DISPROPORTIONATION OF ALKYLDICHLOROSILANES IN PRESENCE OF N-CYANO DERIVATIVES OF PIPERDINE AND MORPHOLINE

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Organyldichlorosilanes $RSiHCl_2$ can undergo disproportionation to the corresponding organylchlorosilanes $RSiH_2 Cl$ and organyltrichlorosilanes $RSiCl_3$ in the presence of ammonium and iron halides [1, 2], pyridine and adiponitrile [3, 4], tetrabutylammonium chloride [5], hexametapol [6], and dialkylcyanamides [7-9].

We established that N-cyanopiperidine (I) and N-cyanomorpholine (II) are active catalysts for the disproportionation of alkyldichlorosilanes. Thus, when 4-10 mole% of (I) or 10 mole% of (II) is used as the catalyst the conversion of the alkyldichlorosilanes reaches 50-80%, while the yield of the alkylchlorosilanes is 90% (Table 1).

EXPERIMENTAL

Ethylchlorosilane. Into the pot of a fractionating column were loaded 129 g of ethyldichlorosilane and 11 g of (I). The mixture was brought up to reflux and the ethylchlorosilane fraction, with bp 40-43°C (715 mm), was removed after 30-40 min. After distilling off the formed ethylchloro- and ethyltrichlorosilane, the still residue can be repeatedly used as the catalyst.

<u>Methylchlorosilane</u>. Into the pot of a fractionating column were loaded 115 g of methyldichlorosilane and 11.2 g of (II). The mixture was refluxed for 40-60 min and then the methylchlorosilane, with bp $5-8^{\circ}$ (715 mm), was distilled into a trap, cooled to -65° . The still residue can be reused many times as the catalyst.

The physical constants of the obtained alkylchlorosilanes corresponded to the literature data, while the elemental analysis results agreed with theory.

CONCLUSIONS

The N-cyano derivatives of piperidine and morpholine were proposed as being efficient catalysts for the disproportionation of alkyldichlorosilanes. Their use makes it possible to convert alkyldichlorosilanes to alkylchlorosilanes in up to 90% yield.

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TABLE I. Disproportionation of ASIAC6 in Presence of (1) and	TABLE 1.	Disproportionation	of RSiHCl ₂	in Presence	of (I)	and $($	II)
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R	Catalyst	Amount, mole %	Conversion of RSiHCl ₂ , %	Yield of RSiHCl ₂ %*	Boiling point, °C (715 mm)
CH3	(I)	10,0	70,8	90,0	5-6
CH3	(II)	10,0	51,6	92,0	5-7
C2H5	(I)	10,0	73,5	88,0	40-41
<i>n</i> -C3H7	(I)	5,0	83,8	67,0	70-71
<i>n</i> -C4H9	(I)	4,0	51,0	93,0	99-100

*Based on reacted RSiHCl₂.

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PMR STUDY OF EXCHANGE REACTION BETWEEN

TRIMETHYLTIN METHYLMERCAPTIDE AND THE

CHLORIDE IN INERT SOLVENTS

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The exchange reactions in trimethyltin derivatives, with cleavage of the tin-chlorine and tin-sulfur bonds, were studied previously [1-4]. In [1] it was shown that exchange between trimethyltin chloride (I) and the phenoxide (II) in CCl₄ solution (concentration of each reactant = 0.2 mole/liter) at ~20°C is absent on the PMR time scale. The same reaction was studied by the PMR method in toluene (concentration of each reactant ~0.5 mole/liter) [2, 3]. It was found that the exchange rate increases with decrease in the temperature, while the reaction order in (I) lies between two and three, and close to one in the case of (II). At the same time, when the exchange between (I) and trimethyltin methylmercaptide (III) was studied in [4] it was determined that in CH₂Cl₂ this exchange reaction proceeds rapidly not only on the PMR time scale, but also on the ¹¹⁹Sn NMR time scale (the concentrations of the reactants are not given in [4]).

In the present paper, in order to ascertain the effect of the nature of an inert solvent on the exchange rate in trimethyltin derivatives, which contain the tin-chlorine and tin-sulfur bonds, we used the PMR method to study reaction (1) in toluene, chlorobenzene, o-dichlorobenzene, $CHCl_3$, and CH_2Cl_2 .

$$(CH_{a})_{a}SnCl + (CH_{a})_{a}Sn^{*}SCH_{a} \rightleftharpoons (CH_{a})_{a}Sn^{*}Cl + (CH_{a})_{a}SnSCH_{a}$$
(1)

The change in the line shape of the signals of the $(CH_3)_3Sn$ group with temperature in the PMR spectrum of an exchange mixture of (I) (0.33 mole/liter) and (III) (0.33 mole/liter) in toluene is shown in Fig. 1. This character of change in the line shape of the CH_3 group, and also the values of τ calculated from the PMR spectra (Table 1), indicate an inverse relationship between the exchange rate and the temperature. The apparent value of the activation energy of reaction (1) in toluene is equal to -9.7 ± 0.3 kcal/mole, while the value of the preexponent is 10^{-6} Hz.

The change in the PMR spectra of an equimolar mixture of (I) (0.33 mole/liter) and (III) in the other employed solvents has qualitatively the same character as in toluene: one quite narrow signal of the protons of the $(CH_3)_3Sn$ group at low temperature, and two narrow signals of the CH_3 protons at high temperature. As a result, an inverse relationship between the rate of reaction (1) and the temperature exists in all five solvents.

A quantitative comparison of the exchange rates in various solvents was made at 34° . Calculation of τ discloses (Table 2) that the minimum exchange rate occurs in toluene, and the maximum rate in o-dichlorobenzene. A comparison of the exchange rates with the dielectric constant of the solvents (ϵ), which changes by at least 4 times when going from toluene to o-dichlorobenzene, testifies to the fact that the rate of reaction (1) increases with increase in ϵ (see Table 2). However, it should be mentioned that the exchange rates in toluene and CHCl₃ are but slightly different, although the value of ϵ for CHCl₃ is twice that for toluene. This result may be related to a blocking of the reaction centers in CHCl₃ when H bonds of the following type [5-7] are formed:

 $\begin{array}{c} CH_3 \\ (CH_3)_3 SnCl \cdots H - CCl_3 \quad and \ (CH_3)_3 SnSl \cdots H - CCl_3 \end{array}$

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