on a 3% FFAP on 46–60 Chrom W vpc column at 190° indicated two products. The minor component was assumed to be the epimeric acid and represented 10–30% of the mixture depending on reaction conditions. The acids were not separated but were converted quantitatively to their methyl esters with diazomethane. Separation of the esters on a 25% XF-1150 preparative column gave 14 mg of the major component and 3 mg of the minor one. The mass spectrum of the major ester, 5-carbomethoxytricyclo[4.1.0.0^{3,7}]heptane (**32**), showed a parent peak at *m/e* 152.

Anal. Calcd for $C_9H_{12}O_2$: C, 71.02; H, 7.95. Found: C, 70.78; H, 7.97.

The infrared spectrum (neat) of this ester was not superimposable on that of an authentic sample of 3-carbomethoxynortricyclanecarboxylic acid.[30] An nmr spectrum was obtained on a small amount of ester formed from a repetition of the degradation sequence. Although this sample contained approximately 10% impurity, the spectrum was similar to that of the original adduct and not to that of the corresponding nortricyclanecarboxylic ester.

An accurate mass measurement (found: *m/e* 152.0845. calcd: *m/e* 152.0834) of the minor ester component showed it to be isomeric with **32**.

Hydrogenation of 5-Carbomethoxytricyclo[4.1.0.0^{3,7}]heptane (32) to *endo*-2-Carbomethoxynorbornane (35). Into a 5-ml side-arm flask fitted with rubber septums was placed 20 mg of **32**, 4 mg of 5% Pd–C, and 3 ml of ether. The flask was flushed with hydrogen and a positive hydrogen pressure was introduced *via* a syringe. Vpc analysis on a 2% XF-1150 column indicated hydrogenation was 80% complete after overnight stirring. The catalyst was removed by centrifugation and 10 mg of fresh catalyst was added. Completion of hydrogenation in 20 min gave 12 mg of product which was purified by means of a 3% PDEAS (1/4 in. × 8 ft) vpc column at 86°. The nmr and infrared spectra were identical with those of an authentic sample of **35**. The nmr spectrum was obtained on an A-60-A spectrometer coupled with a transient averaging computer (27 scans, 250 sec each).

***endo*-2-Carbomethoxybicyclo[2.2.1]heptane (35).** A known sample of 1.0 g (7.25 mmol) of *endo*-5-norbornene-2-carboxylic acid was quantitatively hydrogenated over 80 mg of 5% Pd–C in 20 ml of ethanol in less than 1 hr. The saturated acid was converted to its methyl ester,[31] with diazomethane in ether. The nmr spectrum had a singlet at τ 6.63 (3H), a broad multiplet at τ 7.30–8.47 (3 H), and a multiplet at τ 8.47–9.47 (8 H).

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Direct Fluorination of Ureas[1]

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Contribution of the Environmental Systems Division, Aerojet-General Corporation, Azusa, California. *Received October 1, 1969*

Abstract: Fluorourea and N,N-difluorourea were prepared by the direct fluorination of aqueous solutions or acetonitrile suspensions of urea. Fluorourea decomposed in aqueous solution to give azodicarbondiamide, and in the presence of urea, biurea. Fluorourea reacted with sulfuric acid to give fluorammonium ion, ammonium sulfite, or hydrazine sulfate, depending on reaction conditions. Properties of N,N-difluorourea are described. The fluorination of alkylureas gave difluoraminoalkanes and N-alkyl-N′,N′-difluoroureas, showing that the second fluorination step takes place at the same nitrogen as the first, whether a hydrogen or an acyl group is displaced. The fluorination of cyclic N,N′-disubstituted ureas gave ω-(difluoramino) isocyanates and carbamyl fluorides.

The fluorination of solid urea was reported by Glemser and Lüdemann[2] to give biurea and HF, along with some NH_3, COF_2, CO_2, and biuret. Although no NF compounds were identified, fluorourea was postulated to be an intermediate. Subsequently, Lawton, *et al.*,[3,4] identified N,N-difluorourea as one of the products of fluorination under similar conditions, as well as CF_4, $(CF_3)_2NF$, $(CF_3)_3N$, HNF_2, and HCN. Less than 1 mole of fluorine per mole of urea was used.

