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DEFLUORINATION OF HEXADECAFLUOROBICYCLO[4,4,0]DEC-1(6)-ENE: A FACILE SYNTHESIS OF PERFLUOROAROMATICS

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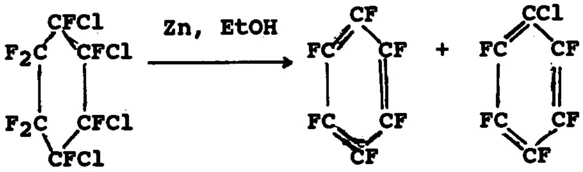
SUMMARY

Depending mainly on the polarity of the aprotic solvent used, defluorination of hexadecafluorobicyclo[4,4,0]dec-1(6)-ene (1) with activated zinc gave tetradecafluorobicyclo[4,4.0]dec-1(2),6(7)-diene(2), perfluorotetralin(3), decafluoro-1,2-dihydronaphthalene(4) and perfluoronaphthalene(5). In methanol, 2,7-dimethoxy-dodecafluorobicyclo[4,4,0]dec-1(2),6(7)-diene (6) was formed. These products were characterized by elemental analysis, IR, UV, ^{1}H NMR and ^{19}F NMR. An electron transfer and then a radical intermediate seem to be involved in such defluorination reactions.

INDRODUCTION

Dehalogenation of polyhalofluoroalkanes with zinc has been used extensively in the preparation of fluoroolefins. However, defluorinations are less common. In an early example, defluorination was probably involved in the dehalogenation of perchlorofluorocyclohexane[1].



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Pyrolytic defluorination over metals is another example which led to the development of a general preparative route to aromatic fluorocarbons from the corresponding perfluoroalicyclic precursors[2].

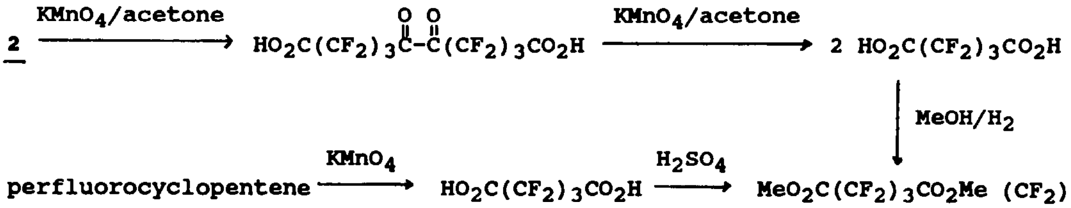
In order to develop new syntheses of perfluoroaromatics, here the defluorination of hexadecafluorobicyclo[4,4,0]dec-1(6)-ene (1) with activated zinc powder has been studied.

RESULTS AND DISCUSSION

Hexadecafluorobicyclo[4,4,0]dec-1(6)-ene(1) was obtained from the products of the fluorination of tetralin by CoF_3[3]. Defluorination of 1 with zinc occurred readily in various solvents. For example, in dioxane only 2 was formed. In acetonitrile or DMF, aromatic perfluorocarbons such as perfluorotetralin (3), decafluoro-1,2-dihydronaphthalene (4) and perfluoronaphthalene (5) were formed successively under rather mild conditions (**SCHEME I**). Defluorination also occurred in methanol, but an addition-elimination reaction of the first formed 2 with methoxide anion happened at the same time and 6 was isolated.

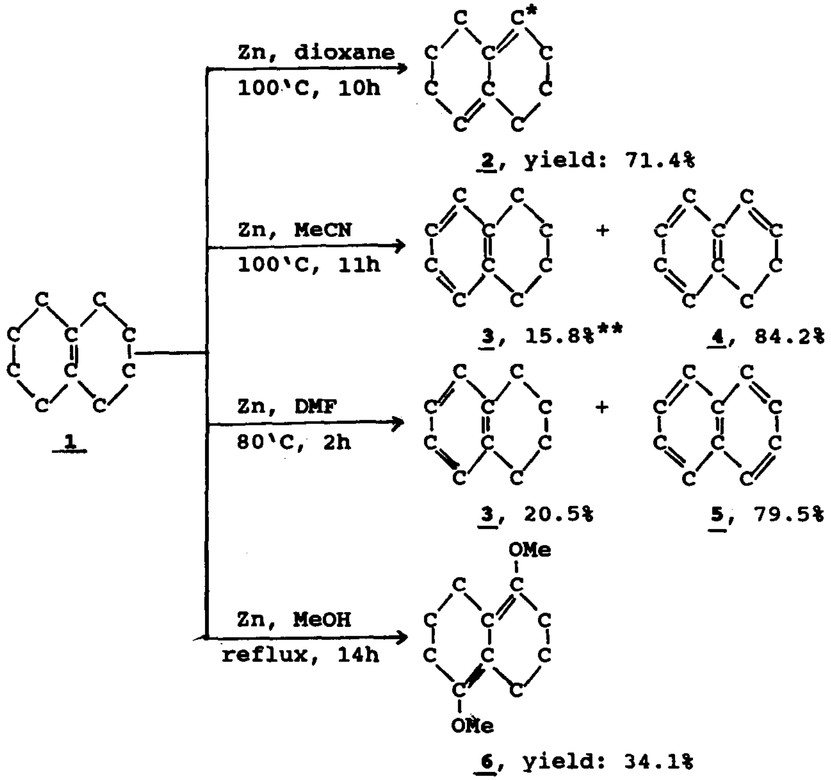
The structures of the known compounds 3-5 were confirmed by ^{19}F NMR, IR, MS and compared with the known data[2b, 4, 5]. Compounds 2 and 6 are new

