believed to be accurate to ±1°. The chemical-shift differences (Table IV) obtained from nmr spectra of $CFCl_3$ solutions of **2** and **3** were essentially unchanged with the weight per cent of **2** varied from 30 to 75 and that of **3** varied from 35 to 75.

Perfluoro-4-chloro-1,2-oxazetidine (5) was prepared by hydrolysis of compound **6** as described previously.[8]

Perfluoro-4-chloro-2-fluoro-1,2-oxazetidine (2).—A 2-l. steel reactor (passivated with fluorine) was charged with NaF pellets (10 g), perfluoro-4-chloro-1,2-oxazetidine (**5**, 5.0 g, 34 mmol), and fluorine (43 mmol) at −196°. The mixture was allowed to react for 5 hr and the excess fluorine was pumped off at −196°. Product **2** was collected as one peak by preparative glpc at 20°. Compound **3** could also be obtained from the reaction mixture, since it was initially present as an impurity in **5**. The infrared spectrum of **2** showed bands at 7.30 (s, ring), 7.75 (s), 8.3 (shoulder), 8.5 (s), 8.95 (s), 9.4 (s), 10.8 (w), and 12.3 μ (s). The mass spectrum of **2** showed peaks at m/e (rel intensity, ion) 130 (9.3, $C_2F_4NO^+$), 118 and 116 (10.6, 30.9, $C_2F_3Cl^+$), 97 (2.1, $C_2F_3O^+$), 87 and 85 (1.8, 5.3, CF_2Cl^+), 83 (4.6, CF_3N^+), 69 (10.1, CF_3^+), 66 (6.9, CF_2O^+), 64 (7.4, CF_2N^+), 50 (20.4, CF_2^+), 47 (100, COF^+), 45 (9.0, CFN^+), 37 and 35 (4.3, 14.9, Cl^+), 31 (62.8, CF^+), 30 (91.5, NO^+), and 26 (4.4, CN^+).

Anal. Calcd for C_2F_4ClNO: C, 14.52; H, 0.00; F, 45.92; N, 8.46. Found: C, 14.55; H, 0.00; F, 45.67; N, 8.10.

Perfluoro-2,4-dichloro-1,2-oxazetidine (3) was prepared by reaction of **5** (5.0 g, 34 mmol) and chlorine (32 mmol) in a 2-l.

flask at room temperature for 5 hr. Product **3** was collected as one peak by preparative glpc at 20°. Its infrared spectrum showed bands at 7.40 (s, ring), 7.94 (s), 8.5 (s), 9.0 (s), 9.8 (s), 12.7 (m), and 13.3–13.4 μ (vs, broad). The mass spectrum of **3** showed peaks at m/e (rel intensity, ion) 181 (trace, C_2F_3-Cl_2NO^+), 129 and 127 (0.6, 1.9, $C_2F_2ClNO^+$), 118 and 116 (6.2, 21.9, $C_2F_3Cl^+$), 101 and 99 (2.2, 7.5, CF_2NCl^+), 87 and 85 (1.1, 3.6, CF_2Cl^+), 82 and 80 (2.7, 7.5, $CFClO^+$), 69 (7.8, CF_3^+), 66 (2.2, CF_2O^+), 65 (0.6, $COCl^+$), 64 (8.0, CF_2N^+), 63 (2.6, $COCl^+$ or $CNCl^+$), 61 (2.4, $CNCl^+$), 50 (13.5, CF_2^+), 51 (2.4, CCl^+), 49 (9.6, NOF or CCl^+), 47 (100, COF^+), 45 (6.0, CFN^+), 37 and 35 (8.5, 30, Cl^+), 31 (40.6, CF^+), 30 (90, NO^+), and 26 (6.9 CN^+).

Anal. Calcd for $C_2F_3Cl_2NO$: C, 13.20; H, 0.00; F, 31.33; N, 7.70. Found: C, 13.45; H, 0.00; F, 31.60; N, 7.49.

Registry No.—*cis*-**2**, 23025-21-0; *trans*-**2**, 23025-22-1; *cis*-**3**, 23025-23-2; *trans*-**3**, 23025-24-3.

Organic Reactions in Liquid Hydrogen Fluoride.
I.   Synthetic Aspects of the Ritter Reaction in Hydrogen Fluoride[1]

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Liquid hydrogen fluoride effectively condenses an olefin and nitrile (Ritter reaction) to form N-substituted amides at ambient conditions. With linear monoolefins, *i.e.*, 1-octene and acetonitrile, three isomeric secondary amides are produced in yields of 80–90% when 0–10% water is present in the HF. Branched olefins, *i.e.*, 2-methyl-2-butene, which give tertiary carbonium ions, require 25–40% water in the reaction medium to obtain high yields of amides. With an olefin in which the tertiary carbon is remote from the point of unsaturation, as in the case of 3-methyl-1-butene, the major product is the amide derived from the tertiary carbonium ion *via* isomerization. The reaction has been applied to a variety of monoolefins and substituted nitriles, including HCN. Diolefins, in general, react poorly, giving viscous gums, although 2,5-dimethyl-1,5-hexadiene gave 2,5-diacetamido-2,5-dimethylhexane and norbornadiene gave N-3-nortricyclylacetamide.

Hydrogen fluoride, long known as a catalyst in alkylation reactions,[2] has received little attention as a solvent for organic reactions. This is undoubtedly due to the hazards associated with handling HF such as its toxicity and the rapid attack on glass. However, its volatility (bp 20°), its strong acid character ($H_0 = -9.9$), and the fact that it can be handled conveniently in polyethylene labware or Monel reactors suggest that HF could have distinct advantages over commonly used acid solvent systems such as sulfuric, polyphosphoric, etc.[2] We have examined several classes of reactions which normally are carried out in strong acids and wish to report our findings concerning the Ritter condensation of olefins and nitriles.

The acid condensation of an olefin, alcohol, or halide with a nitrile to form N-alkylamides has been extensively studied.[3] In most cases sulfuric acid was used either alone or with solvents such as acetic acid, but prior to this work no reports concerning the use of hydrogen fluoride as a solvent system has been noted.[4]

In the present study it was found that hydrogen fluoride is an excellent solvent system for the preparation of N-alkylamides and can be used at room temperature and atmospheric pressure for a variety of olefins and nitriles. Since conditions for optimum yields vary, these are discussed for linear olefins, which form secondary carbonium ions; branched olefins, which form tertiary carbonium ions; and cyclic and bicyclic olefins.

Results and Discussion

Linear Olefins.—Linear monoolefins react smoothly with nitriles, including hydrogen cyanide, in hydrogen fluoride containing from 0 to 10% water to produce N-substituted amides at ambient conditions. Table

$$RCH=CHR' + R''CN \xrightarrow[\text{H}_2\text{O}]{\text{HF}} \underset{\underset{\text{NHCOR''}}{|}}{RCHCH_2R'}$$
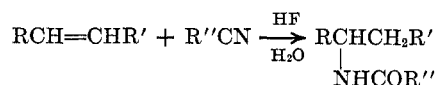
(1) Portions of this paper were presented at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968.

(2) G. A. Olah, "Friedel–Crafts and Related Reactions," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, p 317 ff.

