and set at 70/140. The title silane, 4.15 g (20.9 mmol) was syringed into the addition apparatus. The addition required 25 min and the nitrogen flow was continued for 30 min to elute all volatile products. After the trap had been warmed to room temperature under nitrogen, 3.85 g of condensate was removed. The condensate was found to contain a single component identified as methoxypropyltrimethoxysilane by the following data. NMR δ 3.37 (s, 9 H, $(MeO)_3Si$), 3.10 (s superimposed upon a t, $J = 7$ Hz, 5 H, $-CH_2-OCH_3$), 1.47 (m, 2 H) and 0.47 ppm, (m, 2 H). Anal. Found: C, 43.18; H, 9.33. $C_7H_{18}O_4Si$ calcd.: C, 43.27; H, 9.34%.

This reaction was also carried out at 150 and 170°C. In all three reactions the isolated yield was in excess of 93%.

Reaction of 3-chloropropyltrimethoxysilane with sodium methoxide

In a manner identical to the previously described reaction 4.0 g (20.2 mmol) of the title silane was allowed to react with 5.4 g (0.1 mol) of sodium methoxide at 190°C. The condensate, 3.30 g, was found to contain a trace of methanol and three silicon-containing products. In order of their elution from the column these products were tetramethoxysilane, a mixture of allyl and propenyltrimethoxysilane and methoxypropyltrimethoxysilane. Internal standard yield analysis using tert-butoxychloromethyldimethylsilane as an internal standard indicated that the yields of these products were 16, 18 and 42%, respectively. The tetramethoxysilane gave identical spectra to those of an authentic sample. The mixture of olefins was identified by the following data. NMR δ 6.60—4.30 (m, 2.63 H), 3.27 (s, 9 H, $(MeO)_3Si$) and 1.74—1.24 ppm (m, 2.25 H). Anal. Found: C, 44.45; H, 8.76. $C_6H_{14}O_3Si$ calcd.: C, 44.41; H, 8.70%. Mass spectra: *m/e* (% abundance, assignment): 162 (11.5, M^+), 121 (100, $(MeO)_3Si^+$), 91 (53. $(MeO)_2SiH^+$).

The literature contains reference to disproportionation and redistribution reactions of 1- and 2-propenyltrimethoxysilane but no physical data are available [15]. The corresponding trimethyl 1- and 2-propenyl derivatives are well characterized. The NMR assignment in Table 2 for the isomers parallels that of the NMR for the trimethyl derivatives [16—18]. As further support of the isomeric assignments, an authentic sample of allyltrimethoxysilane was prepared by the heterogeneous reaction of allyltrichlorosilane and lithium methoxide. The NMR spectrum of this product contained a doublet at δ 1.40 ppm which is in accord with the assignment made in Table 2.

Reaction of 3-chloropropyltrimethoxysilane with potassium methoxide

In a manner identical to that described for the reaction of the title silane with lithium methoxide, 4.0 g (20.0 mmol) of the title silane was allowed to react with 7.0 g (0.1 mol) of potassium methoxide. The crude condensate from this reaction at 190° C contained, in order of their elution from the column, tetramethoxysilane (27%), a mixture of allyl and propenyltrimethoxysilane (16%), methoxypropyltrimethoxysilane (18%), and unreacted starting material (13%).

As was the case for the reactions with sodium methoxide, the distribution of isomeric olefin products was determined by NMR spectroscopy. The allyl hydrogen range, δ 1.74—1.24 ppm, contained two sets of doublets. The set furthest downfield was tentatively assigned to the propenyl silane. The crude NMR integral was corrected for three versus two allyl hydrogens. The NMR spectra were obtained in each case with GLC-isolated samples of the olefin mixtures.

Reaction of 3-chloropropyltrimethoxysilane with sodium methoxide contaminated with water and a control experiment without water

Sodium methoxide, 5.94 g (0.11 mol) was mixed thoroughly with 0.018 g (10 mmol) of water in a mortar. The contaminated base was then allowed to react by the procedure described above with 3.8 g (19.2 mmol) of the title silane at 170° C. The resulting condensate, 2.40 g, was analyzed and the results compared to those of a control experiment carried out on the same day with the same batch of sodium methoxide. The yields were as follows: doped (control): tetramethoxysilane 12 (18%), olefins 8.4 (19%) and 3-methoxypropyltrimethoxysilane 26 (34%). As noted earlier [1], the lower overall yield for the experiment with the base to which water had been added likely arises from hydroxide-induced reactions which convert the silane into an involatile material which remains in the furnace area. The NMR spectra in the olefinic region of the products of these two reactions were essentially the same within experimental error.

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