The work was carried out while V. P. Litvinov was residing at the Chemistry Center of the University of Lund (Sweden) in the framework of the agreement on scientific exchange between the Academy of Sciences of the USSR, the Royal Swedish Academy of Sciences, and the Royal Academy of Engineering Sciences. We thank the Swedish Research Council for Natural Sciences for making it possible to carry out the present work.

CONCLUSIONS

1. The Vilsmeier formylation of selenopheno[2,3-c]thiophene produces a mixture of selenopheno[2,3-c]thiophene-4-carboxaldehyde and selenopheno[2,3-c]thiophene-6-carboxaldehyde in a 3:2 ratio.

2. Metalation of selenopheno[2,3-c]thiophene by butyllithium followed by treatment of the lithium derivative formed with DMFA results in the formation of a product of the opening of the selenophene fragment along with the indicated aldehydes in an 18:82 ratio. This product is the first example of the splitting of a C–Se bond between a selenium atom and a β-carbon atom in a thiophene ring.

LITERATURE CITED

1. V. P. Litvinov and Ya. L. Gol'dfarb, Adv. Heterocycl. Chem., 19, 123 (1976); V. P. Litvinov, The Chemistry of Condensed Thiophenes: Thienothiophenes, Selenophenothiophenes, and Related Systems. Topics in Organic Sulphur Chemistry, University Press, Ljubljana (1978), p. 157.
2. V. P. Litvinov, I. P. Konyaeva, and Ya. L. Gol'dfarb, Izv. Akad. Nauk SSSR, Ser. Khim., 1575 (1974); V. P. Litvinov, I. P. Konyaeva, and Ya. L. Gol'dfarb, ibid., 477 (1976); V. P. Litvinov, Ya. L. Gol'dfarb, and I. P. Konyaeva, ibid., 372 (1980).
3. I. A. Abronin, V. P. Litvinov, G. M. Zhidomirov, A. Z. Dzhumanazarova, and Ya. L. Gol'dfarb, Khim. Geterotsikl. Soedin., 199 (1980).
4. V. P. Litvinov, A. N. Sukiasyan, Ya. L. Gol'dfarb, and L. V. Bogacheva, Izv. Akad. Nauk SSSR, Ser. Khim., 1592 (1971).
5. V. P. Litvinov, Ya. L. Gol'dfarb, V. S. Bogdanov, I. P. Konjaeva, and A. N. Sukiasyan, J. Prakt. Chem., 315, 850 (1973).
6. H. Wynberg and J. Feljen, Rec. Trav. Chim., 89, No. 1, 77 (1970).
7. W. C. Still, M. Kahn, and A. Mitra, J. Org. Chem., 43, 2923 (1978).
8. S. Gronowitz and T. Freid. Khim. Geterotsikl. Soedin., 435 (1978).
9. F. B. Iteke, L. Christiaens, and M. Renson, Tetrahedron, 32, 689 (1976).
10. E. Luppold, E. Müller, and W. Winter, Z. Naturforsch., 31B, 1654 (1976).
11. S. Gronowitz, A. Halberg, and T. Freid, Tetrahedron, 35, 2607 (1979).
12. Ya. L. Gol'dfarb, V. P. Litvinov, and A. N. Sukiasyan, Izv. Akad. Nauk SSSR, Ser. Khim., 2585 (1967); Ya. L. Gol'dfarb, V. P. Litvinov, and A. N. Sukiasyan, ibid., 1269 (1971); V. P. Litvinov, A. N. Sukiasyan, and Ya. L. Gol'dfarb, Khim. Geterotsikl. Soedin., 723 (1972).

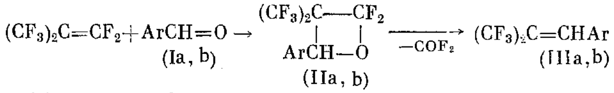
REACTION OF PERFLUOROISOBUTYLENE WITH AROMATIC ALDEHYDES

Yu. V. Zeifman, L. A. Simonyan,
Z. V. Safronova, and N. P. Gambaryan

UDC 542.91:547.413.5:547.571

Continuing a study of the reactions of perfluoroisobutylene with compounds containing electrophilic multiple bonds [1], we investigated the reaction of perfluoroisobutylene with aromatic aldehydes, namely, benzaldehyde (Ia) and its p-(dimethylamino) (Ib) and p-nitro derivatives (Ic). It was assumed that the reaction would occur according to a cycloaddition scheme with subsequent decomposition of the intermediate oxetane (II) into olefin (III) and carbonyl fluoride. The latter with perfluoroisobutylene should give perfluoropivaloyl fluoride (IV)

