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PERFLUOROALKYLATION OF BENZYL BROMIDES USING PERFLUORO-2-METHYLPENT-2-ENE IN POTASSIUM FLUORIDE-DIMETHYLFORMAMIDE

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SUMMARY

A marked solvent effect was found in the reaction of perfluoro-2-methyl-2-pentene and benzyl bromides in the presence of fluoride anion to form α-(perfluoro-1,1-dimethylbutyl)-tolunitrile derivatives. Thus, potassium fluoride worked effectively as a fluoride ion source in N,N-dimethylformamide probably to afford nucleophilic perfluoro-1,1-dimethylbutyl-potassium. To the contrary, in diglyme, potassium fluoride produced the desired product only in a trace amount. Cyano-, nitro-, and unsubstituted benzyl bromides and α,α'-dibromoxylene were converted to the corresponding products in almost quantitative yields.

INTRODUCTION

Due to the characteristic surface activity, fluorine-containing organic compounds have been utilized as specialty surfactants or surface-treating agents, and their chemistry and industry are promising. Although perfluoroalkyl compounds have been produced mainly by electro-fluorination and telomerization methods, perfluoro-2-methylpent-2-ene (**1**) which is selectively produced by anionic dimerization of hexafluoropropene, and other low molecular oligomers of perfluoro olefins have attracted attention as another source of perfluoroalkyl groups. Substitution and addition reactions of perfluoro-tertiary carbanions [1-3] derived from branched olefins and

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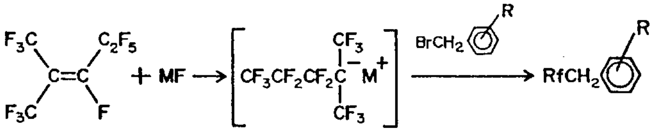
fluoride anion are one of the most promising procedures for this purpose, and several synthetic reactions using **1** have been reported [1-3]. Although potassium fluoride has been used as a catalyst or a fluorinating reagent in the case of reactions using hexafluoropropene [4-8], the fluorinating reagent for low molecular perfluoroolefin oligomers was limited to cesium fluoride [1-3], inevitably making these reactions less practical due to the high cost of cesium fluoride.

We wish to report the use of potassium fluoride as a very effective fluorinating reagent for **1** to afford the perfluoro-tertiary carbanion which then undergoes substitution with benzyl bromides. The products have potential as effective surfactants and insulation liquids for electronic instruments.

RESULTS AND DISCUSSION

The probable reaction pathway is shown below. The addition of fluoride ion to the olefin (**1**) gives the tertiary carbanion rather than the less stable secondary carbanion.



(**1**) (**2a-i**) (**3a-g,j,k**)

MF=CsF, KF, NaF **a** R=p-CN, **e** R=m-NO_2, **i** R=m-CH_2Br
Rf=$CF_3CF_2CF_2C(CF_3)_2$- **b** R=m-CN, **f** R=o-NO_2, **j** R=p-CH_2Rf
c R=o-CN, **g** R=H, **k** R=m-CH_2Rf
d R=p-NO_2, **h** R=p-CH_2Br

SCHEME. Perfluoroalkylation of Benzyl Bromides

The reaction conditions and the results for the preparation of α-perfluoroalkyl-p-tolunitrile are summarized in Table 1.

The cesium fluoride/diglyme system afforded the desired compound (**3a**) in a high yield at low temperature using a short reaction period (Run 1) [1]. Under the same reaction

TABLE 1

Synthetic conditions for the preparation of **3a**

Run	Solvent	MF	Molar ratio of **1** : **2a** : MF	Temp. (°C)	Time (h)	Yield (%)
1	diglyme	CsF	1.5 : 1 : 2	50	2	98
2	diglyme	KF	1.5 : 1 : 2	50	20	4
3	DMF	KF	1.5 : 1 : 2	50	20	66
4	DMF	KF	1.5 : 1 : 5	50	20	69
5	DMF	KF	1.5 : 1 : 10	50	20	72
6	DMF	KF	1.5 : 1 : 2	50	40	80
7	DMF	KF	1.5 : 1 : 2	50	70	98
8	DMF	KF	1.5 : 1 : 2	100	5	93
9	DMF	KF	1.5 : 1 : 2	100	10	98
10	DMF	KF	1.5 : 1 : 2	150	2	92
11[a]	DMF	KF	1.5 : 1 : 2	50	20	78
12	DMF	NaF	1.5 : 1 : 2	50	70	4
13	DMF	NaF	1.5 : 1 : 2	100	10	4
14	DMSO	KF	1.5 : 1 : 3	50	20	23

