Small Ring Systems from Isocyanides. I. The Reaction of Isocyanides with Hexafluorobutyne-2[1]

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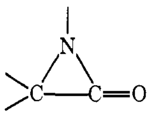
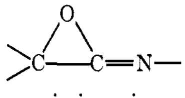
Abstract: The use of the characteristic α,α-addition reaction of isocyanides as a method for the formation of a small membered ring system has been investigated. In inert solvents, isocyanides react with 2 mol of hexafluorobutyne-2 to produce cyclopropenylketenimine derivatives. None of the simple 1:1 adducts (the anticipated iminocyclopenone derivatives) were detected. The cyclopropenylketenimines were easily hydrolyzed to the corresponding cyclopropenylamides and reduced to cyclopropane derivatives. When isocyanides were allowed to react with hexafluorobutyne-2 in ethanol as solvent, two different 1:1:1 adducts (isocyanide:butyne:ethanol) were obtained, a ketenimine and a conjugated imino ester. The structure of these 1:1:1 adducts imply the prior formation of a 1:1 intermediate that may have predominant carbene or carbanion character.

The interesting question of the possible existence of α-lactams has been solved, largely by the work of Sheehan[2] and Baumgarten.[3] At the same time, their work raised the question of the possible existence of α-iminooxiranes, at one time thought to be easily convertible valence tautomers of the α-lactams.



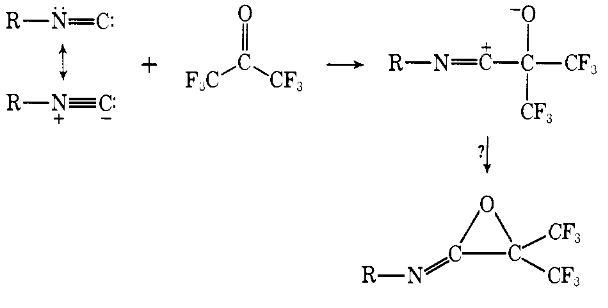
an α-lactam



an α-iminooxirane

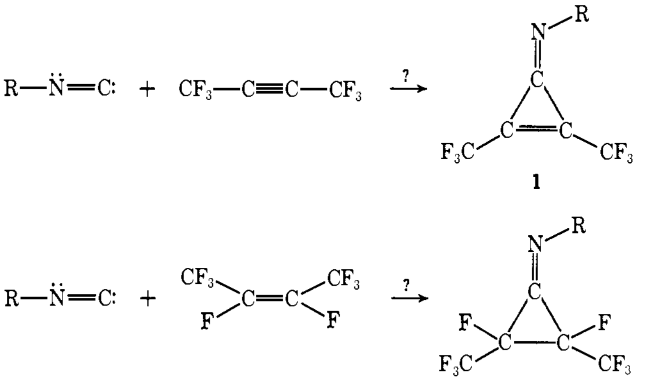
Since it had been conclusively demonstrated the α-lactams possessed a real existence, we began to study ways toward the synthesis of the α-iminooxiranes. A novel approach was suggested by the work of Sheehan and Lengyel.[4]

Their work showed that an α-lactam, when heated to 70°, produced nearly equimolar amounts of a ketone and an isocyanide. They suggested that an intermediate in their reaction might well be an α-iminooxirane. We felt that we might be able to reverse part of the above reaction by using an extremely electrophilic carbonyl compound such as hexafluoroacetone. However, instead of forming the α-iminooxirane, 2 mol of ketone reacted per mol of isocyanide to form stable α-iminodioxolanes. This work has since been published independently by two groups of chemists.[5,6] Our failure to isolate an α-iminooxirane even under conditions of high dilution addition of the ketone to the isocyanide were somewhat discouraging but the facile formation of the 2:1 adduct (the dioxolane) proved that isocyanides could interact with a carbonyl that was strongly activated by electron-withdrawing groups. We therefore turned our attention toward the reaction of isocyanides with electron-deficient double and triple bonds. We report the results of that investigation in this paper.



We initially felt that an isocyanide might add to an activated double or triple bond in the ways shown in Scheme I. We discovered that a reaction did indeed take place with the acetylene but no reaction has so far been observed in the case of the ethylene derivative. The product of the reaction of the isocyanide with perfluorobutyne-2 was not a 1:1 adduct, however, but rather a 1:2 adduct (1 mol of isocyanide to 2 mol of the butyne).

Scheme I



From analogous work on the reaction of carbon monoxide with triple bonds or from the spectral data, various possible structures were suggested for these 1:2 adducts. The three most reasonable structures seemed to be **3**–**5**.

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[1] Acknowledgment is made to the donors of The Petroleum Research Fund, administered by the American Chemical Society, for support of this research. A portion of this paper was taken from the M.S. Thesis of F. J. Nagel, Cleveland State University, 1968. Presented in part at the 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April, 1969, Abstract ORGN-100.

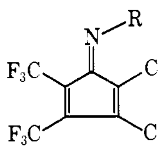
[2] J. C. Sheehan and I. Lengyel, *J. Am. Chem. Soc.*, **86**, 1356 (1964). For a recent review article on α-lactams see: I. Lengyel and J. C. Sheehan, *Angew. Chem. Intern. Ed. Engl.*, 7, 25 (1968).

