ATRANES

XV. The Dehydrocondensation of Silatrane with Alcohols and Phenols*

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Silatrane, $N(CH_2CH_2O_3)SiH$, in the presence of the corresponding sodium alkoxide of phenoxide readily reacts with alcohols and phenols with the liberation of hydrogen and the formation of 1-alkoxy- or 1-aryloxyatranes, $N(CH_2CH_2O)_3SiOR$. Depending on the nature of the alcohol or phenol, the rate of the reaction falls in the following sequence: p-$CH_3OC_6H_4OH$ > p-$(CH_3)_3CC_6H_4OH$ = n-C_4H_9OH = = n-$C_5H_{11}OH$ > i-C_4H_9OH > s-C_4H_9OH > p-$CH_3C_6H_4OH$ > C_6H_5OH > > p-ClC_6H_4OH > t-C_4H_9OH > p-$O_2NC_6H_4OH$ > C_6F_5OH. The rate of the dehydrocondensation reaction of hydrosilanes with alcohols rises in the sequence $(C_2H_5)_3SiH < N(CH_2CH_2O)_3SiH < (C_2H_5O)_3SiH$. In the presence of $ZnCl_2$ as catalyst, the dehydrocondensation reaction of silatrane with alcohols takes place considerably more slowly and does not go to completion. The formation of 1-organyloxysilatranes from silatrane and alcohols does not take place in the presence of H_2PtCl_6 or in the absence of catalysts. Using the dehydrocondensation reaction, twelve 1-organyloxysilatranes have been synthesized, two of which were previously unknown.

In contrast to the C—H bond, the Si—H bond is readily cleaved by alcohols in the presence of alkali-metal hydroxides or alkoxides according to the following scheme:

$$\gt Si{-}H + H{-}O{-}R \xrightarrow{RO^-} \gt Si{-}O{-}R + H_2.$$

This is explained by the fact that the Si—H bond is polarized in the opposite direction to the C—H bond, in consequence of which the hydrogen in the hydrosilanes is capable of being easily split off in the form of the hydride ion [2, 3].

The rate of the reaction of trialkysilanes, R_3SiH, with alcohols decreases with an increase in the length of the hydrocarbon chain of the normal alcohols, and also with its branching, i.e., on passing from the normal to the iso alcohols or from the primary to the secondary and tertiary alcohols [3–5]. Phenols do not react with trialkylsilanes in the presence of alkali-metal phenoxides [3].

The reaction of trialkoxysilanes with alcohols has been studied inadequately [6–15]. In the absence of a catalyst or in the presence of weakly alkaline catalysts, no appreciable cleavage of the Si—H bond in $(RO)_3SiH$ occurs [9, 10] but transesterification of the alkoxy groups takes place. However, in the preparation of triethoxysilane from trichlorosilane and ethanol, tetraethoxysilane is formed as a by-product, the amount of which increases with a rise in the reaction temperature and the time of heating [6, 11, 14]. Under certain conditions, this reaction may even be used as a method for preparing $Si(OC_2H_5)_4$ [11]. More careful investigations have shown that triethoxysilane reacts slowly with ethanol in the absence of catalysts [13, 15]. There is no information in the literature on the influence of the structure of the alcohols on the rate of their reaction with trialkoxysilanes, since the cleavage of the Si—H bond in $(RO)_3SiH$ has been studied only for the case of ethanol (without a catalyst [13, 15] and in the presence of KOH [7, 9]). The rates of the reactions of alcohols with trialkylsilanes and trialkoxysilanes have not been compared, either. It has been stated (without the presentation of experimental data) only [12] that the tendency to nucleophilic substitution of the hydrogen in the hydrosilanes rises in the sequence $(C_2H_5)_3SiH$ < < $(C_6H_5)_3SiH < (C_2H_5O)_3SiH$.