2 is a colourless liquid with b.p.130.0-131.5'C. A strong absorption band at 1670 cm^{-1} shown in the infrared spectrum and λ_{max} (95% EtOH) at 222.6nm in the UV were assigned to the absorption of a conjugated double bond. Oxidation of 2 by $KMnO_4$/acetone and then esterification with MeOH yielded dimethyl perfluoroglutarate (**2a**). Its spectra were checked with the known dimethyl perfluoroglutarate synthesized first by oxidation of perfluorocyclopentene followed by esterification with methanol. Thus the structure of 2 was deduced as tetradecafluorobicyclo[4,4,0]dec-1(2),6(7)-diene.



$$\mathbf{2} \xrightarrow{KMnO_4/acetone} HO_2C(CF_2)_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}(CF_2)_3CO_2H \xrightarrow{KMnO_4/acetone} 2\ HO_2C(CF_2)_3CO_2H \xrightarrow{MeOH/H_2} MeO_2C(CF_2)_3CO_2Me\ (CF_2)$$

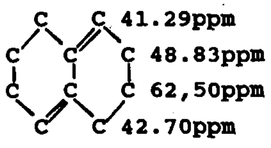
$$\text{perfluorocyclopentene} \xrightarrow{KMnO_4} HO_2C(CF_2)_3CO_2H \xrightarrow{H_2SO_4} MeO_2C(CF_2)_3CO_2Me\ (CF_2)$$



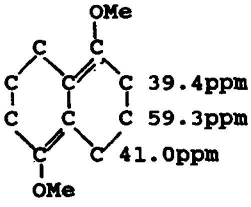
* All unmarked bonds are to fluorine. ** Except as otherwise stated, the percentage yields were determined by ^{19}F NMR.

SCHEME I.

The ^{19}F chemical shifts of 2 were assigned by comparison with the known cyclic compounds which contain the relevant structure features[6].



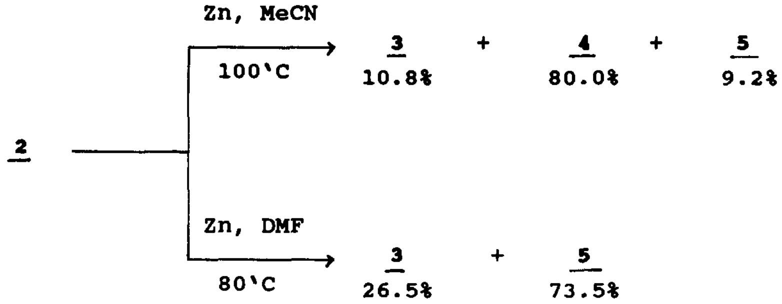
2



6

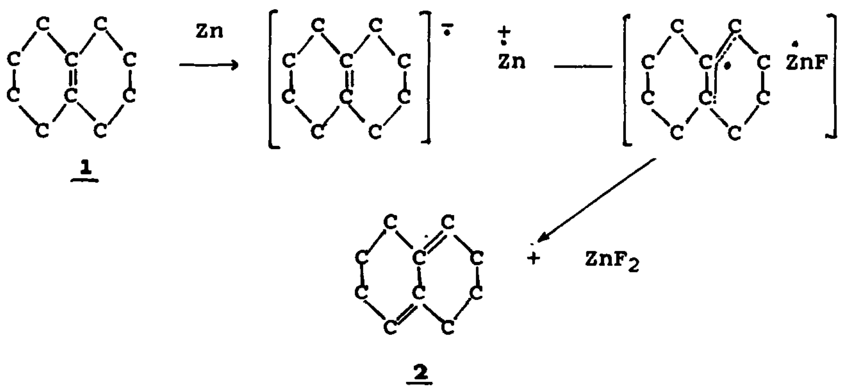
Compound 6 forms white needles with m.p.93.5-94.5'C. A strong absorption band at 1620 cm^{-1} in the IR and λ_{max} (95% EtOH) at 263.5nm in the UV are attributed to the conjugated double bond.