The fluorination of aqueous solutions of urea was found in the present work[5] to be a more readily controllable reaction to produce N,N-difluorourea. This solution fluorination technique has also been applied to carbamates,[6,7] amides,[8] and nitronate salts.[9] The moderating effect of the solvent allowed the use of 2 moles of fluorine, and a 74% yield of N,N-difluorourea was isolated by ether extraction. N,N-Difluorourea was also prepared by the fluorination of a suspension of urea in acetonitrile.

N,N-Difluorourea must be handled with caution, as it is a sensitive explosive and is toxic, but it is not changed on prolonged storage at room temperature. A sample was recovered almost quantitatively after 5 hr in toluene at 110°. The compound is a white solid, mp 41–41.5°, which was isolated in two crystalline forms, platelets by sublimation and needles by crystallization from halogenated solvents. The platelet form is hygroscopic whereas the needle form is not affected by atmospheric moisture. The amino group of N,N-difluorourea is unreactive, and further fluorination did not yield more highly fluorinated ureas.[10] No reaction took place in 5 hr between difluorourea and bromine in carbon tetrachloride at 60°.

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The crude aqueous fluorination product containing N,N-difluorourea (approximately 1 *M*) and the by-product, HF, can be stored for about 1 week at 0° without noticeable decomposition, and for several months frozen at −20°. This solution is hydrolyzed rapidly at 60–90° in the presence of sulfuric acid, and this reagent has become a widely used source of difluoramine.[5,11–15] The reaction of the crude N,N-difluorourea solution with base has also been reported to be a convenient synthesis method for difluorodiazine.[15]

The expected intermediate in the formation of N,N-difluorourea, fluorourea, has not been isolated previously. With this objective an equimolar amount of fluorine was passed into an aqueous urea solution. Even under these conditions, the major product was N,N-difluorourea, but a 20% yield of fluorourea was isolated by extraction with ether and recrystallization from methylene chloride. Fluorourea is thus fluorinated more rapidly than urea in aqueous solutions. Acetonitrile was also used as a fluorination solvent, with the advantages of allowing lower reaction temperatures and more convenient product isolation. The fluorination of a suspension of urea in acetonitrile, using 0.6 mol of fluorine, thus gave a 53% yield of fluorourea based on fluorine.

$$NH_2CNH_2 + F_2 \longrightarrow NH_2CNHF + HF \xrightarrow{F_2} NH_2CNF_2$$

Fluorourea is a white solid, mp 56–57°. The proton nmr spectrum in tetrahydrofuran consists of broad signals at δ 6.67 and 10.66 (area ratio 2:1) and the fluorine signal (+34.22 from trifluoroacetic acid) also shows no resolution. The lack of observable H–F coupling indicates that the hydrogen adjacent to the fluorine is highly labile.

Solid fluorourea was stable to prolonged storage at −20°, but aqueous solutions decomposed at ambient temperature, and an orange solid, identified as azodicarbondiamide, began to deposit within 20 min. The same compound was formed from fluorourea in refluxing ethanol. However aqueous solutions of fluorourea with urea added gave no azodicarbondiamide, but, rather, a white solid which was shown to be biurea. These reactions might take place by direct

$$FNHCNH_2 \longrightarrow NH_2CN{=}NCNH_2$$

$$FNHCNH_2 \xrightarrow{NH_2CONH_2} NH_2CNHNHCNH_2$$

displacement of fluoride by the nucleophiles, fluorourea and urea, respectively, or through a cationic intermediate (or nitrene) resulting from initial loss of fluoride. The reaction of fluorourea with urea is in accord with the postulation of Glemser and Lüdemann.[2]

Fluorourea was also hydrolyzed with sulfuric acid, and the nature of the reaction varied greatly with the experimental conditions. A large excess of concentrated sulfuric acid at 40–50° gave fluorammonium ion, identified by its nmr spectrum.[16] However, when a 2:1 mole ratio of concentrated sulfuric acid to fluorourea was used at 35°, hydrazine sulfate and ammonium sulfite were isolated. At 40°, an otherwise similar reaction resulted in a fume-off. The use of a large excess of 65% sulfuric acid at 60° also resulted in the isolation of ammonium sulfite. Fluorourea reacted with ketones and aldehydes in the presence of sulfuric acid to give amides and nitriles, respectively, the same products that were obtained from fluorammonium salts.[16]