[3] H. E. Baumgarten, J. F. Fuerholzer, R. D. Clark, and R. D. Thompson, *J. Am. Chem. Soc.*, **85**, 3303 (1963).

[4] J. C. Sheehan and I. Lengyel, *ibid.*, **86**, 746 (1964).

[5] N. P. Gambaryan, E. M. Rokhlin, Yu. V. Zeifman, L. A. Simonyan, and I. L. Knunyants, *Dokl. Akad. Nauk SSSR*, **166**, 864 (1966).

[6] W. J. Middleton, D. C. England, and C. G. Krespan, *J. Org. Chem.*, **32**, 948 (1967).



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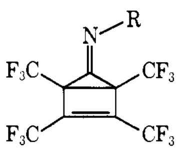

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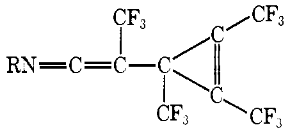

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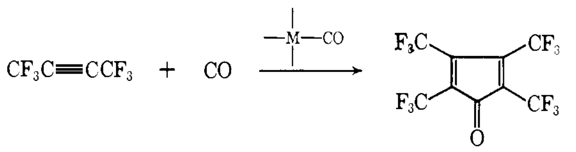
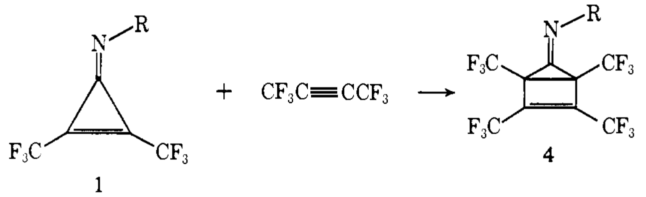
A compound analogous to structure **3** has been obtained from the reaction of a metal–carbonyl complex with perfluorobutyne-2 under high pressures of carbon



monoxide.[7] A similar type of reaction has been briefly reported in a review article[8] (results unpublished) for the reaction of an isocyanide with diethyl acetylene dicarboxylate.

Compound **4** might be expected to arise from the cycloaddition of 1 mol of the butyne to the previously mentioned cyclopropenone imine (**1**). The ten-



dency of perfluoro compounds to undergo cycloaddition reactions to form small-membered rings perhaps strengthens the possible formation of compound **4**.

Structure **5** was suggested for the 2:1 adduct only after careful study of the spectral data. We now feel that analysis of all the data enables us to reject structures **3** and **4** and demonstrate conclusively that structure **5** is the true structure of the 2:1 adducts.

The 2:1 adducts of perfluorobutyne-2 and the isocyanides are relatively stable pale yellow liquids that are formed under quite mild conditions. In a tightly stoppered vial they are stable for an indefinite period of time but in the presence of moist air they rapidly undergo a reaction to produce white crystalline amides (*vide infra*) which differ from the 2:1 adducts in chemical analysis only by the addition of a molecule of water. The same amides are more readily obtained by hydrolysis of the 2:1 adducts in 50% sulfuric acid. The adducts are soluble in organic solvents and quite insoluble in water. They dissolve in solvents such as benzene or xylene without an intensification of color; in contrast to the marked color changes that occur upon the addition of perfluorotetramethyl cyclopentadienone to aromatic solvents.[7] We would expect compounds of structure **3** to form similar colored π complexes.

The very strong absorption at 4.80 μ (the acetylene or cumulene region) together with the medium, sharp absorption at 5.25 μ would also seem to rule out structure **3** since perfluorotetramethyl cyclopentadienone shows no absorption in these regions.[7] The above absorptions are in good agreement with structure **5**; the peak at 4.80 μ is precisely the position of absorption for a ketenimine[9] and the peak at 5.25 μ is the expected position of absorption for a fully substituted cyclopropene double bond.[10,11] The work of Mahler[12] provides a good analogy; he has prepared 1,2-bis(trifluoromethyl)-3,3-difluorocyclopropene which has a double-bond absorption at 5.5 μ.

Structure **4** seems inconsistent with these data. In order that structure **4** fit these data the peak at 4.80 μ must be attributed to the strained $>C{=}N-$ stretch while the peak at 5.25 μ to the substituted cyclobutene double bond. Since tetramethylcyclopropanone absorbs at 5.43 μ,[13] it would be reasonable to expect the imine to absorb at higher wavelength not at lower wavelength and nowhere near 4.80 μ. Furthermore, a fully substituted cyclobutene double bond absorbs at 5.94 not 5.25 μ.[14]

The ^{19}F nmr spectra of the 2:1 adducts also favor structure **5**. The three signals with relative areas of 1:2:1 is consistent with structure **5**. However, if there is slow inversion of the R group at the imino nitrogen then the two α positions in structures **3** and **4** may become nonequivalent while the two β positions may be remote enough to remain essentially equivalent. Thus, a 1:2:1 pattern could perhaps arise from structure **3** or **4** but such a pattern is more consistent with structure **5**.

