REACTION OF TRIMETHYLIODOSILANE WITH TETRAALKOXYSILANES AND HEXAALKOXYDISILOXANES

M. G. Voronkov, S. F. Pavlov,
and É. I. Dubinskaya

UDC 542.91:547.1'128

The reaction of alkylchlorosilanes with organylalkoxysilanes [1-3] proceeds either in the presence of catalysts or at high temperatures (under pressure). Previously it was shown [4] that triethyliodosilane under mild conditions easily cleaves the Si–O–C and C–O–C bonds in the absence of catalysts. In the present paper we studied the reaction of trimethyliodosilane (I) with tetramethoxysilane (IIa) and tetraethoxysilane (IIb), and also with hexamethoxydisiloxane (IIIa) and hexaethoxydisiloxane (IIIb). The following reactions took place in the first two cases

$$\underset{(I)}{(CH_3)_3SiI} + \underset{(II)}{(RO)_4Si} \rightarrow \underset{(IV)}{(CH_3)_3SiOSi(OR)_3} + RI$$

$$2\,(I) + (II) \rightarrow \underset{(V)}{[(CH_3)_3SiO]_2Si(OR)_2} + 2RI$$

$$3\,(I) + (II) \rightarrow \underset{(VI)}{[(CH_3)_3SiO]_3SiOR} + 3RI$$

$$4\,(I) + (II) \rightarrow \underset{(VII)}{[(CH_3)_3SiO]_4Si} + 4RI$$

$$R = CH_3\,(a),\ C_2H_5\,(b)$$

However, when the reaction of (I) with the tetraalkoxysilanes was studied using various mole ratios it proved that the reaction is not selective, and the presented schemes only partially reflect the character of the transformations that take place. A mixture of the trimethylsiloxy derivatives (IV)-(VIII) is formed at a molar ratio of (I) : (II) = 1 : 1; 2 : 1; 3 : 1. Together with them, hexamethyldisiloxane (HMDS) is also formed. When the (I) : (II) mole ratio = 4 : 1 the compounds (VII) and (VIII) are formed in respective yields of 52 and 28% from (IIa), and 82 and 18% from (IIb). As a result, the reaction of (I) with tetraalkoxysilanes is a convenient method for the preparation of tetrakis(trimethylsiloxy)silane (VII). The yield of the corresponding alkyl iodide is nearly quantitative at all of the ratios of (I) and (II). The reaction of (I) with (IIa) proceeds much more easily and quickly than with (IIb).

The secondary formation of siloxane (VIII) can be depicted by the scheme:

$$8\,(CH_3)_3SiI + 2\,Si(OR)_4 \rightarrow \underset{(VIII)}{[(CH_3)_3SiO]_3SiOSi[OSi(CH_3)_3]_3} + 8\,RI + [(CH_3)_3Si]_2O$$

The formation, together with (IV)-(VII), of disiloxane (VIII) cannot be the result of (I) reacting with (VII), since they do not react under the studied conditions. Compound (VIII) could easily be obtained in good yield by reacting (I) with (III). The yield of (VIII) was 98% from (IIIa) and 82% from (IIIb).

EXPERIMENTAL METHOD

The GLC determinations were run on an LCM-8D chromatograph, using a 2-m long column, packed with 10% PPMS-4 deposited on Celite, and helium as the carrier gas.

Trimethyliodosilane (I) was obtained by reacting HMDS with aluminum and iodine [5]; the tetraalkoxysilanes (II) were obtained by reacting $SiCl_4$ with the appropriate alcohols, while the hexaalkoxydisiloxanes (III) were obtained by the hydrolysis of the corresponding tetraalkoxysilanes. All of the starting reagents were chromatographically pure. The reactions were run in a dry argon atmosphere in a Favorskii flask by heating in a silicone bath until the formed alkyl iodide ceased to distill.

Irkutsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 657-660, March, 1975. Original article submitted June 19, 1974.

TABLE 1. Reaction Products of Trimethyliodosilane with Tetraalkoxysilanes and Hexaalkoxydisiloxanes $[(CH_3)_3SiO]_nSi(OR)_{4-n}$

Compound	R	n	Yield, % [(I):(II) mole ratio]	Bp, °C (p, mm of Hg)	n_D^{20}	d_4^{20}	Found/calculated, %				τ, ppm			
							Si	C	H	O	CH_3Si	CH_3O	CH_3CH_2O	CH_2O
(IV)	CH_3	1	30,0 (1 : 1) 17,6 (2 : 1)	154 (722)	1,3827	0,9718	28,70/27,60	32,64/33,50	8,08/8,50	30,55/30,40	9,85	6,51	—	—
(V) [6]	CH_3	2	41,5 (1 : 1) 33,0 (2 : 1)	173 (780)	1,3858	0,9150	31,09/31,40	35,34/35,80	8,92/8,90	25,04/24,00	9,85	6,54	—	—
(VI)	CH_3	3	21,0 (1 : 1) 29,0 (2 : 1)	191 (722)	1,3885	0,8845	34,15/34,30	36,63/36,80	9,30/9,20	20,20/19,65	9,87	6,59	—	—
(VII) [7]	—	4	81,5 (4 : 1) *	61 (3)	1,3889	0,8670	37,18/36,50	37,57/37,55	9,085/9,400	16,17/16,30	9,89	—	—	—
(VIII) [8]	$[(CH_3)_3SiO]_3Si$	1	29,0 (4 : 1) †	303 (740) mp, 254°	—	—	36,26/37,00	35,40/35,60	8,83/8,96	19,20/18,44	9,85	—	—	—
(IX) [9]	C_2H_5	1	44,3 (1 : 1) 32,5 (2 : 1)	176 (732)	1,3865	0,9109	23,00/22,60	41,70/42,10	9,70/9,60	25,50/25,10	9,85	—	8,81	6,24
(X) [9]	C_2H_5	2	21,2 (1 : 1) 18,7 (2 : 1)	180 (725)	1,3883	0,8921	27,60/28,10	41,00/41,60	9,60/9,45	21,80/21,60	9,87	—	8,81	6,28
(XI) [9]	C_2H_5	3	29,0 (1 : 1) 35,5 (2 : 1)	193 (732)	1,3890	0,8800	32,03/32,90	39,00/38,70	9,15/9,40	19,80/18,90	9,86	—	8,80	6,22