It appeared to us to be of interest to study the reaction of alcohols and phenols with a silatrane (1-hydrosilatrane), $N(CH_2CH_2O)_3SiH$ (I) [16, 17]. The latter, like all silatranes, contains a quinquecovalent silicon atom having a higher electron density than the Si atom in triethoxysilane (because of the presence of the intramolecular Si←N coordination bond) [19–22]. Because of this, in accordance with the proposed mechanism of the nucleophilic cleavage of the Si—H bond by alcohols [3], it could have been expected that their reaction with I should take place more slowly than with triethoxysilane. At the same time, it was obvious that a certain influence on the rate of the dehydrocondensation of alcohols with $(C_2H_5O)_3SiH$ and I should also be exerted by the high steric accessibility of the silicon atom in the silatrane. On the other hand, a comparison of the rates of the dehydrocondensation reactions of alcohols with I and with trialkylsilanes would also permit a comparison, even if a qualitative one, of both the electron density and the steric accessibility of the silicon atom in the silatrane and the trialkylsilanes. This should make it possible to determine what affects the electron-accepting capacity of the central silicon atom in I to the greater extent: the -I effect of the $(-OCH_2CH_2)_3N$ grouping, which increases the electrophilicity of the Si atom, or the presence of the Si←N coordination bond, acting in the opposite direction. In addition to this, this investigation also had another objective: to lay the basis for the study of the chemical reactions of the silatranes.

We studied the dehydrocondensation of I with alcohols, using as examples methanol, all the isomeric butyl alcohols and n-amyl alcohol, and also with pentafluorophenol (kindly supplied by G. G. Yakobson, to whom the authors express their gratitude), and phenol and its derivatives containing the group CH_3, $(CH_3)_3C$, CH_3O, Cl, and NO_2 in the para position. As catalysts we used the corresponding sodium alkoxides (phen-

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*For part XIV, see [1].

Dehydrocondensation Reactions of Silatrane (I) and of Triethoxysilane with Alcohols and Phenols (ROH)

R	Amount of ROH*, mole	Catalyst	Amount of catalyst, mM	Time of the reaction, min	Yield of hydrogen, %	Yield of II, %	Mp of II**, °C
			$N(CH_2CH_2O)_3SiH$				
CH_3	0.02	—	0	60	10	0	—
CH_3	0.02	H_2PtCl_6	0.005	50	23	0	—
$n\text{-}C_4H_9$	0.02	H_2PtCl_6	0.005	180	0	0	—
$n\text{-}C_4H_9$	0.02	$n\text{-}C_4H_9ONa$	6.5	15	100	66.8	114—115 (113—113.5)
$i\text{-}C_4H_9$	0.02	$i\text{-}C_4H_9ONa$	4.4	20	100	78.9	105—106 (99—100)
$s\text{-}C_4H_9$	0.02	$s\text{-}C_4H_9ONa$	4.4	23	100	80.2	135—136 (131—132)
$t\text{-}C_4H_9$	0.02	$t\text{-}C_4H_9ONa$	6.5	105	100	80.2	148.5—149.5 (146.5—147.5)
$n\text{-}C_5H_{11}$	0.02	$n\text{-}C_5H_{11}ONa$	8.7	15	100	83.9	102.5—103.5 (102.5—103.5)
$n\text{-}C_5H_{11}$	0.01	$ZnCl_2$	1.5	130	67	21.5	102.5—103.5 (102.5—103.5)
$n\text{-}C_5H_{11}$	0.01	H_2PtCl_6	0.005	65	36	0	—
$n\text{-}C_5H_{11}$	0.02	—	0	200	0	0	—
C_6H_5	0.01	C_6H_5ONa	1.3	55	100	89.1	228—229.5 (228—229.5)
C_6H_5	0.01	$ZnCl_2$	1.5	210	100	54.3	228—229.5 (228—229.5)
C_6H_5	0.01	H_2PtCl_6	0.005	133	25	0	—
C_6H_5	0.01	—	0	300	0	0	—
$p\text{-}CH_3C_6H_4$	0.01	$p\text{-}CH_3C_6H_4ONa$	1.2	30	100	75.8	188—189 (188—189)
$p\text{-}(CH_3)_3CC_6H_4$	0.01	$p\text{-}(CH_3)_3CC_6H_4ONa$	0.9	15	100	71.2	252—253 (252—253)
$p\text{-}CH_3OC_6H_4$	0.01	$p\text{-}CH_3OC_6H_4ONa$	1.0	13	100	88.2	183—184***
$p\text{-}ClC_6H_4$	0.01	$p\text{-}ClC_6H_4ONa$	1.0	87	100	72.5	166—167 (166—167)
F_5C_6	0.01	F_5C_6ONa	1.2	250	100	82.1	263—264***
$p\text{-}O_2NC_6H_4$	0.01	$p\text{-}O_2NC_6H_4ONa$	0.9	145	100	42.3	182.5—184 (182.5—184)
			$(C_2H_5O)_3SiH$				
$n\text{-}C_4H_9$	0.02	$n\text{-}C_4H_9ONa$	4.3	0.5	100	—	—
$t\text{-}C_4H_9$	0.02	$t\text{-}C_4H_9ONa$	6.5	60	100	—	—
$n\text{-}C_5H_{11}$	0.02	$n\text{-}C_5H_{11}ONa$	6.5	0.5	100	—	—
C_6H_5	0.01	C_6H_5ONa	1.0	30	100	—	—

