act with n-butyllithium to produce remarkable polylithiated species such as C_3Li_4 in the case of propyne.

In the course of extending our work we have examined the reaction of organolithium reagents with 1-phenylpropyne. No addition or electron transfer was observed with this compound with either n-butyllithium in ether or hexane, or t-butyllithium in pentane, but rather the alkyne was isomerized to 3-phenylpropyne in 50–75% yield.

$$C_6H_5C{\equiv}CCH_3 \xrightarrow[\text{ether or hydrocarbon}]{\text{RLi}} \xrightarrow{H_2O} C_6H_5CH_2C{\equiv}CH$$

$$R = n\text{-Bu or } t\text{-Bu}$$

When 1 mole of 1-phenylpropyne was treated with 6 moles of n-butyllithium in hexane for 16 hr under reflux followed by addition of deuterium oxide to the reaction mixture, deuterated 3-phenylpropyne was obtained. The nuclear magnetic resonance (nmr) spectra of the product showed no aliphatic protons, and deuterium analysis revealed the presence of 3.22 atoms of deuterium/molecule. The product is, therefore, essentially I probably admixed with a small amount of II

$C_6H_5CD_2C{\equiv}CD$
I

$C_6H_4DCD_2C{\equiv}CD$
II

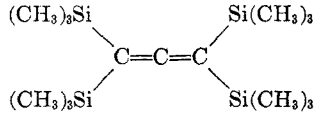
which must in turn have arisen from the polylithiated species III and IV.

$C_6H_5C_3Li_3$
III

$C_6H_4LiC_3Li_3$
IV

Under the conditions of the hydrolysis (1-phenylpropyne or 3-phenylpropyne in the presence of LiOD–D_2O) no deuterium was found to be incorporated into either of the above-mentioned alkynes.

In the case of n-butyllithium and propyne[3] the tetralithiated product (C_3Li_4) reacts with trimethylchlorosilane to give the allene V rather than an acetylene such as we observe. As the authors[3] point out, however, this is very likely a steric effect and in fact the trilithiated product from propyne when treated with trimethylchlorosilane gives VI.


V

$(CH_3)_2SiCHC{\equiv}CSi(CH_3)_3$
VI

It is of interest to note that phenylacetonitrile and acetomesitylene form dilithio salts with n-butyllithium in tetrahydrofuran–hexane.[4]

Experimental Section

Nmr spectra were obtained using a Varian Associates A-60 spectrometer with tetramethylsilane as internal standard. Deuterium analyses were determined by J. Nemeth, Urbana, Ill. Hydrocarbon solvents were purified by washing with sulfuric acid, then water, drying over sodium sulfate, and distillation from sodium. Melting points are uncorrected.

n-Butyllithium in ether was prepared according to the method of Gilman[5] and filtered through a glass-wool plug prior to use. The concentration of organolithium reagent was determined by the double-titration method.[6]

n-Butyllithium in hexane was obtained from Foote Mineral Co., and t-butyllithium in pentane from Lithium Corp. of America.

1-Phenylpropyne.—The procedure of Hurd and Tockman[7] was used starting with phenylacetone. It was found that sodium t-butoxide is more effective than potassium hydroxide in the dehydrohalogenation step.

Reaction of n-Butyllithium with 1-Phenylpropyne in Ether.—To 0.39 mole of n-butyllithium in 425 ml of ether held at ice-bath temperature and under helium atmosphere, there was added rapidly 20 g (0.175 mole) of 1-phenylpropyne. An almost immediate color change to yellow was observed. The color turned to red when the solution reached room temperature. After 16 hr of stirring at room temperature the reaction mixture was slowly treated with 125 ml of water (external cooling). The ether layer was separated and dried over magnesium sulfate. Distillation yielded 14 g (70%) of 3-phenylpropyne, bp 55–56° (4 mm), $n^{25.2}\mathrm{D}$ 1.5259 [lit.[8] bp 71–73° (17 mm), $n^{23}\mathrm{D}$ 1.53481] The nmr spectrum showed five protons centered at τ 2.70, two protons at τ 6.47, and one proton at τ 7.95. The bis-3-phenylpropynylmercury derivative was prepared, mp 105–106.5°, and the melting point was not depressed when it was mixed with an authentic sample.[9]

Reaction of n-Butyllithium with 1-Phenylpropyne in Hexane.—Under a nitrogen atmosphere a solution of 1.00 mole of n-butyllithium and 19.3 g (0.167 mole) of 1-phenylpropyne in 625 ml of n-hexane was heated under reflux for 16 hr. At the end of this time 40 g (2.0 moles) of deuterium oxide was slowly added with external cooling. Work-up was the same as in the case above, and there was obtained 9.7 g (50%) of deuterated 3-phenylpropyne, pure by vapor phase chromatography (vpc). Only aromatic protons appeared in the nmr spectrum.

