pentyl, 25; cyclohexyl, 1.0; cycloheptyl, 120. We see that while there is indeed a pronounced minimum in rate with the C_6 sulfoxide the over-all spread in relative reactivities is considerably less than the spread in endocyclic to exocyclic elimination ratios observed with 1-methylcycloalkylamine oxides. Furthermore, although the C_5 amine oxide showed the largest IV/III ratio,[5b] the C_5 sulfoxide actually undergoes elimination about five times as slow as the C_7 compound. It would therefore appear that in the pyrolysis of the 1-methylcycloalkylamine oxides there are probably significant variations in *both* exocyclic and endocyclic elimination rates with ring size. For this reason we believe that the data in Table I for the sulfoxide pyrolysis represent a more accurate indicator of the general effect of ring size on elimination rate for Ei reactions of this type than do the IV/III ratios for the pyrolysis of the amine oxides II. The observed variations in the rate of pyrolysis are, of course, directly indicative of the variation with ring size in the free energy required to convert the cycloalkyl group from its preferred conformation in the starting sulfoxide to the conformation it must assume for transition state I.

Experimental Section

Cycloheptyl Phenyl Sulfoxide.—Technical grade cycloheptene (Aldrich Chemical Co.) was fractionally distilled using a spinning-band column, and the fraction boiling at 113–114° was collected. A 20-ml (0.172 mole) portion of this olefin was combined with 18 ml (0.177 mole) of thiophenol and 0.3 g of azobisisobutyronitrile, and the resulting solution was heated at 70–80° under nitrogen for 15 hr. At the end of that time 0.2 g of fresh azobisisobutyronitrile was introduced and heating was continued for an additional 16 hr. The final reaction mixture was fractionally distilled under reduced pressure, and, after recovery of considerable unreacted olefin and thiol, cycloheptyl phenyl sulfide (19.9 g, 56%) was collected, bp 179–181° (17 mm).

The sulfide (19.9 g) was dissolved in 350 ml of methanol, and a solution of 22 g of sodium metaperiodate in 100 ml of water was added to it at 0°. The resulting mixture was stirred at 0° for 10 hr. It was then filtered, and the filtrate was extracted several times with chloroform. The combined extracts were dried over anhydrous magnesium sulfate, and the chloroform was removed under reduced pressure to leave a red-brown oil. This was dissolved in hot petroleum ether (bp 30–60°) and cooled. The cycloheptyl phenyl sulfoxide which crystallized out was recrystallized several more times to give 6.2 g (28%) of pure sulfoxide, mp 44–45°.

Anal. Calcd for $C_{13}H_{18}OS$: C, 70.02; H, 8.03. Found: C, 70.09; H, 7.95.

Cyclohexyl Phenyl Sulfoxide.—Cyclohexyl phenyl sulfide[6] was synthesized in 65% yield from cyclohexane and thiophenol by a procedure analogous to that used for cycloheptyl phenyl sulfide, bp 160–165° (17 mm). The sulfide was then converted to the sulfoxide with sodium metaperiodate, using the general procedure outlined by Johnson and McCants.[7] The crude sulfoxide, obtained in 76% yield, was purified by several recrystallizations from petroleum ether, mp 62–64° (lit.[8] 61–64°).

Cyclopentyl Phenyl Sulfoxide.—Reaction of cyclopentene with thiophenol afforded cyclopentyl phenyl sulfide,[9] bp 149–150° (20 mm), in 77% yield. The sulfide was oxidized to the sulfoxide using the same procedure as for the cyclohexyl compound. A number of attempts to induce the sulfoxide to crystallize failed. Accordingly, it was purified by distillation in a molecular still. Infrared examination of the distillate suggested that the sulfoxide still contained some hydroxylic impurities. It was therefore treated with Linde 4A Molecular Sieves and redistilled in the molecular still. To further ensure the removal of hydroxylic impurities the distillate from this second distillation was treated with calcium hydride and distilled once more. The purified sulfoxide was obtained in about 30% yield based on the sulfide.

Anal. Calcd for $C_{11}H_{14}OS$: C, 67.98; H, 7.27. Found: C, 67.35; H, 7.25.