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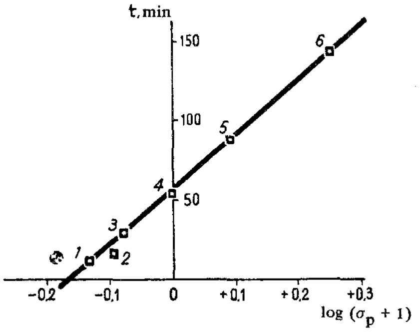
*Amount of hydrosilane in all experiments 0.01 mole.

**Literature data [23] given in brackets.

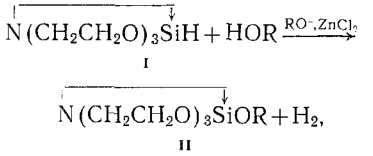
***New compound. R = p-CH_3OH, found, %: C 52.51; H 6.44; N 4.71; H 6.51; N 4.96; Si 9.24. Calculated for $C_{13}H_{19}NO_5Si$, %: C 52.51; H 6.44; N 4.71; Si 9.44. R = F_5C_6, found, %: C 40.04; H 3.45; N 3.87; Si 7.69. Calculated for $C_{12}H_{12}F_5NO_4Si$, %: C 40.34; H 3.39; N 3.92; Si 7.86.

oxides) and also $ZnCl_2$ and H_2PtCl_6. Because of the absence of comparative literature data we also studied the reaction of triethoxysilanes n-butyl-, tert-butyl, and n-amyl alcohols and phenol in the presence of the corresponding sodium alkoxide or phenoxide. All the dehydrocondensation reactions were carried out in xylene at its boiling point. The results of the experiments, the yields, and the melting points of the 1-organyloxysilatranes obtained are given in the table.



Correlation between the times of the reactions of I with p-XC_6H_4OH (t) and the Hammett's constants of the substituents X(σ_p). X = CH_3O (1), $(CH_3)_3C$ (2), CH_3 (3), H (4), Cl (5), NO_2 (6).

The dehydrocondensation of I with alcohols and phenols in the presence of the corresponding sodium alkoxide or phenoxide or $ZnCl_2$ takes place in the following way:



$$\underset{\text{I}}{N(CH_2CH_2O)_3SiH} + HOR \xrightarrow{RO^-, ZnCl_2} \underset{\text{II}}{N(CH_2CH_2O)_3SiOR} + H_2,$$

where R = alkyl, aryl. The 1-alkoxysilatranes (II) formed in this way possess a high purity, since in the majority of cases they have melting points a few degrees higher than the products synthesized from lower tetraalkoxysilanes, the corresponding alcohol, and triethanolamine [23].

The best catalyst for the reaction is the sodium alkoxide or phenoxide, in the presence of which dehydrocondensation takes place rapdily (15–100 min), being accompanied by the evolution of the theoretical amount of hydrogen and the formation of II with a yield of 70–90% (see table). The only exception is p-nitrophenol, the reaction of which with I is complete only after 145 min, while the yield of 1-(p-nitrophenoxy)-silatrane does not exceed 42%. The reaction of I with pentafluorophenol takes place even more slowly (250 min).