The hydrolysis of fluorourea thus provides a reducing agent sufficiently powerful to reduce sulfuric acid. Possible structures for this reducing agent include fluoramine and its self-condensation product, diimide. It has been reported, however, that diimide does not reduce oxidized sulfur compounds.[17] Evidence has been presented that in the absence of an excess of strong acid, fluorammonium salts can dissociate to a small extent, to fluoramine in organic solvents.[16] Since difluoramine can function as a reducing agent,[18,19] fluoramine would be expected to be a strong reducing agent, but other transient species could be involved. The reduction of sulfuric acid was also reported in the preparation of hydroxylamine from hydrazoic acid.[20]

The formation of the hydrazine salt is an example of the Raschig reaction which is unusual in that alkaline conditions are normally required. Hydrazine has been produced from chlorourea and base but the mechanism is not known.[21,22]

Only one report of the fluorination of substituted ureas has appeared. Banks, Haszeldine, and Lalu[14] reported that the aqueous fluorination of N,N′-dimethylurea gave difluoraminomethane and N-fluoro-N,N′-dimethylurea. N,N′-Diethylurea gave the analogous products but trimethylurea yielded only difluoraminomethane. Fluorinations of monosubstituted ureas have not been reported previously.

Results of the aqueous fluorination of monosubstituted ureas and cyclic disubstituted ureas in the present work are presented in Table I. The fluorination of simple alkylureas yielded difluoraminoalkanes and N-alkyl-N′,N′-difluoroureas, and in the case of propylurea, the N-alkyl-N-fluorourea, a solid, was also isolated. The difluoraminoalkanes, difluoraminoethane,[23] 1-difluoraminopropane,[24] difluoraminocyclohexane,[11] and 1,3-bis(difluoramino)propane,[7] were prepared previously by other methods. A mixture of ethyl difluoraminoacetate and its dehydrofluorination product, ethyl cyanoformate, was also isolated previously from the fluorination of ethyl N-carbomethoxyglycine.[7] The mixture could not be separated without further dehydrofluorination of ethyl difluoraminoacetate taking place.

The failure to isolate N,N′-difluoroureas is in accord with observations that in fluorinations of carbamates[6,7]

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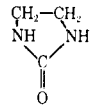
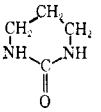
Table I. Fluorination of Substituted Ureas

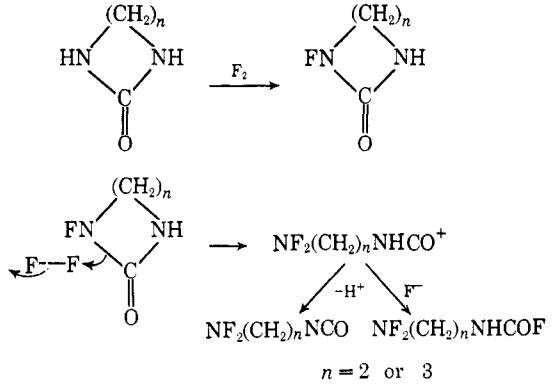
Starting material	Products	Bp (mm) or mp, °C
$C_2H_5NHCONH_2$	$C_2H_5NF_2$	
	$C_2H_5NHCONF_2$	30–31 (0.5)
$CH_3CH_2CH_2NHCONH_2$	$CH_3CH_2CH_2NF_2$	45 (760)
	$CH_3CH_2CH_2NFCONH_2$	78
	$CH_3CH_2CH_2NHCONF_2$	40 (0.1)
$C_6H_{11}NHCONH_2$	$C_6H_{11}NF_2$	35–42 (26)[a]
	$C_6H_{11}NCO$	28–30 (0.1)
	$C_6H_{11}NHCONF_2$	59–60
$C_2H_5OCCH_2NHCONH_2$ (O)	$C_2H_5OCCH_2NF_2$ (O)	32–42 (25)
	C_2H_5OCCN (O)	
	$C_2H_5OCCH_2NHCONF_2$ (O)	66–67 (0.1)
	$NF_2CH_2CH_2NHCOF$	39–40 (0.05)
	$NF_2CH_2CH_2CH_2NF_2$	38–50 (25)[a]
	$NF_2CH_2CH_2C{\equiv}N$	58–60 (25)[b]
	$NF_2CH_2CH_2CH_2NCO$	
	$NF_2CH_2CH_2CH_2NHCOF$	65–66 (0.1)

