1.45 (d, 3 H, Me, ^3J = 6.2 Hz); 4.00 and 4.51 (dd and t, 1 H and 1 H, CH_2, AB part of the ABX system, $^2J_{AB}$ = 8 Hz, $^3J_{AX}$ = 7 Hz, and $^3J_{BX}$ = 8 Hz); 4.84 (m, 1 H, CH).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 97-03-33060) and the Foundation for Support of Young Scientists of the Russian Academy of Sciences.

References

1. M. Aresta, E. Quaranta, and I. Tommasi, *New J. Chem.*, 1994, **18**, 133.
2. R. Quinn, J. B. Appleby, and G. P. Pez, *J. Am. Chem. Soc.*, 1995, **117**, 329.
3. T. Tsuda, *Gazetta Chimica Italiana*, 1995, **125**, 101.
4. A. Behr, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 661.
5. W. J. Kruper and D. V. Dellar, *J. Org. Chem.*, 1995, **60**, 725.
6. T. Aida and S. Inoue, *J. Am. Chem. Soc.*, 1983, **105**, 1304.
7. K. Kasuga, S. Nagao, T. Fukumoto, and M. Handa, *Polyhedron*, 1996, **15**, 69.
8. US Pat. 4.663.467.
9. US Pat. 5.283.356.
10. I. Shibata, A. Baba, H. Iwasaki, and H. Matsuda, *J. Org. Chem.*, 1986, **51**, 2177.
11. A. Baba, K. Seki, and H. Matsuda, *J. Heterocycl. Chem.*, 1990, **27**, 1925.
12. T. Tsuda, Y. Chujo, and T. Saegusa, *J. Am. Chem. Soc.*, 1980, **102**, 431.
13. US Pat. 4.786.741.
14. Eur. Pat. Off. 0297647.
15. S. A. Lermontov, S. I. Zavorin, I. V. Bahtin, N. S. Zefirov, and P. J. Stang, *Phosphorus, Sulfur, and Silicon*, 1995, **102**, 283.
16. L. M. Yagupol'skii, V. I. Popov, N. V. Kondratenko, B. L. Korsunskii, and N. N. Aleinikov, *Zh. Org. Khim.*, 1975, **11**, 459 [*J. Org. Chem. USSR*, 1975, **11** (Engl. Transl.)].
17. K. Alam and A. F. Janzen, *J. Fluor. Chem.*, 1985, **27**, 467.
18. S. A. Lermontov, I. M. Rakov, N. S. Zefirov, and P. J. Stang, *Tetrahedron Lett.*, 1996, **37**, 4051.

Received October 10, 1997;
in revised form March 27, 1998

The use of hexafluoropropene oxide in substitutive fluorination of Sb^V and Bi^V oxygen-containing compounds

S. A. Lermontov,* I. M. Rakov, and N. S. Zefirov

Institute of Physiologically Active Substances, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (095) 913 2113. E-mail: lermon@ipac.ac.ru

Reactions of hexafluoropropene oxide with Sb^V and Bi^V oxygen-containing compounds were studied. The E=O (E—O) groups were found to be transformed into the EF_2 (E—F) (E = Sb or Bi) groups.

Key words: hexafluoropropene oxide, substitutive fluorination, triphenylantimony difluoride, triphenylbismuth difluoride.

Earlier, we have studied the reaction of hexafluoropropene oxide (HFPO) with phosphoryl compounds.[1,2] It was shown that the P=O groups were thereby transformed into the PF_2 groups. Taking into account that this reaction occurs relatively smoothly with compounds containing a very stable phosphoryl P=O group, one could assume that such transformations are also possible in the case of compounds of other Group V elements containing the E=O group.