A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow.
Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 6, pp. 1367-1371, June, 1981. Original article submitted October 8, 1980.



$$(CF_3)_2C{=}CF_2 + ArCH{=}O \rightarrow \begin{matrix}(CF_3)_2C{-}CF_2\\ |\quad\quad|\\ ArCH{-}O\end{matrix} \xrightarrow[-COF_2]{} (CF_3)_2C{=}CHAr$$

(Ia, b) (IIa, b) (IIIa,b)

$Ar{=}C_6H_5$ (a), $C_6H_4N(CH_3)_2$-*p* (b).

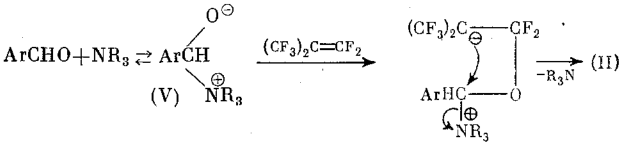
$$(CF_3)_2C{=}CF_2 + COF_2 \rightarrow (CF_3)_3C{-}COF$$

(IV)

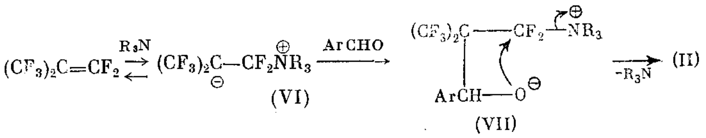
Perfluoroisobutylene reacts with DMFA [2, 3], and perfluoromethacryloyl fluoride reacts with aldehydes (I) [4] according to such a scheme. However, by contrast, perfluoroisobutylene does not react with benzaldehyde or with p-methoxybenzaldehyde even with prolonged heating to 150°C.* At the same time, the reaction of perfluoroisobutylene with (Ib) occurs at 20°C. In addition, 1,1-bis(trifluoromethyl)-2-[p-(dimethylamino)phenyl]-ethylene (IIIb) and fluoride (IV) are obtained in high yield.

Such a difference is apparently explained by the fact that (Ib), as a tertiary amine, catalyzes cycloaddition. Previously, we determined that the reactions of perfluoroisobutylene with electrophilic multiple bonds can be carried out in a number of cases only under conditions of nucleophilic catalysis [1, 6]. Therefore, the reaction of perfluoroisobutylene with aldehydes (Ia) and (Ic) was investigated in the presence of R_3N [γ-(dimethylamino)pyridine, diazabicyclooctane, and Me_3N].

It was determined that all these amines promote the reaction of perfluoroisobutylene with aldehydes, but only γ-(dimethylamino)pyridine catalyzes precisely the cycloaddition reaction: in this case, the main isolated reaction products (at ~100°C) are bis(trifluoromethyl)phenylethylene (IIIa) and fluoride (IV). Apparently, the role of γ-(dimethylamino)pyridine as a catalyst in this reaction consists in activation of one of the components, namely, the aldehyde or perfluoroisobutylene. In the first case, the aldehyde is converted to bipolar ion (V), able to undergo addition at the multiple bond of perfluoroisobutylene. Subsequent cyclization with regeneration of the catalyst and decomposition of the cycloadduct give as products olefin (III) and fluoride (IV).



An alternative mechanism includes the reversible addition of R_3N to perfluoroisobutylene (cf. [7]), the reaction of betaine (VI) with the carbonyl group, and cyclization with elimination of R_3N



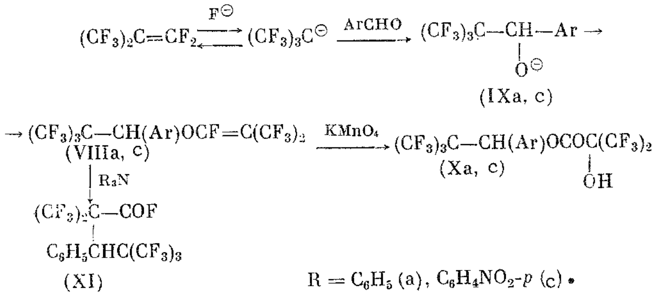
In the presence of diazabicyclooctane (at ~100°C), olefin (IIIa) is formed in very small amounts, and the main isolated product is fluoride (XI), containing a perfluoro-tert-butyl group. The same fluoride is also formed in the presence of Me_3N at 100°C. The reaction of (Ic) with perfluoroisobutylene in the presence of diazabicyclooctane occurs at ~20°C with the formation of α-(perfluoro-tert-butyl)benzyl vinyl ether (VIIIc).