Anal. Calcd for $C_9H_5D_3$: D, 37.5 atom % excess. Found: D, 40.3 atom % excess.

t-Butyllithium and 1-Phenylpropyne Deuterolysis.—To 0.26 mole of t-butyllithium in 230 ml of pentane at room temperature under a nitrogen atmosphere, there was added 13.0 g (0.112 mole) of 1-phenylpropyne in 160 ml of ligroin (bp 100–115°). The color of the solution changed almost immediately to a deep red and a precipitate was later formed. The solution was allowed to react at room temperature for 22 hr. At the end of this time 13.4 g (0.67 mole) of deuterium oxide was added very slowly to the cooled solution. After reacting for 2 hr the organic layer was separated, and the solvent was removed under reduced pressure. Flame-ionization gas chromatography showed three components: 3-phenylpropyne (85%), 1-phenylpropyne (5%), and a higher boiling component (10%). This was a 55% yield of 3-phenylpropyne (7.1 g).

Registry No.—I, 10147-10-1; 1-phenylpropane, 673-32-5; 3-phenylpropane, 10147-11-2.

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The Catalytic Fluorination of Perfluorocarbon Nitriles and Imines

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The reaction of fluorine with unsaturated carbon–nitrogen compounds has been the subject of numerous investigations. Most of these studies have been carried out in flow systems employing halogenated nitriles. Under mild conditions trifluoroacetonitrile or pentafluoropropionitrile were converted to the corresponding azo compounds whereas under more vigorous conditions the saturated perfluoro compounds $C_2F_5NF_2$ and C_3F_7-

NF_2 were formed.[1] Small amounts of $CF_3CF{=}NF$ can also be obtained along with the difluoramine and azo compounds by use of a jet reactor.[2]

The controlled low-temperature addition of chlorine monofluoride to perfluorocarbon nitriles to form the corresponding perfluoroalkyl nitrogen dichloride derivatives,[3] suggested that a similar reaction with fluorine should occur under the proper conditions.

Results and Discussion

Since the alkali metal fluorides have been shown to catalyze the addition of fluorine across S–N[4] or C–O[5] double bonds an attempt was made to extend this method to unsaturated carbon–nitrogen systems. The reaction of fluorine with either trifluoroacetonitrile or pentafluoropropionitrile at −78° in the presence of activated cesium fluoride was found to produce the corresponding perfluoroalkyl difluoramines smoothly.

$$R_fCN + 2F_2 \xrightarrow[CsF]{-78^\circ} R_fCF_2NF_2$$
$$R_f = CF_3 \text{ or } C_2F_5$$

Although the yields were essentially quantitative a considerable variation in the conversion of the nitrile to difluoramine was observed. The variation seemed to be related to the method of treatment of the added cesium fluoride. The most active catalyst was obtained by first allowing the cesium fluoride to absorb carbonyl fluoride, which was then removed by treatment with excess fluorine. Using this catalyst the conversions were generally above 90%. No evidence for the formation of any unsaturated derivatives such as $R_fCF{=}NF$ or $R_fCF_2N{=}NCF_2R_f$ was found in the above cases even when a deficiency of fluorine was employed. In the absence of activated cesium fluoride no reaction occurred at −78° and the nitrile could be recovered. Fluorination of CF_3CN and C_2F_5CN with a mild fluorinating agent did not yield any NF derivatives. For example, the reaction of CF_3CN or C_2F_5CN with silver difluoride for 12 hours in a static system at ambient temperature produced the corresponding azo compounds, $C_2F_5N{=}NC_2F_5$ and $C_3F_7N{=}NC_3F_7$ in 90% yield.

