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POLYCYCLIC FLUOROAROMATIC COMPOUNDS. PART XII. [1] THE EXTENT OF 1-SUBSTITUTION IN OCTAFLUORONAPHTHALENE

J. BURDON and T. W. RIMMINGTON[†]

Chemistry Department, The University, P.O.Box 363, Birmingham B15 2TT (U.K.)

SUMMARY

Nucleophilic attack on octafluoronaphthalene gives a small amount of 1-substitution in addition to the predominant 2-substitution: methyllithium (8.4% 1-substitution), sodium methoxide (3.7%), diethylamine (0%), lithium diethylamide (4.8%).

INTRODUCTION

The many papers [1-4] on nucleophilic attack on perfluoropolynuclear carbocyclic aromatics all report only the major product with the exception of a paper by Bolton and Sandall [3] which mentions in passing that octafluoronaphthalene reacts with sodium methoxide in methanol to give not more than 20% of a product which may be the 1-methoxy compound, in addition to the predominant 2-methoxy-isomer.

In the polyfluoro-benzenoid area there are numerous reports [5] of isomer distributions resulting from nucleophilic attack.

RESULTS AND DISCUSSION

We have now carried out a study of the isomer distribution in nucleophilic attack on octafluoronaphthalene. The results are summarized in Table 1. The reaction mixtures were analysed by gas chromatography and

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[†] Present address: Department of Chemical Technology, South Australian Institute of Technology, P.O. Box 1, Ingle Farm, South Australia 5098, Australia.

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the products identified by mass spectrometry; in all cases the 1- and 2-isomers were well separated and their mass spectra were similar but not the same. The 2-substitution products were further identified by their ^{19}F nmr spectra (Table 2). Because their amounts were so small, no attempt has been made to isolate any of the 1-isomers.

TABLE 1

Relative amounts of 1- and 2-substitution in octafluoronaphthalene

Nucleophile	% 1-substitution	% 2-substitution
Methyl-lithium	8.4	91.6
Sodium methoxide	3.7	96.3
Diethylamine	0	100
Lithium diethylamide	4.8	95.2

TABLE 2

^{19}F NMR spectra of 2-substituted heptafluoronaphthalenes

Substituent	Chemical shift[a]						
	1	3	4	5	6	7	8
CH_3	122.3[b]	138.0	144-150		155.6[c]	156.9[c]	144-150
OMe	140.3[d]	148.8	146.5	146.5	156.3[c]	158.3[c]	146.8[d]
NEt_2	131.0[e]	141.3	147.5[c,f]	148.7[c,f]	157.8	157.8	146.2[e]

[a] In ppm upfield from $CFCl_3$; integers are fluorine positions. [b] $J_{1,8}$ = 65 Hz. [c] Or vice-versa. [d] $J_{1,8}$ = 62 Hz. [e] $J_{1,8}$ = 65 Hz. [f] $J_{4,5}$ = 59 Hz.

It would be otiose to discuss the extent of 1-substitution at any great length. Factors such as reactivity/selectivity relationships, steric effects, and the role of solvent and temperature could all be important. We do note, however, that the extent of 1-substitution does appear to follow a reactivity/selectivity trend: the least reactive (temp. of 65°C required) nucleophile - diethylamine (no 1-substitution) - is most selective; probably the most reactive (exothermic at 15°C) - methyl-lithium - is least selective (8.4% 1-substitution). This is, of course, a common state of affairs in organic chemistry.

