ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 3, pp. 469–471. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © Yu.S. Kudyakova, D.N. Bazhin, Ya.V. Burgart, V.I. Saloutin, O.N. Chupakhin, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 3, pp. 481–482.

SHORT COMMUNICATIONS

Dedicated to Full Member of the Russian Academy of Sciences
I.P. Beletskaya on her jubilee

Perfluoroalkylation of Unsaturated Compounds in the Presence of Copper(II) Salen Complexes

Yu. S. Kudyakova, D. N. Bazhin, Ya. V. Burgart, V. I. Saloutin, and O. N. Chupakhin

Postovskii Institute of Organic Synthesis, Ural Branch, Russian Academy of Sciences,
ul. Akademicheskaya/S. Kovalevskoi 22/20, Yekaterinburg, 620990 Russia
e-mail: kud@ios.uran.ru

Received January 17, 2013

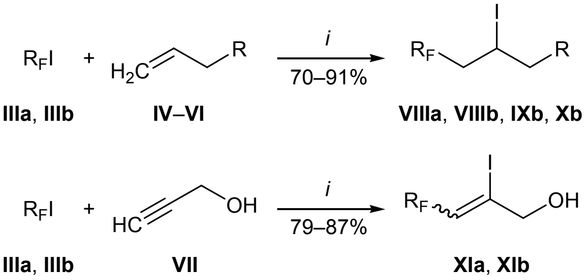
DOI: 10.1134/S1070428013030263

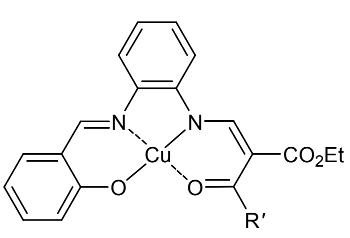
Introduction of perfluoroalkyl groups into molecules of organic compounds essentially changes their physicochemical properties and extends the scope of their practical applications [1–3]. Organometallic catalysis provides an important tool for performing perfluoroalkylation reactions, and variation of the reaction conditions and ligand nature is a significant factor affecting the yield and product structure [4–8]. For example, catalysis of reactions of alkenes with perfluoroalkylating agents by copper(I) and copper(II) salts in the presence of different ligands leads to the formation of functionalized trifluoromethyl-substituted compounds [4, 5].

We previously synthesized transition metal salen complexes, namely {ethyl 2-[2-(2-hydroxyphenylmethylideneamino)phenylaminatomethylidene]-3-oxo-3-(polyfluoroalkyl)propionato}copper(II) **I** and **II** [9]. In the present communication we report on the use of complexes **I** and **II** as catalysts in radical addition of perfluoroalkyl iodides to unsaturated compounds. In fact, copper(II) complexes **I** and **II** efficiently catalyzed reactions of perfluoroalkyl iodides **IIIa** and **IIIb** with alkenes **IV**–**VI** and with propargyl alcohol **VII**, and the corresponding addition products **VIIIa**, **VIIIb**, **IXb**, **Xb**, **XIa**, and **XIb** were obtained in good yields (70–91%) under mild conditions. No reaction occurred in the absence of a catalyst and/or radical initiator.

Presumably, complexes **I** and **II** promote decomposition of hydrogen peroxide to produce hydroxyl radicals $HO^{\cdot}$ which initiate radical addition of perfluoroalkyl iodides to unsaturated compounds. Complex **II** ensured somewhat higher yields than did complex **I**, i.e., the catalyst with a longer fluorinated carbon chain is more efficient.

Perfluoroalkylation of unsaturated compounds (*genral procedure*)**.** Complex **I**, 5 mol %, was added to a mixture of 0.10 mol of perfluoroalkyl iodide **IIIa** or **IIIb** and 0.10 mol of unsaturated compound **IV**–**VII** in 30 ml of acetonitrile, 20 ml of 38% hydrogen peroxide was then added dropwise, and the mixture was stirred





I, **II**

$R_F = C_4F_9$ (**a**), $C_3F_7OCF(CF)_3CF_2OCF(CF_3)$ (**b**); **IV**, **VIII**, R = OH; **V**, **IX**, R = OAc; **VI**, **X**, $R = H(CH_2)_7$; **I**, $R' = CF_3$; **II**, $R = H(CF_2)_2$; *i*: MeCN, 38% H_2O_2, complex **I** or **II** (5 mol %), 25°C.

for 2 h. The product was extracted into chloroform (3 × 50 ml), the extract was washed with water and dried over sodium sulfate, and the solvent was distilled off.