[a] Impure product identified by spectral comparison with an authentic sample. [b] Codistilled, separated by gas chromatography.

and amides,[8] monofluorinated products undergo further fluorination, with displacement of either hydrogens or acyl groups, more rapidly than the starting materials do. Thus the initial fluorination products of alkylureas are N-alkyl-N-fluoroureas and N-alkyl-N′-fluoroureas, which undergo further fluorination on the same nitrogen to give alkyldifluoramines and N-alkyl-N′,N′-difluoroureas, respectively. The second fluorination step takes place at the same nitrogen as the first, whether hydrogen or an acyl group is displaced.

$$RNHCONH_2 \xrightarrow{F_2} \underset{\downarrow}{RNFCONH_2} + \underset{\downarrow}{RNHCONHF}$$
$$RNF_2 \qquad RNHCONF_2$$

The formation of carbamyl fluorides and isocyanate from the fluorinations of 2-imidazolidone and tetrahydropyrimidone are rationalized as electrophilic displacements of acylium ions from the monofluorinated intermediates. The resulting aminoacylium ions can react with fluoride to give the carbonyl fluorides or lose



a proton to give isocyanate. This mechanism is similar to that postulated for the formation of ω-difluoramino acid fluorides from the fluorination of lactams.[6]

Experimental Section

General. Fluorinations were conducted in a glass standard taper three-necked flask fitted with a mechanical stirrer, a glass tube extending below the liquid level used as a gas inlet, and a standard taper thermometer well with an opening for gas exit. Standard fluorine-handling hardware[25] was used, and the fluorine (Allied Chemical Corp.) was diluted threefold to sixfold with nitrogen. Within this dilution range, the fluorine concentration was not found to be critical. The fluorinations were exothermic and the rate of fluorine input was such as to maintain the solution temperatures within the described limits. Vigorous stirring was used. Exit gases were vented through an aqueous potassium iodide trap to destroy unreacted fluorine and to provide visual evidence for completion of the fluorination. Safety shielding is required for the fluorinations and for handling NF compounds.

N,N-Difluorourea. A solution of 60 g (1.0 mol) of urea in 800 ml of water was treated with 1 mol of diluted fluorine at 0–5° over an 8-hr period. The product was extracted with four 200-ml portions of ether, and dried over sodium sulfate, and a 5% aliquot was stripped of solvent at 25 mm. The residue was dried for several minutes at 3 mm and was then sublimed at 0.1 mm onto a −78° condenser to give 3.55 g (74% yield) of colorless platelets, mp 41–41.5°.[3]

Anal. Calcd for $CH_2N_2F_2O$: C, 12.50; H, 2.08; N, 29.17; F, 39.57. Found: C, 12.23; H, 2.35; N, 28.7; F, 38.8.

Fluorination of a suspension of 24 g (0.40 mol) of urea in 200 ml of acetonitrile (0.8 mol of fluorine, −15 to −20°, 2.5 hr), removal of the bulk of solvent from a 25% aliquot (25 mm), and recrystallization from methylene chloride and carbon tetrachloride gave 5.0 g (52% yield) of white needles, mp 41–41.5°.

The two crystalline forms were interconvertible, and gave identical spectra in solution.[3,14] The platelet form was quite hygroscopic, whereas the needle form was not.

Fluorourea. A suspension of 60 g (1.0 mol) of urea in 300 ml of acetonitrile was fluorinated until a clear solution was formed (0.6 mol of fluorine, −5°, 2 hr). Addition of 500 ml of methylene chloride gave a heavy oil which was separated, washed with 50 ml of methylene chloride, and recrystallized from 2.5 l. of methylene chloride to give 25 g (53% yield) of fluorourea, mp 56–57°.

(25) Allied Chemical Corp., Data Sheet PD-TA-85413A.

Anal. Calcd for CH_3N_2OF: C, 15.39; H, 3.88; N, 35.89; F, 24.34. Found: C, 15.31; H, 4.20; N, 35.80; F, 23.7.

The proton nmr spectrum in tetrahydrofuran consisted of two broadened signals at δ 6.67 and 10.66 (area ratio 2:1), and the fluorine spectrum consisted of a singlet at +34.22 ppm from external trifluoroacetic acid.