(3) (a) L. I. Krimen and D. J. Cota, *Org. Reactions*, **17**, 213 (1969); (b) J. J. Ritter and P. P. Minieri, *J. Amer. Chem. Soc.*, **70**, 4045 (1948); (c) E. N. Zil'berman, *Russ. Chem. Rev.* (Engl. Transl.), 311 (1960).

(4) During the course of this research, a patent was issued describing the use of hydrogen fluoride for preparing secondary alkyl, primary amines from linear olefins and nitriles: R. H. Potts, E. J. Miller, and A. Mais (to Armour and Co.), U. S. Patent 3,338,967 (1967).

TABLE I

REACTION OF LINEAR OLEFINS WITH NITRILES IN ANHYDROUS HYDROGEN FLUORIDE[a]

$$RCH{=}CH_2 + R'CN \xrightarrow{HF} \xrightarrow{H_2O} amide$$

R	R'	Yield, %	Amide produced	Compd no.	Bp, °C (mm)	n^{20}D	Calcd, % C	H	N	Found, % C	H	N
H	CH₃	4	N-Ethylacetamide	1	b							
CH₃	CH₃	23	N-Isopropylacetamide	2	93–94 (13)[c]	1.4297	59.35	10.98	13.84	58.55	11.10	13.78
n-C₃H₇	CH₃	72	N-(2- and 3-pentyl)acetamides	3	71–72 (0.3)	1.4394	65.07	11.70	10.84	64.92	11.86	10.70
n-C₆H₁₁	H[d]	40	Octylformamides	4	102–105 (0.6)	1.4473	68.74	12.18	8.90	68.56	11.94	8.70
n-C₁₆H₃₁	H	43	Octadecylformamides	5	186–194 (0.4)	e	76.67	13.24	4.71	77.00	13.50	4.86
n-C₆H₁₁	CH₃	92	N-(2-, 3-, and 4-octyl)acetamides	6	94–99 (0.3)	e	70.12	12.38	8.18	70.00	12.43	8.22
n-C₆H₁₁	CH₃OCH₂	61	N-(2-, 3-, and 4-octyl)methoxyacetamides	7	79–86 (0.3)	1.4479	66.53	11.51	6.96	65.59	11.48	6.90
n-C₆H₁₁	ClCH₂	65	N-(2-, 3-, and 4-octyl)chloroacetamides	8	93–96 (0.3)	1.4633	58.38	9.80	6.81	58.48	9.83	6.69
n-C₆H₁₁	Ph	71	N-(2-, 3-, and 4-octyl)benzamides	9	139–146 (0.3)	1.5125	77.21	9.93	6.00	77.15	9.78	6.04
n-C₁₀H₂₁	CH₃[f]	40	N-Dodecylacetamides	10	130–134 (0.3)	1.4515	73.95	12.86	6.16	74.74	12.68	5.95

[a] Reactions were run at 25–40° for 0.5–2 hr on a 0.10–0.50 M scale. [b] Not isolated in pure state, but determined by glpc comparison with an authentic sample. [c] Lit. bp 201–203°: B. T. Gillis, *J. Org. Chem.*, **24**, 1027 (1959). [d] HCN source was NaCN and SO₂ was employed as a cosolvent. [e] Solidified at room temperature. [f] SO₂ was employed as a cosolvent.
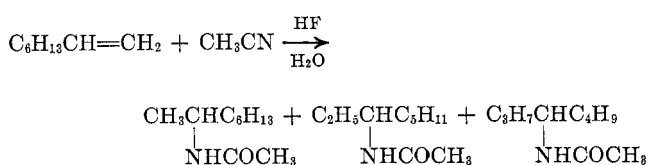
TABLE II

TEMPERATURE DEPENDENCE OF THE 1-OCTENE–ACETONITRILE CONDENSATION[a]

Temp, °C	Yield, %, of N-octyl-acetamides	Residue,[b] wt, g	Composition of residue, % 1-Octene	RF	Amides	"Heavies"	Other[c]	Isomer distribution of amides 2	3	4
−75	2	6.5	58	37	5	0	0	100	0	0
−50	8	7.7	0	76	18	4	2	87	10	3
−25	40	12.0	3	19	59	9	10	26	39	35
0	57	13.7	4	1	72	19	4	21	42	37
20	71	13.8	2	0	88	6	3	20	42	38
40	62	14.2	1	0	76	23	0	22	41	37
60	48	13.4	0	0	64	36	0	27	39	34
100	26	11.1	0	0	40	60	0	32	37	31

[a] Reaction was run with 0.10 mol each 1-octene and CH₃CN, with 48 ml of HF and 2 ml of H₂O for 2 hr. [b] Represents the "crude" weight of product produced after extraction with ether and flash evaporation; 100% yield of N-octylacetamides would be 17.1 g. [c] Represents unidentified volatile peaks on the glpc.

I illustrates a representative sampling of many of the nitrile–olefin combinations which were investigated. Significantly, when Ritter's original conditions of H₂SO₄–HOAc were employed, the olefins tabulated gave amides in very low yields (0–10%). Also to our knowledge, this is the first example of ethylene entering into an acid-catalyzed nitrile condensation, albeit in low yield.

Because of its ease of handling and availability, 1-octene was used as a model compound typifying a secondary olefin in the reaction with acetonitrile to demonstrate the effect of temperature and hydrogen fluoride/olefin ratios and to establish the extent of isomerization. With 1-octene, three N-octylacetamides are possible and all three are usually produced; the relative quantities are dependent upon conditions. Because of the carbonium ion nature of the reaction no 1 isomer was identified.

$$C_6H_{13}CH{=}CH_2 + CH_3CN \xrightarrow[H_2O]{HF}$$

$$\underset{\overset{|}{NHCOCH_3}}{CH_3CHC_6H_{13}} + \underset{\overset{|}{NHCOCH_3}}{C_2H_5CHC_5H_{11}} + \underset{\overset{|}{NHCOCH_3}}{C_3H_7CHC_4H_9}$$

The reaction is temperature dependent (Table II) with the highest yields being produced near ambient conditions. In this study 4% water was present in the HF to minimize polymerization at the higher temperatures. The composition of the isolated residue was determined by glpc with an internal standard of dodecane to establish the amount of "heavies" present and was verified by distillation. Although the "heavies" could not be distilled, nitrogen was shown to be present

by elemental analysis, and amidic groups were indicated by the infrared spectrum. It is significant that at low temperatures only octyl fluorides and unreacted octene were found along with a low yield of acetamides. The isomer distribution of the amides that were formed at low temperatures favored the 2 isomer, whereas at higher temperatures isomerization was more extensive.

High yields (80–85%) of N-octylacetamides are obtained when a mole ratio of hydrogen fluoride/1-octene is 10–30:1 with an isomer distribution of 2-, 3-, and 4-N-octylacetamides being about 1:2:2. With a mole ratio of 7.5:1 the yield drops to 56% and a 5:1 ratio gives a 33% yield; in both experiments a nearly 1:1:1 isomer distribution is obtained. The yield is only 7% with a 2.5:1 mole ratio and a 9:4:1 isomer ratio for the 2, 3, and 4 isomers is observed. A 1:1 mole ratio of hydrogen fluorido/1-octene gives no detectable N-octylacetamides. The lower yields indicate that insufficient HF is available for effectively carrying out the reaction as unreacted octene is recovered. Factors such as lowered dielectric constants or decreased H_0 values may be significant. Also HF has been shown by Wiechert, *et al.*,[5] to complex with acetonitrile in varying molar ratios [CH₃CN/HF(HF)ₙ] and a portion of the HF may be complexed in this manner thus decreasing the effective amount available for protonation at the lower concentrations. When 0–10% water is present in the HF, yields are optimal, but drop sharply at higher water concentrations (Figure 1) as will be discussed under Branched Olefins.