In the presence of activated zinc powder, 2 could be defluorinated further in aprotic solvents. Thus in MeCN, 2 gave 3, 4 and 5 while in DMF 3 and 5 were obtained(**SCHEME** II). Such results showed that migration of a double bond within the ring system took place during defluorination. Also it is plausible to postulate that the defluorination reactions proceeded in the sequence: 1 → 2 → 3 → 4 → 5.



SCHEME II.

The results shown in **SCHEME** I and **SCHEME** II suggest that the more polar the solvent is, the more extensively the defluorination proceeds. May be the zinc difluoride formed could be more easily divorced from the zinc surface with the increasing polarity of solvents and thus the surface was renewed. If a radical trapper, C_6H_5NO, was added and ESR measurements made during the defluorination of 1 by Zn in DMF, an apparent g value of 2.0032 was recorded. Therefore, such defluorinations probably proceed through a radical intermediate.



The fact that perfluorodecalin could not be defluorinated under the same conditions implies that at least one preexisting double bond is necessary for the defluorination of perfluoropolycyclic compounds or may be monocyclic compounds too.

EXPERIMENTAL

Boiling points and melting points were uncorrected. IR were recorded with a Zeiss Specord-75 as films or as KCl pellets. ^{1}H NMR (with chemical shifts in ppm from external TMS) and ^{19}F NMR (with chemical shifts in ppm from external TFA and positive for upfield shifts) were determined at 60MHz on a Varian EM-360 Spectrometer or at 90MHz on a JEOL FX-90Q Spectrometer. A Finnigan GC-MS 4021 Mass Spectrometer was used to measure the mass spectra. UV were measured with a PE UV-Vis 559 Spectrophotometer. GLC were performed with a 102G (Shanghai Analytical Factory) using a 3m long column packed with DNP on Chromosorb (dinonyl phthalate, 15%).

Defluorination of 1

Typical Procedure: 10.0g 1 (23.6mmol) and 6g (91.7mmol) activated zinc powder were placed in 60ml solvent and stirred under the conditions stated in **SCHEME** I and **SCHEME** II. After that, the mixture was poured into 50ml ice water and acidified with dil. HCl. The organic layer was separated and the aqueous solution was extracted with Et$_2$O. The organic and ethereal extracts were combined, dried and distilled.

In dioxane, 6.5g (yield 71.4%) **2** boiled at 127-130'C was obtained. It was purified further by semipreparative GLC(column temp.: 80'C). **Elem. Anal.** for **2** $C_{10}F_{14}$: C, 30.83; F, 68.77 (required: C,31.11; F, 68.89). **IR** (cm^{-1})(film): 1670(vs, C=C), 1150(vs,C-F). **UV:** λ_{max} (95% EtOH)=222.6nm (ε=3.50*10^{4}). **MS** m/e(inten.,assign.): 69(58.2,CF$_3$), 267(61.2,M-C$_2$F$_5$), 317 (100, M-CF$_3$), 348(35.3,M-2F), 367(39.5,M-F), 386(54.4, M).**^{19}FNMR** (measured at 81.9MHz in neat): 41.29(2F,broad), 42.70(4F, broad), 48.83(4F, s), 62.50 (4F, s).

In acetonitrile, 5.9g organic mixture containing **3** and **4** boiled at 85-95'C/15mmHg was obtained. The mixture was separated by semi-preparative GLC(column temp.: 100'C). Compound **3**: **MS**: 69(41.5,CF_3), 179(58.6, $M-C_3F_7$), 198(49.3, $M-C_3F_6$), 229(50.1, $M-C_2F_5$), 241(100, C_9F_7), 248(80.8, $M-C_2F_4$), 279(58.3, $M-CF_3$), 298(50.3, $M-CF_2$), 310 (56.3, M-2F), 329(68.2 M-F), 348(79.1, M). ^{19}**F NMR** (neat): 31.5(4F, s), 60.6(6F, s), 71.0 (2F, s). Compound **4**: **IR**(film): 1740(vs, C=C), 1640 and 1520(s, C=C of perfluorobenzene), 1130(s,C-F). **MS**: 69(6.1, CF_3), 241(100, $M-CF_3$), 260(18.8, $M-CF_2$), 291(35.3, M-F), 310(53.7, M). ^{19}**F NMR** (neat): 41.5(2F, d, J=45.1Hz), 50(2F, s), 60.7(1F, m), 64.4(2F, q, J=60.0Hz), 71.7(1F, s), 73.7(1F, s), 84(1F, s).