[a] Dicyclohexano-18-crown-6 (5mol% based on **2a**) was added.

conditions but using potassium fluoride instead of the cesium salt, the yield of the desired product is very low (Run 2). However, when the potassium fluoride/dimethylformamide system was employed, satisfactory results were obtained by adapting a longer reaction period (Run 3, 6, 7) or a higher reaction temperature (Run 3, 8, 9, 10). In spite of the fact that the reaction system is apparently solid-liquid heterogeneous, the effect of surface area of potassium fluoride powder was observed to be less important, since the amount of the salt added has little effect on the yields (Run 3, 4, 5).

In the cases of potassium fluoride/diglyme (Run 2), sodium fluoride-dimethylformamide (Run 12, 13), and potassium fluoride-dimethylsulfoxide systems (Run 14), only unsatisfactory results were obtained even with a longer reaction period and a higher reaction temperature. There was little effect in addition of dicyclohexano-18-crown-6 as a phase transfer catalyst (Run 11).

TABLE 2

Preparation of Fluorocarbon Compounds (**3a-g,j,k**)[a]

Compnd	Yield (%)	b.p.[b] (°C/mmHg)	^{19}F-NMR[c] ($CDCl_3$,ppm)	^{1}H-NMR ($CDCl_3$,δppm)	M.S. (M^+)	IR (neat,cm^{-1})	Molecular Formula	E.A. Found(Calcd.)
3a	98	100-105/0.01	-0.72 (quint,6F) 17.20(t,3F) 43.12(m,2F) 60.12(m,2F)	3.60(s,2H) 7.32-7.60(m,4H)	435	2540 1190-1315	$C_{14}F_{13}H_6N$	C:38.75(38.64) H: 1.24(1.39) N: 3.29(3.22)
3b	94	90-95/1.0	-0.64 (quint,6F) 17.12(t,3F) 42.92(m,2F) 60.16(m,2F)	3.56(s,2H) 7.36-7.72(m,4H)	435	2530 1190-1315	$C_{14}F_{13}H_6N$	C:38.67(38.64) H: 1.28(1.39) N: 3.27(3.22)
3c	93	85-87/1.0	-1.32 (quint,6F) 17.08(t,3F) 44.16(m,2F) 59.56(m,2F)	3.83(s,2H) 7.28-7.33(m,4H)	435	2525 1190-1305	$C_{14}F_{13}H_6N$	C:38.60(38.64) H: 1.27(1.39) N: 3.19(3.22)
3d	98	80-85/0.03	-0.40 (quint,6F) 17.24(t,3F) 43.44(m,2F) 60.36(m,2F)	3.68(s,2H) 7.52-8.20(m,4H)	455	1510 1310 1200-1280	$C_{13}F_{13}H_6NO_2$	C:34.34(34.30) H: 1.32(1.33) N: 3.14(3.08)
3e	98	70-75/0.01	-0.60 (quint,6F) 17.32(t,3F) 43.20(m,2F) 60.24(m,2F)	3.67(s,2H) 7.40-8.32(m,4H)	455	1530 1350 1190-1300	$C_{13}F_{13}H_6NO_2$	C:34.39(34.30) H: 1.28(1.33) N: 3.20(3.08)