A small molar excess, preferably a 1.1:1.0 molar excess of nitrile/olefin, of either reactant does not

(5) K. Wiechert, H. H. Heilmann, and P. Mohr, *Z. Chem.*, **3**, 308 (1963).

SCHEME I

leads to N-2-octylacetamide

C—C—C—C—C—C—C=C $\underset{-H^+}{\overset{+H^+}{\rightleftharpoons}}$ C—C—C—C—C—C—$\overset{+}{C}$—C—H $\underset{-F^-}{\overset{+F^-}{\rightleftharpoons}}$ C—C—C—C—C—C—C—C—H

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ |

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ F

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $-HF \updownarrow +HF$

C—C—C—C—C—C—C—C— $\overset{F^-}{\rightleftharpoons}$ C—C—C—C—C—$\overset{+}{C}$—C—C $\overset{H^+}{\rightleftharpoons}$ C—C—C—C—C—C=C—C

$\quad$ |

$\quad$ F

$\quad$ $\updownarrow$ $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\downarrow$

etc.

leads to N-3-octylacetamide

appear to be detrimental to the reaction (Table III). If a large excess of the olefin is employed, danger of polymerization is increased and on work-up the unreacted material is extracted with the product. Table III illustrates that when the nitrile/olefin ratio is

TABLE III

VARIATION OF NITRILE/OLEFIN RATIO

CH₃CN, g	1-Octene, g	CH₃CN/ 1-Octene	N-Octyl- acetamides	Isomer distribution		
				2	3	4
4.1	22.4	0.5	94	23	41	36
8.2	11.2	2.0	86	29	41	30
20.5	11.2	5.0	54	63	30	7
41.0	11.2	10.0	8	86	12	2

large (*ca.* 10), the nitrile acts as a solvent, decreases the yield, and alters the isomer distribution. The data shown were obtained at 25° with 2.5 mol of HF. A solvent such as liquid sulfur dioxide can be employed without adverse effects.

Yield and isomer distribution were insensitive to reaction time. When the reaction was run on a 0.10 *M* scale with a 25 *M* excess of HF at 25°, the yield remained at 82–88% over a time interval of 15–120 min. The isomer distribution of N-octyl-acetamides follows: 2 isomer, 26%; 3 isomer, 40%; and 4 isomer, 34%.

The initial location of the double bond in the octene has little effect on yield but alters the isomer composition to a small extent (Table IV).

TABLE IV

REACTION OF ISOMERIC OCTENES WITH ACETONITRILE IN HYDROGEN FLUORIDE

Olefin	Yield, %, of N-octyl- acetamides	Isomer distribution		
		2	3	4
1-Octene	87	32	38	30
2-Octene	85	21	46	33
3-Octene	83	23	45	32
4-Octene	85	18	49	33

Although anticipated, we observed no carbon-chain rearrangement as was found in the Koch carboxylation of olefins in strong acids.[6]

The variation of isomer distribution, *i.e.*, increased percentage of N-2-octylacetamide, appears to occur when the amount of HF is decreased and is always

(6) J. R. Norell, unpublished work; K. E. Moeller, *Angew. Chem. Intern. Ed. Engl.*, **2**, 719 (1963).

Figure 1.—Reaction of 2-methyl-2-butene and 1-octene with CH₃CN in aqueous HF at 40° for 2 hr using a total volume of 50 ml of H₂O–HF and 0.10 mol each of olefin and CH₃CN: □, N-octylacetamides from 1-octene; O, t-amylacetamide from 2-methyl-2-butene; △, t-butylacetamide in crude product from reaction of 2-methyl-2-butene with CH₃CN.

accompanied by lower overall yield of the octylacetamides. Since the 2 isomer arises from stabilization of the 2-octyl carbonium ion, there is a strong indication that the isomerization occurs by a stepwise addition–elimination mechanism as suggested by Olson[7] in a similar study on the alkylation of aromatics with olefins, and not by a hydride migration (Scheme I). Under optimum conditions (*i.e.* large excess of HF) the free isomerized olefin is present only in transient amounts and the fluorooctane predominates as the nonnitrogen-containing intermediate. Furthermore the resulting loss of HF to form the isomerized olefin should be facilitated by the tendency to form HF₂⁻. The preponderance of N-2-octylacetamide in media of low acid concentration may be due to two factors. (1) At lower acid concentrations the H_0 value is greatly decreased (100% HF = -9.9)[2] and hence the rate of protonation or the HF addition is much slower; thus, the rate of isomerization is decreased. (2) When

(7) A. C. Olson, *Ind. Eng. Chem.*, **52**, 833 (1960).

SO₂ or CH₃CN is present in excess the dielectric constant would be expected at be lower than that of pure HF (ϵ 85 at 0°) and hence the rate of ionization of the fluorooctane would decrease. Thus the rate-determining step for isomerization would seem to be ionization of the C–F bond, which would be less likely to occur in media of lower dielectric constant since the tendency of HF to form the HF_2^- ion should be less.

$$RCHCH_3 + HF \longrightarrow R\overset{+}{C}HCH_3 + HF_2^-$$
$$\underset{F}{|}$$
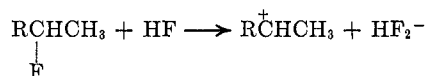
Octyl alcohols or halides which may react as carbonium ion precursors were treated with acetonitrile in HF (Table V) to form N-octylacetamides. Under the specific conditions employed, primary alcohols and halides showed no tendency toward amide formation. Under these same conditions, the secondary chloro-, bromo-, and iodooctanes all gave either very low amide yields or no reaction at all, whereas 2-fluorooctane gave an amide yield comparable with that obtained with octene. 2-Octanol gave a high yield of amides and a "normal" isomer distribution.

TABLE V

VARIATION OF THE CARBONIUM ION SOURCE

$$C_8H_{17}X + CH_3CN \xrightarrow[\text{2. } H_2O]{\text{1. } HF, 25°} C_8H_{17}NHCOCH_3$$

X	Yield, %, of acetamidooctanes	Recovered starting material, %
1-OH	0	80
2-OH	77	0
2-F	81	0
1-Cl	0	78
2-Cl	6	83
2-Br	0	99
2-I	0	92

The results appear at first glance to be inconsistent with the normally observed order of solvolysis rates for halides in that iodides solvolyze more readily than fluorides or chlorides because of the difference in bond strengths.[8] However, atoms which are strongly electronegative tend to be better leaving groups when they are in acidic media than when they are in neutral or basic solvents[9] because protonation and/or hydrogen bonding results in weakening of the C–X bond. Solvolysis of fluorides has been shown to be accelerated by acidic catalysts, whereas solvolysis of the other halides is not.[10] In this case, using HF as the acid catalyst gives an enhanced catalytic effect due to the tendency toward formation of the HF_2^-.[11] Thus the high yield of N-octylacetamide from 2-fluorooctane and not from the other halides is probably due to a combination of all the effects mentioned above.