4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodoheptan-1-ol (VIIIa). Yield 28.3 g (70%), reddish oily substance, bp 97–98°C (10 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.79 m and 3.08 m (1H each, CF_2CH_2), 3.76 m (2H, $C\mathbf{H}_2OH$), 4.32 m (1H, CHI). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 35.95 q.t (2F, γ-F, $^3J_{FF}$ = 12.7, 3.8 Hz), 37.29 m (2F, β-F), 47.06 d.m and 49.86 d.m (1F each, CF_2CH_2, $^2J_{FF}$ = 270.9 Hz), 80.79 t.t (3F, CF_3, $^3J_{FF}$ = 9.7, $^4J_{FF}$ = 3.2 Hz). Found, %: C 20.55; H 1.57; F 42.56. $C_7H_6F_9IO$. Calculated, %: C 20.81; H 1.50; F 42.32.

4,6,6,7,9,9,10,10,11,11,11-Undecafluoro-2-iodo-4,7-bis(trifluoromethyl)-5,8-dioxaundecan-1-ol (VIIIb). Yield 45.8 g (72%), yellow liquid, bp 85–87°C (10 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.79 m and 3.08 m (1H each, CF_2CH_2), 3.76 m (2H, $C\mathbf{H}_2OH$), 4.32 m (1H, CHI). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 17.02 m (1F, CF), 30.61 m (1F, $CFCH_2$), 32.27 m (2F, $CF_3C\mathbf{F}_2$), 78.71 d.m (3F, CF_3, $^3J_{FF}$ = 42.3 Hz), 80.50 m (6F, $C\mathbf{F}_3CF_2C\mathbf{F}_2OCFC\mathbf{F}_2$), 81.61 m (3F, $C\mathbf{F}_3CFCF_2$), 82.02 m (1F, $CFC\mathbf{F}_2$). Found, %: C 20.70; H 1.03; F 50.66. $C_{11}H_6F_{17}IO_3$. Calculated, %: C 20.77; H 0.95; F 50.78.

4,6,6,7,9,9,10,10,11,11,11-Undecafluoro-2-iodo-4,7-bis(trifluoromethyl)-5,8-dioxaundecyl acetate (IXb). Yield 54.2 g (80%), colorless liquid. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.10 s (3H, CH_3), 2.83 m and 2.99 m (1H each, $CFCH_2$), 4.31 m (3H, $CHICH_2O$). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 17.10 m (1F, CF), 30.59 m (1F, $CFCH_2$), 32.33 m (2F, $CF_3C\mathbf{F}_2$), 78.75 d.m (3F, CF_3, $^3J_{FF}$ = 42.3 Hz), 80.45 m (6F, $C\mathbf{F}_3CF_2C\mathbf{F}_2OCFC\mathbf{F}_2$), 80.57 m (3F, $C\mathbf{F}_3CFCF_2$), 82.09 m (1F, $CFC\mathbf{F}_2$). Found, %: C 29.95; H 1.13; F 47.77. $C_{13}H_8F_{17}IO_4$. Calculated, %: C 23.03; H 1.19; F 47.63.

1,1,1,2,2,3,3,5,6,6,8-Undecafluoro-10-iodo-5,8-bis(trifluoromethyl)-4,7-dioxaoctadecane (Xb). Yield 58.9 g (82%), colorless liquid, bp 115–119°C (3 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.92 t (3H, Me, = J 7.1 Hz), 1.28–1.62 m [14H, $(CH_2)_7$], 2.56–2.63 m (2H, CH_2CI), 6.52 m, 6.72 m (1H, CFCH). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 17.10 m (1F, CF), 30.59 m (1F, $CFCH_2$), 32.33 m (2F, $CF_3C\mathbf{F}_2$), 78.75 d.m (3F, CF_3, $^3J_{FF}$ = 42.3 Hz), 80.45 m (6F, $C\mathbf{F}_3CF_2C\mathbf{F}_2OCFC\mathbf{F}_2$), 80.57 m (3F, $C\mathbf{F}_3CFCF_2$), 82.09 m (1F, $CFC\mathbf{F}_2$). Found, %: C 30.01; H 2.83; F 45.07. $C_{18}H_{20}F_{17}IO_2$. Calculated, %: C 30.10; H 2.81; F 44.97.

