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STUDIES ON FLUOROALKYLATION AND FLUOROALKOXYLATION.

PART 3. PERFLUOROALKYLATION OF OLEFINS WITH PERFLUOROALKYL-IODIDES AND COPPER IN VARIOUS SOLVENETS

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SUMMARY

Perfluoroalkyl iodides react readily with simple olefins in the presence of catalytic amounts of copper in diglyme or acetic anhydride to give adducts in high yields. The reaction can be moderately accelerated by irradiation, partly suppressed with p-DNB and inhibited completely by hydroquinone. Fluorine-containing non-volatile amorphous solids were obtained when easily polymerized olefins, such as styrene and acrylates, were used as substrates. The reaction of perfluoroalkyl iodides and diallylic ether gave five-membered ring products under the same conditions. All the results seem to indicate that the reaction is a radical chain process induced by electron transfer. In DMSO, the main reaction may involve perfluoroalkylcopper intermediates which can be trapped by iodobenzene and hydroquinone and p-DNB show little inhibition effects.

INTRODUCTION

In 1972, Coe and Milner [1] discovered a method of direct perfluoroalkylation of olefins by perfluoroalkylcopper or perfluoroalkyl iodide in the presence of copper in dimethylsulfoxide (DMSO). They explained the results in terms of a radical mechanism without specifying how and when the

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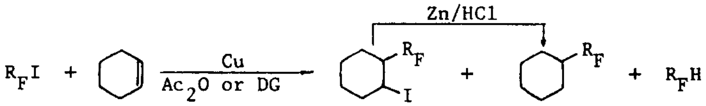
radicals were formed. As a continuation of our studies of the solvent effects on the fluoroalkylation of aromatics [2], we present here a method of perfluoroalkylation of olefins with perfluoroalkyl iodides in the presence of catlytic amounts of copper in acetic anhydride or diglyme (DG). The possible mechanisms of these copper-catalyzed reactions in different solvents are discussed.

RESULTS AND DISCUSSION

Treatment of perfluoroalkyl iodide (1) with cyclohexene in the presence of catalytic amounts of copper (1:Cu molar ratio 4:1) in acetic anhydride or DG at 100°C for 6.5 h resulted in good yield (~70%) of product 2 with 3 and 4 as by-products, the copper was converted into white cuprous iodide.



1 2 3 4

R_F = $(CF_2)_4Cl$ (a)
= $(CF_2)_4O(CF_2)_2SO_2F$ (b)
= $(CF_2)_2O(CF_2)_2SO_2F$ (c)

2 was shown to be a mixture of cis and trans isomers (cis:trans = 2:1) by elemental analyses, GC, MS, ^{1}H NMR and ^{19}F NMR spectra. 2 was converted to 3 with Zn/HCl. The results are summarized in Table 1.

As Table 1 shows, the amount of copper powder used had little influence on the reaction, i.e. the main product was still 2, even if excess copper was used, although the product distribution had changed a little (see entry 2 and 3). Reaction of 1 with olefin did not take place at 15–20°C, and proceeded only rather slowly at 50°C. The reaction occurred under ambient laboratory light, however, it was moderately accelerated by irradiation. For example, only 1 h (conversion 95%) was required to complete the reaction of 1b with cyclohexene by irradiation (entry 10) but without irradiation only 91% conversion was achieved after 6 h (entry 9). Similar results can be seen from entries 12 and 7. These results suggest an activating influence of UV on the copper-induced reaction. Similarly, the reaction of 1 with other olefins, such as n-octene and β-chlorotrifluoroethoxylpropene-1 gave the corresponding adducts.

TABLE 1

Reaction of R_FI with cyclohexene

Entry	R_FI	Solvent	Cu/R_FI	T^oC	t(h)	Conversion %[a]	Product %	
							2	3
1	1a	Ac_2O	1/4	100	6.5	100	59.1	11.4
2	1b	Ac_2O	2/1	100	10	100	47.4	18.7
3	1b	Ac_2O	1/4	100	6.5	98	68.7	3.4
4	1b	Ac_2O	1/4	50	13	96	69.8	2.6
5	1b	Ac_2O	1/4	15-20	25	0	0	0
6	1c	Ac_2O	2/1	100	8	88	65.2	/
7	1a	DG	1/4	100	6.5	100	65.1	7.5
8	1a	DG	1/4	100 dark	6.5	100	61.8	8
9	1b	DG	1/4	100	6	91	49.1	10
10	1b	DG	1/4	100 UV	1	95	38	18[b]
11	1b	DG	0	100 UV	6.5	81	41	22
12	1a	DG	1/4	100 UV	0.8	84	47	15[c]
13	1a	DG	0	100 UV	0.8	51	44	18

[a] Conversion(%) was determinated by ^{19}F NMR; Besides 2,3, 5~10% of R_FI (4) was also obtained unless specified otherwise.

