Letters to the Editor

Polyfluoroalkylation of vinyl ethers by heptafluoropropyl iodide in the presence of sodium alkoxides

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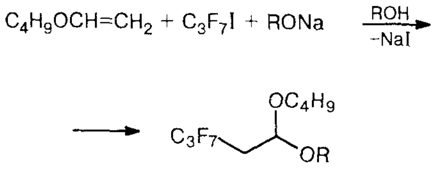
The addition of iodo(perfluoro)alkanes to alkyl vinyl ethers catalyzed by tetrakis(triphenylphosphino)palladium in absolute hexane proceeds with heat evolution to afford the corresponding α-iodoethers in yields up to 88 %.[1] The following dehydroiodination of the α-iodoethers (20 % molar excess of the triethylamine, 40—60 °C) leads to a mixture of the *cis*- and *trans*-isomers of alkyl-β-perfluoroalkyl vinyl ethers (51—86 % yield). An attempt to synthesize the latter in one step, though, failed,[1] since the iodo(perfluoro)alkanes do not react with the vinyl ethers in the presence of pyridine or triethylamine.

We tried to carry out the photoinduced addition of iodo(perfluoro)alkanes to alkyl vinyl ethers. But in this case the evolution of the iodine and a strong tar formation were observed. The reaction does not proceed in the absence of a radical initiator. Unexpectedly, we have found that by mixing butyl vinyl ether with heptafluoropropyl iodide in the presence of sodium alkoxides the hitherto unknown polyfluoroacetals (**1** and **2**) are formed in a high yield (Scheme 1).

The reagents were taken in an equimolar ratio, and the reaction was carried out in the appropriate alcohol at 5—10 °C in the absence of a radical initiator. The structures of acetals **1** and **2** were confirmed by the ^{1}H NMR spectra.

Scheme 1



1, 2

R = Me (**1**), Pr^i (**2**)

This is the first communication on the interaction of vinyl ethers with polyhalogenoalkanes in the presence of alkali metal alkoxides.

Experimental

Standard method for the synthesis of polyfluoroacetals 1 and 2. Sodium (0.02 mol) was dissolved in an appropriate alcohol (10-fold excess). The solution was cooled to 5—10 °C, and C_3F_7I (0.02 mol) was added. Then butyl vinyl ether (0.02 mol) was added slowly dropwise. The mixture was stirred at 5—10 °C for 0.5 h, and then CO_2 was passed through the mixture for 10 min. The mixture was then filtered, the solvent evaporated, and the residue distilled *in vacuo*.

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1-Butoxy-2-heptafluoropropyl-1-methoxyethane (1) was obtained in an amount of 4.7 g (78 % yield), b.p. 70 °C (30 Torr), n_D^{20} 1.3443. ^{1}H NMR (C_6D_6), δ: 4.84 (t, 1 H, CH); 2.40 (m, 2 H, CH_2CF_2); 3.33 (s, 3 H, MeO); 3.56 (m, 2 H, CH_2O); 1.51 (m, 4 H, 2 CH_2); 0.92 (m, 3 H, Me).

1-Butoxy-1-isopropoxy-2-heptafluoropropylethane (2) was obtained in an amount of 3.5 g (53.3 % yield), b.p. 67 °C (5 Torr), n_D^{20} 1.3553. ^{1}H NMR (C_6D_6), δ: 4.90 (t, 1 H, OCHO); 2.44 (m, 2 H, CH_2CF_2); 3.61 (m, 2 H, CH_2O); 1.50 (m, 4 H, 2 CH_2); 1.01 (m, 9 H, 3 Me); 4.05 (m, 1 H, OCH).

References

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Synthesis of rare-earth monophthalocyanines containing fragments of sterically hindered phenols

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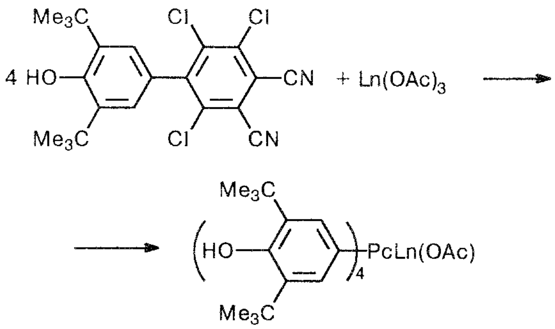
The monophthalocyanines of rare-earth elements (REE) are usually the side products of the synthesis of diphthalocyanines.[1] There have been several reports on the preparation of monophthalocyanines of REE in high yields.[2,3]

We have demonstrated that the introduction of a bulky substituent, 2,6-di-*tert*-butyl-4-hydroxyphenyl, into the molecule of the starting phthalonitrile makes it possible to direct the template synthesis toward the formation of the monophthalocyanine of REE as a major product.

By melting 3,5-di-*tert*-butyl-4-hydroxy-2',5',6'-trichloro-3',4'-dicyanodiphenyl[4] with the anhydrous acetates of Nd, Eu, and Lu (in a 4 : 1 molar ratio) at 290—300 °C for 1.5 h, the corresponding monophthalocyanines (**1a—c**) are formed in 83, 53, and 64 % yield, respectively. The data of the elemental analysis of the compounds obtained are in good agreement with the calculations.

The IR spectra (CCl_4) of compounds **1a—c**, ν/cm^{-1}: 3630—3645 (O—H); 2800—3100 (C—H); 1610—1660 (C=C). ^{1}H NMR spectrum (DMSO-d_6, δ) of Nd complex **1a**: 1.24 (s, 72 H, Bu^t); 4.86 (s, 4 H, OH); 6.84—7.04 (m, 8 H, Ph). The electron absorption spectra with the Q-bands at 673, 676, and 657 nm, respectively, point to the formation of the mononuclear complexes of REE.



1a—c

Ln = Nd(**a**), Eu(**b**), Lu(**c**)

Alterations in the reaction conditions (the molar ratio of the reagents, the temperature, or the reaction time) do not result in the formation of any products of diphthalocyanine type, their synthesis being apparently sterically hindered.

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