The fluorination of aqueous urea (as in the N,N-difluorourea synthesis) with 1.0 mol of fluorine at 0–5° gave, after extraction with ether and recrystallization from methylene chloride, a 20% yield of fluorourea.

Azodicarbondiamide. A solution of 3.0 g (0.038 mol) of fluorourea in 20 ml of absolute ethanol was refluxed for 2.5 hr and was then cooled to room temperature. The precipitate was filtered and washed with ethanol and ether to give 0.3 g of azodicarbondiamide, an orange solid, mp 260–265° dec (lit.[26] mp 224–230°).

Anal. Calcd for $C_2H_4N_4O_2$: C, 20.7; H, 3.45; N, 48.3. Found: C, 20.8; H, 3.31; N, 48.6.

From the filtrate 2.5 g of fluorourea was recovered on removal of the solvent.

A solution of 1.6 g (0.02 mol) of fluorourea in 25 ml of water was allowed to stand at ambient temperature. An orange precipitate began to form in 20 min. Azodicarbondiamide (0.1 g) was isolated after 5 days by filtration and washing with ethanol and ether.

Anal. Calcd for $C_2H_4N_4O_2$: C, 20.69; H, 3.45; N, 48.3. Found: C, 20.83; H, 3.34; N, 48.21.

Biurea. An aqueous fluorourea solution as above containing 3.0 g (0.05 mol) of urea gave 0.4 g of biurea, a white solid, mp 265° dec (lit.[27] mp 246–258° dec).

Anal. Calcd for $C_2H_6N_4O_2$: C, 20.33; H, 5.08; N, 47.5. Found: C, 20.07; H, 5.02; N, 47.29.

Reaction of Fluorourea with Sulfuric Acid. A solution of 0.3 g of fluorourea in 3.0 g of concentrated sulfuric acid was heated at 40–50° for 10 min. The fluorine nmr spectrum of the resulting solution was identical with that reported for fluorammonium bisulfate.[16]

A solution of 2.0 g (0.0026 mol) of fluorourea in 20 ml of 65% sulfuric acid was heated at 60° until gas evolution ceased (1 hr). The solution was cooled to 25° and diluted with 50 ml of ethanol. A white solid separated, which was washed with ethanol and with ether and recrystallized from aqueous ethanol to give 1.5 g (30% yield) of ammonium sulfite hydrate, mp 265–270° dec (same mixture melting point with an authentic sample), also identified by its ir spectrum.

A solution of 1.6 g (0.020 mol) of fluorourea in 4.0 g (0.04 mol) of concentrated sulfuric acid was heated at 35° with magnetic stirring. After 30 min foaming was observed and the mixture was cooled to 30° and 25 ml of ethanol was added. The precipitate was recrystallized from water to give 0.9 g of hydrazine sulfate, mp 254°. Dilution of the filtrate with 50 ml of ether and recrystallization of the resulting precipitate gave 0.85 g of ammonium sulfate hydrate. A similar reaction at 40° resulted in a fume-off.

Fluorination of Ethylurea. Fluorination of 13.2 g (0.15 mol) of ethylurea in 350 ml of water (0–5°, 0.35 mol of fluorine, 2 hr) gave 6 g (49% yield) of difluoraminoethane identified by its infrared spectrum.[23] The compound was isolated from the exit gas in a −78° trap and was purified by trap-to-trap distillation. Extraction of the aqueous solution with methylene chloride gave 3.0 g (16% yield) of N,N-difluoro-N′-ethylurea, bp 30–31° (0.5 mm), $n^{25}D$ 1.3978.

Anal. Calcd for $C_3H_6N_2F_2O$: C, 29.04; H, 4.88; N, 22.58; F, 30.64. Found: C, 29.20; H, 5.15; N, 22.3; F, 29.5.

Fluorination of Propylurea. Fluorination of 102 g (1.0 mol) of propylurea in 700 ml of water (1.5 mol of fluorine, 6 hr, 0–5°) gave 15 g (0.16 mol) of difluoroaminopropane, bp 45°, which was condensed from the exit gas in a −78° trap.

Anal. Calcd for $C_3H_7NF_2$: C, 37.9; H, 7.4; N, 14.7; F, 39.95. Found: C, 37.8; H, 7.4; N, 14.7; F, 40.0.