Branched Olefins.—Table VI is representative of the branched olefins that were investigated with a variety of nitriles. As a convenient example of a branched olefin and precursor of tertiary carbonium ions, 2-methyl-2-butene was studied extensively in

regard to its reaction with acetonitrile in various concentrations of aqueous HF to form *t*-amylacetamide (12). It was found that conditions that produce optimum yields of amides from a linear olefin, *i.e.*, 1-octene, give low yields with branched olefins and the converse is true. Several runs, which are displayed graphically in Figure 1, demonstrate that amide yields from branched olefins are optimized when 25–40% water is present in HF and that only 0–10% water should be present for linear olefin reactions.

A rationale for this striking difference seems to lie in the relative stabilities of the incipient carbonium ions which may be present during the course of the reaction. Three different carbonium ions are possible intermediates in this order of apparent stability: tertiary > imino > secondary.[12] For both linear and branched olefins there appear to be three distinct steps: protonation, nitrile attack, and hydrolysis and tautomerization. These are outlined in Scheme II for different situations, *i.e.*, linear olefins in concentrated HF and branched olefins in concentrated HF.

With linear systems in concentrated HF we have ready protonation, and nitrile attack is not extensively reversible because of the enhanced stability of the imino cation over a secondary carbonium ion.[12b] The hydrolysis proceeds in a normal fashion. However, when the acid is diluted, the protonating power to form secondary carbonium ions decreases and the first step in the reaction lies far to the left. Starting 1-octene is recovered along with little or no octyl fluoride, and traces of amidic products are obtained when 1-octene is allowed to react with acetonitrile in 60% aqueous HF.

Olefins with a branch on the olefinic carbon protonate readily even in dilute acid. We have found that conditions optimum for *t*-amylacetamide formation require 25–40% water in the HF (Figure 1). The nitrile attack is essentially nonreversible in aqueous acid because of the large amount of water present, which traps the adduct as the enol which in turn tautomerizes to the amide. In anhydrous conditions protonation is as extensive as in the linear system but now the reversibility of the nitrile attack is more pronounced. This reversal tends to build up concentrations of the *t*-amyl cation which in turn can dimerize with free olefin and then fragment to *t*-butyl and hexyl cations.[13] Both polymerized products and *t*-butylacetamide were observed but interestingly no N-hexylacetamide was found under our analytical techniques. Figure 1 shows the extent of *t*-butylacetamide formation arising from fragmentation of the *t*-amyl cation in very strong acid solutions. A maximum in amide yield is observed at a water concentration of about 40% (in HF). Since the initial reaction is protonation of the olefin, the latter concentration may be used as an indication of the cessation of the reaction of carbonium ion formation, which in turn, could conceivably be due to the acid strength of the system.

3-Methyl-1-butene reacted with acetonitrile and HF under "secondary carbonium ion" conditions to give

(8) E. S. Gould, "Mechanism and Structure of Organic Chemistry," Henry Holt and Co., New York, N. Y., 1959, p 261.

(9) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p 50.

(10) W. T. Miller and T. Bernstein, *J. Amer. Chem. Soc.*, **70**, 3600 (1948).

(11) N. B. Chapman and J. L. Levy [*J. Chem. Soc.*, 1677 (1952)] have shown that the solvolysis of secondary alkyl fluorides is autocatalytic when the initial concentration of acid is low because of the generated HF.

(12) (a) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill Book Co., Inc., New York, N Y., 1962, p 226; (b) P. A. S. Smith, "Open Chain Nitrogen Compounds," Vol. 1, W. A. Benjamin, Inc., New York, N. Y., 1965, p 169.

(13) S. H. Patinkin and B. S. Friedman in "Friedel–Crafts and Related Reactions," Vol. II, G. A. Olah, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, p 48.

TABLE VI

REACTION OF BRANCHED OLEFINS WITH NITRILES IN HYDROGEN FLUORIDE[a]

Olefin	RCN	% HF concn	Yield, %[b]	Amides produced	Compd no.	Mp or bp (mm), °C	Calcd, % C	H	N	Found, % C	H	N
2-Methyl-2-butene	HCN	70	70	$C_2H_5C(CH_3)_2NHCHO$	11	58–60 (0.5)	62.57	11.37	12.16	62.09	11.40	12.18
2-Methyl-2-butene	CH₃CN	64	91	$C_2H_5C(CH_3)_2NHCOCH_3$	12	78–79[c]						
2-Methyl-2-butene	CH₃CN	100	24	$C_2H_5C(CH_3)_2NHCOCH_3$	12	d						
			8	$(CH_3)_3CNHCOCH_3$	13							
3-Methyl-1-butene	CH₃CN	100	24	$C_2H_5C(CH_3)_2NHCOCH_3$	12	70–94[d]						
			4	$(CH_3)_2CHCH(CH_3)NHCOCH_3$	14							
2,3-Dimethyl-2-butene	CH₃CN	70	65	$(CH_3)_2CHC(CH_3)_2NHCOCH_3$	15	68–69	67.08	11.97	9.78	67.26	11.78	9.80
3,3-Dimethyl-1-butene	CH₃CN	100	50	$(CH_3)_2CHC(CH_3)_2NHCOCH_3$	15							
			12	$(CH_3)_3CCH(CH_3)NHCOCH_3$	16	69–76 (0.4)[e]						
Vinylcyclohexane	CH₃CN	80	60[f]	N-1-Ethylcyclohexylacetamide[d]	17							
1-Ethylcyclohexanol	CH₃CN	70	84	N-1-Ethylcyclohexylacetamide	17	69–70[g]						
2-Methyl-2-butene	ClCH₂CN	70	42	$C_2H_5C(CH_3)_2NHCOCH_2Cl$	18	49–51	h					
2-Methyl-2-butene	Cl₂CHCN	70	87	$C_2H_5C(CH_3)_2NHCOCHCl_2$	19	105–107	42.44	6.61	7.07	41.72	6.45	7.20
2-Methyl-2-butene	C₆H₅CN	70	70	$C_2H_5C(CH_3)_2NHCOC_6H_5$	20	92–93[i]	75.35	8.96	7.32	75.36	8.74	7.44
2-Methyl-2-butene	CH₃OCH₂CN	70	79	$C_2H_5C(CH_3)_2NHCOCH_2OCH_3$	21	55 (0.4)[j]	60.34	10.77	8.80	59.88	10.62	8.44

[a] Run at 25–40° for 2 hr. [b] No attempts were made to optimize the yields. [c] Lit.[3b] mp 78–79°. [d] Composition was determined by glpc and comparison with authentic sample. [e] Composition was determined by nmr (see Experimental Section). Boiling point represents boiling point of the mixed amides. [f] Two isomeric but unidentified amides were present in 22% yield for a total amide yield of 82%. [g] Lit. mp 71–72°. N. K. Kochetkov, *et al., Zh. Obshch. Khim.,* **29,** 3613 (1959). [h] Lit.[3b] bp 62–63° (1 mm). [i] Reference 3b cites mp 81–82° which we believe is in error. [j] n^{20}D 1.4400.