With the goal of testing this assumption, we introduced some oxygen-containing compounds of antimony and bismuth into reaction with HFPO. It turned out that HFPO reacts with $Ph_3Sb{=}O$ even at room temperature to give Ph_3SbF_2.

$$Ph_3Sb{=}O \longrightarrow Ph_3SbF_2$$

Ph_3SbF_2 was identified by ^{19}F NMR spectroscopy. The chemical shift of the Ph_3SbF_2 formed ($\delta_F(CF_3COOH)$ −75.1) corresponded to $\delta_F(CFCl_3)$ −153.2 described in the literature.[3] The product[4] of a reaction that we reproduced possessed a similar chemical shift (δ_F −75).

$$Ph_3Sb + XeF_2 \longrightarrow Ph_3SbF_2.$$

The yield of Ph_3SbF_2 was determined by integrating the signals for Ph_3SbF_2 and *m*-fluorotoluene, which was added to the reaction mixture after the reaction was

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1652—1653, August, 1998.

completed. Ph_3SbF_2 was isolated from the reaction mixture only in small yield (9%), which is probably explained by the simultaneous formation of a bisalkoxy derivative according to the scheme

$$Ph_3SbF_2 + 2\,F_2C\overset{O}{\diagup\diagdown}CF{-}CF_3 \rightleftharpoons Ph_3Sb(OC_3F_7)_2.$$

The reversible formation of perfluoroalkoxides from HFPO and fluoride anion is described in the literature.[5]

Bi^V compounds enter into reaction with HFPO with the same ease. Ph_3BiF_2 is formed when a flow of HFPO is passed through a suspension of Ph_3BiCO_3 in boiling benzene.

$$Ph_3BiCO_3 \longrightarrow Ph_3BiF_2$$

A signal δ_F −82.7 was present in the ^{19}F NMR spectrum of the reaction mixture. A similar chemical shift (δ_F −83) is observed[6] for the product of a reaction that we reproduced

$$Ph_3Bi + XeF_2 \longrightarrow Ph_3BiF_2.$$

The yield of Ph_3BiF_2 was determined by ^{19}F NMR spectroscopy by integrating the signals for Ph_3BiF_2 and C_6F_6, which was added to the reaction mixture after the reaction was completed. Ph_3BiF_2 was isolated (in small yield, like Ph_3SbF_2) from the reaction mixture. It gave satisfactory elemental analysis data.

After HFPO was passed through a benzene solution of $Ph_3Bi{=}O$ at room temperature, Ph_3BiF_2 (δ_F −82.8) was also detected in the reaction mixture by ^{19}F NMR spectroscopy.

$$Ph_3Bi{=}O \longrightarrow Ph_3BiF_2$$

However, in this case, the yield of Ph_3BiF_2 was only 6%. This is probably due to the very high thermal instability of the initial $Ph_3Bi{=}O$, which slowly decomposes in a benzene solution even at room temperature (in other solvents, according to the literature data,[7] either $Ph_3Bi{=}O$ is insoluble or its decomposition rate is higher).

Experimental

^{19}F NMR spectra were recorded on a Bruker CXP-200 spectrometer (188 MHz) with proton decoupling in $CDCl_3$ and acetone-d_6, CF_3COOH was used as the external standard. Commercially available HFPO as well as reagents prepared according to described procedures (Ph_3SbO,[8] Ph_3BiCO_3,[9] and Ph_3BiO [7]) were used.

Reaction of HFPO with Ph_3SbO. HFPO was passed through a solution of Ph_3SbO (0.192 g, 0.52 mmol) in 15 mL of anhydrous CH_2Cl_2 at room temperature for 9 h until Ph_3SbO completely dissolved. The solvent was removed *in vacuo*. A singlet signal of Ph_3SbF_2 (δ_F −75.1) was present in the ^{19}F NMR spectrum of the reaction mixture. The yield of Ph_3SbF_2 (31%) was determined by integrating the signals for Ph_3SbF_2 and *m*-fluorotoluene, which was added to the reaction mixture after the reaction was completed. The solvent was removed *in vacuo*. The residue was washed with *n*-heptane (4×1 mL), and the solutions were combined and concentrated to dryness. The residue was crystallized from *n*-heptane to give Ph_3SbF_2 (0.018 g, 9%), m.p. 114—115 °C (*cf.* Refs.: m.p. 115 °C [10] and 121—122 °C [4]).