[b] In addition to 37% of R_FH.

[c] In addition to 23% of R_FH.

$n\text{-}C_6H_{13}CH{=}CH_2 \; + \; \underline{1a} \text{ or } \underline{1b} \longrightarrow n\text{-}C_6H_{13}CH(I)CH_2R_F \quad \underline{5}$

$ClCHFCF_2OCH_2CH{=}CH_2 \; + \; \underline{1b} \longrightarrow ClCHFCF_2OCH_2CH(I)CH_2(CF_2)_4O(CF_2)_2SO_2F$ 6

Only a non-volatile amorphous solid (conversion 60%) was obtained from the reaction of 1 with methylmethacrylate, ethyl acrylate or styrene in the presence of copper in DG or Ac_2O. The ^{19}F NMR (in CCl_4) spectra showed a clear signal, indicating attachment of fluorinated group to carbon (see Experimental). However, if excess copper was used in the case of ethyl acrylate, a colorless liquid 7 could be isolated and identified as a 1:1 adduct.

$CH_2{=}CHCO_2Et \; + \; \underline{1b} \longrightarrow FSO_2(CF_2)_2O(CF_2)_4CH_2CH_2CO_2Et$ 7

The presence of an equivalent (relative to catalytic amounts of copper) of free radical inhibitor, hydroquinone, in diglyme suppressed completely the reaction of 1 with cyclohexene, and 1 was recovered quantitatively. Addition of single electron transfer (SET) scavenger, e.g. p-dinitrobenzene (p-DNB) (equivalent relative to catalytic amounts of copper) to the reaction mixture either in Ac_2O or in DG decreased the conversion of 1 to 50% as compared with that of the control. The results are summarized in Table 2.

TABLE 2

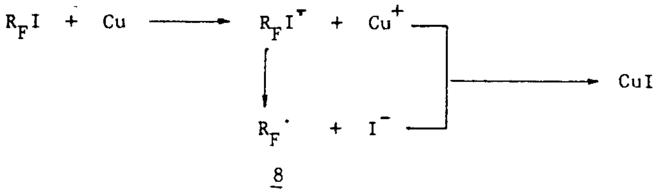
Reaction of 1 with cyclohexene in the presence of p-DNB*

Entry	R_FI	Solvent	t(h)	Conversion %	Product %** 2	3
1	1a	Ac_2O	6.5	57	53	10
2	1a	DG	6.5	50	51	17.7
3	1b	Ac_2O	7	46.6	47	10
4	1b	DG	16	48	32.2	10

* Cu : R_FI(mol) = 1 : 4 Cu : P-DNB(mol) = 1 T = 100°C

** A small amount of R_FH was observed

The results mentioned above seem to show that perfluoroalkylation of olefins by R_FI in the presence of copper in DG or Ac_2O may involve a SET initiated radical chain process as follows:



$$\underline{8} + RCH{=}CHR' \longrightarrow R_FRCHCHR' \quad \underline{9}$$

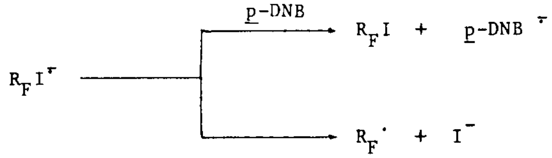
$$\underline{9} + R_FI \longrightarrow R_FRCHCHIR' \qquad \underline{9} + nRCH{=}CHR' \xrightarrow[\text{or "I"}]{\text{"H"}} R_F(RCHCHR')_{n+1}H(I)$$

$$\underline{9} + \text{"H"} \longrightarrow R_FRCHCH_2R'$$

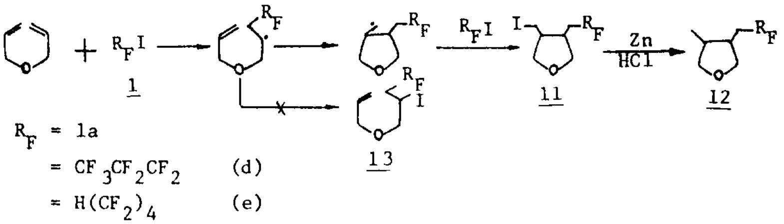
$$\underline{8} + \text{"H"} \longrightarrow R_FH$$

For simple olefins, the radical (9) abstracts iodine from 1 to give the product. But for the easily polymerized olefins, addition of another molecule of olefin is much faster than abstracting iodine from R_FI or hydrogen from solvent, thus fluorine-containing polymers are obtained.