SCHEME II

For linear olefins in concentrated HF

$$C_6CH=CH_2 + HF \rightleftharpoons C_6\overset{+}{C}H-CH_3 \rightleftharpoons C_6CHCH_3 \quad \text{(protonation)}$$
$$\underset{F}{|}$$

$$C_6\overset{+}{C}HCH_3 + CH_3CN \rightleftharpoons C_6CHCH_3 \overset{F^-}{\rightleftharpoons} C_6CHCH_3 \quad \text{(nitrile attack)}$$
$$\underset{\overset{+}{N}=CCH_3}{|} \qquad \underset{N=CFCH_3}{|}$$

$$RN=CFCH_3 + H_2O \longrightarrow RN=CCH_3 \longrightarrow RNHCOCH_3 \quad \text{(hydrolysis and tautomerization)}$$
$$\underset{OH}{|}$$

For branched olefins in concentrated HF

$$(CH_3)_2C=CHCH_3 + HF \rightleftharpoons (CH_3)_2\overset{+}{C}CH_2CH_3 \rightleftharpoons (CH_3)_2CFCH_2CH_3 \quad \text{(protonation)}$$

$$(CH_3)_2\underset{+}{C}CH_2CH_3 + CH_3CN \rightleftharpoons (CH_3)_2CCH_2CH_3 \rightleftharpoons (CH_3)_2CCH_2CH_3 \quad \text{(nitrile attack)}$$
$$\underset{\overset{+}{N}=CCH_3}{|} \qquad \underset{N=CFCH_3}{|}$$

fragmentation and/or polymerization

$$R'N=CFCH_3 + H_2O \longrightarrow R'N=CCH_3 \longrightarrow R'NHCOCH_3 \quad \text{(hydrolysis and tautomerization)}$$
$$\underset{OH}{|}$$

the isomerized *t*-amylacetamide (**12**) and N-(1,2-dimethylpropyl)acetamide (**14**) in a ratio of 6.3:1 with an overall amide yield of only 28%. Employing "tertiary carbonium ion" conditions the yield was 10% and the ratio of migrated to nonmigrated amide was 12:1. This type of olefin presents a peculiar problem

$$C-\underset{\underset{C}{|}}{C}-C=C + CH_3CN \xrightarrow{\text{HF-H}_2\text{O}}$$

$$\underset{\underset{\underset{12}{C}}{|}}{C}-\overset{\overset{\text{NHCOCH}_3}{|}}{C}-C-C + \underset{\underset{\underset{14}{C}}{|}}{C}-C-\overset{\overset{\text{NHCOCH}_3}{|}}{C}-C$$

in optimization of yields in that it is a secondary olefin but, after protonation, migration occurs and a tertiary carbonium ion is formed, which then tends to polymerize and fragment in the strong acid system. Under tertiary carbonium ion conditions, *i.e.,* dilute acid, the

olefin is not protonated easily and hence the reaction proceeds very poorly.

2,3-Dimethyl-2-butene reacted smoothly with acetonitrile in HF under tertiary carbonium ion conditions to give the expected N-(1,1,2-trimethylpropyl)acetamide (**15**). Extensive methyl migration occurred with 3,3-dimethyl-1-butene; the ratio of migrated (**15**) to nonmigrated (**16**) amide was 4:1.

$$C-\underset{\underset{C}{|}}{\overset{\overset{C}{|}}{C}}-C=C + CH_3CN \xrightarrow[\text{2. H}_2\text{O}]{\text{1. HF}}$$

$$\underset{\underset{16}{\underset{C}{|}\ \text{NHCOCH}_3}}{C-\overset{\overset{C}{|}}{C}-C-C} \quad + \quad \underset{\underset{15}{\text{NHCOCH}_3}}{C-\overset{\overset{C\ \ C}{|\ \ |}}{C}-C-C}$$

As shown in Table VII a variety of nitriles react with 2-methyl-2-butene to give good yields of the respective amide at 40° with 70% aqueous HF.

TABLE VII

REACTION OF CYCLIC AND BICYCLIC OLEFINS WITH NITRILES IN ANHYDROUS HYDROGEN FLUORIDE[a]

Olefin	RCN	Yield, %	Amides produced	Compd no.	Mp or bp (mm), °C	Calcd, % C	H	N	Found, % C	H	N
Cyclohexene	HCN[b]	67	Cyclohexylformamide	22	94–97 (0.4)	c					
Cyclopentene	CH₃CN	40	N-Cyclopentylacetamide	23	89–92 (0.5)	d					
1-Methylcyclohexene	CH₃CN[e]	80	N-1-Methylcyclohexylacetamide	24	84–86	f					
Cycloheptene	CH₃CN	62	N-Cycloheptylacetamide[g]	25	129–130 (0.8)	h					
Cyclododecene	CH₃CN[i]	85	N-Cyclododecylacetamide	26	141–142	74.66	12.00	6.22	74.29	12.24	6.16
Cyclohexene	CH₃CN	72	N-Cyclohexylacetamide	27	106–107	j					
Cyclohexene	ClCH₂CN	67	N-Cyclohexylchloroacetamide	28	106–108	k					
Cyclohexene	Cl₂CHCN	66	N-Cyclohexyldichloroacetamide	29	139–140	l					
Cyclohexene	C₆H₅CN	86	N-Cyclohexylbenzamide	30	148–150	m					
Cyclohexene	CH₃OCH₂CN	50	N-Cyclohexylmethoxyacetamide	31	60–62	63.12	10.01	8.18	63.82	9.96	8.12
Cyclohexene	(CH₃)₃CCN	67	N-Cyclohexylpivalamide	32	121–123	n					
Cyclohexene	CF₃CN	80	N-Cyclohexyltrifluoroacetamide	33	94–95	o					
Bicyclo[3.2.1]octene-2	CH₃CN	86	N-Bicyclo[3.2.1]oct-2-ylacetamide	34	132–134	p					
Norbornene	CH₃CN	74	N-2-Norbornylacetamide	35	140–141	q					
Norbornadiene	CH₃CN	Low	N-3-Nortricyclylacetamide	36	106–107	71.49	8.66	9.26	71.43	8.69	9.22
1,5-Cyclooctadiene	CH₃CN	Low	N-(cis-2-Bicyclo[3.3.0]octyl)acetamide	37	135–136	71.92	10.26	8.39	71.76	10.35	8.40