Procedure for Kinetic Runs.—Diglyme was purified by distilling it first from sodium metal at reduced pressure and then from lithium aluminum hydride at atmospheric pressure. The general procedure for the runs was patterned closely after that described by Walling and Bollyky.[3] The only changes made were the following: (1) *n*-hexane, rather than tetralin, was used as the internal standard in the solutions of the sulfoxide in diglyme; (2) after the contents of an ampoule had been poured into water, *n*-pentane, rather than *n*-hexane, was used as the extracting solvent; (3) a nitrile silicone column (XF-1150, Wilkens Instrument and Research) was used for glpc separation of the olefin and the internal standard.

At least six points plus an infinity time point were taken for each run. The final yield of olefin was from 85 to 100% of theory in every case. Unlike the situation noted by Walling and Bollyky[3] we did not observe any tendency for the experimental first-order rate constants to decrease with increasing conversion.

Registry No.—Cyclopentyl phenyl sulfoxide, 10181-73-4; cyclohexyl phenyl sulfoxide, 3324-82-1; cycloheptyl phenyl sulfoxide, 10181-75-6; cycloheptyl phenyl sulfide, 10181-76-7; cyclohexyl phenyl sulfide, 7570-92-5.

(6) R. W. Saville, *J. Chem. Soc.*, 2880 (1958).
(7) C. R. Johnson and D. McCants, Jr., *J. Am. Chem. Soc.*, **87**, 1109 (1965).
(8) B. Weibull, *Arkiv. Kemi*, **3**, 171 (1951).
(9) I. N. Tits-Skvortsova, S. Ya. Levina, A. I. Leonova, and T. A. Danilova, *Zh. Obshch. Khim.*, **22**, 135 (1952).

Low-Temperature Fluorination of Aliphatic Isocyanates and Carbamyl Halides

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The fluorination of many simple organic substrates has been studied in great detail by many workers.[1] Conditions chosen were such that little discrimination was shown by the fluorine in its site of attack. An interesting exception was Bockemuller[2] who was able to add fluorine cleanly to tetrachloroethylene at −80°. A similar, low-temperature approach has been shown to be selective and successful with a wide variety of olefins[3–5] as well as Schiff bases.[6] In view of the ease of addition of fluorine to the carbon–nitrogen double bond of Schiff bases, it was expected that a similar process with aliphatic isocyanates would also be successful.

Halogenation of aryl isocyanates has been examined briefly by Gumpert,[7] but no direct adducts were formed. However, the products found could be rationalized with the intermediacy of N-bromocarbamyl bromides. Aliphatic isocyanates were not con-

(1) For a comprehensive review, see (a) M. Hudicky, "Chemistry of Organic Fluorine Compounds," The Macmillan Co., New York, N. Y., 1963; (b) A. E. Pavlath and A. J. Leffler, "Aromatic Fluorine Compounds," American Chemical Society Monograph No. 155, Reinhold Publishing Corp., New York, N. Y., 1962; (c) A. M. Lovelace, D. A. Rausch, "Aliphatic Fluorine Compounds," W. Postelnek, American Chemical Society Monograph No. 138, Reinhold Publishing Corp., New York, N. Y., 1958.
(2) W. Bockemuller, *Ann.*, **506**, 20 (1933).
(3) R. F. Merritt and T. E. Stevens, *J. Am. Chem. Soc.*, **88**, 1822 (1966)
(4) R. F. Merritt, *J. Org. Chem.*, **31**, 3871 (1966).
(5) R. F. Merritt, *J. Am. Chem. Soc.*, **89**, 609 (1967).
(6) R. F. Merritt and F. A. Johnson, *J. Org. Chem.*, **32**, 416 (1967).
(7) F. Gumpert, *J. Prakt. Chem.*, **32**, 278 (1885).

sidered or examined. As N-haloaniline derivatives are prone to rearrange, this work is confined to the addition of fluorine to aliphatic isocyanates. The fluorination of methyl, ethyl, and *n*-propyl isocyanates led to the same types of products so that only the *n*-propyl case will be discussed in any detail.

Experimental Section

Apparatus.—The experimental apparatus and general procedure have been amply described in previous papers.[4,5]

Materials.—The isocyanates were obtained from the Corwin Co., and were distilled prior to use. The fluorine (Allied Chemical Corp.) was freed of HF by passage through a sodium fluoride scrubber and purity was established by vapor pressure measurements and oxidizing titer.

