the β-ketoester salts with methylhydrazine and 3,5-dioxypyrazolidines which successively split off methanol and H_2O with formation of 3-oxypyrazolines and pyrazol-5-ones, respectively.

LITERATURE CITED

1. K. I. Pashkevich and V. I. Saloutin, Usp. Khim., 54, 1997 (1985).
2. V. I. Saloutin, A. N. Fomin, and K. I. Pashkevich, Izv. Akad. Nauk SSSR, Ser. Khim., 144 (1984).
3. M. Cocivera, K. W. Woo, and P. Livant, Can. J. Chem., 56, 473 (1978).
4. A. N. Fomin, V. I. Saloutin, K. I. Pashkevich, et al., Izv. Akad. Nauk SSSR, Ser. Khim., 2626 (1983).
5. S. I. Selivanov, R. A. Bogatkin, and B. A. Ershov, Zh. Org. Khim., 18, 909 (1982).
6. A. L. Henne, M. S. Newman, L. L. Quill, and R. A. Staniforth, J. Am. Chem. Soc., 69, 1819 (1947).

NEW ROUTE TO PERFLUOROTERT-BUTYL IODIDE

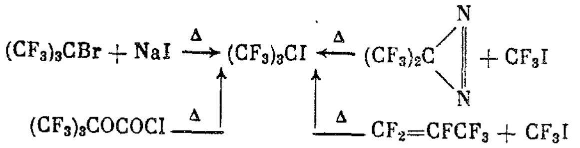
L. E. Deev, T. I. Nazarenko, and K. I. Pashkevich

UDC 542.91:547.226'161:547.413.5'161

Perfluorotert-butyl iodide is a convenient source of the perfluorotert-butyl radical [1].

Preparations of $(CF_3)_3CI$ (I) have included the reaction of hexafluoroethane with tetraiodomethane under electric discharge [2], treatment of $(CF_3)_3CBr$ with iodide using flash CO_2 laser irradiation [3], and iodofluorination of perfluoroisobutylene [1, 4]. However, the complexity of the experimental apparatus and the high toxicity of perfluoroisobutylene do not favor these methods. Our work has concerned a new synthetic method for (I).

It has been shown that treatment of $(CF_3)_3CBr$ with NaI in aprotic solvents (MeCN, acetone) gave (I) in 5-6% yield. The main product was 2-hydroperfluoroisobutane apparently formed because the highly reactive perfluorotert-butyl anion can remove a proton from the solvent. Treatment of perfluorotert-butyl chloroformate with KI at 180-200°C gave a 30% yield of (I). This reaction probably occurs via formation of an unstable perfluorotert-butyl iodoformate which loses CO_2 on heating.



Heating bis(trifluoromethyl)diazirine with CF_3I to 150-200°C also led to a 10-12% yield of (I).

A high yield of (I) (70-75%) was successfully obtained by co-pyrolysis of hexafluoropropylene with CF_3I in a flow-through reactor at 280-400°C. The ratio of products formed depended upon the temperature, the ratio of reagents, and the reactor material (Table 1).

The proposed formation of (I) can arise by the following scheme:

$$CF_3CF{=}CF_2 + CF_3^{\cdot} \rightarrow (CF_3)_2CF_2\dot{C}F_2 \rightarrow (CF_3)_3C^{\cdot} \xrightarrow{CF_3I} (CF_3)_3CI + CF_3^{\cdot}$$

Apparently the nickel wall of the reactor promotes the isomerization of the perfluoroisobutyl radical to the more stable perfluorotert-butyl as a result of which (I) predominates

---

Chemistry Institute, Ural Branch, Academy of Sciences of the USSR, Sverdlovsk. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 402-404, February, 1988. Original article submitted June 16, 1986.

