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NITROGEN COMPOUNDS AS HIGH YIELD PRECURSORS TO BRANCHED FLUOROCARBONS BY DIRECT FLUORINATION

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To Professor George H. Cady on his 70th birthday

SUMMARY

The low temperature direct fluorination of highly branched nitrile and amine containing hydrocarbons were conducted under conditions condusive to good yields of perfluorinated hydrocarbons. Perfluoroneopentane was produced from pivalonitrile and perfluoroisobutane from t-butyl amine. The results suggest the lability of $\cdot NF_2$ groups under the conditions of the experiment. In contrast, when normal nitriles, such as glutaronitrile and nitrogen containing ring compounds, such as morpholine are fluorinated, the corresponding nitrogen containing fluorocarbon is produced in higher yields than previously reported by other fluorination methods.

INTRODUCTION

The direct fluorination of highly branched hydrocarbon structures, difficult by other methods[2], is possible by low temperature, direct fluorination[3-6]. The addition of nitrogen containing functions to the expanding list of functional moieties successfully fluorinated presents a substantial challenge to the method. We present here two examples in which side reactions and radical dissociation substantially interfered with a "successful" fluorination although valuable products were obtained.

EXPERIMENTAL

Fluorination of Pivalonitrile (t-Butyl Cyanide)

A 1.61 gm (19.4 m moles, F.W. 83.13) sample of pivalonitrile was evaporated using a 200 ml/min helium flow into a six zone low temperature reactor sir lar to the one described previously[3]. The melting point of pivalonitrile is 1 16°C and so the first zone was maintained at +40° and the second zone at +10°. Each zone following was about 20-25° colder than the previous zone. Zone was maintained at -78°C. After 12 hours, the He was reduced to 20 ml/min zones were cooled to -78°C and a fluorine flow of 0.5 ml/min (30 millimole F_2/day) was started. At this point the procedure is virtually identical to the one used for pivaloyl fluoride[4]. The product was passed through NaF pellets it left the reactor. The removal of HF allowed the volatiles to be collected glass traps. The volatiles (~2.0 g) were fractionated through -45, -78, -10 -130 and -196°C traps on a vacuum line developing 10^{-3} torr. The -196°C that contained nitrogen containing fragments and traces of NF_3 and N_2F_4. The -1 trap was discarded.

The -78, -104 and -130 traps contained a mixture of F-isobutane, F-neotane, and monohydro-F-neopentane. The materials were purified on a fluorosilicone (OF-1-0065, 13% on chromosorb p 80-100 mesh) column. Only the compounds F-isobutane (~0.5g); F-neopentane (0.96g, 17.2%) and monohydro-F-neopentane (0.475g, 9.1%) were purified. Only 0.5 grams of additional r ial containing no major g/c peaks was obtained. Invariably, the nitrogen co- species were incompletely fluorinated. F-isobutane and F-neopentane were identical to authentic samples compared by IR[3,7] and ^{19}F nmr[3].

The one new compound, monohydro-F-neopentane was characterized by and ^1H nmr spectroscopy (external $CFCl_3$, TMS) and infrared spectroscopy.

$(CF_3)_3\,C\text{-}CF_2\text{-}H$ Jab = 9.7 hz

a b c δ = 6.19ppm Jac = 0.8 hz

+66.01 +126.6 ppm Jbc = 51.1 hz

Fluorination of t-Butyl Amine

A 2.1 gm (3.0 ml, 28.7 m moles) sample of t-butyl amine was evaporated into the reactor using a 40cc/min flow of helium. Because the m.p. was low (-67.5°C), the first two zones were kept at -78°C during the transfer of product from the evaporator to the reactor. After completion of the evaporation, the helium flow was reduced to 20 cc/min and a fluorine flow of 1.5 cc/min initiated. After 24 hours the helium was terminated and an additional zone was cooled to -78°C with dry ice as the first zone was allowed to warm. In this way, material was carried along the reactor renewing the surface of the reactant. This sequence was repeated until zone six was warmed to ambient and the product collected in a glass trap at -78°C after passing through sodium fluoride to remove hydrogen fluoride. The fluorine flow was terminated and the system was flushed with helium.