An attempt to prepare CF_3NF_2 by the catalytic fluorination of sodium cyanide was not very successful. No reaction between fluorine and a mixture of sodium cyanide and cesium fluoride was observed at −78°. Although reaction occurred at ambient temperature only small amounts of the desired product were formed. The majority of the reaction mixture consisted of cyanogen, tetrafluoromethane, nitrogen, and hexafluoroethane. On the other hand, the fluorination of potassium thiocyanate at −78°, produced an equimolar mixture of SF_6 and CF_3NF_2 regardless of the amount of fluorine employed. No other carbon-containing species could be detected in the reaction mixture.

$$KSCN + 6F_2 \xrightarrow{-78^\circ} KF + SF_6 + CF_3NF_2$$

The alkali metal fluorides were also found to catalyze the fluorination of $(CF_3)_2C{=}NH$.[6] In fact, chlorination or bromination of this substrate occurred in the presence of the alkali metal fluorides.

$$(CF_3)_2C{=}NH + X_2 \xrightarrow{MF} (CF_3)_2C{=}NX + HX$$
$$X = F, \text{ Cl, or Br}$$
$$M = K \text{ or Cs}$$

Although the reaction using stoichiometric amounts of chlorine gave high yields of the N-chloro derivative an excess of bromine was needed owing to the formation of the Br_3^- anion. No evidence was found for the formation of either the dichloramine or dibromamine derivatives. When fluorine was employed in the above reaction, a mixture of products was obtained. The reaction of $(CF_3)_2C{=}NH$ with 1 equiv of fluorine in the presence of cesium fluoride produced approximately an equimolar mixture of $(CF_3)_2C{=}NF$ and $(CF_3)_2CFNF_2$ (yield 34%). However, the use of KF as a catalyst afforded the unsaturated compound in up to 70% yield. Fluorination of either $(CF_3)_2C{=}NH$ with 2 equiv of fluorine or $(CF_3)_2C{=}NF$ with 1 equiv of fluorine in the presence of CsF produced the saturated compound, $(CF_3)_2CFNF_2$, in yields up to 95%. The fluorination of the parent imine thus appears to be stepwise, and the nature of the catalyst appears to be more important in the second step than the first.

The products were purified by vapor phase chromatography. They were characterized by F^{19} nmr, vapor density molecular weight, and elemental analysis. The assignment of the coupling constants was based on homonuclear decoupling experiments. For example, irradiation of the NF_2 group in $C_3F_7NF_2$ resulted in the collapse of the triplet at ϕ 127.2, while irradiation of the CF_3 group (ϕ 82.1) resulted in the collapse of the quadruplet at 116.6. This assignment is in agreement with a previous one in the literature.[7] In a similar manner irradiation of the NF peak in $(CF_3)_2C{=}NF$ resulted in the collapse of each set of two quadruplets into a set of single quadruplets (J_{FF} = 8 cps). Although the preparation of $(CF_3)_2C{=}NF$ has been reported,[8] the F^{19} nmr spectrum given does not agree with that obtained here. In fact, no adequate explanation was given for the observed spectrum. However, the spectrum obtained in this study is consistent with the expected structure. The F^{19} nmr spectra of $C_2F_5NF_2$ and $(CF_3)_2CFNF_2$ agree reasonably well with those previously reported.[8,9]

Experimental Section

Materials.—The perfluorocarbon nitriles were obtained from commercial sources and their purity was checked by vapor phase chromatography. Fluorine was obtained from General Chemical Division of Allied Chemical Corp., and used after passage through a NaF scrubber. Cesium fluoride was obtained from Alpha Inorganics. The imine, $(CF_3)_2C{=}NH$, was prepared by the literature method.[6]

Catalytic Fluorination of Nitriles.—A 10-g sample of cesium fluoride, which had been dried overnight at 175–200° under vacuum and then ground in a nitrogen-filled drybox, was loaded into a 150-ml monel Hoke cylinder containing approximately 30 $^3/_8$-in. stainless steel balls. The cylinder was loaded with 25.3

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mmoles of COF_2 and then shaken for 2 days. This resulted in the adsorption of 7.82 mmoles of COF_2. The cylinder was cooled to −196° and fluorine (8.1 mmoles) was admitted. The cylinder was allowed to warm to 25° and the contents were removed by means of a water aspirator. Trifluoroacetonitrile (1.97 mmoles) and fluorine (4.05 mmoles) were loaded into the bomb. It was allowed to warm slowly to −78° and than was shaken at this temperature for 8 hr. A small amount of noncondensable gas remained. The condensable fraction (1.94 mmoles) was analyzed by vapor phase chromatography using a 16-ft perfluorotributylamine–Chromosorb P column operating at −40°. (This column was used for purification of all the materials discussed.) It consisted of 96% $C_2F_5NF_2$ and 4% CF_3CN. In a similar fashion 0.79 mmoles of C_2F_5CN was converted to a mixture consisting of 97% $C_3F_7NF_2$ and 3% $C_2F_5CN_2$ as analyzed by vpc at −26°.