TABLE 1. Yield (%) of Primary Products of Co-Pyrolysis of Hexafluoropropylene with Trifluoroiodomethane (10% Conversion)

Product	Quartz reactor				Nickel reactor, 360°C, C_3F_6: CF_3I 1:1.6 (molar)
	C_3F_6 : CF_3I=1 : 1,6 (molar)		360°, C_3F_6 : CF_3I (molar)		
	310°	380°	1 : 7	1 : 1,6	
$(CF_3)_2C{=}CF_2$	0	6,1	0	Traces	1,5
$CF_3CF_2CF_2I$	4,0	Traces	2,2	0,7	3,1
$(CF_3)_2CFI$	8,0	0,7	2,2	1,5	3,1
$(CF_3)_2CFCF_2I$	10,1	1.4	14,3	6,7	6,2
$CF_3CFIC_2H_5$	48,5	70,7	66,6	71,3	9,1
$(CF_3)_3CI$	24,2	20,4	15,5	19,8	77,0

TABLE 2. ^{19}F NMR Spectral Data for Co-Pyrolysis of Hexafluoropropylene with Trifluoroiodomethane (δ, ppm, C_6F_6)

Component of mixture	Observed values	Literature data
$(CF_3)_2C{=}CF_2$	Detection problem	See [6]
$CF_3CF_2CF_2I$	80,4, 118,5, 64,5	79,8, 117,7, 60 [7]
$(CF_3)_2CFI$	76,4, 149,6	78, 147 [7]
$(CF_3)_2CFCF_2I$	71,97, 164,9, 51,8	
$CF_3CFICF_2CF_3$	73,88, 146,4, 111,6 78,92	73, 143, 116, 78,5 [8, 7]
$(CF_3)_3CI$	64.21	

in the co-pyrolysis products. The ^{19}F NMR data for the mixture of components is given in Table 2.

The IR spectra of the co-pyrolysis products included frequencies of 1800, 1700, 1350-1110, 1090, 1070, 1050, 1030, 1000, 960, 940, 900, 870, 815, 748, 725, and 709 cm^{-1}. This series of frequencies confirmed the presence in the mixture of C–I, C–F, and C=C groups and did not conflict with literature data for the following compounds: $\nu(CF_3)_2C{=}CF_2$: 1751, 1389, 1309, 1232, 1193, 1050, 1000, 769, 721 cm^{-1} [9]. $\nu CF_3CF_2CF_2I$: 1314, 1263, 1248, 1139, 1129, 1068, 1030, 873, 813, 730 cm^{-1} [10]. $\nu(CF_3)_2CFI$: 1280, 1245, 1182, 1122, 957, 900, 751, 713, 709 cm^{-1} [11]. $\nu(CF_3)_3CI$: 1270, 960, 725 cm^{-1} [2]. $\nu CF_3CFICF_2CF_3$: 1399, 1325, 1274, 1176, 1153, 1019, 986, 934, 886, 860, 816, 748, 743, 721 cm^{-1} [8].

It should also be noted that the IR spectrum of the C_3F_6/CF_3I co-pyrolysis product showed new absorptions at 940 and 1090 cm^{-1} apparently assignable to $(CF_3)_2CF{-}CF_2I$.

EXPERIMENTAL

Perfluorotert-butyl bromide was prepared according to [5], $(CF_3)_3COCOCl$ by [12] and bis(trifluoromethyl)diazirine by [13]. GLC was carried out on an LKM-12 chromatograph with catharometer detector, He carrier, and a 3 m × 4 mm stainless steel column containing hydroxylated silochrom C-80 (0.25-0.35 mm). ^{19}F NMR spectra were recorded on a WP 80 SY spectrometer at 75.4 MHz and referenced to C_6F_6. IR spectra were recorded on a Specord-75IR instrument.

Reaction of Perfluorotert-butyl Bromide with NaI. $(CF_3)_3CBr$ (6.2 g, 21 mmoles) in CH_3CN (5 ml) was added to a solution of NaI (3.1 g, 21 mmoles) in CH_3CN (20 ml) and refluxed for 5 h to give $(CF_3)_3CH$ (351 ml, 75.7%). The cooled mixture was filtered and the filtrate extracted and distilled to give $(CF_3)_3CI$ (I, 0.4 g, 5.5%). In a further experiment $(CF_3)_3CBr$ (8.1 g, 27.1 mmoles) in acetone (5 ml) was added to a solution of NaI (4.0 g, 26.6 mmoles) in acetone (20 ml) and refluxed for 5 h. $(CF_3)_3CH$ (86 ml, 14%) was evolved and the cooled mixture was filtered off. The filtrate was distilled to give (I) (0.5 g, 5.3%).