Fluorination of *n*-Propyl Isocyanate.—*n*-Propyl isocyanate (44 mmoles, 3.7 g) was dissolved in 30 ml of CCl_3F (Freon 11) and the HF scavenger (88 mmoles) was added. The exact yield of products depends on the scavenger employed. The mixture was degassed at −78° with vigorous stirring. The pure fluorine (44 mmoles) was slowly metered into the reactor by stopcock manipulation with care taken to keep the pressure below 100 mm. The products were vacuum distilled from the reactor and separated from the solvent by fractional condensation at −45° (chlorobenzene slush). Vapor phase chromatography (silicone 710 at 65°) was used to analyze and separate the first three of the four following products.

A. α-Fluoropropyl Isocyanate (I).—This compound was identified by infrared which showed bands for NCO (4.5 μ) and CF (9.0–9.9 μ). The proton nmr showed the proton geminal to the fluorine at δ 5.45 as two triplets (J_{FH} = 53 cps and J_{HH} = 6 cps). The remaining five protons are normal and consistent with the structure (yield, 10–60%).

B. α-Fluoropropyldifluoramine (II).—The infrared spectrum indicates the lack of functional group but shows CF (8.7 and 9.25μ) and NF (11.1 and 11.8 μ) group absorptions. The proton nmr spectrum was in excellent agreement with structure (II) in that the proton geminal to both the nitrogen and fluorine atoms contained the predicted 20 lines owing to extensive proton and fluorine coupling. The adjacent methylene was a complex doublet (J_{CFH} = 21 cps) centered at δ 1.72 and the remaining three methyl protons were a normal triplet centered at 1.09. The fluorine nmr spectrum exhibited CF as two overlapping triplets centered at φ 172.8 [φ = ppm (CCl_3F)]. The HF (geminal) coupling has the larger value of 52 cps. The nitrogen-bound fluorine appears as an asymmetric complex doublet centered at φ −23.2 (yield, 5–35%).

Anal. Calcd for $C_3H_6F_3N$: C, 31.86; H, 5.35; N, 12.39. Found: C, 32.00; H, 5.69; N, 12.39.

C. N-Propyl-N-fluorocarbamyl Fluoride (III).—The spectral properties were fully covered in the Discussion (yield, 0–40%).

Anal. Calcd for $C_4H_7F_2NO$: C, 39.02; H, 5.73. Found: C, 37.39; H, 5.51.

D. N-Propylcarbamyl Fluoride (IV).—After the volatile products were removed [bp <30° (0.1 mm)] the oily residue was extracted with ether from the inorganic HF scavenger. The ether was removed leaving a colorless liquid which decomposed to *n*-propylisocyanate and HF upon distillation. The liquid exhibited carbonyl fluoride absorption at 5.5–5.6 as well as N–H at 2.97 and CF at 8.1 μ. The fluorine nmr spectrum showed a single fluorine atom as a singlet at φ 15.9. Treatment of *n*-propyl isocyanate with anhydrous HF produced an oil with spectra identical with that seen above (yield, 0–35%).

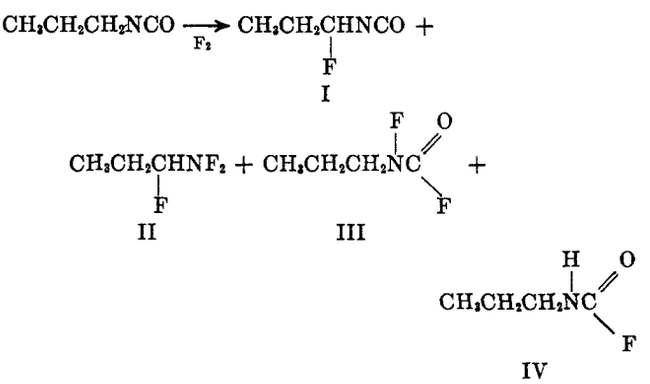
Fluorination of *n*-Propylcarbamyl Chloride.—The carbamyl chloride (44 mmole, NH, 2.95 and COCl, 5.68 μ) was prepared directly in the fluorination solvent (CCl_3F) with 46 mmoles of dry HCl. After removal of the excess HCl, sodium fluoride was added, the solution was cooled to −78°, and the fluorination was started. After consumption of 1 equiv of fluorine, the products were fractionated and the crude product (5.3 g, 87% yield) shown to contain ~90% *n*-propyl-N-fluorocarbamyl chloride by chlorine analysis and proton nmr. The only impurity was propyl isocyanate. The carbamyl chloride is heat sensitive and cannot withstand vapor phase chromatography. However, the infrared spectrum of the mixture verified the acyl chloride group at 5.5–5.6 and NF at 11.0 to 11.9 μ. The nmr spectra are treated fully in the Discussion section. Elemental analysis was obtained on the urea derivative formed with aniline, mp 63.0–63.5°.