Anal. Calcd for $C_2F_5NF_2$: vapor density mol wt, 171. Found: vapor density mol wt, 169, 171. Calcd for $C_3F_7NF_2$: vapor density mol wt, 221. Found: vapor density mol wt, 218, 220.

The infrared spectrum of $C_2F_5NF_2$ was in agreement with the published spectrum,[9] while that of $C_3F_7NF_2$ contained bands in the NF region at 10.45 and 10.70 μ. The F^{19} nmr spectrum of $C_2F_5NF_2$ consists of a triplet at ϕ 81.8 ($J_{CF_3NF_2}$ = 10 cps), a singlet at 119.9, and a broad singlet at −16.3. The relative area ratios are 2.98:2.17:2.0. The F^{19} nmr spectrum of $C_3F_7NF_2$ consists of a triplet at ϕ 82.1 ($J_{CF_3CF_2}$ = 8 cps), a triplet at 127.2 ($J_{CF_2NF_2}$ = 9 cps), a quadruplet at 116.6 ($J_{CF_3CF_2}$ = 8 cps), and a broad singlet at −16.5. The relative area ratios are 3.12:2.01:1.96:2.0.

Preparation of CF_3NF_2.—A mixture containing 2.1 g of KSCN and 4.5 g of KF was loaded into a 300-ml monel Hoke cylinder. Fluorine (3.67 mmoles) was admitted to the cylinder at −196°. The cylinder was allowed to warm to −78° and stood at that temperature overnight. No noncondensables remained. The condensable fraction (1.21 mmoles) consisted of 49.7% CF_3NF_2 and 50.3% SF_6 as determined by mass spectral analysis. Partial purification was achieved by vacuum line fractionation through a −145° trap which retained most of the SF_6. Further purification was achieved by vpc at −60°. The infrared was in agreement with the published spectrum.[9]

Anal. Calcd for CF_3NF_2: vapor density mol wt, 121. Found: vapor density mol wt, 120, 122.

The F^{19} nmr spectrum of CF_3NF_2 consists of a broad peak at ϕ 84.1 and another broad peak at −18.5. The relative area ratio of the two peaks is 3.11:2.0.

Preparation of $(CF_3)_2C{=}NX$. A.—Chlorine (2.20 mmoles) and $(CF_3)_2{=}NH$ (1.95 mmoles) were condensed into a 150-ml stainless steel bomb containing 10 g of cesium fluoride. The mixture was allowed to warm slowly to ambient temperature and stand for 5 hr. Vacuum line fractionation through −126 and −196° cold traps yielded 1.75 mmoles of $(CF_3)_2C{=}NCl$ (97% purity) in the former trap and 0.2 mmole of chlorine in the latter trap. Further purification of $(CF_3)_2C{=}NCl$ was achieved by vpc at −20°.

Anal. Calcd for CF_3F_5NCl: F, 57.1; Cl, 17.8; N, 7.0; vapor density mol wt, 199.0. Found: F, 55.3; Cl, 17.4; N, 6.8; vapor density mol wt, 201, 197, 198.

The infrared spectrum of $(CF_3)_2C{=}NCl$ contained bands at 6.14 (m), 7.55 (s), 8.02 (vs, 8.84 (s), 10.05 (s), 12.60 (m), 13.27 (s), and 14.12 (m–vs) μ. The F^{19} nmr spectrum of $(CF_3)_2C{=}NCl$ consists of two quadruplets ($J_{CF_3CF_3}$ = 8 cps) at ϕ 67.5 and 69.1. Their relative areas are 1.0:0.9.

B.—Bromine (5.14 mmoles) and $(CF_3)_2C{=}NH$ (2.50 mmoles) were condensed into a bomb containing 10 g of KF and approximately 30 $^3/_8$-in. stainless steel balls. The mixture was allowed to warm to ambient temperature before shaking overnight. The total product mixture (2.61 mmoles) was removed from the cylinder and rectified by vpc at 10°. A 68% yield of $(CF_3)_2C{=}NBr$ was obtained. Its infrared and F^{19} nmr spectra were similar to those reported.[6]

Anal. Calcd: vapor density mol wt, 244. Found: vapor density mol wt, 240, 241.