The infrared spectrum showed bands in the NF region at (μ) 9.87 (m), 10.11 (m), 10.8 (sh), 11.0 (m), 11.34 (s), and 12.3 (vs).

The aqueous mixture was extracted with five 50-ml portions of methylene chloride and five 50-ml portions of ether. Distillation of the dried extracts gave 8.0 g (0.065 mol) of N,N-difluoro-N′-propylurea, bp 40° (0.1 mm), $n^{25}D$ 1.4045, and 4.0 g of N-fluoro-N-propylurea, bp 40–50° (0.1 mm). Recrystallization of the latter from carbon tetrachloride gave 3.0 g (0.025 mol), mp 78°.

The proton nmr spectrum of N-fluoro-N-propylurea ($CDCl_3$ solution) consisted of a triplet at δ 0.99 for CH_3, a sextet at δ 1.74 for $CH_3CH_2CH_2$–, a doublet of triplets (J_{HF} = 39.2 cps) at δ 3.66 for CH_3CH_2NF, and a broad NH signal at δ 6.04. The fluorine spectrum consisted of a triplet (J = 39.7 cps) at ϕ^* +66.7. The infrared spectrum showed carbonyl bands at 5.85 and 6.38 μ.

The proton nmr spectrum of N,N-difluoro-N′-propylurea (CCl_4 solution) consisted of a triplet at δ 0.99 for CH_3, a sextet at δ 1.65 for $CH_3CH_2CH_2$, a slightly broadened quartet at δ 3.29 for $-CH_2-CH_2NH-$, and a broadened signal at δ 7.07 for NH. The fluorine spectrum consisted of a broadened singlet at ϕ^* −32.64 for NF_2.

Anal. Calcd for $C_4H_8NF_2O$: C, 34.78; H, 5.80; N, 20.3; F, 27.5. Found: C, 34.61; H, 5.90; N, 20.1; F, 27.8.

Fluorination of Cyclohexylurea. Fluorination of a suspension of 27.6 g (0.20 mol) of cyclohexylurea in 600 ml of water (0.8 mol of fluorine, 0–5°, 3.5 hr, extraction with methylene chloride, and distillation gave 5.5 g of impure difluoraminocyclohexane,[11] bp 35–42° (26 mm), 3.5 g of cyclohexyl isocyanate,[8] bp 28–30° (0.1 mm), and 9.0 g of crude N,N-difluorocyclohexylurea, bp 20–30° (0.1 mm). The latter crystallized in the receiver, and was recrystallized from heptane to give 8.3 g (25% yield) of white needles, mp 59–60°.

Anal. Calcd for $C_6H_{11}N_2F_2O$: C, 47.18; H, 6.79; N, 15.69; F, 21.33. Found: C, 46.83; H, 6.91; N, 15.4; F, 22.5.

The fluorine nmr spectrum (CCl_4 solution) consisted of a singlet at ϕ^* −32.8.

Fluorination of Ethyl Hydantoate. Fluorination of a suspension of 73 g (0.50 mol) of ethyl hydantoate in 650 ml of water (1.0 mol of fluorine, 2 hr, 0–5°) and extraction with methylene chloride gave 17.0 g of a 45:55 mixture of ethyl cyanoformate and ethyl difluoraminoacetate,[7] bp 32–42° (25 mm), and 15 g (16.5% yield) of ethyl N,N-difluorohydantoate, bp 66–67° (0.1 mm).

Anal. Calcd for $C_5H_8N_2F_2O_3$: C, 32.97; H, 4.40; N, 15.4; F, 20.9. Found: C, 33.02; H, 4.50; N, 15.5; F, 20.7.

The proton nmr spectrum (CCl_4 solution) consisted of a triplet at δ 1.31 and a quartet at δ 4.20 for the ethyl, a doublet at δ 3.99 for $-NHCH_2CO-$, and a broadened signal at δ 7.09 for NH. The fluorine spectrum consisted of a broadened singlet at ϕ^* −32.4.

Fluorination of 2-Imidazolidone. A solution of 43 g (0.50 mol) of 2-imidazolidone in 650 ml of water was fluorinated (1.0 mol of fluorine, 0–5°, 2 hr), and extracted with five 50-ml portions of methylene chloride. The product was treated with sodium sulfate and solid sodium bicarbonate and was distilled to give 18 g (25% yield) of 2-difluoraminoethylcarbamyl fluoride, bp 39–40° (0.05 mm).