3f	92	70-75/0.02 (colorless needles,mp 44.5-45.5°C)	-0.96 (quint,6F) 17.04(t,3F) 44.40(m,2F) 59.72(m,2F)	4.18(s,2H) 7.28-7.99(m,4H)	455	1550 1370 1200-1310	$C_{13}F_{13}H_6NO_2$	C:34.28(34.30) H: 1.21(1.33) N: 3.08(3.08)
3g	92	75-80/25	-0.60 (quint,6F) 17.20(t,3F) 43.60(m,2F) 60.40(m,2F)	3.44(s,2H) 7.28(s,5H)	410	2950 1340 1300-1195 1120	$C_{13}F_{13}H_7$	C:38.10(38.07) H: 1.85(1.72)
3j	93	90-95/0.07	-0.40 (quint,6F) 17.68(t,6F) 43.68(m,4F) 60.88(m,4F)	3.56(s,4H) 7.28(s,4H)	742	1330 1300-1200 990 730	$C_{20}F_{26}H_8$	C:32.32(32.36) H: 1.04(1.09)
3k	93	110-115/0.6	-0.60 (quint,6F) 17.60(t,6F) 44.48(m,4F) 59.80(m,4F)	3.52(s,4H) 7.27(s,4H)	742	1350 1310-1200 1120 750	$C_{20}F_{26}H_8$	C:32.21(32.36) H: 1.05(1.09)

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[a] Colorless oil unless otherwise cited

[b] Kugelrohr distillation

[c] External standard: $PhCF_3$(63.73ppm)

In Table 2, the synthetic results of **3a-g**, j, **k** are summarized together with their spectral and analytical data, which proves the structure of compounds **3**. Compounds **3a-e, g**, j, **k** were colorless liquids, and **3f** was colorless needles upon purification by recrystallization from hexane.

Compounds **3a-g**, may be useful as the raw material for surfactants, and **3**j, **k** as the insulation liquid for electronic equipments. Furthermore, the reactions of **1** and other electrophilic reagents under the reaction conditions are under investigation.

EXPERIMENTAL

Melting point and boiling points are uncorrected. ^1H NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer operating at 100 MHz; chemical shifts are reported in parts per million from tetramethylsilane as internal standard with the downfield direction taken as positive. ^{19}F NMR spectra were obtained with a JEOL JNM-PS-100 spectrometer at 94 MHz; chemical shifts are calculated in parts per million upfield from benzotrifluoride (63.7 ppm) as internal standard. Mass spectra were recorded on a Hitachi RMU-6E spectrometer; m/z values are quoted for the lowest isotopic species. Infrared spectra were recorded on a Hitachi 260-10 spectrometer.

Perfluoro-2-methylpent-2-ene (**1**) was donated by NEOS Co. Ltd., Kobe, Japan, and redistilled under atmospheric pressure at 51 °C before use. Benzylbromides were guaranteed grade reagents from commercial sources. N,N-Dimethylformamide, guaranteed grade, was heated to reflux for 10 h on CaH_2 and then distilled at 55 °C/26 torr directly to a receiver flask which contained molecular sieves 4A preheated at 400 °C for 3 h for storage. Diglyme, reagent grade, was heated to reflux for 12 h in the presence of sodium metal and then distilled at reduced pressure to a receiver flask containing molecular sieves. Dimethyl sulfoxide, reagent grade, was stirred at room temperature for 4 days in the presence of CaH_2 and then distilled at 96 °C/30 torr to a flask containing molecular sieves. Potassium fluoride of guaranteed grade was dried at 200 °C for 20 h and stored on P_2O_5 in a desiccator. Dicyclohexano-18-crown-6 was obtained from a commercial source.

α-(Perfluoro-1,1-dimethylbutyl)-p-tolunitrile (**3a**), Typical Procedure:

Olefin **1** (4.50 g, 15 mmol), potassium fluoride (1.16 g, 20 mmol), α-bromo-p-tolunitrile (1.96 g, 10 mmol), and N,N-dimethylformamide (10 ml) were placed in a sealed glass tube, and heated at 100 °C for 10 h with stirring. The reaction mixture was poured into ether, and washed with portions of water, 5% $NaHCO_3$ aqueous solution and then water. The ether was evaporated to give a yellow oil. To eliminate the unreacted benzyl bromide, an ether solution of pyridine was added to this mixture, and stirred at room temperature for 3 h. This solution was washed consecutively with water, 5% HCl, and water. After the organic phase was separated, dried over magnesium sulfate, and the solvent evaporated, the desired compound **3a**, a colorless liquid was obtained by Kugelrohr distillation (4.26g, yield 98%).

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