In the presence of zinc chloride, the reaction of I with alcohols and phenol takes place comparatively slowly, and in the case of n-amyl alcohol it does not even go to completion. When chloroplatinic acid was used as catalyst, the formation of II could not be detected at all, although about 36% of hydrogen was liberated in the process. This is a new example of the ineffectiveness of H_2PtCl_6 as a catalyst of reactions of I at the Si—H bond (we have shown previously [17] that I does not add to olefins in the presence of H_2PtCl_6). The reaction of I with alcohols and phenol scarcely proceeds in the absence of catalysts, either.

The rates of the dehydrocondensation reactions of I with alcohols and phenols were compared on the basis of the time of the complete evolution of hydrogen. The rates of the reactions of I with n-butyl, n-amyl, isobutyl, and sec-butyl alcohols in the presence of the corresponding sodium alkoxide were approximately the same (15–23 min), the rate of the reaction of tert-butyl alcohol with I was an order of magnitude lower (105 min), while phenol occupied an intermediate position (55 min). p-Methoxyphenol, p-tert-butylphenol, and p-cresol reacted faster than phenol, (13, 15, and 30 min, respectively), and p-chlorophenol, p-nitrophenol, and pentafluorophenol more slowly (87, 145, and 250 min, respectively). On the whole, the rate of dehydrocondensation falls in the following sequence:

$$p\text{-}CH_3OC_6H_4OH > p\text{-}(CH_3)_3CC_6H_4OH = n\text{-}C_4H_9OH = n\text{-}C_5H_{11}OH > i\text{-}C_4H_9OH > s\text{-}C_4H_9OH > p\text{-}CH_3C_6H_4OH > C_6H_5OH > p\text{-}ClC_6H_4OH > t\text{-}C_4H_9OH > p\text{-}O_2NC_6H_4OH > C_6F_5OH.$$

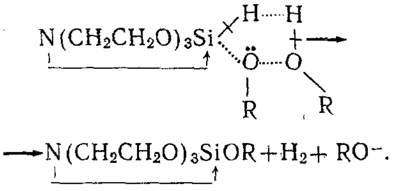
Thus, the rate of the dehydrocondensation of phenols with I falls with a rise in their acidity. However, in the case of the aliphatic alcohols the opposite phenomenon is observed, which is explained by the predominant influence of steric hindrance, which increases with an increase in the degree of branching of the alkyl radicals.

The times necessary for the practically complete dehydrocondensations of I with phenols of the p-XC_6H_4OH series (t) are connected with the Hammett's constants of the substituents X(σ_p) by the empirical equation $\sigma_p = a + be^{ct}$ or $\log(\sigma_p + n) = a' + b't$. The good linear correlation between log (σ_p + 1) and t is shown in the accompanying figure.

The dehydrocondensation of trialkylsilanes with the primary and secondary butyl alcohols is complete in a few hours, while it does not take place at all with tert-butyl alcohol and phenol under the given conditions [3, 4]. In the dehydrocondensation of triethoxysilane with n-butyl and n-amyl alcohols under similar conditions, the evolution of hydrogen is complete in less than 1 minute, and with tert-butyl alcohol and phenol in 60 and 30 min, respectively.

Thus, the rate of the dehydrocondensation reaction of the three types of hydrosilanes mentioned above with alcohols in the presence of the sodium alkoxides rises in the following sequence: $(C_2H_5)_3SiH < N(CH_2CH_2O)_3SiH < (C_2H_5O)_3SiH$. This series confirms the nucleophilic nature of the substitution of the hydrogen in I and agrees with our ideas on the structure of the silatranes. The intermediate position of I in the series given indicates that the N:→Si coordination bond in the silatranes is partially compensated by the -I effect of the $(-OCH_2CH_2)_3N$ grouping, so that the electrophilic activity of the central silicon atom in I proves to be lower than in $(C_2H_5O)_3SiH$, but higher than in $(C_2H_5)_3SiH$. The steric hindrance created by an increasing degree of branching of the hydrocarbon radical in the alkoxy group attacking the silicon atom is shown less in the alkaline alcoholysis of I than in the case of the trialkylsilanes.