---

*From (IIb), the yield from (IIa) is 52%.

†From (IIa), the yield from (IIIa) is 98%, and from (IIIb) it is 82%.

Reaction of Trimethyliodosilane (I) with Tetramethoxysilane (IIa). a) To 10.8 g (0.071 mole) of (IIa) at 70°C was added 14.2 g (0.071 mole) of (I) in 30 min. After distilling off the CH_3I (99%), preparative GLC was used to isolate and identify compounds (IV)-(VIII) from the reaction mixture (Table 1).

All of the obtained compounds have identical IR spectra: 1060-1080 cm^{-1} (Si–O, C–O), 840, 1250 cm^{-1} (CH_3–Si).

b) After distilling off the CH_3I (99.5%), when 54.3 g (0.266 mole) of (I) was reacted with 20.3 g (0.133 mole) of (IIa) the following compounds were identified in the reaction mixture by GLC: (IV) 17.6, (V) 33.0, (VI) 28.9, and (VII) 13.5%, and also polysiloxanes, including (VIII) (~7%).

c) From 27.2 g (0.136 mole) of (I) and 5.17 g (0.034 mole) of (IIa), after distilling off the CH_3I (99.8%) and vacuum-distillation we isolated 6.73 g (52%) of (VII), 3.72 g (29%) of (VIII), 1.5 g (11.6%) of HMDS, and ~7% of polysiloxanes.

Reaction of Trimethyliodosilane (I) with Tetraethoxysilane (IIb). a) After heating a mixture of 10.0 g (0.05 mole) of (I) with 10.4 g (0.05 mole) of (IIb) for 1 h at 100°, with removal of the C_2H_5I by distillation (95% yield), the reaction mixture was separated by preparative GLC; the yields were: (IX) 44.3%, (X) 21.2%, (XI) 29%, and polysiloxanes 5.5% (see Table 1).

b) When 19.2 g (0.096 mole) of (I) was reacted with 5.0 g (0.024 mole) of (IIb) for 2 h we isolated 14.0 g (99%) of C_2H_5I. Vacuum-distillation of the residue (9.0 g) gave 7.35 g (81.5%) of (VII), 1.35 g (15%) of (VIII), and 0.4 g (3.5%) of polysiloxanes.

Reaction of Trimethyliodosilane (I) with Hexamethoxy- (IIIa) and Hexaethoxydisiloxane (IIIb). a) When a mixture of 25 g (0.125 mole) of (I) and 5.36 g (0.0208 mole) of (IIIa) was heated at 70° for 45 min we isolated 17.5 g (99%) of CH_3I and 12.6 g (98%) of (VIII).

b) A mixture of 14.2 g (0.072 mole) of (I) and 4.2 g (0.012 mole) of (IIIb) was heated at 100° for 1 h. After distilling off the C_2H_5I (91% yield) we isolated 0.14 g (82%) of (VIII), while the residue was a mixture of polysiloxanes with a variable degree of polymerization.

CONCLUSIONS

The reaction of trimethyliodosilane with tetraalkoxysilanes, taken in a 1-3 : 1 mole ratio, leads to a mixture of trimethylsiloxy derivatives $[(CH_3)_3SiO]_nSi(OR)_{4-n}$ with n = 1-4. Tetrakis(trimethylsiloxy)silane (n = 4) is the main reaction product at a 4 : 1 mole ratio of the reactants. It is formed together with hexakis(trimethylsiloxy)disiloxane, which was obtained in 82-98% yield when trimethyliodosilane is reacted with a hexaalkoxydisiloxane.

LITERATURE CITED

1. C. I. Guillissen and A. Gancberg, Ind. Chem. Belge, 17, 481 (1952).
2. M. Kumada and H. Hattori, J. Inst. Polytechn. Osaka Univ., C 3, 78 (1952); 2, 147 (1952).
3. I. Haiduc, Rev. Roum. Chim., 11, 897 (1966).
4. M. G. Voronkov and Yu. I. Khudobin, Zh. Obshch. Khim., 26, 584 (1956).
5. M. G. Voronkov and Yu. I. Khudobin, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 713 (1956).
6. K. A. Andrianov and V. V. Severnyi, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, 1624 (1961).
7. L. H. Sommer, Q. Green, and F. C. Whitmore, J. Am. Chem. Soc., 71, 3253 (1949).
8. R. Müller, R. Kohne, and S. Slivinski, J. Prakt. Chem., 9, 63 (1959).
9. M. Sakiyama and R. Okawara, Bull. Chem. Soc. Japan, 33, 1645 (1960).