Novel Perfluorocyclohexylation with Bis(perfluorocyclohexane carbonyl) Peroxide

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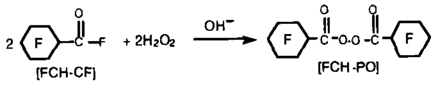
A new bis(perfluorocyclohexane carbonyl) peroxide was prepared by the reaction of the corresponding acyl fluoride and hydrogen peroxide. This peroxide was applicable for the direct introduction of perfluorocyclohexyl group into various organic molecules such as acrylic acid oligomer, benzene and polystyrene; in particular interest, not only equatorial but also axial conformational isomers were isolated in phenylperfluorocyclohexane thus obtained.

The large availability of trifluoromethylated or longer linear fluoroalkylated compounds has offered the increasing attention toward developments of these compounds into medicinal and material sciences.[1] However, the development of the organofluorine compounds containing hindered cyclic fluoroalkyl segments such as perfluorocyclohexyl group has hitherto been limited except for the patent's reports on the poly(1,1-dihydroperfluorocyclohexylmethyl methacrylates),[2] but it is very interesting to explore such hindered cyclic fluoroalkylated compounds, especially the direct introduction of this fluoroalkyl group from the viewpoint of the development of new organofluorine chemistry. Furthermore, such novel hindered cyclic fluoroalkylated compounds are strongly expected to have greater application in a variety of fields. Previously, we reported that perfluoroalkanoyl and perfluorooxaalkanoyl peroxides are a convenient tool for the direct introduction of the corresponding perfluoroalkyl and perfluorooxaalkyl groups into various organic molecules via a radical or a single electron-transfer process.[3] Now, we have found that new various perfluorocyclohexylated compounds are obtained by the use of bis(perfluorocyclohexane carbonyl) peroxide under very mild conditions, and the results will be described herein.

Bis(perfluorocyclohexane carbonyl) peroxide (FCH-PO) was prepared by the reaction of the corresponding acyl fluoride [FCH-CF, which was supplied by SynQuest Laboratories, Inc. (Alachua, FL, USA)] and hydrogen peroxide in $CF_2ClCFCl_2$ under alkaline conditions as shown in the following scheme.



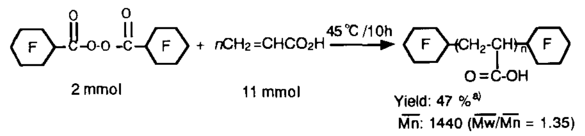
Scheme 1.

The concentration of the peroxide was determined by iodometry. Because of its instability, the solution of the peroxide in $CF_2ClCFCl_2$ thus obtained was used without further purification. The IR spectra of FCH-PO showed the characteristic diacyl peroxide carbonyl bands at 1865 and 1830 cm^{-1}. The thermal decomposition of FCH-PO in $CF_2ClCFCl_2$ was carried out at 35.0 ~ 45.0 ℃, and the rates of decomposition of FCH-PO were measured by idometric titration.

The decomposition of FCH-PO followed a first-order equation at each temperature (35.0, 40.0, 42.5 or 45.0 ℃), and the values of the activation enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) for the thermal decomposition of FCH-PO were 105.4 $kJmol^{-1}$ and 0 $JK^{-1}mol^{-1}$, respectively. These values are similar to those of $(C_3F_7COO)_2$ [$\Delta H^{\neq}$ = 101.7 $kJmol^{-1}$; $\Delta S^{\neq}$ = 16.3 $JK^{-1}mol^{-1}$][4] and $[C_3F_7OCF(CF_3)COO]_2$ [$\Delta H^{\neq}$ = 100.0 $kJmol^{-1}$; $\Delta S^{\neq}$ = 12.6 $JK^{-1}mol^{-1}$][4], and these perfluoroalkanoyl and perfluorooxaalkanoyl peroxides are well known to decompose via a concerted homolytic dissociation to afford the corresponding perfluoroalkyl and perfluorooxaalkyl radicals.[3,4,5] The results for the decomposition behavior of FCH-PO strongly suggest that a perfluorocyclohexyl radical is likely to form by the concerted three-bond radical fission of FCH-PO. Therefore, FCH-PO is expected to react with radical polymerizable substrates to afford the perfluorocyclohexylated oligomers with carbon-carbon bond formation via a radical process.

In fact, we tried to synthesize novel perfluorocyclohexylated acrylic acid oligomers via a radical process. The reaction scheme was shown in the following.

As shown in Scheme 2, we succeeded in preparing fluoroalkylated acrylic acid oligomers by the reaction of FCH-PO with acrylic acid under very mild conditions.