Inhibition of the reaction by p-DNB can be ascribed to the comparable electron-accepting ability of p-DNB [3]. The radical anion, $R_FI^{\bar{\cdot}}$, may either transfer its electron to p-DNB, inhibiting the reaction, or decompose to produce a radical which initiates further reactions.



It is well-known that ring closure in the exo-mode from hex-5-enyl radical and relative species (so called free radical 'clock reaction') is an excellent probe for elucidating mechanisms [4]. In order to further confirm the radical mechanism, the reaction of diallylether (DAE) and 1 in the presence of catalytic amounts of copper was carried out in DG. Little cuprous iodide was observed while the cyclic adduct 11 was formed. The structure of 11 was assigned from its ^{19}F NMR and ^{13}C NMR spectra. 11 can be readily reduced to 12. In the ^1H NMR spectra of 12a there appears two



doublets (J_{H-H} = 6Hz) at 0.80 and 0.86. GC also shows 11 as well as 12 are cis and trans mixtures (cis:trans = 3:1). 11d is a known compound, which, in addition to 13 as a by-product, was obtained by the reaction of 1d and DAE with ABN initiator[5]. The attempted trapping of 13 by changing the molar ratio of reactants (Cu/R_FI and R_FI/DAE) and decreasing the reaction temperature to 60° met with little success. It seems to indicate that cyclization of the radical intermediate is much faster than its abstraction of iodine from 1. Reaction of 1 with DAE are summarized in Table 3.

The fact that most of the copper appeared unreacted during the reaction seems to show that chain is long.

McLouglin et al. [6] indicated that perfluoroalkylcopper in DMSO and even in ether-type solvents can couple with iodobenzene to give perfluoroalkylbenzenes. Coe et al. [1] considered that the reaction of perfluoroalkyl iodide with excess olefin in the presence copper in DMSO also proceeded through the intermediate perfluoroalkylcopper. By analogy, one may also suggest that if perfluoroalkylcopper were also the intermediate in the above reactions then the coupling product with C_6H_5I would be obtained if the latter was added to the system [7]. But this possibility is excluded by the following evidence: to the reaction mixture of 1a, cyclohexene and excess copper powder in DG or Ac_2O was added an equivalent amount of C_6H_5I (relative to olefin), when only 45.4% of 2a and 18% 3a were obtained. Iodobenzene was recovered nearly quantitatively. Similarly, 7 was the only isolated product, when 1b was reacted with ethyl acrylate and iodobenzene in the presence of copper. These data seem to indicate that perfluoroalkylation of olefins induced by copper with R_FI in Ac_2O and DG involves radical rather than perfluoroalkylcopper intermediate.

TABLE 3.
Reaction of 1 with DAE in DG

R_FI	Cu/R_FI	R_FI/DAE	T°C	t(h)	Yield %
1a	1/4.1	0.64	100	5.5	76.2
1d	1/4.1	0.54	80	7	76
1e	1/2.7	1.6	60	13	71.6