[a] All reactions were run at room temperature (25°) for 0.5–2 hr with 100% HF. [b] Run at 54° for 5 hr in 85% HF. [c] Lit. bp 150–158° (18 mm): H. E. Albert, U. S. Patent 2,819,306 (1958). [d] Lit. bp 146–149° (22 mm): E. K. Harvill, R. M. Herbst, E. C. Schreiner, and C. W. Roberts, *J. Org. Chem.*, 15, 662 (1950). [e] Used 85% HF at 40°. [f] Lit. mp 84–85°: H. E. Baumgarten, F. A. Bower, R. A. Setterquist, and R. E. Allen, *J. Amer. Chem. Soc.*, 80, 4588 (1958). [g] No evidence for ring contraction by glpc. [h] Lit. bp 147–148° (3 mm): M. Murakami, K. Akagi, and Y. Mori, *Bull. Chem. Soc. Jap.*, 35, 11 (1962). [i] Temperature 10°. [j] Lit. mp 107–109°: E. K. Harville, R. M. Herbst, E. C. Schreiner, and C. W. Roberts, *J. Org. Chem.*, 15, 622 (1950). [k] Lit. mp 105–106°: M. Baker, *Compt. Rend.*, 233, 66 (1951). [l] Lit. mp 140°: B. J. H. Heywood, British Patent 712,745 (1954). [m] Lit. mp 148–149°: D. B. Denney and G. Feig, *J. Amer. Chem. Soc.*, 81, 227 (1959). [n] Lit. mp 122.5°: W. M. Degnan and C. J. Shoemaker, *ibid.*, 68, 104 (1946). [o] Lit. mp 93–94°: E. J. Bourne, S. H. Henry, C. E. N. Tatlow, and J. C. Tatlow, *J. Chem. Soc.*, 4014 (1952). [p] Lit. mp 134°: F. Derich and H. Bueren, German Patent 1,167,337 (1964). [q] Lit. mp 143–144° for *exo* amide, 131–132° for *endo* amide: J. A. Berson and D. A. Ben-Effraim, *J. Amer. Chem. Soc.*, 81, 4094 (1959).

Cyclic and Bicyclic Olefins.—Cyclic olefins behave similarly to linear systems with no evidence of ring contraction being observed. Table VII illustrates that cyclohexane, cycloheptene, cyclopentene, and cyclododecene all give fair to good yields of the respective amides when run in 90–100% HF (secondary carbonium ion conditions). With cycloheptene, ring contraction was expected[14] but no N-1-methylcyclohexylacetamide (24) was found. 1-Methylcyclohexene reacted smoothly as a tertiary olefin to give an 80% yield of the expected amide (24) when run in 72% HF.

With hydrogen cyanide, cyclohexene gave the best yield (67%) of cyclohexylformamide (22) when run in 85% HF at 54° for 5 hr on a 2.0 M scale. If 100% HF is employed, only traces of the formamide are obtained along with a fair yield of N,N'-dicyclohexyl-2-cyclohexylaminomalonamide and polymeric material.[15] Hence, even though cyclohexene is a secondary olefin, it is preferable to use about 15% water and heat to 40–60° when preparing formamides from HCN. The source of HCN can be either the pure acid or formation *in situ* from the sodium or potassium salt. In this case, when the reaction is not run to completion, *i.e.*, shorter time (2 hr) and decreased temperature (16°), reaction intermediates and by-products can be identified. The composition of that portion of the reaction product which could be distilled contained 35% cyclohexyl fluoride, 6% cyclohexyl formate, 9% cyclohexanol, 50% cyclohexylformamide, and a trace of cyclohexylisonitrile. The fluoride, alcohol, and formamide are all readily explained, and cyclohexyl formate may arise by addition of formic acid (*via* HCN hydrolysis) to cyclohexene. Cyclohexylisonitrile may arise *via* two routes: (a) The dehydration of cyclohexylformamide by HF (the dehydration of formamides by P₂O₅ and other strongly dehydrating agents is a

well-known method for preparing isonitriles[16] and HF has long been noted as a strong dehydrating agent);[2] (b) an alternative route is *via* dehydrofluorination of the
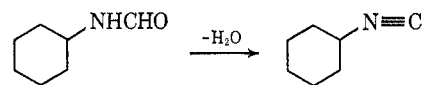

intermediate imidoyl fluoride by an α elimination of HF. The isonitrile was first observed by its foul odor
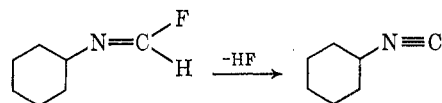

and then independently prepared by the method of Ugi, *et al.*,[16] and characterized in the mixture.

Although not extensively studied, the bicyclic olefins norbornene and bicyclo[3.2.1]oct-2-ene gave the respective amides with no detectable rearrangement. The amide isolated from norbornene appeared to be chiefly the *exo* isomer from melting point characteristics (see Table VII). The bicyclic diene

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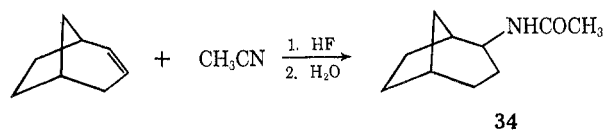
norbornadiene gave N-3-nortricyclylacetamide [N-3-tricyclo[2.2.1.0²,⁶]heptyl)acetamide] (36) in low yield.


35

36
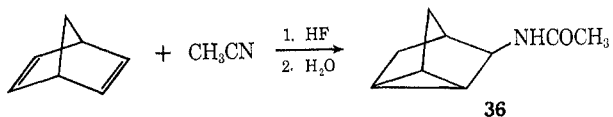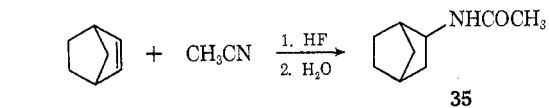
(14) R. Jacquier and H. Christol, *Bull. Soc. Chim. Fr.*, 596 (1957).

(15) The reaction of an olefin with HCN in HF represents a new synthesis for 2-aminomalonamides and is the subject of another paper: J. R. Norell, *J. Org. Chem.*, 35, 1619 (1970).

(16) I. Ugi, U. Fetzer, U. Eholzer, H. Knupfer, and K. Offenum, *Angew. Chem. Intern. Ed. Engl.*, 4, 472 (1965).

Another transannular reaction occurred with 1,5-cyclo-octadiene which gave N-(cis-2-bicyclo[3.3.0]octyl)-acetamide (37) in low yield. In general diolefins
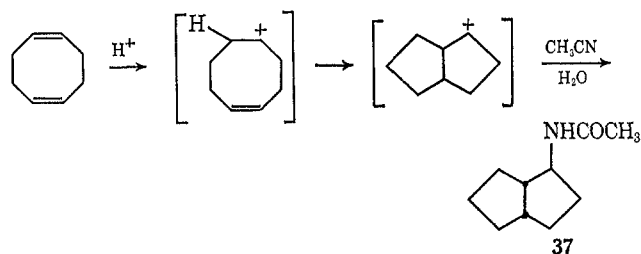
react rather poorly in this reaction, forming a polymeric gum, high in nitrogen content. One exception was 2,5-dimethyl-1,5-hexadiene which gave 2,5-di-acetamido-2,5-dimethylhexane (38) in 22% yield.
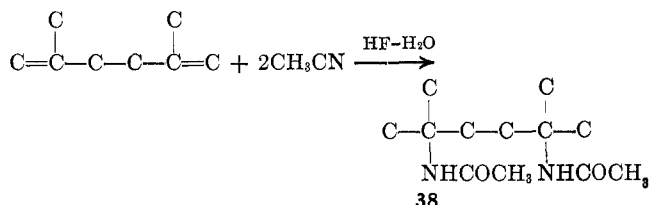
All the amides prepared in this work were characterized by comparison with known compounds or the structure was established by elemental analyses and infrared and nmr spectroscopy and the purity was checked by gas chromatography.

In summary, it has been found that N-substituted amides are conveniently prepared from linear or branched olefins by reaction with a nitrile or hydrogen cyanide in a hydrogen fluoride solvent. Yields are optimal for linear olefins when the HF contains 0–10% water, whereas, for branched olefins, 25–40% water is required, and temperatures of 20–40° are favored.