Yield: 47 %[a)]
$\overline{Mn}$: 1440 ($\overline{Mw}/\overline{Mn}$ = 1.35)

a) The yield is based on the starting materials (acrylic acid and the decarboxylated peroxide unit (R_F-R_F)

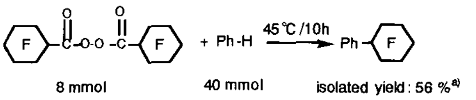
Scheme 2.

Under our present oligomeric conditions, in which the concentration of the peroxide was almost the same as that of acrylic acid, mainly oligomer with two fluoroalkyl groups would be obtained via primary radical termination or radical chain transfer to the peroxide. Fluorinated acrylic acid oligomer thus obtained was easily soluble not only in water but also in organic solvents such as MeOH, EtOH, THF, acetone, DMF, and DMSO. In addition, this oligomer was able to reduce the surface tension of water effectively to around 20 mN m^{-1} with a clear break point resembling a CMC(critical micelle concentration) at 30 ℃ . Therefore, this perfluorocyclohexylated acrylic acid oligomer is applicable to new fluorinated oligo-surfactant.

Furthermore, FCH-PO has been calculated by using the MNDO-PM3 semiempirical MO method[6] to have a similar LUMO energy level (-2.613 eV) as that (-2.513 eV) of $(C_3F_7COO)_2$, which is a useful electron acceptor even from well-known poor electron-donor aromatic compounds such as benzene.[3] The LUMO energy level of FCH-PO suggests that FCH-PO should become a useful electron acceptor from benzenes. Therefore, we tried to synthesize novel perfluorocyclohexylated compounds via a single electron-transfer reaction. These reaction schemes were shown in the following.[7]

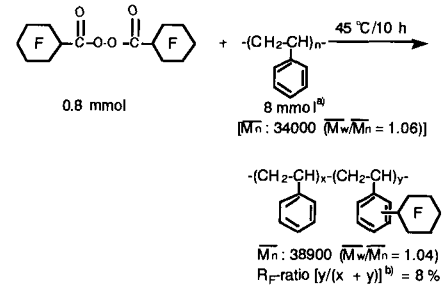
As shown in the Schemes 3 and 4, aromatic perfluorocyclohexylation of benzene and polystyrene by the use of FCH-PO was found to proceed under very mild conditions to afford the corresponding perfluorocyclohexylated benzene and polystyrenes, respectively.

Usually, it is not possible to separate conformers from one another above room temperatures, and hindered cyclohexanes such as *t*-butylcyclohexane exist in a single conformation, with the *t*-butyl group equatorial. In fact, in the conformational isomers of phenylcyclohexane, only isomer with phenyl group equatorial should be isolated. However, surprisingly, G.C. (gas chromatography) analyses from 30 ℃ to 150 ℃ of phenylperfluorocyclohexane in Scheme 3 showed the presence of two conformational isomers (equatorial : axial by ^{19}F NMR is 53 : 47).



a) Based on the peroxide used.

Scheme 3.

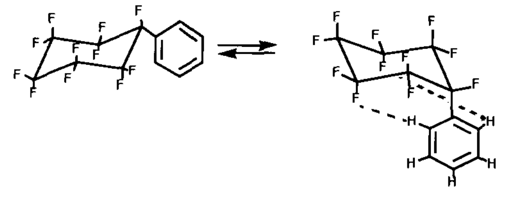


a) Calculated from styrene monomer units.

b) R_F-ratio was determined by ^{19}F NMR in comparison with the peak area of the perfluorocyclohexyl groups of polymer with that of $PhCF_3$ as the internal standard.

Scheme 4.

From the results of GC-MS (Exact MS), GC-FT-IR, ^{13}C and ^{19}F NMR analyses, two isomers of phenylperfluorocyclohexane were suggested to correspond to cyclohexanes with the perfluorocyclohexyl group equatorial and axial, respectively, as shown in the following Scheme 5.[8]



Scheme 5.

As shown in Scheme 5, the presence of the axial isomer may be ascribed to the hydrogen bond formation between the hydrogen atoms in phenyl group and the fluorine atoms, which stabilizes the axial isomer.[9,10]

Similarly, ^{19}F NMR spectra of perfluorocyclohexylated polystyrene showed the two conformational isomers (equatorial : axial by ^{19}F NMR is 56 : 44).