Reaction of Perfluorotert-butyl Chloroformate with KI. Ignited KI (16 g, 96 mmoles) in a nickel ampul was evacuated and cooled and $(CF_3)_3COCOCl$ (14 g, 47 mmoles) condensed into it. The ampul was agitated for 3 h at 150-180°C, cooled, evacuated, and the accumulated product collected in a trap cooled with acetone/dry ice. Distillation of the product in vacuo then gave I (5.0 g, 30.8%).

Reaction of Bis(trifluoromethyl)diazirine with Trifluoroiodomethane. CF_3I (100 g, 0.51 mole) and bis(trifluoromethyl)diazirine (27.2 g, 0.15 mole) were condensed into an evacuated and cooled autoclave of capacity 0.5 liter. After heating for 10 h at 150-155°C the contents were cooled. The gaseous products of the reaction were collected in a trap cooled with acetone/dry ice. The trap was changed and high boiling products were obtained by evacuation of the autoclave. Distillation then gave I (5.2 g, 9.8%).

Co-pyrolysis of Hexafluoropropylene with Trifluoroiodomethane. A mixture of hexafluoropropylene and CF_3I were passed through a reaction tube (500 × 18 mm) heated to 320-380°C at a velocity of 2 ml/sec. The pyrolysis products were collected in an acetone/dry ice cooled trap. The yields of pyrolysis products at 10% conversion are given in Table 1.

CONCLUSIONS

Perfluorotert-butyl iodide is formed in high yield upon pyrolysis of hexafluoropropylene with perfluoromethyl iodide. Perfluorotert-butyl iodide is also formed in low yield when perfluorotert-butyl bromide or chloroformate is treated with alkali metal iodides and also from bis(trifluoromethyl)diazirine and perfluoromethyl iodide.

LITERATURE CITED

1. E. P. Mochalina, B. L. Dyatkin, I. V. Galakhov, and I. L. Knunyants, Dokl. Akad. Nauk SSSR, 169, 1345 (1966).
2. R. J. Lagow, L. L. Gerchman, and R. A. Jacob, USA Patent 3,992,424 (1976).
3. V. N. Bagratashvili, V. N. Burimov, L. E. Deev, et al., Kvantovaya Élektron., Moscow, 9, No. 2, 423 (1982); Chem. Abstr., 96, 190552J (1982).
4. T. Takeuchi, Yukigosei Kagaku Kekaisi, 32, No. 7, 580 (1974).
5. S. T. Kocharyan, E. M. Rokhlin, and I. L. Knunyants, Zh. Vses. Khim. Ova., 11, No. 6, 709 (1966).
6. B. L. Dyatkin, N. I. Delyagina, and S. R. Sterlin, Usp. Khim., 45, 1205 (1976).
7. L. Phillips and V. Wray, J. Chem. Soc., Perkin Trans. 2, No. 2, 220 (1972).
8. R. Gregory, R. N. Haszeldine, et al., J. Chem. Soc., No. 7, 1216 (1971).
9. T. J. Brice, J. D. LaZerte, L. J. Hals, and W. H. Pearlson, J. Am. Chem. Soc., 75, 2698 (1953).
10. Fluorine and Its Compounds [Russian translation], Vol. 2, IL, Moscow (1957), p. 456.
11. W. T. Miller and M. B. Freedman, J. Am. Chem. Soc., 85, No. 2, 180 (1963).
12. M. Hudlicky, J. Fluor. Chem., 20, No. 5, 649 (1982).
13. Synthesis of Organofluoro Compounds, Khimiya, Moscow (1973), p. 75.