Reaction of HFPO with Ph_3BiCO_3. HFPO was passed through a boiling suspension of Ph_3BiCO_3 (5.24 g, 10.5 mmol) in 50 mL of anhydrous C_6H_6 until Ph_3BiCO_3 completely dissolved (14 h). The solvent was removed *in vacuo*. A singlet signal of Ph_3BiF_2 (δ_F −82.73) was present in the ^{19}F NMR spectrum of the reaction mixture. The yield of Ph_3BiF_2 (41%) was determined by integrating the signals for Ph_3BiF_2 and C_6F_6, which was added to the reaction mixture after the reaction was completed. The reaction mixture was washed three times with hot *n*-hexane, and the solutions were combined and concentrated to dryness. The residue was reprecipitated twice with *n*-hexane from a hot benzene solution to give Ph_3BiF_2 (0.08 g, 2%), m.p. 148—153 °C (*cf.* Refs.: m.p. 127.5 °C [11] and 158.5—159 °C [12]). Found (%): C, 45.19; H, 3.30. $C_{18}H_{15}BiF_2$. Calculated (%): C, 45.20; H, 3.16.

Reaction of HFPO with Ph_3BiO. HFPO was passed through solution of Ph_3BiO (0.048 g, 0.105 mmol) in 10 mL of anhydrous C_6H_6 at room temperature for 5 h. The solvent was removed *in vacuo*. A singlet signal of Ph_3BiF_2 (δ_F −82.8) was present in the ^{19}F NMR spectrum of the reaction mixture. The yield of Ph_3BiF_2 (6%) was determined by integrating the signals for Ph_3BiF_2 and *m*-fluorotoluene, which was added to the reaction mixture after the reaction was completed.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 98-03-32997) and the Fogarthy International Research Foundation of the USA National Institutes of Health (Grant R03TW00437).

References

1. S. A. Lermontov, I. M. Rakov, and I. V. Martynov, *Tez. VI vses. konf. po khimii ftororg. soedin.* [*Abstracts of Papers, VI All-Union Conf. on the Chemistry of Organofluorine Compounds*], Novosibirsk, 1990 (in Russian).
2. S. A. Lermontov, I. M. Rakov, and I. V. Martynov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1990, 2848 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1990, **39**, 2584 (Engl. Transl.)].
3. I. Ruppert and V. Bastian, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 214.
4. L. M. Yagupol'skii, V. L. Popov, N. V. Kondratenko, B. L. Korsunskii, and N. N. Aleinikov, *Zh. Org. Khim.*, 1975, **11**, 459 [*Russ. J. Org. Chem.*, 1975 (Engl. Transl.)].
5. H. Millauer, W. Schwertfeger, and G. Siegemund, *Angew. Chem.*, 1985, **97**, 164.
6. S. A. Lermontov, I. M. Rakov, N. S. Zefirov, and P. J. Stang, *Phosphorus, Sulfur, and Silicon*, 1994, **92**, 225.
7. R. G. Goel and H. S. Prasad, *J. Organomet. Chem.*, 1972, **36**, 323.
8. G. A. Razuvaev, T. G. Brilkina, E. V. Krasilnikova, T. I. Zinovjeva, and A. I. Filimonov, *J. Organomet. Chem.*, 1972, **40**, 151.
9. D. H. R. Barton, N. Y. Bhatnagar, J.-C. Blazejewski, B. Charpiot, J.-P. Finet, D. J. Lester, W. B. Motherwell,

M. T. B. Papoula, and S. P. Stanforth, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2657.
10. V. P. Glushkova, T. V. Talalaeva, Z. P. Razmanova, G. S. Zhdanov, and K. A. Kocheshkov, in *Sb. statei obshch. khimii* [*Collection of Papers on General Chemistry*], 1953, **2**, 992 (in Russian).
11. R. G. Goel and H. S. Prasad, *Can. J. Chem.*, 1970, **48**, 2488.
12. F. Challenger and J. F. Wilkinson, *J. Chem. Soc.*, 1922, **121**, Part 1, 91.