Reaction of $(CF_3)_2C{=}NH$ with Fluorine. A.—Fluorine (1.71 mmoles) was expanded into a 150-ml monel Hoke cylinder containing 1.74 mmoles of $(CF_3)_2C{=}NH$ and 10 g of CsF at −196°. After standing at −78° for 1 hr the cylinder was allowed to slowly warm to 25°. The condensable fraction was shown by F^{19} nmr to contain $(CF_3)_2C{=}NF$, $(CF_3)_2CFNF_2$, and $(CF_3)_2C{=}NH$ in approximately equal amounts. Separation by vapor phase chromatography at −35° resulted in the isolation of $(CF_3)_2C{=}NF$ and $(CF_3)_2CFNF_2$ in over-all yields of 34 and 32%, respectively. Under these conditions the starting material did not come off the column.

B.—When the above procedure was carried out using 1.53 mmoles of $(CF_3)_2C{=}NH$ and 3.17 mmoles of fluorine, $(CF_3)_2CFNF_2$ was formed in 97% yield, as determined by vpc at −35°.

C.—Fluorine (1.81 mmoles) was expanded into a 150-ml monel Hoke cylinder containing 1.87 mmoles of $(CF_3)_2C{=}NH$ and 10 g of KF at −196°. The mixture was treated as in A. Separation of the reaction mixture by vpc resulted in the isolation of $(CF_3)_2C{=}NF$ in 70% yield.

Anal. Calcd for $(CF_3)_2C{=}NF$: vapor density mol wt, 183. Found: vapor density mol wt, 180, 181. Calcd for $(CF_3)_2CFNF_2$: vapor density mol wt, 221. Found: vapor density mol wt, 223, 220. Calcd for C_3F_7N: F, 72.7; N, 7.7. Found: F, 71.4; N, 7.3. Calcd for C_3F_9N: F, 77.4; N, 6.3. Found: F, 76.0; N, 6.0.

The infrared spectrum of $(CF_3)_2C{=}NF$ contained bands at 6.11 (m), 7.41 (s), 7.98 (s), 8.22 (s), 8.45 (sh), 9.74 (s), 10.62 (s), and 13.60 (s) μ, while that for $(CF_3)_2CFNF_2$ contained bands at 7.45 (s, sh), 7.63 (m), 7.78 (s), 8.01 (vs), 8.18 (s), 8.53 (s), 9.86 (s), 10.56 (s), 10.80 (s), and 13.60 (s) μ. The F^{19} nmr spectrum of $(CF_3)_2CFNH_2$ consists of a triplet ($J_{CF_3NF_2}$ = 14 cps) each member of which is split into a doublet (J_{CE_3CF} = 3 cps) at ϕ 74.2, a broad peak at 170.5, and a broad peak at −22.7. The relative area ratios for these peaks are 6.1:1.1:2.0. The F^{19} nmr spectrum of $(CF_3)_2C{=}NF$ consists of two quadruplets ($J_{CF_3CF_3}$ = 8 cps and J_{CF_3NF} = 24 cps) at ϕ 63.6, two quadruplets ($J_{CF_3CF_3}$ = 8 cps and J_{CF_3NF} = 12 cps) at 66.8, and a broad peak at −48.3. The relative area ratios are 3.15:2.95:1.0.

Registry No.—$C_2F_5NF_2$, 354-80-3; $C_3F_7NF_2$, 423-32-5; CF_3NF_2, 335-01-3; $(CF_3)_2C{=}NCl$, 10181-78-9; $(CF_3)_2C{=}NF$, 2802-70-2; $(CF_3)_2CFNF_2$, 662-23-7; $(CF_3)_2C{=}NH$, 1645-75-6.

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Geminal Dihalides from the Oxidation of Pivalaldehyde Hydrazone by Interhalogens

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In the course of other studies in progress in this laboratory, we required a series of geminal dihalides with two different halogens bonded to the same carbon atom. A number of isolated examples of this type of compound have appeared in the literature. The synthetic methods heretofore used are illustrated by the photochemical bromination of chlorocyclohexane to 1-bromo-1-chlorocyclohexane,[1] peroxide-catalyzed addition of chlorodibromomethane to ethylene to yield 1,3-dibromo-1-chloropropane,[2] and iododecarboxylation of α-halo acids by means of lead tetraacetate and iodine.[3] We required a method of converting a carbonyl compound (RR′CO) to the dihalide (RR′CXY) which would be safe, experimentally simple, and applicable in principle to a wide variety of structural types. None of the preceding synthetic

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