Anal. Calcd for $C_3H_5N_2F_3O$: C, 25.3; H, 3.55; N, 19.7; F, 40.1. Found: C, 25.4; H, 3.40; N, 19.5; F, 39.7.

The proton nmr spectrum ($CDCl_3$ solution) showed a broad NH signal at δ 5.93, and a triplet of triplets (J_{HF} = 29 cps) for $NF_2-CH_2CH_2$ at δ 3.71, the central member of which was overlapped by the other methylene signal. The fluorine spectrum showed a triplet (J = 27.5 cps) at ϕ^* −53.67 for NF_2 and a doublet (J = 7.4 cps) at ϕ^* +14.73 for –NHCOF. The infrared spectrum showed NH (3.0 μ), C=O (5.6 μ), and bands in the NF region (μ) 10.3 (m), and 10.55 (m), 11.0 (w), 12.0 (s), and 12.5 (w).

Fluorination of Tetrahydro-2-pyrimidone. A solution of 70 g (0.70 mol) of tetrahydro-2-pyrimidone in 650 ml of water was allowed to react with 3.0 ml of fluorine at 0–5° for 1.5 hr. The product was extracted with four 35-ml portions of methylene chloride and the resulting solution was dried over sodium sulfate, treated with solid sodium bicarbonate, filtered, and distilled through a Holzman[28] column to give 8.0 g (6% yield) of 80% pure (gc analysis) 1,3-bis(difluoroamino)propane,[7] bp 38–50° (25 mm), 9.5 g of a mixture containing 40% 3-difluoraminopropionitrile (5% yield) and 50% 3-difluoraminopropyl isocyanate (5% yield),[8] bp 58–60° (25 mm), and 25 g (21% yield) of 3-difluoraminopropylcarbamyl fluoride, bp 65–66° (0.1 mm). The nitrile and isocyanate were separated by gas chromatography (retention times, 35 and 18 min, respectively, 8 ft × 0.25 in. column of 10% diethylene glycol adipate on Fluoropak 80, 100°, 50 cc of He/min).

The proton nmr spectrum of 3-difluoroaminopropionitrile in 1:1 $CDCl_3$–CCl_4) consisted of a triplet (J = 8 cps) at δ 2.80 and a triplet of triplets (J_{HH} = 8 cps, J_{HF} = 26.9 cps) at δ 3.81. The fluorine spectrum showed a triplet at ϕ^* −51.66. The infrared spectrum showed C≡N at 4.45 μ (m) and bands in the NF region at (μ) 9.70 (m), 9.90 (m), 10.51 (s), 11.28 (m), 11.5 (w), 12.0 (s), and 12.7 (s).

Anal. Calcd for $C_3H_4N_2F_2$: C, 33.96; H, 3.80; N, 26.41; F, 35.84. Found: C, 33.70; H, 3.91; N, 26.3; F, 37.0.

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(28) Vacuum jacketed 25 × 0.6 cm column with a platinum wire spiral, four turns per cm.

The proton nmr spectrum of 3-difluoroaminopropylcarbamyl fluoride ($CDCl_3$ solution) consisted of a quintet (J = 7 cps) at δ 1.98 for $CH_2CH_2CH_2$, a broad signal at δ 5.68 for NH, a triplet of triplets (J_{HF} = 29.3 cps) at δ 3.58 for NF_2CH_2CH, and quartet at δ 3.34 for CH_2CH_2NH. The fluorine spectrum showed a triplet (J = 28.5 cps) at ϕ^* −55.3 for NF_2 and a doublet (J = 7.3 cps) at ϕ^* +14.59 (-NHCOF). The infrared spectrum showed NH at 3.0 μ and C=O at 5.60 μ.

Anal. Calcd for $C_4H_7N_2F_3O$: C, 30.77; H, 4.52; N, 17.95; F, 36.51. Found: C, 30.99; H, 4.60; N, 17.5; F, 36.0.

