BRIEF COMMUNICATIONS

ADDITION OF N,N-DICHLOROARYLSULFAMIDES TO 1-ALKENYLSILATRANES

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N,N-Dichloroarylsulfamides readily add to the double bond of 1-alkenylsilatranes. Depending on the ratio of the starting reagents, the reaction may proceed with the participation of one or both chlorine atoms of the dichloramide.

Sulfamides containing a silatrane group, which, as a rule, imparts specific physiological activity [1], have not been reported. We studied the reaction of the dichloramides of benzene-, p-chlorobenzene-, and p-toluenesulfonic acids with 1-alkenylsilatranes. The reaction was carried out in $CHCl_3$ or CH_2Cl_2 in an inert atmosphere or vacuum. When the reagent ratio is 1:1, the addition products are formed according to the following scheme:

$$\begin{gathered}\mathrm{RSO_2NCl_2 + CH_2 = CH(CH_2)_{\mathit{n}} - Si(OCH_2CH_2)_3N \rightarrow} \\ \mathrm{\rightarrow RSO_2NClCH_2CHCl(CH_2)_{\mathit{n}} - Si(OCH_2CH_2)_3N} \\ \mathrm{(I)-(VI)} \\ \mathrm{R = Ph},\ n = 0\ \mathrm{(I)};\ \mathrm{R} = p\text{-}\mathrm{ClC_6H_4},\ n = 0\ \mathrm{(II)}; \\ \mathrm{R} = p\text{-}\mathrm{MeC_6H_4},\ n = 0\ \mathrm{(III)};\ \mathrm{R = Ph},\ n = 1\ \mathrm{(IV)}; \\ \mathrm{R} = p\text{-}\mathrm{ClC_6H_4},\ n = 1\ \mathrm{(V)};\ \mathrm{R} = p\text{-}\mathrm{MeC_6H_4},\ n = 1\ \mathrm{(VI)}.\end{gathered}$$

The treatment of (I)-(VI) with moist solvents gave the following $RSO_2NHCH_2CHCl(CH_2)_nSi(OCH_2CH_2)_3N$ (VII)-(XII). When the mole ratio is 1:2, the reaction proceeds with the participation of both chlorine atoms of the starting dichloramides

$$\begin{gathered}\mathrm{RSO_2NCl_2 + 2CH_2 = CH{-}Si(OCH_2CH_2)_3N \rightarrow} \\ \mathrm{\rightarrow RSO_2N[CH_2CHCl{-}Si(OCH_2CH_2)_3N]_2} \\ \mathrm{(XIII)-(XV)} \\ \mathrm{R = Ph\ (XIII)},\ p\text{-}\mathrm{ClC_6H_4\ (XIV)},\ p\text{-}\mathrm{MeC_6H_4\ (XV)}\end{gathered}$$

The product yield in all cases is almost quantitative. The IR spectra of adducts (I)-(XV) have SO_2N group stretching bands at 1160 and 1330 cm^{-1}. The strong band at 3220 cm^{-1} corresponds to the NH fragment in (VII)-(XII). The structures of these products were in accord with their PMR spectra (Table 1).

EXPERIMENTAL

The IR spectra were taken in KBr pellets or in vaseline oil on a Specord 75-IR spectrometer. The PMR spectra of 20% solutions in $CDCl_3$ were taken on a Tesla BS-576A spectrometer at 100 MHz.

N-Chloro-N-(2-silatranyl-2-chloroethyl)benzenesulfonamide (I). A mixture of 201 mg (10 mmoles) 1-vinylsilatrane and 226 mg (10 mmoles) N,N-dichlorobenzenesulfonamide was dissolved in 10 ml chloroform. Spontaneous warming to 50°C was observed. The reaction mass was maintained for 20 min at about 20°C and 25 ml hexane was introduced. The precipitate formed was filtered off, washed with ether, dried in vacuum, and recrystallized from 3:1 hexane–chloroform to give 425 mg (~100%) (I). Chloramides (II)-(VI) were obtained by analogous procedures.