The contents of the glass traps were fractionated through -30°, -78°, and -196°C traps. Most of the material was collected in the -130°C trap. The products were separated on the fluorosilicone column and identified by ^{19}F and ^{1}H nmr, mass spectroscopy and infrared spectroscopy.

The primary products were F-isobutane 1.43g (21%), 1 hydro-F-isobutane 2.21 g (35%) and a trace of 2 hydro-F-isobutane. Again all nitrogen containing species were incompletely fluorinated and in small amount. The ^{19}F and ^{1}H nmr of 1-hydro-F-isobutane is as follows:

$$\underset{a}{(CF_3)_2}-\underset{b}{CF}-\underset{c}{CF_2}-\underset{d}{H} \qquad \delta = 5.38 \text{ ppm}$$

$$\phi = +73.08 \quad +183.6 \quad +128.1 \text{ ppm}$$

* combine to make CF_{3a} a quartet

$$\left.\begin{array}{l} J_{ac} = 7.5 \\ J_{ad} \cong 7.5 \end{array}\right\} *$$

Jab = ~0
Jac = 7.5
Jad ≅ 7.5
Jbc = ~0
Jbd = ~0
Jcd = 52.2 hz

Fluorination of Glutaronitrile, $NC(CH_2)_3CN$

The reaction of glutaronitrile with elemental fluorine diluted with helium gas has been carried out at -78°C, under various fluorine concentrations and lengths of time. Separation of the reaction products on the gas chromatogry has yielded three fluorocarbons which have been identified as n-C_5F_{12}, $CF_3(CF_2)_4NF_2$ and $F_2N(CF_2)_5NF_2$. Of these compounds, the last one was never These compounds were identified as follows:

Perfluoropentane, n-C_5F_{12}: This compound has been identified by mean its infrared spectrum which was identical with the one published in the literature[7].

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Azaperfluorohexane, $CF_3(CF_2)_4NF_2$: This N-fluoroamine was identified the basis of its infrared, NMR and mass spectra. The infrared spectrum of this compound resembled that of n-C_5F_{12} and, in addition, contained a double between 1000 and 900 cm^{-1} which was attributed to the NF_2 group. The NMR spectrum of $CF_3\overset{\varepsilon}{C}F_2\overset{\gamma}{C}F_2\overset{\beta}{C}F_2\overset{\alpha}{C}F_2NF_2$ exhibited five peaks at -14.1 (NF_2), +117 (α), +124.0 (β and γ), +128.0 (ε) and +83.5 (CF_3) ppm with respect to $CFCl_3$ n the ratio of 1:1:2:1:1, which was in agreement with the spectrum reported by Bigelow and co-workers[8]. The fluorines of the β and γ groups were not res The mass spectrum of the compound contained highest peaks at m/e 302, C_5 (parent minus F) and 269, $C_5F_{11}^+$ (parent minus NF_2) as well as many other e ted peaks.

1, 7-Diazaperfluoroheptane $F_2N(CF_2)_5NF_2$: This new compound has been identified on the basis of its infrared, NMR and mass spectra. The infrared spectrum showed considerable similarity to that of n-C_5F_{12} and contained the characteristic doublet between 1000 and 900 cm^{-1}, although it has been transformed now into a sharp peak and a shoulder due probably to the highest symmetry of the compound. The NMR spectrum of $F_2N\overset{\alpha}{C}F_2\overset{\beta}{C}F_2\overset{\gamma}{C}F_2CF_2CF_2N$ exhibited three peaks at -13.5 (NF_2), 116.3 (α) and 122.6 (β and γ) ppm with respect to $CFCl_3$ in the ratio 2:2:3. As expected the fluorines on the β and γ CF_2 groups were not resolved. The mass spectrum of the compound content highest peaks at m/e 335, $C_5F_{13}N_2^+$ (parent minus F), 302 $C_5F_{12}N^+$ (parent mir NF_2) and a pronounced peak at 250 $C_5F_{10}^+$ as well as many others as expected The yield was 15%.