However the reaction seems to take a different course in DMSO. It was found that in the presence of catalytic amounts of copper conversion was low. For example, the reaction of 1a with cyclohexene, Cu and DMSO in molar ratio of 4:8:1:45 at 100° for 10 h afforded mainly 3a with 27% conversion of 1a, and the coversion could only be increased to 83% when equivalent amounts of copper(relative to 1b) was used. Addition of hydroquinone or p-DNB to the reaction mixture showed little inhibiting effect. The result is not consistent with Coe's data [1]. The difference may arise from the fact that Coe et al. [1] used a great excess of olefin whereas we used excess DMSO. In order to verify this suggestion, the following experiments were done: the reaction of 1a, cyclohexene, copper and DMSO in molar ratio of 1:20:1:4 at 100^o for 14 h. The conversion was 100% and the major product was adduct 2a and the reaction was suppressed by hydroquinone or p-DNB. A likely explanation is that the presence of excess olefin in the system suppressed the solvent effect of DMSO, thus the reaction became a radical chain process induced by SET. Other evidence supporting this proposition was a competitive reaction using iodobenzene as a trap: 1a reacted with equivalent amounts of cyclohexene and iodobenzene in excess DMSO to give δ-chlorooctafluorobutylbenzene (14) and olefin was recovered nearly quantitatively. Under similar conditions but with the ratio of 1a:C_6H_5I:cyclohexene:DMSO being 1:1:20:4, the major product was 2a in addition to 14 (5%). The results in DMSO probably show that when DMSO used is in excess relative to other reagents the reaction process may mainly involve the electron transfer in solvent cage and finally a perfluoroalkylcopper intermediate is formed. However when olefin used is in excess the main reaction path in DMSO, as in DG and Ac_2O, is a SET induced process. The different effects between DG or Ac_2O and DMSO may be rationalized by the fact that DMSO has a stronger coordination ability and can very well stabilize the perfluoroalkylcopper intermediate which plays a major role during the reaction course [6]. On the contrary, Ac_2O and DG may be unable to stabilize perfluoroalkylcopper owing to their poor coordination ability. Thus the reaction in these solvents was mainly a radical chain process.

EXPERIMENTAL

All boiling points were uncorrected. NMR spectra (chemical shifts in ppm from external TMS for ^{1}H NMR and from external TFA for ^{19}F NMR positive for upfield shifts) were recorded on EM-360 NMR spectrometer at 60 MHz. Infrared spectra were measured on a Carl Zeiss Specord 75 IR and Perkin Elmer 683 IR spectrometer. Mass spectra were taken on GC-MS-4021. GC spectra were measured on the Shanghai Model 103. 1b, 1c and β-chlorotrifluoroethoxylpropene-1 were prepared according to references [8] and [9], respectively.

All experiments were carried out under atmosphere of pure nitrogen.

Perfluoroalkylation of simple olefins

The following procedure is typical:1a, 9.0g(25 mmol), cyclohexene, 4.1g(50 mmol), and acetic anhydride, 20 ml, were placed in a 100 ml three-neckedflask fitted with magnetic stirrer and refluxing condener. Copper powder, 0.38g(6 mmol), was added with stirring at 100°C for 1.5 h. After addition the contents were further stirred for 5 h at this temperature. White cuprous iodide appeared in the flask. ^{19}F NMR, GC showed the reaction was complete, 8% of 4a was observed. The mixture was filtered. The solid was washed twice with ether, the combined extracts hydrolyzed with dilute acid. The organic layer was separated, and aqueous layer was extracted twice with ether. The combined extracts were washed with water, dried over anhydrous Na_2SO_4 and ether distilled off. Distillation *in vacuo* gave 0.9g of 3a (11%), 6.5g of 2a (59.1%).

2a: b.p. 82-4°C/2 mm, IR (film) 2930,2860,1445,1250,1180-1125,1080, 1050,960 cm^{-1}. MS M/e(rel.int.) 317(38.78),319(9.28),297(13.65),299(4.34), 281(5.64),85(8.18),81(24.26),67(11.72),55(12.30),41(100). cis: ^{1}H NMR δ 4.65(m,1H),1.4-2.2(m,9H). ^{19}F NMR δ -10.3(2F),39.8(2F),42.0(2F),42.3(2F) trans: ^{1}HNMR δ 4.95(m,1H),1.4-2.2(m,9H), ^{19}F NMR δ -10.3(2F),32.0(2F),41.8 (2F),42.0(2F). Analysis: Found; C,27.47; H, 2.16; F,34.27. $C_{10}H_{10}F_8ClI$ requires C,26.99; H,2.25; F,34.20.

3a: b.p. 72°C/16 mm. IR (film) 2940,2860,1410,1350,1250,1230-1160, 1080,1050,1000,970,900. MS M/e(rel.int.) 318(2.12),317(11.61),297(5.04) 279(12.35),131(12.69),83(100),81(74.59),55(80.36). ^{1}H NMR δ 5.70(m,1H), 1.1-2.0(m, 10H). ^{19}F NMR δ -8.9(2F),42.0(2F),43.4(2F),43.6(2F) Analysis: Found: H,3.36; F,48.12. $C_{10}H_{11}F_8Cl$ requires H,3.45; F,47.73.