Apparently, the formation of ether (VIIIc) and fluoride (XI), an isomer of vinyl ether (VIIIa), is due to the fact that $F^{\ominus}$ is generated in the perfluoroisobutylene – R_3N system [8]. This leads to the formation of the anion $(CF_3)_3C^{\ominus}$, which subsequently controls the reaction of perfluoroisobutylene with aldehydes. Indeed, in the presence of CsF, perfluoroisobutylene reacts with benzaldehyde even at ~ 20°C and gives vinyl ether (VIIIa) in high yield. Vinyl ether (VIIIc) is obtained similarly from (Ic). At the same time, the presence of CsF does not change the result of the reaction of perfluoroisobutylene with (Ib). In addition, as before, olefin (IIIb) is formed, and not the corresponding ether (VIII).

Thus, it is apparent that in the reaction of perfluoroisobutylene with aldehydes (Ia) and (Ic) in the presence of F^-, reversible addition of the anion $(CF_3)_3C^{\ominus}$ occurs at the carbonyl group of the aldehyde (cf. [9]) with the formation of alcoholate (IX), which subsequently replaces the vinyl F atom in the second fluoroolefin molecule.

---

* See [5] for the comparative activity of perfluoroisobutylene and perfluoromethacrylic acid derivatives.



In accordance with this scheme, the maximum yield of ether (VIIIa) is attained with a 2:1 ratio of the reagents perfluoroisobutylene and (Ia), and with an equimolar ratio of the reagents the reaction stoichiometry is retained, and unreacted benzaldehyde is isolated together with ether (VIIIa).

The structure of ethers (VIII) was confirmed by spectral methods and also by oxidation (cf. [10]) to the corresponding esters of α-hydroxyhexafluoroisobutyric acid (X). As expected, during heating with R_3N, ether (VIIIa) isomerized to fluoride (XI) (cf. [11]).

Thus, the direction of the reaction of perfluoroisobutylene with the aromatic aldehydes depends on the nature of the substituent in the para position of the aromatic ring and on the catalyst: the F^- anion causes addition of the perfluoro-tert-butyl anion at the carbonyl group, and γ-(dimethylamino)pyridine catalyzes the cycloaddition reaction. Apparently, despite the similarity of the bipolar intermediate (VII) to alcoholate (IX), the presence of the $CF_2\overset{\oplus}{N}R_3$ group in (VII) makes possible the intramolecular nucleophilic substitution with elimination of R_3N. In the case of alcoholates (IX), the substitution of the F atom in the trifluoromethyl group is hindered, and the reaction proceeds by the route of formation of vinyl ethers (VIII).

EXPERIMENTAL

The IR spectra were recorded with a UR-20 instrument, and the NMR spectra were recorded with a Perkin–Elmer R-32 instrument (PMR of 90 MHz and ^{19}F NMR of 86.46 MHz) from external standards of HMDS and CF_3COOH.

1,1-Bis(trifluoromethyl)-2-[-p-(dimethylamino)phenyl]ethylene (IIIb). A mixture of 5 g of aldehyde (Ib), 15 g of perfluoroisobutylene, and 15 ml of abs. MeCN was kept in a sealed ampul for 15 days at 20°C. The volatile products, containing fluoride (IV) (^{19}F NMR data), were distilled in vacuo, and the residue was recrystallized from hexane. Obtained: 8 g (85%) of olefin (IIIb), mp 74-76°C. Found: C 50.58; H 3.85; F 40.62; N 5.06%. $C_{12}H_{11}F_6N$. Calculated: C 50.88; H 3.88; F 40.30; N 4.95%. Infrared spectrum (ν, cm^{-1}): 1600, 1640. PMR spectrum (in CCl_4): 2.9 singlet (Me), 7.25 multiplet (CH), 6.3-7.4 multiplet (C_6H_4). ^{19}F NMR spectrum (in CCl_4): −16.3 doublet quartet (CF_3^A), −20.6 quartet (CF_3^B); $J_{CF_3-CF_3} = 9$, $J_{CF_3-H^A} = 1.1$ Hz. In the presence of CsF or diazabicyclooctane, the reaction accelerated somewhat, and the yield of olefin (IIIb) decreased to 70%.