Direct Fluorination of Morpholine

Morpholine has been fluorinated to F-N-fluoromorpholine. The volatile products from the reactor were separated on an SE-30 glc column. The infrared spectrum of perfluoro-N-fluoromorpholine: (cm^{-1}, intensity, possible assignments) 1371, w; 1338, m; 1291, s, CF_2 stretch; 1233, shoulder on 1217; 1217, vs, CF_2 stretch; 1146 and 1124, s doublet, COC sym. stretch (?); 967, m, NF stretch; 688, m; 661, w; 606, mb; (w, weak; m, medium; s, strong; vs, very strong; mb, medium and broad). The NF stretch has been previously reported as 922 and 975 cm^{-1}.[9] The mass spectrum of C_4F_9NO with the major m/e, intensity relative to m/e =114, and possible ions were: 250, 0.1, $^{13}CC_3F_9NO^+$, $C_4F_9{}^{15}NO$ (cal 0.07); 259, 1.5, $C_4F_9NO^+$(parent); 231, 0.3 isotopes of 230 (cal 0.2); 230, 4.0, $C_4F_8NO^+$; 202, 1.7, $C_3F_8N^+$; 185, 1.0, $C_3F_7O^+$; 180, 2.2, $C_3F_6NO^+$; 169, 1.4, C_3F_7; 165, 1.7, isotopes of 164 (cal. 1.4); 164, 40.3, $C_3F_6N^+$; 152, 1.7, $C_2F_6N^+$; 151, 1.1; 146, 0.8, isotopes of 145 (cal 0.7); 145, 17.7, $C_3F_5N^+$; 142, 1.7, $C_3F_4NO^+$; 120, 1.8, $^{13}CCF_5$(cal 1.6); 119, 74.6, $C_2F_5{}^+$; 115, 3.0, isotopes of 114 (cal. 2.5); 114, 100.0, $C_2F_4N^+$; 101, 5.3; 100, 38.8, $C_2F_4{}^+$; 97, 8.0, $C_2F_3O^+$; 95, 9.4, $C_2F_3N^+$; 92, 3.2, $C_2F_2NO^+$; 81, 1.3, $C_2F_3{}^+$; 76, 4.6, $C_2F_2N^+$; 76, 1.3; 69, 52.3, $CF_3{}^+$; 51, 3.3; 50, 10.0 $CF_2{}^+$; 47, 6.6, CFO^+; 44, 47.0, $CO_2{}^+$; 43, 6.6, C_2F^+; 31, 3.3, CF^+; and the usual peaks under m/e = 30. In addition, two metastables were apparent at 79.17 and 41.76 m/e. These represent the neutral fragments of fluorine and FCN leaving the m/e = 114, $C_2F_4N^+$, to yield m/e =95, $C_2F_3N^+$, and m/e = 69, $CF_3{}^+$, respectively.

The ^{19}F nuclear magnetic resonance spectrum was measured on the neat F-N-fluoromorpholine with an external reference to trifluoroacetic acid. The chemical shifts and the integrations were in agreement with the previously reported values,[10, 11]. The yield was over 31%.

Another component of the reaction has been identified as bispentafluoroethyl ether on the basis of its infrared spectrum which was identical in all aspects to the published spectrum[13] and its mass spectrum. The major m/e intensities, and possible ions were: 235, 1, $CF_2CF_2OC_2F_5{}^+$; 185, 189, $C_3F_7O^+$; 135, 6, $C_2F_5O^+$; 120, 168; 119, offscale, $C_2F_5{}^+$; 116, 10, $C_2F_4O^+$; 100, 26, $C_2F_4{}^+$; 92, 78; 70, 33; 69, offscale, $CF_3{}^+$; 66, 6, $COF_2{}^+$; 50, 61, $CF_2{}^+$; 47, 60, COF^+;

45, 10; 44, 621, CO_2^+; 43, 92, C_2F^+; 31, 143, CF^+; and the usual peaks u 30. Also, identified by infrared and mass spectra has been hexafluoroetha- pentafluoroethyldifluoroamine, and nitrogen trifluoride. Tentatively identity was $CF_3OCF_2CF_2CF_2N(F)CF_3$. This last compound was in small amount and represents β-cleavage of the morpholine ring. The nitrogen elimination from the morpholine ring represents the major side reaction and adds to the evidence of the weakness of the carbon-nitrogen bond compared to the carbon-carbon.