2b: b.p. 103°/2 mm. IR (film) 2930,2860,1460,1355,1320,1250,1210, 1150,990,820, MS M/e(rel.int.) 482(12.75),481(100),461(13.22),281(5.56), 131(9.47),119(15.09),81(55.39),55(14.17). cis: ^{1}H NMR δ 4.75(m), 1.6-2.3 (m). ^{19}F NMR δ 4.4(2F),5.1(2F),40.0(2F),43.8(2F),47.2(2F),34.5(2F), -122.0(1F). trans: ^{1}H NMR δ 5.05(m),1.6-2.3(m); ^{19}F NMR δ 4.4(2F),5.1(2F), 32.0(2F),43.8(2F),47.2(2F),34.5(2F),-122.0(1F). Analysis: Found: C,23.63; H,1.72, F,40.80. $C_{12}H_{10}F_{13}SO_3I$ requires: C,23.68; H,1.64; F,40.62.

3b: m.p. 68°C/2 mm. IR (film) 2930,2860,1460,1320,1210,1155,990,820, MS M/e(rel.int.) 482(2.87),481(15.83),461(8.41),443(11.61),131(14.51),119

(6.54),83(68.55),81(100),55(27.27), ^{1}H NMR δ 5.75(m,1H),1.2-2.2(m,10H). ^{19}F NMR δ 4.6(2F),5.3(2F),40.1(2F),43.1(2F),47.8(2F),35.9(2F),-121.5(1F). Analysis: Found: C,29.81; H,2.11; F,51.76; S,6.61. $C_{12}H_{11}F_{13}SO_3$ requires: C,29.87; H,2.29; F,51.35; S,6.65.

2c: b.p. 80°C/2 mm. IR (film) 2930,2850,1460,1350,1335,1240,1190, 1135,1105,975,800. MS M/e(rel.int.) 382(8.12),381(100),361(18.13),181(6.73), 161(10.47),141(17.52),81(37.64),67(15.93),55(7.07). cis: ^{1}H NMR δ 4.73(m,1H), 1.7-2.1(m,9H); ^{19}F NMR δ 5.1(2F),8.0(2F),43.8(2F),34.8(2F),-121.5(1F). trans: ^{1}H NMR δ 4.95(m,1H), 1.7-2.1(m,9H); ^{19}F NMR δ 5.1(2F),6.7(2F),36.8 (2F),34.8(2F),-121.5(1F). Analysis: Found: C,23.87; H,2.04; F,34.15. $C_{10}H_{10}F_8SO_3I$ requires C,23.62; H,1.96; F,33.66.

5a: 64%. m.p. 98°C/4 mm. IR (film): 2940,2920,2860,1185-1120,1080,955, 810,710. MS M/e(rel.int.) 347(14.02),349(4.31),127(1.86),85(4.47),83 (5.30),71(22.03),69(19.88),58(96.58),44(100,?). ^{1}H NMR δ 4.6-4.3(m),2.9-2.5(m),2.1-1.2(m),0.96(m); ^{19}F NMR δ -10.1(2F),36.0(t,J_{H-F} = 12Hz,2F), 42.1(2F),42.3(2F). Analysis: Found: C,30.78; H,3.28; F,32.08.$C_{12}H_{16}F_8ClI$ requires C,30.35; H,3.37; F,32.03.

5b: 61%. b.p. 95°C/3 mm. IR(film) 2940,2920,2860,1460,1235,1200,1130, 980. MS M/e(rel.int.) 511(49.68),183(2.48),119(3.63),111(7.02),83(7.12), 71(52.34),58(100,?),43(24.39). ^{1}H NMR δ 4.43(m),2.63(m),1.0-1.8(m). ^{19}F NMR δ 6.4(2F),7.1(2F)38.1(t,J_{H-F} = 12Hz,2F),45.3(2F),49.3(2F),36.8(2F), -120.2(1F). Analysis: Found: C,26.35; H,2.51; F,38.67 $C_{14}H_{16}F_{13}ISO_3$ requires C,26.33; H,2.53; F,38.70.