Experimental Section

Melting points were determined on a Thomas–Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord, nmr spectra were run on a Varian A-60 spectrometer, and the mass spectra were obtained on a high resolution CEC mass spectrometer, Model 21-110. Purity of the amides produced was determined on an F & M Model 500 gas chromatograph using a 9-ft Apiezon L on Chromosorb W column programmed from 75 to 275° at 15°/min with a He flow rate of 80 cc/min.

Chemicals.—*CAUTION!* When handling anhydrous HF, a face shield, rubber gloves with plastic arm bands, and a protective apron are worn, using excellent hood facilities. Colorless hydrogen fluoride (99.9% from Air Products, Inc., Allentown, Pa.) is withdrawn in the liquid phase by inverting the cylinder and taking off the liquid HF through a Monel Hoke valve in addition to the cylinder valve. The liquid is allowed to drip directly into a polyethylene graduate where it readily condenses as a fuming liquid and is then poured into one of the two reaction vessels. No special precautions are taken to exclude moisture and air. All olefins and nitriles were commercially available and were distilled when the purity was in doubt. Hydrogen cyanide was obtained from E. I. du Pont de Nemours and Co. and was stabilized with P_2O_5.

Apparatus.—For reactions at room temperature or below, a reaction vessel was fabricated from high-density polyethylene into the shape of a cylinder (ca. 500 ml) with the bottom beveled so that an egg-shaped magnetic stirring bar could be inserted. Atop the cylinder were "welded" two female sections of Polycone (obtained from Cole-Parmer, Inc., Chicago, Ill.). A polyethylene plug containing a Weston stainless steel thermometer was inserted in one of the standard tapered openings. To a poly-

ethylene separatory funnel was "welded" the male section of a Polycone so that a snug fit could be made into the other opening of the reactor. This ensured a reaction system which was completely inert to attack by HF. For reactions above room temperature or where a gas was involved, a 300-ml Monel reactor was used which was fitted with a pressure gauge and a thermocouple and could be shaken in a heated bath.

General Method for Preparation of N-Alkylamides.—One of the reaction vessels was cooled in ice and charged with a total of 50 ml of water and HF depending on the percentage acid concentration desired. The nitrile (0.10–0.25 mol) was added, followed by dropwise addition of the olefin (0.10–0.20 mol), and the reactor was capped and maintained at the desired temperature for the indicated time. The contents were poured on ice water (ca. 300 ml) and made strongly basic with an excess of concentrated NH_4OH. The amides were extracted with CH_2Cl_2 or ether, dried ($MgSO_4$-K_2CO_3), concentrated, and purified by distillation or recrystallization (hexane or hexane-ethanol). Tables I, VI, and VII list the physical properties for the amides obtained. Where the reaction was not so straightforward as described above, amplification of the procedure is given below.

N-Ethylacetamide (1).—HF (75 ml) and CH_3CN (0.55 mol) were placed in the Monel reactor and pressured to 400 psig with ethylene at 20°. The pressure dropped to 250 psig (ca. 1 hr) and was repressured to 400 psig; the process was repeated until 0.57 mol had been added. The reactor was shaken an additional 17 hr and the pressure dropped to 150 psig. On work-up (extraction with CH_2Cl_2) 2.9 g of a yellow oil was obtained containing 50% 1 as determined by glpc comparison with an authentic sample.

N-Isopropylacetamide (2).—HF (75 ml) and CH_3CN (0.55 mol) were placed in the Monel reactor and pressured with propylene, and the reactor was shaken at 10°. The pressure rapidly fell to 10 psig and was repressured to 100 psig; this process was repeated 12 times to give 0.52 mol of propylene. Isolated yield was low (23%) because of difficulties in extracting the highly water-soluble amide.

N-(2- and 3-Pentyl)acetamides (3).—1-Pentene (0.20 mol), CH_3CN (0.26 mol), and HF (50 ml) gave 15.6 g of distilled acetamidopentanes. The 2 and 3 isomers could not be separated by our glpc technique and were independently prepared by acetylation of the corresponding amines, N-2-pentylacetamide, bp 70° (0.2 mm), and N-3-pentylacetamide, mp 69–70°. The carbon-migrated N-t-amylacetamide was likewise independently synthesized, mp 78–79°, and was readily distinguished from the other isomers by glpc. None of the latter compound was found in the reaction mixture with 1-pentene.

N-(2-, 3-, and 4-Octyl)acetamides (6).—As described in the discussion these were prepared by a variety of conditions from octenes, CH_3CN, and HF. The mixture of the 2, 3, and 4 isomers was a liquid which solidified on prolonged standing. The individual isomers were independently prepared from the ketone via the oxime followed by $LiAlH_4$ reduction according to the method of Geiseler, *et al.*[17]

N-Dodecylacetamides (10).—1-Dodecene (0.10 mol), CH_3CN (0.11 mol), HF (25 ml), and SO_2 (75 ml) gave a 40% purified yield of the mixed dodecylacetamides.

Reaction of 3,3-Dimethyl-1-butene with CH_3CN in HF–SO_2.—3,3-Dimethyl-1-butene (0.10 mol), CH_3CN (0.10 mol), and 25 ml of HF in 50 ml of SO_2 gave 9.0 g of a crude amide mixture which was distilled, bp 69–76° (0.4 mm), and solidified to white crystals, mp 54–56°. Glpc analysis indicated only one peak; however, the nmr spectrum indicated that 80% of the material was the carbon-migrated compound, N-(1,1,2-trimethylpropyl)-acetamide (15), and 20% was N-(1,2,2-trimethylpropyl)acetamide (16). Three observations in the nmr spectrum point to this conclusion: (1) a very small but detectable N–H doublet is present at δ 7.92 in addition to the strong N–H singlet at 7.59 of 15; (2) a small rise in the integral occurs at δ 3.80 indicative of $HCNHCOCH_3$ of 16 which is not present in pure 15; (3) two –$COCH_3$ bands occur at 8.1 µ. The methyl band at 9.08 µ is greatly enhanced in area. Elemental analysis of the mixture gave the correct percentages (see Table VI).

Reaction of 3-Methyl-1-butene with CH_3CN–HF.—HF (50 ml) and CH_3CN (0.20 mol) were placed in the polyethylene reactor and cooled in an ice bath. 3-Methyl-1-butene (0.20 mol) which had been condensed in a Dry Ice bath was added slowly by means of a cooled pipet, and the mixture was allowed to gradually warm

(17) G. Geiseler, F. Asinger, and G. Henning, *Chem. Ber.*, **94** 1008 (1961).

to room temperature. The contents were poured on ice, neutralized with NH₄OH, dried (K₂CO₃), extracted with ether, and concentrated to give 11.45 g of a yellow oil. Glpc analysis of the oil indicated the following components (%): ether (5); *t*-amyl alcohol (29), arising from hydrolysis of the intermediate *t*-amyl fluoride; unknown (2); *t*-amylacetamide (54); and N-(1,2-dimethylpropyl)acetamide (9). The ratio of *t*-amylacetamide to N-(1,2-dimethylpropyl)acetamide was 6.3 with the yield of amidic products being 7.23 g (28% yield). The mixture was recrystallized from hexane to a white crystalline mixture, mp 70–74°.