Received October 22, 1997;
in revised form February 20, 1998

An unexpected reaction of 2-(cyclopent-2-enyl)aniline hydrochloride with dimethyldioxirane

D. I. D'yachenko,* A. G. Mustafin, V. V. Shereshovets, N. N. Kabal'nova, V. P. Kazakov, I. B. Abdrakhmanov, and G. A. Tolstikov

Institute of Organic Chemistry, Ufa Research Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation.
Fax: +7 (347 2) 35 6066

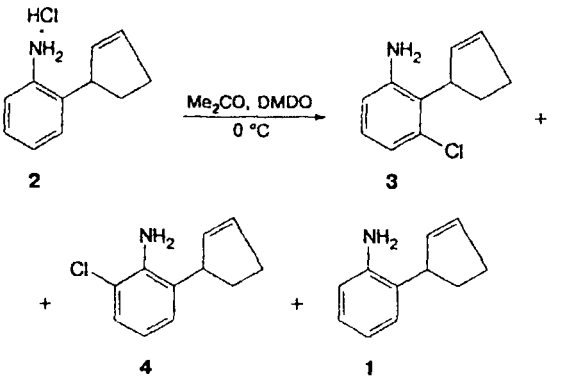
An unusual direction of the reaction of 2-(cyclopent-2-enyl)aniline hydrochloride with dimethyldioxirane was found: the formation of two isomeric products, *viz.*, 3- and 6-chloro-2-(cyclopent-2-enyl)anilines, was observed.

Key words: 2-(cyclopent-2-enyl)aniline hydrochloride, dimethyldioxirane, 3-chloro-2-(cyclopent-2-enyl)aniline, 6-chloro-2-(cyclopent-2-enyl)aniline.

It has recently been shown that dimethyldioxirane (DMDO) can be used for selective epoxidation of primary and secondary *N*-alkenylamines,[1–3] which is achieved after preliminary protection of the amino group as an ammonium salt or a complex with BF_3. Hydrochlorides of aliphatic amines are oxidized by DMDO to nitro compounds.[4,5]

We studied the possibility of epoxidation of *ortho*-alkenylarylamines, in particular, 2-(cyclopent-2-enyl)aniline (**1**), with the aim of further using this methodology as the key stage in the synthesis of hardly accessible nitrogen-containing heterocycles. The amino group was protected by converting amine **1** into hydrochloride **2**, which is well soluble in organic solvents. When we studied the reaction of salt **2** with DMDO, we found that it occurs in an unusual direction leading to the formation of 3-chloro-2-(cyclopent-2-enyl)aniline (**3**) and 6-chloro-2-(cyclopent-2-enyl)aniline (**4**) in 21 and 27% yields, respectively. The structures of the compounds obtained were established by ^{1}H NMR and IR spectroscopy and mass spectrometry and confirmed by the data of elemental analysis.

For example, the mass spectra of compounds **3** and **4** indicate that each of them contains one chlorine atom in the molecule. The identity of the high-field portions of the ^{1}H NMR spectra of compounds **1**, **3**, and **4** due to the protons of the cyclopentenyl fragment[6] is evidence for the localization of the chlorine atom in the aromatic ring of molecules **3** and **4**. The absence of singlet signals in the region of aromatic protons (at δ 6.5—7.5) and the appearance of a doublet of doublets in the same region indicate that the chlorine atom is located in positions 3 or 6 of the aromatic ring. For isomers **3** and **4**, the signals confirming this position were assigned by the double resonance method. Irradiation of a doublet of doublets at δ 7.00 results in the appearance of singlets at δ 6.66 and 6.86 in the ^{1}H NMR spectrum of compound



Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 8, pp. 1654—1655, August, 1998.