In DMF, 4.2g **5** (yield 65.6%) with m.p.85.5-87'C was obtained after sublimation at 80-86'C/0.5mmHg and one recrystallization from MeOH. The crude mixture contained 20.5% **3** and 79.5% **5** as estimated by ^{19}F NMR. Compound **5**: **IR** (pellets on KCl): 1660 and 1490 (vs, C=C of perfluoronaphthalene). **MS**: 69(3.8, CF_3), 203(25.3, $M-CF_3$), 222(29.8, $M-CF_2$), 241 (58.9,M-CF), 272(100, M). ^{19}**F NMR** (in CCl_4): 67.0(4F, s), 75.0(4F, s).

In methanol, 3.3g **6** (yield 34.1%) with m.p.93.5-94.5'C was obtained after being chromatographed on silica gel using petroleum ether as eluent and recrystallized in MeOH. **Elem. Anal.** for **6** $C_{12}H_6F_{12}O_2$: C, 34.96; H,1.20; F, 55.66 (required: C, 35.14; H, 1.47; F, 55.58). **IR** (pellets on KCl): 3000 (w, C-H), 1620 (vs, C=C), 1140 (vs, C-F). **UV**:λ_{max}(EtOH)263.5nm ($\epsilon=3.54*10^4$).**MS**: 410(100, M). ^{1}**H NMR**(in CCl_4): 4.3(OCH_3,s).^{19}**FNMR** (in CCl_4): 39.4(4F, s), 41.0(4F, s), 59.3(4F, s).

Defluorination of 2

Treated as in the previous experiments, 10g **2** in acetonitrile gave a mixture (6.0g) containing **3**, **4** and **5** while in DMF, 4.0g mixture containing **3** and **5** was obtained(see SCHEME II for details).

Oxidation of 2

10g **2** (25.9mmol) in 30ml acetone was cooled to 0'C and 11g ground

$KMnO_4$ was added slowly with vigorous stirring. The reaction proceeded at 0'C for 7h. After that, 50ml ice water was added and SO_2 was bubbled in until the solution became transparent. The aqueous solution was extracted with Et_2O and the ethereal solution was dried first over $MgSO_4$ and then over P_2O_5. Distillation gave 7.2g acid (yield 58.0%) boiled at 120-130'C/2mmHg. Such acid was esterified with $MeOH/H_2SO_4$ and gave 4.8g of **2a** (yield 86.0%) with b.p. 58-63'C/2mmHg. **Elem. Anal.** for **2a** $C_7H_6F_6O_4$: C, 30.95,; H, 2.24; F, 42.94 (required: C,31.36; H,2.26; F,42.52). **IR** (film): 3000(w, C-H), 1790(vs, CO_2Me), 1200(vs, C-F). **MS**: 59(27.1, CO_2Me), 124(100, $CF2CO_2Me$), 209(49.2, M-CO_2Me), 221(23.0,M-47), 269(32.4, M+1), 283 (79.6, M+Me). **^{1}H NMR** (neat): 3.87(OCH_3, s). **^{19}F NMR** (neat): 42.6 (4F, s), 48.2(2F, s).

REFERENCES

1 E.T. McBee, W.B. Ligett, V.V. Lindgren, U.S.Pat., 2 586 364 (1952); **Chem. Abstr.**, 46 (1952) 8675d.

2(a) P.L. Coe, C.R. Patrick and J.C. Tatlow, **Tetrahedron**, 9(1960) 245.

(b) B. Gething, C.R. Patrick, M. Stacey and J.C. Tatlow, **Nature**, 183(1959) 588.

3 P.L. Coe, R.M. Habib and J.C. Tatlow, **J. Fluorine Chem.**, 20 (1982) 203.

4 R.G. Plevey, I.J. Sallomi, D.F. Thomas and J.C. Tatlow, **J. Chem. Soc., Perkin Trans. I**, (1976) 2270.

5 T.W. Bastock, A.E. Pedler and J.C. Tatlow, **J. Fluorine Chem.**, 8(1976) 11.

6(a) S.F. Campbell, A.G. Hudson, E. F.Mooney, A. E.Pedler, R. Stephens and K.N. Wood, **Spectrochem. Acta**, 23A(1967) 2119.

(b) G. Camaggi and F. Gozzo, J. Chem. Soc. (C), (1971) 925.