ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 6, pp. 1218–1219. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © S.N. Adamovich, A.I. Albanov, A.N. Mirskova, R.G. Mirskov, M.G. Voronkov, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 6, pp. 1043–1044.

LETTERS TO THE EDITOR

Reaction of 1-Alkylsilatranes with 2-Methylphenoxyacetic Acid

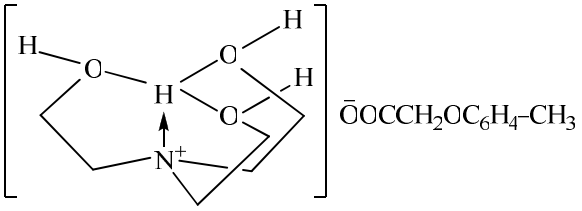
S. N. Adamovich, A. I. Albanov, A. N. Mirskova, R. G. Mirskov, and M. G. Voronkov

Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia
e-mail: mir@irioch.irk.ru

Received December 22, 2008

DOI: 10.1134/S1070363209060334

Tris(2-hydroxyethyl)ammonium 2-methylphenoxyacetate ("2-methylphenoxyacetoxyptotatrane") $N^+H\cdot(CH_2CH_2OH)_3\cdot^-OOCCH_2OC_6H_4CH_3$ (**I**) under the name of "crezacin" or "trecrezan" is used in agriculture and medicine[1, 2]. Its Si-organyl analogs "silatranes" $RSi(OCH_2CH_2)_3N$ (**II**) are also widely used in these fields [3].



With the aim to prepare compounds combining the biological activity of **I** and **II** we have studied the reaction of 1-alkylsilatranes with 2-methylphenoxyacetic acid, $CH_3C_6H_4OCH_2COOH$ (**III**). So far, the reactions of **II** with carboxylic acids practically were not studied.

The ability of **II** to form onium salts with participation of N or O atoms was long discussed in the literature [4, 5]. In [6, 7] it was shown that **II** and boratrane form with trifluoromethanesulfonic acid the corresponding ammonium complexes. One could expect the reaction to follow two routes:

$$Si(OCH_2CH_2)_3N + HX \rightarrow \underset{\textbf{IV}}{[RSi(OCH_2CH_2)_3N^+H]\ X^-}, \quad (1)$$

$$RSi(OCH_2CH_2)_3N + 2HX \rightarrow \underset{\textbf{V}}{[R(X)Si(OCH_2CH_2)_2N^+(H)CH_2CH_2OH]\ X^-}, \quad (2)$$

R = Me, Et; X = $OOCCH_2OC_6H_4–CH_3$.

We have not detected the expected stable products of reactions (1), (2) in our experiments. The methods of ^1H, ^{13}C, ^{15}N, ^{29}Si NMR and IR spectroscopy proved the formation of $[R(OH)Si(OCH_2CH_2)_2N^+(H)CH_2CH_2OH]\ X^-$ (**VI**), where R = CH_3 (**VIa**), R = C_2H_5 (**VIb**), which, apparently, are formed after partial hydrolysis of **II** or **V** with the air moisture.

The independent synthesis of **VIa** and **VIb** was performed by the scheme:

$$RSi(OR_1)_3 + \underset{\textbf{I}}{(HOCH_2CH_2)_3N^+H\cdot X^-} \rightarrow \underset{\textbf{IV}}{[RSi(OCH_2CH_2)_3N^+H]\ X^-} + 3R_1OH \rightarrow \underset{\textbf{VIa, VIb}}{[R(OH)Si(OCH_2CH_2)_2N^+(H)CH_2CH_2OH]\ X^-}.$$

$R = R_1$ = Me, Et; X = $OOCCH_2OC_6H_4–CH_3$.

At the same time, the reaction of methyltrichlorosilane or tetramethoxysilane with **I** in THF or benzene leads to insoluble, high-melting colorless powders containing Si and showing in their IR spectra the band at 1580 cm^{-1} (C=O).

Compound **VIa** was obtained was obtained by refluxing 5 g (26 mmol) of methylsilatrane and 4.38 g (26 mmol) of **III** in methanol for 6 h. The solvent was removed, the residue was thoroughly washed with hexane and dried in vacuum. ^1H NMR (CD_3OD): 7.13–6.80 m (C_6H_4O), 4.50 s (CH_2COO), 3.90 t (OCH_2), 3.39 t (NCH_2), 2.29 s (CH_3–Ph), 0.10 s (CH_3Si). ^{13}C NMR: 173.65 (C=O), 156.53 (C_i–O), 130.14, 126.22, 120.28, 110.86 (Ar),126.49 (C_i–Me), 66.12 (CH_2COO), 55.42 (OCH_2), 55.11 (NCH_2), 14.97 (CH_3–Ph), –10.37 (CH_3Si). ^{15}N NMR: –337.70. ^{29}Si NMR: –38.83. IR: 1590 (C=O), 3300 (OH).

Compound **VIb** was prepared similarly. ^1H NMR (CD_3OD): 7.10–6.83 m (C_6H_4O), 4.56 s (CH_2COO), 3.87 t (OCH_2), 3.40 t (NCH_2), 2.25 s (CH_3–Ph), 0.89 q

(CH_2–Si), 0.27 t (CH_3). ^{13}C NMR: 174.35 (C=O), 157.80 (C_i–O), 131.67–112.24 (Ar), 125.39 (C_i–Me), 66.99 (CH_2COO), 56.80 (OCH_2), 56.48 (NCH_2), 16.45 (CH_3–Ph), 9.35 (CH_2). ^{15}N NMR: –338.30, ^{29}Si NMR: –38.98. IR: 1600 (C=O), 3300 (OH).

Compounds **VIa** and **VIb** was prepared by an alternative procedure by refluxing equimolar amounts of methyltriethoxy- or ethyltrimethoxysilane and **I** in THF during 12 h. the residue was washed with hexane and dried.

ACKNOWLEDGMENTS

This work was performed with financial support from the Council of grants of the President of RF (grant no. NSh-255-2008.3).

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