Anal. Calcd for $C_{10}H_{13}FN_2O$: C, 61.21; H, 6.68; F, 9.68; N, 14.28. Found: C, 60.98; H, 6.71; F, 9.60; N, 13.39.

The nmr spectra (both proton and fluorine) are in accordance with structure of the derivative as N-propyl-N-fluoro-N′-phenylurea.

Discussion

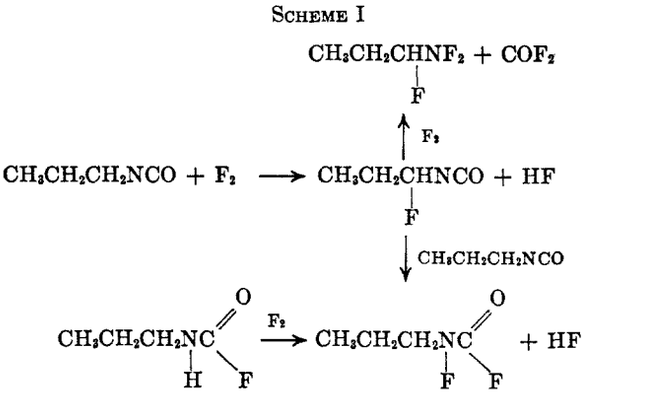
***n*-Propyl isocyanate** smoothly absorbed fluorine (1.0 equiv) at −78° when diluted with Freon 11 (CCl_3F). A slight excess of sodium fluoride was present to absorb any HF produced by side reaction. The products isolated were α-fluoropropyl isocyanate (I), α-fluoropropyldifluoramine (II), N-fluoro-N-propylcarbamyl fluoride (III), and N-propylcarbamyl fluoride (IV).



The yields of the N-fluorocarbamyl fluoride (III) were variable up to 40% as an upper limit. Attempts to remove the HF formed concurrently with I and II caused a further lowering of the yield of III. Sodium carbonate, the best HF scrubber found to date, completely quenched the formation of III and also carbamyl fluoride (IV). It is then apparent that IV is a precursor to III and that direct fluorination of the double bond is not occurring.[8]

Propylcarbamyl fluoride (IV) was prepared by addition of anhydrous HF to *n*-propyl isocyanate. Fluorination in the manner as described above gave the same spectrum of products as seen when starting from the isocyanate, and yields of III relative to I and II were increased. The proper reaction is then as shown in Scheme I.

SCHEME I



The products were identified by a combination of proton and fluorine nmr. The fluorine nmr spectrum

(8) R. E. Banks, R. N. Haszeldine, and J. P. Lalu, *Chem. Ind.* (London), 1803 (1964). The authors report the preparation of alkyl difluoramines, N-fluoroureas, and N-fluorocarbamates by fluorination of organic amides urethans, and ureas. The technique employed dilute aqueous solutions of substrate and fluorine–helium mixtures at 0–5°.

TABLE I

SPECTRAL PROPERTIES OF N-ALKYL-N-FLUOROCARBAMYL FLUORIDES

Compd	ν_{COF}, μ	$\delta_{\alpha\text{-CH}}$, ppm	J_{FH}, cps	J_{FF}, cps	ϕ_{NF}, ppm	ϕ_{CF}, ppm
$CH_3CH_2N(F)C(=O)F$	5.4, 5.5	3.83	30	44	+71.4	+18.9
$CH_3CH_2CH_2N(F)C(=O)F$	5.4, 5.5	3.76	31	44	+69.4	+20.0
$CH_3CH_2CH_2CH_2N(F)C(=O)F$	5.37, 5.48	....	28	56	+69.3	+20.7

of III, the major product, contained a sharp doublet centered at ϕ +20 (J_{FF} = 44 cps) which is assigned the carbonyl fluorine atom. The coupling constant is not unreasonable for coupling through the carbonyl to a single fluorine on the nitrogen. The NF absorption appears as two overlapping triplets centered at ϕ +69.4. The major coupling (J_{FF} = 44 cps) of the NF signal is caused by the fluorine–fluorine coupling whereas the minor splitting ($J_{FH} \sim 30$ cps) is due to two equivalent adjacent protons in the side chain. By spin decoupling the protons, the nitrogen-bound fluorine signal can be reduced from a double triplet to a doublet and no further.