Thus, from the viewpoints of both the development of new organofluorine chemistry and the applications to various fields, it is very interesting to synthesize other new perfluorocyclohexylated compounds, and to clarify the properties of these new fluorinated materials. Further studies are now in progress.

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References and Notes

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6 The semiempirical MO calculations were carried out by using the CaChe MOPAC.

7 A typical experiment for the synthesis of perfluorocylcohexylated compounds is as follows. FCHPO (8 mmol) in $CF_2ClCFCl_2$ solution (200 g) was added to benzene (40 mmol), and the solution was stirred at 45 ℃ for 10 h under nitrogen atmosphere. The reaction mixture was then washed with 5 % sodium hydrogencarbonate, and water. The separated organic layer was dried over anhydrous magnesium sulfate, and the solvent was evaporated. Phenylperfluorocyclohexane (1.58 g) was isolated by distillation (bp: 41 ~ 43 ℃/3mmHg) and identified by IR, GC-MS (Exact MS); ^{1}H, ^{13}C and ^{19}F NMR. GC (a 2-m column packed with 20 % SE-30) analyses of the isolated products showed the presence of two conformational isomers(equatorial and axial); however, we could not isolate each product under various conditions. IR(ν/cm^{-1}) *axial* Ph-C_6F_{11}: 3078, 1342, 1288, 1257, 1226, 1200, 1165, 1153, 1119, 1072, 1041, 984, 922, 837; *equatorial* Ph-C_6F_{11}: 3078, 1504, 1454, 1319, 1257, 1207, 1145, 1038, 1018, 972, 926, 852, 744; MS m/z *axial* Ph-C_6F_{11}: 358 (M^+), 339, 208, 189, 158, 127(base), 69 (Found: M^+, 358.0174. $C_{12}H_5F_{11}$: requires M, 358.0214; *equatorial* Ph-C_6F_{11}: 358 (M^+), 339, 250, 189, 158, 127(base), 69 (Found: M^+, 358.0200. $C_{12}H_5F_{11}$: requires M, 358.0214; ^{1}H NMR ($CDCl_3$) δ 7.51 (2H, t, J = 8 Hz), 7.57 (1H, tt, J = 8 Hz, 2Hz), 7.65 (2H, m); ^{19}F NMR ($CDCl_3$, ext. CF_3CO_2H) δ 2.49 (1F, d, J = 24 Hz, 1*a*), -42.49 (2F, d, J = 291 Hz, 2,6*a*), -46.29 (2F, d, J = 291 Hz, 3,5*a*), -47.40 (1F, d, J = 277 Hz, 4*a*), -57.29 (2F, d, J = 306 Hz, 2,6*e*), -62.97 (2F, d, J = 282 Hz, 3,5*e*), -66.09 (1F, d, J = 277 Hz, 4*e*), -105.33 (1F, t, J = 37 Hz, 1*e*). ^{13}C NMR($CDCl_3$) δ 124.41 [C_1(Ph *e*), d, J = 20.6 Hz), 127.06 [C_2(Ph *e*), d, J_{CCCF} = 11.9 Hz], 127.23 [C_2(Ph *a*), m], 128.93 [C_3 (Ph *e*), d, J = 2.6 Hz], 129.03 [C_3(Ph *a*), d, J = 2.1 Hz], 131.41 [C_4 (Ph *e*)], 131.55 [C_4 (Ph *a*)].

8 In perfluoro(cyclohexyl methyl ether), it was reported that the bulky perfluoromethoxy substituent of the favoured conformer is in the equatorial position(1*e*), and a signal at -62.3 ppm (CF_3CO_2H as standard) can be assigned to the axial fluorine(1*a*). An additional signal at -80.1 ppm could be assigned to the equatorial fluorine (1*e*) of the minor conformer in the low-temperature region (~ 217 K); A. Dimitrov, U. Gross, St. Rudiger, W. Storek, and J. Burdon, *J. Fluorine Chem.*, **78**, 1 (1996).

9 In the fluorinated compounds such as fluorinated β-keto-γ-butyrolactones, the hydrogen bond formation between the hydrogen atom and fluorine atom was observed; T. Kitazume, *Synthesis*, **1986**, 855.

10 It is suggested that the p-π orbital overlap in the p-electrons of fluorines with the π-system of benzene ring could also stabilize the axial isomer; for example, Sheppard reported that fluorine p-orbital in benzotrifluoride and pentafluoroethylbenzene give optimum overlap with carbon p-orbitals at the benzene ring since fluorine p-orbitals are of size and compactness compared with large atoms such as bromine; W. A. Sheppard, *J. Am. Chem. Soc.*, **87**, 2410 (1965).