Russian Journal of General Chemistry, Vol. 73, No. 3, 2003, pp. 488–489. Translated from Zhurnal Obshchei Khimii, Vol. 73, No. 3, 2003, pp. 521–522.

LETTERS TO THE EDITOR

Unusual O–C$_{sp^2}$ Bond Cleavage in Vinyl Ethers with Organylhalosilanes

S. V. Basenko, E. V. Boyarkina, and M. G. Voronkov

Favorskii Irkutsk Institute of Chemistry, Siberian Division, Russian Academy of Sciences, Irkutsk, Russia

Received June 4, 2002

We found a previously unknown reaction of O–C$_{sp^2}$ bond cleavage in vinyl ethers with organylhalosilanes, involving substitution of the halogen atom by an alkoxy group.

$$CH_2{=}CHOR + X_nSiR'_{4-n} \longrightarrow CH_2{=}CHX + X_{n-1}(RO)SiR'_{4-n},$$

R = Bu; R' = CH_2Cl, Me, Ph; X = F, Cl; n = 2–4.

For example, the reaction of butyl vinyl ether with trichloro(phenyl)silane at a 1:1 molar ratio at 20°C gives vinyl chloride and dichloro(butoxy)phenylsilane in a near-quantitative yield (96%). At 2:1 and 3:1 reagent molar ratios, a mixture of chloro(butoxy)-phenylsilanes $PhSi(OBu)_{3-n}Cl_n$ (n = 0–2) is formed. The major component of the mixture is dichloro(butoxy)phenylsilane.

The reactions of butyl vinyl ether with $ClCH_2SiCl_3$, $PhMeSiCl_2$, $MeSiCl_3$, and $SiCl_4$ at 1:1 molar ratios at 20°C, too, give chloro(butoxy)(methyl)phenylsilane, dichloro(chloromethyl)butoxysilane, dichloro(butoxy)-methylsilane, and trichloro(butoxy)silane (yields 32, 57, 45, and 37%, respectively). From butyl vinyl ether and trifluoro(phenyl)silane under similar conditions we obtained difluoro(butoxy)phenylsilane in an yield of up to 10% and poly(butyl vinyl ether).

Reaction of butyl vinyl ether with trichloro-(phenyl)silane. A mixture of 10.0 g of butyl vinyl ether and 21.2 g of trichloro(phenyl)silane was allowed to stand at room temperature for 1 day. Vacuum distillation gave 23.9 g (96%) of dichloro(butoxy)-phenylsilane, bp 110°C (3 mm), n_D^{20} 1.4930, d_4^{20} 1.1246 {published data [1]: bp 130–135°C (14 mm)}. IR spectrum, ν, cm^{-1}: 460, 560 (Si–Cl), 1080, 1115 (Si–O), 1430 (Si–Ph), 1590 (C=C), 2870, 2950 (CH_3), 3050, 3070 (CH_2). ^{1}H NMR spectrum, δ, ppm: 0.93 t (CH_3CH_2), 1.40 m (CH_3CH_2), 1.65 m ($CH_2CH_2CH_2$), 4.00 t (OCH_2), 7.2–7.8 m (C_6H_5). Found, %: C 48.39; H 5.47; Cl 28.50; Si 11.34. $C_{10}H_{14}Cl_2OSi$. Calculated, %: C 48.20; H 5.66; Cl 28.45; Si 11.27. The vinyl chloride formed in the course of the reaction was condensed in a liquid nitrogen trap and then brominated to obtain 1,2-chlorodibromoethane, bp 60°C (8 mm), n_D^{20} 1.5535 {published data [2]: bp 44°C (4 mm), n_D^{20} 1.5540}.

The reactions of trichloro(phenyl)silane with butyl vinyl silane at 1:2 and 1:3 molar ratios, as well as the reactions of butyl vinyl ether with $PhMeSiCl_2$, $ClCH_2SiCl_3$, $MeSiCl_3$, $SiCl_4$, and $PhSiF_3$ were performed in a similar way.

Dichloro(chloromethyl)butoxysilane, bp 58°C (3 mm), n_D^{20} 1.4412, d_4^{20} 1.1560. IR spectrum, cm^{-1}: 460, 570 [ν(Si–Cl)], 1090 [ν(Si–O)], 1385, 1460 [δ(CH_2)], 2870, 2930, 2950 [ν(CH)]. ^{1}H NMR spectrum, δ, ppm : 0.93 t (CH_3CH_2), 1.39 m (CH_3CH_2), 1.63 m ($CH_2CH_2CH_2$), 3.08 ($ClCH_2$), 3.98 t (OCH_2). Found, %: C 27.19; H 5.07; Cl 48.25; Si 7.34; $C_5H_{11}Cl_3OSi$. Calculated, %: C 27.10; H 5.00; Cl 48.00; Si 7.22.

Dichloro(butoxy)(methyl)phenylsilane, bp 87°C (2 mm), n_D^{20} 1.4845 {published data [3]: bp 101°C (5 mm), n_D^{20} 1.4838}.

Dichloro(butoxy)methylsilane, bp 46°C (15 mm), n_D^{20} 1.4130 {published data [4]: bp 29.5°C (9 mm), n_D^{20} 1.4125}.

Trichloro(butoxy)silane, bp 45°C (15 mm), n_D^{20}

1070-3632/03/7303-0488 $25.00

1.4120 {published data [5]: bp 38°C (10 mm), n_D^{20} 1.4118}.

Difluoro(butoxy)phenylsilane, bp 85°C (10 mm). IR spectrum, ν, cm^{-1}: 860, 955 (Si–F), 1090, 1145 (Si–O), 1435 (Si–Ph), 1595 (C=C), 2875, 2940, 2960 (CH_3), 3050, 3080 (CH_2). ^1H NMR spectrum, δ, ppm: 0.88 t (CH_3CH_2), 1.35 m (CH_3CH_2), 1.50 m ($CH_2CH_2 \cdot CH_2$), 3.40 t (OCH_2), 7.2–7.5 m (C_6H_5).

Poly(butyl vinyl ether). ^1H NMR spectrum, δ, ppm: 1.02 (CH_3CH_2), 1.40–1.60 (CH_3CH_2), 1.65–2.30 ($CH_2CH_2CH_2$, $OCHCH_2$), 3.40–4.00 (OCH_2, OCH). Found, %: C 71.86; H 12.20. $C_6H_{12}O$. Calculated, %: C 71.95; H 12.08.

The IR spectra were obtained on a Specord IR-75 instrument. The ^1H NMR spectra were measured on a Bruker DPX-400 instrument (400 MHz) for 15–20% solutions in $CDCl_3$ and C_6D_6, internal reference HMDS.

REFERENCES

1. Bazant, V. and Benes, J., *Collect. Czech. Chem. Commun.*, 1959, vol. 24, no. 2, p. 624.
2. Bachman, G.B., Logan, T.J., Hill, K.R., and Standish, N.W., *J. Org. Chem.*, 1960, vol. 25, no. 8, p. 1312.
3. Chappelow, C.C., Jr., Elliott, R.L., and Goodwin J.T., Jr., *J. Chem. Eng. Data*, 1963, vol. 8, no. 1, p. 82.
4. Shostakovskii, M.F., Sokolov, B.A., Dmitrieva, G.V., and Alekseeva, G.M., *Zh. Obshch. Khim.*, 1964, vol. 34, no. 9, p. 2839.
5. Currell, B.R., Frazer, M.J., Haines, E., and Leader, L., *J. Inorg. Nucl. Chem.*, 1959, vol. 12, no. 1–2, p. 45.