Rates and Equilibria in the Interconversion of Allylic Sulfoxides and Sulfenates[1]

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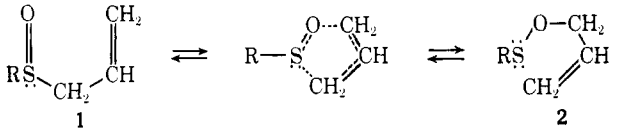
Abstract: Activation parameters for the thermal racemization of allyl *p*-trifluoromethylphenyl sulfoxide ($\Delta H^{\pm}$ = 21 kcal/mol, $\Delta S^{\pm}$ = −8 eu) and the thermal rearrangement of allyl *p*-trifluoromethylbenzenesulfenate ($\Delta H^{\pm}$ = 19 kcal/mol, $\Delta S^{\pm}$ = −5 eu) in combination provide the first complete description of the energy surface for a [2,3] sigmatropic rearrangement. A study of substituent and solvent effects on the rate of racemization of allyl sulfoxides and on the sulfenate–sulfoxide equilibrium constant has revealed that electron-withdrawing groups and nonpolar solvents accelerate the racemization and increase the proportion of sulfenate at equilibrium. It is suggested that these effects originate in changes in the ground-state energy of the sulfoxide.

The thermal racemization of allyl sulfoxides (**1**)[2,3] and the thermal rearrangement of allyl sulfenates (**2**)[3,4] are both manifestations of the same process: the interconversion of **1** and **2** by way of a five-membered ring transition state. The reaction is concerted, reversible, and intramolecular, and may be characterized as a [2,3] sigmatropic process.[5] However,



1 **2**

a, R = 4-$CH_3C_6H_4$
b, R = 4-$CF_3C_6H_4$
c, R = 4-$NO_2C_6H_4$
d, R = 2,4-$(NO_2)_2C_6H_3$
e, R = 2-$NO_2C_6H_4$
f, R = C_6F_5

although in one case, that of **1a**, rates and activation parameters were measured[2,3] for the racemization reaction (*i.e.*, for the conversion of **1** to **2**), corresponding parameters for the reverse process, the isomerization of **2** to **1**, have been lacking. The present work was undertaken in order to fill this gap in our information, and thus to complete the description of the energy surface for the interconversion reaction.

While rearrangement of **2a** is too fast for the convenient measurement of reliable rate constants, it was found that **2b** and **2c** present fewer difficulties in this respect and may be handled at temperatures near −20° without extensive rearrangement. At temperatures above 0°, rearrangement to the corresponding sulfoxides, **1b** and **1c**, proceeds at rates which can be followed conveniently by ultraviolet absorption spectroscopy, since absorption bands of **2** are located at substantially longer wavelengths than the corresponding bands of **1**. The reliability of these measurements is vouchsafed by the presence of isosbestic points, which indicate the absence of side reactions, and good precision is obtained by the appreciable decrease in absorbance which accompanies the change from sulfenate to sulfoxide, even at the low concentrations (*ca.* 10^{-4} *M*) employed. The rearrangement of **2b** and **2c**, like that of **2a**, is essentially complete (>99%), to judge by the spectroscopic (ir, nmr, uv) evidence. Benzene was chosen as the solvent in order to provide a match for the racemization studies described below. Our findings are summarized in Table I. It should be noted that the negative entropy of activation is consistent with the cyclic concerted mechanism of the rearrangement.[3]

Table I. First-Order Rate Constants and Activation Parameters for the Rearrangement of Allyl Arenesulfenates (**2**) to Allyl Aryl Sulfoxides (**1**) in Benzene

Sulfenate	T, °C	$k_{rearr} \times 10^4$, sec^{-1}	Activation parameters
2b	6.9	10.8 ± 0.3	$\Delta H^{\pm}$, 18.8 ± 0.3 kcal/mol
	12.4	20.2 ± 0.6	$\Delta S^{\pm}$, −4.8 ± 0.1 eu
	20.1	48.4 ± 0.1	
	25.1	92.3 ± 0.3	
2c	6.8	9.1 ± 0.1	$\Delta H^{\pm}$, 17.6 ± 0.3 kcal/mol
	12.3	16.8 ± 0.2	$\Delta S^{\pm}$, −9.6 ± 0.1 eu
	20.0	40.0 ± 0.6	

The counterpart for the rearrangement of **2b**, *i.e.*, the racemization of **1b**, was studied as part of a general

(1) This work was supported by the Air Force Office of Scientific Research under Grant No. AF-AFOSR-1188-B.

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