EXPERIMENTAL

Reaction of octafluoronaphthalene with:

(a) methyl-lithium

2.1 M methyl-lithium in ether (50 cm^3) was added with stirring at 15°C and under N_2 to a solution of octafluoronaphthalene (27.2 g) in ether (100 cm^3); an exothermic reaction occurred. After 2 h stirring, the solution was filtered and evaporated to leave a white solid (22.9 g), m.p. 64-72°C. Examination by gas chromatography (diethyleneglycol succinate at 165°C as stationary phase) showed three peaks of relative areas 29.6: 5.3:57.7. The first corresponded to starting material. GC/MS (Kratos MS 80 instrument) showed that the three components were octafluoronaphthalene (M^+ (base peak) = 272), heptafluoro-1-methylnaphthalene (M^+ (base peak) = 268, major peaks at m/e = 249 and 247), and heptafluoro-2-methylnaphthalene (similar mass spectrum to its 1-isomer, but with different relative intensities for the 249 and 247 ions). The total ion currents (t.i.c.) suggested that the three peaks were present in the ratios 6:1:11. Separation of a portion of the reaction mixture (0.23 g) by GC (diethyleneglycol succinate as stationary phase) gave (i) octafluoronaphthalene (0.05 g) and (ii) heptafluoro-2-methylnaphthalene (0.09 g), m.p. 59°C (after sublimation *in vacuo*) (lit. [4] 58°C).

(b) sodium methoxide in methanol

Solutions of octafluoronaphthalene (0.8 g) in methanol (10 cm^3) and sodium (0.05 g) in methanol (10 cm^3) were mixed and then refluxed for 4 h. GC (as in (a)) of the crude product showed three peaks with relative areas of 70.9:1.1:28.0. Separation by column chromatography (30 cm column packed with silica gel with hexane as eluent) gave (i) octafluoronaphthalene (0.55 g) and (ii) a mixture of the last two GC peaks (0.20 g). Examination of (ii) by GC/MS showed two components (with t.i.c.s in the ratio 2.6:100) each with M^+ = 284 and major peaks at m/e = 241 and 269; they differed in the relative intensities of these three peaks.

Recrystallization of (ii) from aqueous methanol gave heptafluoro-2-methoxynaphthalene, m.p. 42-43°C (lit. [4] 40-41°C).

(c) diethylamine

Octafluoronaphthalene (0.55 g) and diethylamine (0.15 g) were heated together in a sealed tube at 65°C for 4 h. The dark-brown liquid product was washed with brine, dried and examined by GC as in (a); this showed only two components, the first of which corresponded to octafluoronaphthalene, in the ratio (peak areas) 28:72. Separation by column chromatography (30 cm column packed with silica gel with 5% benzene in hexane as eluent) gave pure samples of octafluoronaphthalene and 2-diethylaminoheptafluoronaphthalene (nc), m.p. ca. 10°C (Found: C, 53.1; H, 2.9; N, 4.3. $C_{14}H_{10}NF_7$ requires C, 51.7; H, 3.1; N, 4.3%).

(d) lithium diethylamide

1.6 M Butyl-lithium (1.25 cm^3) was added, under nitrogen, to diethylamine (0.15 g) in dry tetrahydrofuran (10 cm^3), all at -75°C. The mixture was stirred for 2 h and then octafluoronaphthalene (0.55 g) in dry tetrahydrofuran (20 cm^3) was added in one portion and this reaction mixture was allowed to warm to room temperature and stirred for 15 h. The brown, viscous mass was washed with brine, filtered, dried, ($MgSO_4$) and re-filtered. Examination by GC (as in (a)) revealed 8 peaks (some very small peaks were ignored) in the ratios (peak areas) 12.0:3.3:2.1:3.5:1.9:69.9: 2.4:4.9. GC/MS showed that the first peak was octafluoronaphthalene and that the fourth and sixth were isomeric NN-diethylaminoheptafluoronaphthalenes (M^+ = 325, base peak at m/e = 310, major peaks at m/e 282 and 185 with the relative intensities of these last two peaks differing markedly between the two isomers). The identity of the other peaks was not pursued assiduously, but their mass spectra suggested that the fifth peak was a heptafluoropropoxynaphthalene (M^+ = 312, base peak at m/e 270), and the seventh a butoxyheptafluoronaphthalene (M^+ = 326, base peak at m/e 270) [both could be derived from oxygenation of butyl-lithium, to butoxide and propoxide, and subsequent nucleophilic substitution]. The eighth peak was probably a bis(diethylamino)hexafluoronaphthalene (M^+ = 378, base peak at m/e 363).

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