RESULTS AND DISCUSSION

Little is known about the specific mechanisms of low temperature direct fluorination except that substantial quantities of free radicals are produced Pivalonitrile and t-butyl amine were selected because of their volatilities and highly branched structures.

The first, a nitrile, had excellent physical properties, high melting point and volatility. The fluorination procedure used was characterized by high dilution (2.5% F_2), low temperature (-78°C), and low flow (30 millimoles/day) conditions. At 50% of theoretical fluorination the fluorine was increased st wise to 90 millimoles/day and the concentration increased to 100% F_2. The conditions, which were sufficient to produce F-pivaloyl fluoride in 50% yield were not able to produce F-neopentyl difluoroamine in isolable quantities. In a combined yield of F-neopentane and monohydro-F-neopentane of from 25% to 30% yield was obtained. Fragments amounting to about 1.0 g (10-15% of the statical) were obtained from the reactor indicating that less than 50% of nitrile which was evaporated into the reactor was recovered as volatile products. spection of the reactor revealed a substantial amount of water sensitive which powder, presumably a polymer or triazine due to polymerization of the nitrate group under the influence of fluorine and the radicals generated in the reaction. Alternate fluorination programs were tried but succeeded only in changing the relative amount of F-neopentane and monohydro-F-neopentane but the combined yield was nearly constant.

The yields of the new 1,7-diazaperfluoroheptane were only 15%. Part of difficulty lies in the fact that replacement of the last hydrogen atoms on the bon chain becomes increasingly difficult due to steric difficulties with the larger fluorine atoms. Nevertheless, it is worth noticing that direct fluorination of perfluoroglutaronitrile $NC(CF_2)_3CN$ by Bigelow's method yielded only $C_5F_{11}NF_2$ and $CF_2CF_2CF_2CF_2NF_2$.

F-N-fluoroamines are of interest because they can be converted to acids by reaction with KI, or to nitriles by reaction with two moles of triphenylphosphine

Perfluoro-N-fluoro morpholine is of special interest because it has been hydrolyzed to perfluorodiglycolic acid by means of aqueous KF hydrolysis[9]. Yields exceeding to the electrochemical fluorination of morpholine (8%) were easily attained[12]. In a subsequent reaction the gradient cold reactor was modified to allow complete volatization and/or renewal of the frozen surface before the next increase in fluorine concentration and smaller more frequent increments in the fluorine concentration were used resulted in yields of perfluoro-N-fluoro morpholine greater than 31%.

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REFERENCES

1 Alfred P. Sloan Fellow

2 R.D. Bagnall, P.L. Coe, and J.C. Tatlow, J. Fluorine Chem. 3, 329 (1974).

3 N.J. Maraschin and R.J. Lagow, J. Amer. Chem. Soc. 94, 8601 (1972); Inorg. Chem. 12, 1459 (1973).

4 J.L. Adcock and R.J. Lagow, J. Amer. Chem. Soc. 96, 7588 (1974).

5 J.L. Adcock and R.J. Lagow, J. Org. Chem. 38, 3617 (1973).

6 J.L. Adcock, R.A. Beh, R.J. Lagow, J. Org. Chem., in press.

7 D.G. Weiblen, Fluorine Chemistry, Vol. II, Ch. 7, J.H. Simons, Ed., Academic Press, Inc., New York, New York, 1954, p.469.

8 L.A. Bigelow, J.B. Hynes and B.C. Bishop, J. Amer. Chem. Soc. 84, 3409 (1962).

9 R.E. Banks and E.D. Bushney, *J. Chem. Soc.* 6077 (1965).

10 J. Lee and H.G. Orrell, *Tran Faraday Soc.* *63*, 16 (1967).

11 M. Muller, P.C. Lauterbus and G.F. Svatos, *J. Amer. Chem. S*
(1957).

12 J.H. Simons, *J. Amer. Chem. Soc.* *79*, 3429 (1957).

13 J.H. Simons, U.S. Patent 2,500,388 (1950).