6: 73%. b.p. 110°C/3 mm. IR (film) 2940,1460,1360,1290,1245,1210,1150, 1100,980,860,810. MS M/e(rel.int.) 573(46.06),567(10.52),183(23.63),127 (7.59),119(72.37),67(46.80),69(15.97). ^{1}H NMR δ 6.01(d-t,$^{2}J_{H-F}$ = 48Hz, $^{3}J_{H-F}$ =4Hz),4.38(m),4.26(m),2.8(m). ^{19}F NMR δ 6.2(2F),6.8(2F),11.5(2F), 37.7(t,J_{H-F} = 12Hz,2F),47.7(2F),48.9(2F),36.5(2F),77.0(d-t,$^{2}J_{H-F}$ = 48Hz), $^{3}J_{H-F}$ = 4Hz,1F). Analysis: Found: C,19.34; H,1.04; F,43.40. $C_{11}H_6F_{16}ISO_4Cl$ requires C,18.84; H,0.86; F,43.40.

7: 45.2% (excess copper used in Ac_2O); 19% (excess copper used in DG). b.p. 77°C/2 mm. IR (film) 2970,2890,1725,1460,1320,1250-1100,1030,980,875, 815. MS M/e(rel,int.) 501(27.02),500(8.66),473(24.54),455(100),183(12.63), 119(41.93),101(13.66),100(16.08),45(39.87). ^{1}H NMR δ 2.3(m,4H),3.91(q,J_{H-H} = 8Hz,2H),0.95(t,J_{H-H} =8Hz,3H). ^{19}F NMR δ 5.0(2F),5.6(2F),37.5(t,J_{H-F} = 12Hz,2F),46.1(2F),47.8(2F),35.1(2F),-121.4(1F). Analysis: Found: C,26.05; H,1.75; F,49.38. $C_{11}H_9F_{13}SO_5$ requires C,26.40, H,1.80; F,49.40.

Reduction of 2a and 2b

To the mixture of 2a (1.3g, 2.8 mmol), Zn powder (0.4g,6 mmol) and ethanol (5 ml) was added four drops of conc. HCl. The contents were refluxed for 4 h., and then poured into water. The organic layer was separated and aqueous layer was extracted with ether. The combined extracts were washed with water and dried over Na_2SO_4. Distillation gave 0.83g (89%) of 3a.

3b(84%) was obtained by reduction of 2b in a similar fashion.

Perfluoroalkylation of easily polymerized olefins

1. Reaction of 1a, 1b with ethyl acrylate in the presence of catalytic amounts of copper

1a, 4.5g (12.5 mmol), reacted with ethyl acrylate, 2.5g (25 mmol), and copper, 0.4g (6.2 mmol) in DG (10 ml) at 80° for 15 h. 1.4g of 1a was recovered. Non-votatile solid, 4.3g, was obtained. ^{19}F NMR(CCl_4) δ -9.8(2F), 35.8(2F),42.3(2F),45.3(2F).

Similarly, a non-volatile product also obtained from 1b.

2. Reaction of 1a, 1b with styrene

1a, 4.5g (12.5 mmol), reacted with styrene. 2.6g (25 mmol) and copper 0.4g (6.2 mmol) in DG (10 ml) at 100° for 8 h. ^{19}F NMR showed conversion was 62%. 3.6g of non-volatile product was obtained. ^{19}F NMR δ -10.0(2F), 35.0(2F),42.3(2F),45.6(2F).

Similarly, a non-volatile product was also obtained from 1b.

The procedure for the reaction of 1 with cyclohexene, copper, in the dark or under irradiation, in the presence of inhibitor, p-DNB and hydroquinone, was similar to the previous. The results are given in Table 1 and Table 2.

Reaction of 1a, 1d and 1e with allylic ether (DAE)

1a, 9.0g(25 mmol), reacted with DAE, 4.2g (42 mmol), and Cu, 0.4g (6.2 mmol), in DG (10 ml) at 100° for 5.5 h. 11a, 9.1g (76.2%), was obtained. b.p. 107°C/2 mm. IR (film) 2950,2860,1440,1405,1270,1210-1120,1050,970,840, 790. MS M/e(rel.int.) 460(17.73),403(63.59),405(22.25),333(14.48),303(73.12),305(24.53),293(52.18),295(19.69),127(12.43),85(12.49),73(72.22), 41(100). ^{1}H NMR δ 2.0-4.2(m). ^{19}F NMR δ-8.9(2F),36.5(2F),43.0(2F),46.0 (2F). ^{13}C NMR: cis: 73.418,45.030,35.645,71.328,2.345,28.379(t), trans: 73.735,47.796,44.790,73.312,6.296,35.389(t). Analysis: Found: C,28.46; H,2.48; F,35.26. $C_{10}H_{10}F_8ClIO$ requires C,28.16; H,2.58; F,35.68.