The proton nmr is also consistent in that the methylene protons adjacent to the nitrogen appear as a pair of triplets centered at δ 3.75. The major (~30 cps) and minor (7 cps) coupling allow assignment to the methylene protons next to the nitrogen bearing a single fluorine atom. The remaining spectral features are those of the ethyl group which remained intact.

The spectral details of the remaining side products are outlined briefly in the Experimental Section. The fluorine spectra of all carbamyl fluorides were virtually identical in each case as listed in Table I above.

The successful fluorination of the carbamyl fluoride (IV) demanded extension to the carbamyl chloride as the latter is more cleanly prepared. *n*-Propylcarbamyl chloride (V) was formed from the isocyanate in the fluorination solution directly by adding 1 equiv of anhydrous HCl. This solution was fluorinated at −78° in the presence of sodium fluoride to produce a high yield of N-propyl-N-fluorocarbamyl chloride (VI). Trace amounts of propyl isocyanate were formed as a by-product.

$$F_2 + \underset{\text{V}}{CH_3CH_2CH_2N(H)C(=O)Cl} \longrightarrow \underset{\text{VI}}{CH_3CH_2CH_2N(F)C(=O)Cl} + HF$$

Compound VI was identified by its nmr spectrum in that the methylene protons adjacent to the nitrogen atom are shifted to δ 3.86 (*cf.* Table I, δ_{av} 3.79 carbamyl fluoride) and exhibit the characteristic coupling constant of 31 cps. The fluorine nmr exhibited the expected signal at ϕ +46.2 as a triplet (J_{FH} = 31 cps).

The carbamyl chloride is difficult to purify because of limited heat stability but was converted to the phenylurea derivative (VII) with aniline. The spectral and analytical results of derivative VII along with the isolation of aniline hydrochloride are in accord with the postulated structure.

$$CH_2CH_2CH_2N(F)C(=O)Cl + C_6H_5NH_2 \longrightarrow \underset{\text{VII}}{CH_3CH_2CH_2N(F)C(=O)NHC_6H_5}$$

Summary.—The fluorination of the CN double bonds of alkyl isocyanates does not involve direct addition but rather side-chain fluorination followed by substitution on nitrogen of the carbamyl fluoride by-product. Direct, low-temperature fluorination of carbamyl fluorides or chlorides provides a convenient synthetic procedure for N-fluorocarbamyl halides. Such halides are useful precursors to other N-fluoroureas and carbamates.

Registry No.—I, 10074-87-0; II, 10074-88-1; III, 10074-89-2; IV, 10074-90-5; *n*-propyl-N-fluorocarbamyl chloride, 10074-91-6; VII, 10074-92-7; N-ethyl-N-fluorocarbamyl fluoride, 10074-93-8; N-butyl-N-fluorocarbamyl fluoride, 10074-94-9.

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Some Reactions of the 4-(α,α-Dicyanomethylene) Derivatives of 1,2,3,4-Tetrahydroquinoline, 1-Methyl-1,4-dihydroquinoline, and 1-Methyl-6-methoxy-1,4-dihydroquinoline[1]

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It has been shown by Campaigne and co-workers[2,3] that the treatment of α-tetrylidenemalononitrile (1) and 6-methylthiochroman-4-ylidene malononitrile (2) with concentrated sulfuric acid produced the cyclized

(1) This work was supported by a Continental Oil Co. Fellowship and a Public Health Service Research Grant CA 02997-08 from the National Cancer Institute, National Institutes of Health.

(2) E. Campaigne, G. Bulbenko, W. Kreighbaum, and D. Maulding, *J. Org. Chem.*, **27**, 4428 (1962).

(3) E. Campaigne and C. DeWitt Blanton, Jr., *Tetrahedron Letters*, No. 36, 2489 (1964).