N-Cyclohexylformamide (22).—A 1-l. Monel autoclave with a bottom tap was charged with HF (14.5 mol), water (2.8 mol), and liquid HCN (2.4 mol) and the temperature was maintained at 16° with circulating cooling water. Cyclohexene (2.0 mol) was added over a period of 45 min at 16° and the reactor was then heated to 54° for 5 hr. The reaction mixture was discharged through the bottom tap, poured on ice water, neutralized with NH₄OH, extracted (Et₂O), dried (MgSO₄), and concentrated to give 242.6 g of a light brown liquid. Glpc analysis indicated the following (%): ether (5); cyclohexanol (trace); cyclohexyl formate (9); and cyclohexylformamide (86). Distillation gave the pure formamide, bp 95–97° (0.4 mm).

In a similar run at 16° for 2 hr in addition to the above-mentioned materials cyclohexyl fluoride and cyclohexyl isonitrile were also isolated.

N-Cycloheptylacetamide (23).—Cycloheptene (0.20 mol) was added to a mixture of HF (50 ml) and CH₃CN (0.30 mol) at 10°. After warming to room temperature, the mixture was stirred for 30 min, poured on ice, neutralized with NH₄OH, extracted (Et₂O), dried (MgSO₄), and concentrated to give 25.0 g of crude amide. Glpc analysis indicated only one peak. Distillation gave the pure amide, bp 126–129° (0.8 mm), which melted at 51–55°. None of the ring-contracted material, N-1-methylcyclohexylacetamide, was found as determined by independently synthesizing the material and spiking the mixture prior to glpc analysis. Also the nmr spectrum indicated no ring contraction (CDCl₃), δ 7.50 (d, 1, *J* = 9.5 Hz, N–H), 3.90 (m, 1, ring H α to nitrogen), 1.82 (s, 3, COCH₃), and 1.53 (m, 16, ring hydrogens).

N-Cyclohexyltrifluoroacetamide (33).—A 300-ml Monel reactor was charged with 50 ml of HF, cooled in a Dry Ice bath, and charged with trifluoroacetonitrile (0.28 mol), bp −64°, by pressuring the gas into the reactor until the desired loss in weight was achieved. Cyclohexene (0.25 mol) was placed in a stainless steel bomb, pressured to 100 psig with N₂, and attached to the Monel reactor in such a way that the olefin could slowly be added to acid mixture. The reaction mixture was then shaken at 30° for 4 hr. After the material was poured on ice, neutralization, extraction, drying, and concentration gave 38.9 g of red-orange, low melting crystals. The material that was distilled [bp 77° (3.0 mm)] solidified to a crystalline mass, mp 93.5–94.5° (hexane).

N-(cis-2-Bicyclo[3.3.0]octyl)acetamide (37).—A mixture of HF (75 ml) and acetonitrile (0.60 mol) was cooled to −50° and 1,5-cyclooctadiene (0.20 mol) was added slowly. The mixture was allowed to warm to 0° over a period of 40 min and poured on ice. Neutralization, extraction, drying, and contration gave 28.1 g of a yellow viscous residue which could not be distilled but could be recrystallized from cyclohexane or pentane or sublimed [150–220° (0.2 mm)] to give white crystals, mp 135–136°. Infrared spectrum indicated the normal amide bands at 3.1 (N–H) and 6.1 μ (C=O); glpc analysis suggested only one component; and the nmr spectrum (CDCl₃) consisted of δ 6.78 (d, N–H), 1.92 (s, 3, COCH₃), and 1.8 (m, 13, ring protons).
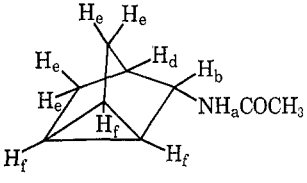
2,5-Diacetamido-2,5-dimethylhexane (38).—A mixture of HF (75 ml) and CH₃CN (0.60 mol) was cooled to −50° and 2,5-dimethyl-1,5-hexadiene was added over a period of 5 min. After the mixture warmed to 0° over a period of 30 min, it was poured on ice and neutralized with NH₄OH. White solids formed, which floated to the top and were filtered and air dried to give 31 g of crude diamide. Recrystallization (EtOH), followed by washing with ether, gave 10 g of white crystals, mp 226–228°. No attempt was made to recover additional product. The diamide exhibited interesting solubility characteristics in that it was insoluble (0.3 g in 1–2 ml of solvent) in CHCl₃, acetone,

dimethyl sulfoxide, dimethylformamide, benzene, pyridine, and water and was soluble in MeOH, hot EtOH, warm dimethylformamide, dilute HCl, CH₃CO₂H, CF₃CO₂H, and concentrated H₂SO₄. The infrared spectrum (Nujol) consisted of 3.14 (N–H) and 6.15 μ (C=O); nmr (CF₃CO₂H) δ 8.28 (s, 2, N–H), 2.47 (s, 6, COCH₃), 1.94 (s, 4, -CH₂-), 1.50 [s, 12, -C(CH₃)₂].

Anal. Calcd for C₁₂H₂₄N₂O₂: C, 63.21; H, 10.61; N, 12.29. Found: C, 63.28; H, 10.55; N, 11.85.

N-3-Nortricyclylacetamide (36).—HF (60 ml), CH₃CN (15 g), and water (5 g) were placed in a polyethylene reaction vessel and cooled to 0°. Freshly distilled norbornadiene (0.20 mol) was added slowly (30 min) at a rate such that the temperature never rose above 10° and was allowed to stir an additional 25 min at 0–10°. The yellow mixture was poured on ice, forming a viscous gum. The aqueous mixture was neutralized with concentrated NH₄OH and extracted with ether (ca. 1 l.), dried (MgSO₄), and concentrated to give 5.0 g of an oil which tended to crystallize. Four recrystallizations (hexane) gave white needles (0.45 g), mp 106–107° (2% yield). The structure of **36** is further supported by the following spectroscopic data: infrared (Nujol) exhibited the characteristic nortricyclyl absorbances[18] at 12.4, 7.7, 6.8, and 3.3 μ in addition to the usual amide absorbances. The nmr data are given in Table VIII. Pertinent peaks in the

TABLE VIII

NMR SPECTRUM FOR N-3-NORTRICYCLYLACETAMIDE

Proton	Chemical shift	Area	Multiplicity
H_a	5.7 –6.5	1	Broad
H_b	3.65–3.95	1	Broad doublet
H_{c,d}	1.8 –2.5	4	Singlet at 1.98 represents a -CH₃ group and is overlapped by a broad resonance due to H_d
H_e	1.25–1.75	4	Multiplet
H_f	1.00–1.25	3	Multiplet characteristic of the cyclopropyl portion of nortricyclene

mass spectrum (70 eV) are as follows: *m/e* (rel intensity), 151 (48, parent ion, M), 108 (48, M − COCH₃), 94 (54, nortricyclyl radical ion), and 43 (100, O=C—CH₃⁺).

(18) D. J. Trecker and J. P. Henry [*J. Amer. Chem. Soc.*, **85**, 3204 (1963)] cite a band at 12.4 μ as very characteristic of the nortricyclene ring system, a band at 3.3 μ due to the cyclopropyl portion, and doublets at 6.8 and 7.7 μ which were always present in the derivatives studied.