The greater rate of the dehydrocondensation reaction of alcohols with I than with trialkylsilanes leads to extremely interesting theoretical consequences. In fact, the attack of the alkoxyl ion on the silicon atom in the silatrane, thanks to the specific spatial structure of the latter, cannot take place in the manner general for organic reactions of the S_N2 type, i.e., from the side opposite to the Si—H bond. Consequently, it must be assumed that on alcoholysis the nucleophilic attack on the silicon in the I of the RO^- group takes place not "from the rear" but "from the side". As a result an intermediate active complex with six electrons in a five-center field [24] is formed (cf. [25]):



This complex contains a sexacovalent octahedral silicon atom formed by the interaction of its vacant 3d orbitals with the attacking solvated anion RO^-. Thus, the dehydrocondensation of a silatrane with alcohols catalyzed by bases is yet another striking example confirming the fact that the lateral attack of the reagent in nucleophilic substitution at a silicon atom is a general phenomenon in organosilicon chemistry. Moreover, this reaction shows that a considerable negative charge on the silicon atom (which exists in the silatranes [22]) is not an obstacle to nucleophilic attack on this atom, because of its capacity for passing into the sp^2d^2 state.

EXPERIMENTAL

The initial isomeric butyl alcohols and the n-amyl alcohol were dehydrated with calcium hydride and purified by distillation. The absolute ethanol, methanol, and phenols were reagents of "pure for analysis" grade. The triethoxysilane was a commercial product purified by distillation through a column, bp 131–133° C, n_D^{20} 1.3772. Compound I was obtained by the reaction of triethoxysilane with boratrane [16–18], mp 256–258° C.

All the reactions of I and also of triethoxysilane with alcohols and phenols were carried out in a two-necked round-bottomed flask fitted with a dropping funnel and reflux condenser connected to a graduated gasometer. The flask was charged with 0.01 mole of I (or triethoxysilane) and 50 ml of xylene. The mixture was heated to the boil, after which the reflux condenser was connected to the gasometer, and the appropriate alcohol with the catalyst dissolved in it was added through the dropping funnel. In the case of the phenols, the calculated amounts of them were placed in the flask together with the I and xylene, and the sodium phenoxide was added after the mixture had been heated to the boil. The time of the reaction was determined from the moment of the mixing of the I with the alcoholic solution of catalyst until the complete cessation of the liberation of hydrogen. After this, the reaction mixture was heated for some further time (20–30 min), and the xylene was distilled off from it. The residue was recrystallized from n-heptane, from a mixture of $CHCl_3$ and CCl_4, or from xylene. The identity of the compounds II obtained with the corresponding 1-organyloxysilatranes [23] was established by mixed melting points. In no case was a depression of the melting point observed.

Some typical experiments are described as examples below.

Dehydrocondensation of I with tert-butyl alcohol. A solution of 0.15 g of sodium in 2.22 g (0.03 mole) of tert-butyl alcohol was rapidly added to a mixture of 1.75 g (0.01 mole) of I and 50 ml of xylene heated to the boil. After 105 min of heating, the theoretical amount of hydrogen (224 ml) had been liberated. After the xylene had been distilled off from the reaction mixture, 1.98 g (80.2%) of a crystalline substance with mp 148.5–149.5° C was obtained. Its identity with the 1-tert-butoxysilatrane obtained by a different method (mp 146.5–147.5° C) [23] was shown by a mixed melting point test.

Dehydrocondensation of I with phenol. A mixture of 1.75 g (0.01 mole) of I, 0.94 g (0.01 mole) of phenol, and 50 ml of xylene was heated to the boil, after which 0.15 g (0.0013 mole) of sodium phenoxide was rapidly added to it. The theoretical amount of hydrogen (224 ml) had been liberated after 55 min. The hot mixture was filtered. The crystals that separated from the cooled filtrate were filtered off with suction, washed with ether, and dried in vacuum. The yield of 1-phenoxysilatrane with mp 190–194° C was 2.38 g (89.1%). After recrystallization from a mixture of $CHCl_3$ and CCl_4, mp 228–229.5° C. A mixture with the 1-phenoxysilatrane obtained by another method [23] (mp 228–229.5° C) melted without depression.

Dehydrocondensation of triethoxysilane with n-amyl alcohol. A solution of 0.15 g of sodium in 2.64 g (0.03 mole) of n-amyl alcohol was added to a mixture of 1.64 g (0.01 mole) of triethoxysilane and 50 ml of xylene. The theoretical amount of hydrogen (224 ml) had been liberated after 40 sec. It was impossible to separate the reaction mixture into individual substances by distillation through a column.

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