α-(Perfluoro-tert-butyl)benzyl Perfluoroisobutenyl Ether (VIIIa). To a suspension of 7.3 g of freshly calcined CsF in 50 ml of abs. monoglyme was added 12 g of aldehyde (Ia), and then 50 g of perfluoroisobutylene was added for 1.5 h with stirring. The mixture was kept at 30°C for 12 h, the unreacted perfluoroisobutylene was removed in vacuo, the residue was decanted into dilute HCl (1:5), and the precipitated oil was extracted with ether, dried, and distilled. Obtained: 39.4 g (70%) of ether (VIIIa), bp 55-56°C (3 mm), n_D^{20} 1.3795. Found: C 35.56; H 1.24; F 60.29%. $C_{15}H_6F_{16}O$. Calculated: C 35.46; H 1.18; F 60.02%. IR spectrum (ν, cm^{-1}): 1705 (C=C). PMR spectrum (in CCl_4): 5.85 singlet (CH), 7.0 multiplet (Ph). ^{19}F NMR spectrum: −4.75 multiplet (CF), −13.7 singlet [$(CF_3)_3C$], −19.1 multiplet [$(CF_3)_2$].

Potassium permanganate was added portionwise to a solution of 9 g of ether (VIIIa) in 50 ml of acetone and 5 ml of water until the appearance of a stable violet coloration. The mixture was boiled for 0.5 h, diluted with water after cooling, decolorized by passing SO_2, and extracted with ether, and the extract was dried and distilled. Obtained: 6.6 g (70%) of α-(perfluoro-tert-butyl)benzyl α-hydroxyhexafluoroisobutyrate (Xa), bp 72-73°C (3 mm), n_D^{20} 1.3810. Found: C 34.65; H 1.44; F 54.99%. $C_{15}H_7F_{15}O_3$. Calculated: C 34.61; H 1.35; F 54.77%. IR spectrum (ν, cm^{-1}): 1770 (C=O), 3500 (OH). PMR spectrum (in CCl_4): 4.68 singlet (OH), 6.56 singlet (CH), 7.35 multiplet (Ph). ^{19}F NMR spectrum (in CCl_4): −3.7 multiplet [$(CF_3)_2$], −14.5 broadened singlet [$(CF_3)_3C$].

A mixture of 3.5 g of ether (VIIIa), 5 g of perfluoroisobutylene, 0.5 g of diazabicyclooctane, and 20 ml of monoglyme was heated in a sealed ampul at 100°C for 15 h. By distillation, 1.5 g of a fraction with bp 60-75°C (2 mm) was isolated, crystallizing during standing. By recrystallization from aqueous alcohol, 0.6 g (17%) of α-[α-(perfluoro-tert-butyl)benzyl]hexafluoroisobutyric fluoride (XI) was obtained, mp 64-66°C; mol. wt. 506 (mass spectrometrically). IR spectrum (ν, cm^{-1}): 1865 (C=O). ^{19}F NMR spectrum (in CCl_4): −13.8 singlet [$(CF_3)_3C$], −15.1 multiplet [$(CF_3)_2C$], −125 multiplet (CF).

α-(Perfluoro-tert-butyl)-p-nitrobenzyl Perfluoroisobutenyl Ether (VIIIb). A suspension of 3.4 g of CsF, 20 g of perfluoroisobutylene, 3 g of aldehyde (Ic), and 25 ml of monoglyme was stirred at 20°C for 8 h. The next day, the residue after distillation of the volatile products was decanted into dilute HCl and extracted with ether. After distillation of part of the ether, 0.8 g of p-nitrobenzoic acid was filtered off. From the filtrate was obtained 2.6 g (33%) of ether (VIIIb), bp 96-101°C (0.015 mm). Found: C 33.27; H 1.03%. $C_{15}H_5F_{16}NO_3$. Calculated: C 32.60; H 0.91%. PMR spectrum (in acetone): 6.8 broadened singlet (CH), 7.6-8.2 multiplet (C_6H_4). ^{19}F NMR spectrum (in acetone): −7.8 multiplet (CF), −14.7 singlet [$(CF_3)_3C$], −19.8 multiplet [$(CF_3)_2$]. A mixture of 1.5 g of aldehyde (Ic), 12 g of perfluoroisobutylene, 0.4 g of diazabicyclooctane, and 35 ml of monoglyme was kept at 20°C for 20 days. By distillation, 2.1 g (35%) of a fraction with bp 95-100°C was obtained, consisting of ether (VIIIb) with insignificant impurities (^{1}H and ^{19}F NMR).