4,4,5,5,6,6,7,7,7-Nonafluoro-2-iodohept-2-en-1-ol (XIa). Yield 33.4 g (83%), reddish liquid, bp 105–107°C (10 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.28–2.54 br.s (1H, OH), 4.35–4.37 m (2H, $C\mathbf{H}_2OH$), 6.54 m, 6.77 m (1H, CH=). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 36.17 m (2F, γ-F, *Z*), 36.44 m (2F, γ-F, *E*), 37.56 m (2F, β-F, *Z*), 37.95 m (2F, β-F, *E*), 50.25 m (2F, α-F, *E*), 54.11 m (2F, α-F, *Z*), 81.03 t.t (3F, CF_3, *E*/*Z*, $^4J_{FF}$ = 9.7, $^3J_{FF}$ = 3.3 Hz). Found, %: C 20.95; H 1.07; F 42.46. $C_7H_4F_9IO$. Calculated, %: C 20.91; H 1.00; F 42.53.

4,6,6,7,9,9,10,10,11,11,11-Undecafluoro-2-iodo-4,7-bis(trifluoromethyl)-5,8-dioxaundec-2-en-1-ol (XIb). Yield 50.1 g (79%), colorless liquid, bp 101–103°C (10 mm). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.28–2.54 br.s (1H, OH), 4.35–4.37 m (2H, $C\mathbf{H}_2OH$), 6.54 m and 6.77 m (1H, CH=). ^{19}F NMR spectrum ($CDCl_3$), δ_F, ppm: 16.58 m (1F, CF), 32.09 s (2F, $CF_3C\mathbf{F}_2$), 32.62 m (1F, CFCH), 76.68 m (3F, CF_3), 79.43 m (3F, $C\mathbf{F}_2OCFC\mathbf{F}_2$), 80.49 m (3F, $C\mathbf{F}_3CF_2$), 81.78 m (3F, $C\mathbf{F}_3CFCF_2$), 83.26 m (1F, $OCFC\mathbf{F}_2$). Found, %: C 20.79; H 0.70; F 50.86. $C_{11}H_4F_{17}IO_3$. Calculated, %: C 20.84; H 0.64; F 50.94.

The reactions of perfluoroalkyl iodides **IIIa** and **IIIb** with alkenes **IV**–**VI** and propargyl alcohol (**VII**) in the presence of complex **II** were carried out in a similar way. Yield, %: 73 (**VIIIa**), 74 (**VIIIb**), 87 (**IXb**), 91 (**Xb**), 87 (**XIa**), 85 (**XIb**).

The ^{1}H and ^{19}F NMR spectra were recorded on a Bruker DRX-400 spectrometer at 400 and 376 MHz, respectively, using tetramethylsilane (^{1}H) and hexafluorobenzene (^{19}F) as references. The elemental compositions were determined on a Perkin Elmer CHN PE 2400 analyzer. Initial perfluoroalkyl iodides **IIIa** and **IIIb** were synthesized as described in [3, 10].

This study was performed under financial support by the Ural Branch of the Russian Academy of Sciences, program of the Presidium of the Russian Academy of Sciences "Development of Methods for the Synthesis of Chemical Compounds and Design of New Materials" (project no. 12-P-1020).

REFERENCES

1. *Modern Fluoroorganic Chemistry*, Kirsch, P., Ed., Weinheim: Wiley–VCH, 2004, p. 308.
2. Murphy, P.M., Baldwin, C.S., and Buck, R.C., *J. Fluorine Chem.*, 2012, vol. 138, p. 3.

3. Bazhin, D.N., Gorbunova, T.I., Zapevalov, A.Ya., and Saloutin, V.I., *J. Fluorine Chem.*, 2009, vol. 130, p. 438.
4. Zhu, R. and Buchwald, S.L., *J. Am. Chem. Soc.*, 2012, vol. 134, p. 12462.
5. Wang, X., Ye, Y., Zhang, S., Feng, J., Xu, Y., Zhang, Y., and Wang, J., *J. Am. Chem. Soc.*, 2011, vol. 133, p. 16410.
6. Besset, T., Schneider, C., and Cahard, D., *Angew. Chem., Int. Ed.*, 2012, vol. 51, p. 5048.
7. Studer, A., *Angew. Chem., Int. Ed.*, 2012, vol. 51, p. 8950.
8. Macé, Y. and Magnier, E., *Eur. J. Org. Chem.*, 2012, vol. 13, p. 2479.
9. Kudyakova, Yu.S., Goryaeva, M.V., Burgart, Ya.V., and Saloutin, V.I., *Izv. Akad. Nauk, Ser. Khim.*, 2010, p. 1707.
10. Bazhin, D.N., Gorbunova, T.I., Zapevalov, A.Ya., Beketov, I.V., and Saloutin, V.I., *Russ. J. Gen. Chem.*, 2011, vol. 81, p. 1829.