N-(2-Silatranyl-2-chloroethyl)benzenesulfonamide (VII). A sample of 212 mg (5 mmoles) (I) was left in the air for 72 h and then dissolved in chloroform. Reprecipitation in hexane gave 200 mg (VII) as colorless crystals, mp 112°C. Amides (VIII)-(XII) were obtained by analogous procedures.

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TABLE 1. Physical Indices of (I)-(VI)

Compound	Mp, °C	PMR spectra (δ, ppm; $CDCl_3$)					
		H_{arom}	CHCl	OCH_2	ClN—CH_2	NCH_2	CH_2Si
(I)	75 (112)	7,48–7,85 m	5,42 m	3,75 t	3,42 d 3,07 d	2,84 t	–
(II)	117 (154)	7,38–7,84 m	5,44 m	3,77 t	3,30 d 3,06 d	2,87 t	–
(III)	88 (120)	7,47–7,87 m	5.62 m	3,79 t	3,44 m	2.84 t	–
(IV)	139 (160–162)	7,47–7,95 m	6,22 m	3,82 t	3,46 m	2,91 t	1,16 t
(V)	102 (128–130)	7,37–7,81 m	6,20 m	3,86 t	3,20–3,61 m	3,02 t	1,25 t
(VI)	105–107 (145–148)	7,40–7,82 m	6,20 m	3,87 t	3,30–3,57 m	2,97 t	1,21 t

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*The melting points of the corresponding N-H derivatives (VII)-(XII) are given in parentheses.

N,N-Bis(2-silatranyl-2-chloroethyl)benzenesulfonamide (XIII) was obtained by analogy to the procedure for (I) from 201 mg (10 mmoles) 1-vinylsilatrane and 113 mg (5 mmoles) N,N-dichlorobenzenesulfonamide. The yield of (XIII) was 310 mg (98%) as a fine crystalline powder, mp 134°C. PMR spectrum (δ, ppm): 7.52-7.87 m (C_6H_5), 5.43 m (CH-Cl), 3.79 t (OCH_2), 3.09 m (SO_2NCH_2), 2.87 t (NCH_2). Amides (XIV)-(XV) were obtained by analogous procedures. The mp of (XIV) was 160-162.5°C. The mp of (XV) was 128-129°C.

LITERATURE CITED

1. M. G. Voronkov and V. M. D'yakov, Silatranes [in Russian], Nauka, Novosibirsk (1978).

SYNTHESIS AND NMR SPECTROSCOPY OF N,N-DIALKYL-N'-(DIMETHYLCHLOROSILYLMETHYL)UREAS WITH AN INTRAMOLECULAR Si←O BOND

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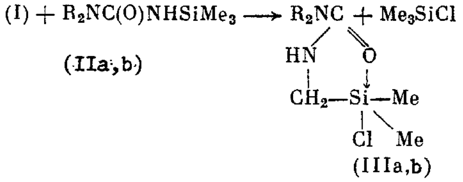
The reaction of N,N-dialkyl-N'-trimethylsilylureas with dimethyl(chloromethyl)-chlorosilane gave N,N-dialkyl-N'-(dimethylchlorosilylmethyl)ureas with an intramolecular Si←O bond. Relatively stable N,N-dialkyl-N'-[dimethyl(chloromethyl)silyl]ureas are intermediates. The structures of the compounds obtained were demonstrated by NMR spectroscopy.

A convenient method has been developed recently for the preparation of various chelate compounds of hypervalent silicon [1] with the $ClSi(C_3)O$ coordination unit. This method is based on the reaction of N- or O-trimethylsilyl derivatives of amides [2], lactams [3], N-acetylacetamide [4], and acetylhydrazines [5] with dimethyl(chloromethyl)chlorosilane (I).

In a preliminary communication [6], we reported that the analogous reaction of N,N-dialkyl-N'-trimethylsilylureas (II) leads to (O-Si)-N,N-dialkyl-N'-[(dimethylchlorosilyl)methyl]ureas (III)



$$\text{(I)} + R_2NC(O)NHSiMe_3 \longrightarrow R_2NC(\text{=O}\rightarrow)(NHCH_2SiMe_2Cl) + Me_3SiCl \qquad (1)$$

(IIa,b)

(IIIa,b)

R = Me (a), Et (b)

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