Ester (Xb), 63% yield, mp 96-98°C, was obtained by oxidation of ether (VIIIb) by $KMnO_4$ Found: C 32.09; H 1.18; N 2.24%. $C_{15}H_6F_{15}NO_5$. Calculated: C 31.90; H 1.06; N 2.48%. IR spectrum (ν, cm^{-1}): 1770 (C=O), 3490 (OH). PMR spectrum (in acetone): 6.8 singlet (CH), 7.5-8.2 (C_6H_4, OH). ^{19}F NMR spectrum (in acetone): −3.3 multiplet [$(CF_3)_2$], −14.5 broadened singlet [$(CF_3)_3C$].

Reaction of Perfluoroisobutylene with Aldehydes in the Presence of R_3N. A mixture of 1.1 g of aldehyde (Ia), 5 g of perfluoroisobutylene, 0.37 g of γ-(dimethylamino)pyridine, and 25 ml of MeCN was heated in a sealed ampul at 100-110°C for 10 h. Fluoride (IV) was observed (by NMR) in the volatile products distilled in vacuo. The residue was decanted into dilute HCl. From the bottom layer was obtained 0.6 g of a fraction with bp 68-70°C (18 mm) consisting of olefin (IIIa) with impurities of aldehyde (Ia) and ether (VIIIa) (data of the NMR spectra and chromatography–mass spectrometry of [12]). Significant amounts of unidentified resinous products were obtained in the residue after distillation.

A mixture of 1.3 g of aldehyde (Ia), 5 g of perfluoroisobutylene, 0.5 g of diazabicyclooctane, and 20 ml of monoglyme was heated in a sealed ampul at 105-115°C for 15 h. After the usual workup, distillation yielded 0.6 g of a fraction with bp 70-73°C (20 mm) containing (according to NMR) 40% aldehyde (Ia), 55% fluoride (XI), and 3% olefin (IIIa). Similarly, 2% crystals with mp 62-64°C, identical to fluoride (XI), were isolated with Me_3N as the catalyst (6 h, 100°C).

CONCLUSIONS

Depending on the nature of the catalyst, 1,1-bis(trifluoromethyl)-2-arylethylenes or products of the addition of the perfluoro-tert-butyl anion to the carbonyl group are formed in the reaction of perfluoroisobutylene with ArCHO under conditions of nucleophilic catalysis.

LITERATURE CITED

1. Yu. V. Zeifman, E. G. Ter-Gabriélyan, D. P. Del'tsova, and N. P. Gambaryan, Izv. Akad. Nauk SSSR, Ser. Khim., 396 (1979).
2. Yu. A. Cheburkov and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 346 (1967).
3. I. L. Knunyants, N. I. Delyagina, and S. M. Igumnov, Izv. Akad. Nauk SSSR, Ser. Khim., 860 (1981).
4. D. C. England, L. Solomon, and C. G. Krespan, J. Fluorine Chem., 3, 63 (1973).
5. É. P. Lur'e, E. G. Gal'pern, N. P. Gambaryan, E. M. Rokhlin, and E. I. Mysov, Izv. Akad. Nauk SSSR, Ser. Khim., 619 (1980).
6. Yu. V. Zeifman, L. A. Simonyan, E. G. Ter-Gabriélyan, N. P. Gambaryan, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 1813 (1976).
7. N. P. Gambaryan, Usp. Khim., 45, 1251 (1976).
8. E. M. Rokhlin, E. G. Abduganiev, and U. Utebaev, Usp. Khim., 45, 1177 (1976).
9. N. I. Delyagina, B. L. Dyatkin, and I. L. Knunyants, Zh. Org. Khim., 10, 935 (1974).
10. U. Utubaev, E. G. Abduganiev, E. M. Rokhlin, and I. L. Knunyants, Izv. Akad. Nauk SSSR, Ser. Khim., 387 (1974).
11. I. L. Knunyants, E. M. Rokhlin, and Yu. A. Cheburkov, Zh. Vses. Khim. O-va, 15, 15 (1970).
12. D. J. Burton and Y. Inouye, Tetrahedron Lett., 3397 (1979).