11e: b.p. 112°C/4 mm. IR (film) 2940,2880,1440,1390,1225,1165-1125, 1040,940,910. MS M/e(rel.int.) 427.(43.81),299(72.31),269(36.66),249 (10.56),127(7.37),98(5.8),73(43.59),55(33.50),41(100). ^{1}H NMR δ 6.28(t-t, $^2J_{H-F}$ = 54Hz, $^3J_{H-F}$ = 6Hz,1H),2.1-4.5(m,10H). ^{19}F NMR δ 36.1(2F),48.3(2F), 52.4(2F),60.8(d, $^2J_{H-F}$ = 54Hz,2F). Analysis: found: C,28.46; H,2.48; F,35.26. $C_{10}H_{11}F_8OI$ requires C,28.16; H,2.58; F,35.68.

Reduction of 11a

To the mixture of 11a (1.5g, 3.2 mmol), Zn powder(0.4g 6 mmol) and ethanol(5 ml) was added four drops of conc.HCl. The contents were maintained at 80° for 3 h and then poured into water. The aqueous layer was extracted with ether three times. The combined extracts were washed with water and dried over Na_2SO_4. Distillation gave 0.9g (82%) of 12a. b.p. 64°C/3 mm. IR (film) 2970,2940,2860,1440,1405,1385,1260,1200-1180,970,840,790. MS M/e (rel,int.) 335(7.80),304(13.94),306(3.99),249(2.11),99(7.05),85(37.81),69 (100),55(79.54),44(44.12). ^{1}H NMR δ 3.85(m),3.2(m),1.5-2.3(m). cis: 0.80 (d,J_{H-H} = 6Hz) trans: 0.86(d,J = 6Hz). ^{19}F NMR: δ -8.7(2F),36.9(2F), 43.2(2F),46.1(2F). Analysis: Found: C,35.89; H,3.27; F,45.55; Cl,10.31. $C_{10}H_{11}F_8ClO$ requires C,35.88; H, 3.29; F,45.45, Cl,10.61.

Reaction of 1a with cyclohexene in DMSO

To a mixture of 1a, 9.0g (25 mmol), and cyclohexene, 4.1g (50 mmol) in DMSO (20 ml) at 100° was added with stirring copper powder, 0.38g (6 mmol). The contents were maintained at this temperature for 10 h and became homogeneous. On adding water a solid was precipitated. After filtration the solid was washed twice with ether. The aqueous layer was extracted with ether three times. The combined extracts were washed with water, dried over Na_2SO_4 and ether distilled off. ^{19}F NMR showed the conversion was 28%. 6.2g of 1a was recovered. Distillation gave 0.6g of 3a (27%).

Reaction of 1a with cyclohexene in the presence of p-DNB in DMSO

9.0g (25 mmol) of 1a reacted with 4.1g (50 mmol) of cyclohexene, 0.8g p-DNB and 0.38g (6 mmol) of Cu in 20 ml of DMSO at 100° for 10 h. The contents became homogeneous. ^{19}F NMR showed that conversion was 27%. 0.5g (25%) of 3a was obtained.

Reaction of 1a with cyclohexene in the presence of hydroquinone in DMSO

4.0g (11 mmol) of 1a reacted with 2.0g (25 mmol) of cyclohexene 0.64g (10 mmol) of Cu and 1.1g of hydroquinone in 10 ml of DMSO at 100° for 10 h. ^{19}F NMR showed the conversion was 72%. 0.8g (32.5%) of 3a was obtained.

Reaction of 1a with cyclohexene in presence of iodobenzene in DG or DMSO

4.5g (12.5 mmol) of 1a reacted 2.0g (25 mmol) of cyclohexene and 5.1g (25 mmol) of iodobenzene in the presence of Cu powder, 1.8g (28 mmol), in 10 ml of DG at 100° for 8 h. ^{19}F NMR showed the conversion was 100%, and 21% of 4a was formed. After workup 4.8g of iodobenzene was recovered. 0.7g (18%) of 3a, 2.5g (45.4%) of 2a were obtained.

If the same reaction was carried out in DMSO, ^{19}F NMR showed neither 2a nor 3a was formed and the conversion was 75.5%. Compound 14, b.p. 90-94°C/50 mm, (b.p. in literature [2] 92-95°C), 54.6%, was obtained.

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