The facile addition of water to the 2:1 adducts to form amides is consistent with either structure **4** or **5** and quite inconsistent with structure **3**. This, together with the spectral data and the fact that the 2:1 adducts do not form colored π complexes with π bases eliminates structure **3** as a possibility. It should be kept in mind, however, that **3** may be formed but not detected in the polymeric pot residue.

Products anticipated from the hydrolysis of **4** and **5** are shown in Scheme II. The hydrolysis products displayed absorption in the infrared that is characteristic of a secondary amide; N–H, 2.90 μ and $>C=O$, 5.90 μ. The appearance of these amide peaks was accompanied by the disappearance of the strong peak at 4.80 μ while the peak at 5.25 μ was still present in the amides.

The proton nmr is consistent with either structure **6** or **7**. Other than the protons in the R group the proton nmr displayed a single quartet with a coupling constant of 8 cps at δ 3.63 when R was cyclohexyl and δ 3.87 when R was phenyl, both in $CDCl_3$. Both the chemical shift and the coupling constant fall in the expected range for such a proton.[15]

The ^{19}F nmr first appeared to fit structure **6** better than structure **7** in that four different kinds of fluorine

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(7) R. S. Dickson and G. Wilkinson, *J. Chem. Soc.*, 2699 (1964).

(8) E. Winterfeldt, *Angew. Chem. Intern. Ed. Engl.*, **6**, 434 (1967).

(9) N. B. Colthup, L. H. Daly, and S. E. Wiberley, "Introduction to Infrared and Raman Spectroscopy," Academic Press, New York, N. Y., 1964, p 205.

(10) Reference 9, p 218.

(11) R. Breslow and L. J. Altman, *J. Am. Chem. Soc.*, **88**, 504 (1966).

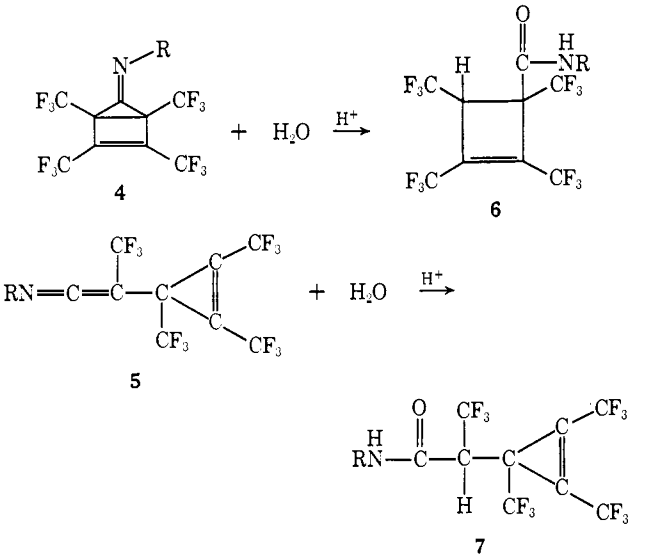
(12) W. Mahler, *ibid.*, **84**, 4600 (1962).

(13) N. J. Turro, W. B. Hammond, and P. A. Leermakers, *ibid.*, **87**, 2774 (1965).

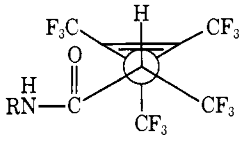
(14) Reference 9, p 217.

(15) A good model could not be found for the chemical shift of this methine proton but if one looks at a similar methylene proton and extrapolates, the observed value seems reasonable. *Cf.* R. M. Silverstein and G. C. Bassler, "Spectroscopic Identification of Organic Compounds," John Wiley & Sons, Inc., New York, N. Y., 1967, pp 141–142.

Scheme II



are indicated by the four different signals, each of equal area. However, the following projection shows that the two CF_3 groups on the cyclopropene double bond



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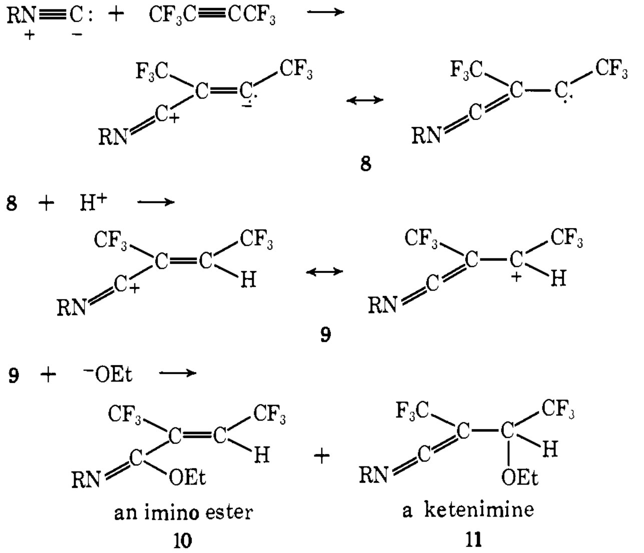
may be nonequivalent. Thus the introduction of the asymmetric center could cause the nonequivalence of the two remote CF_3 groups.

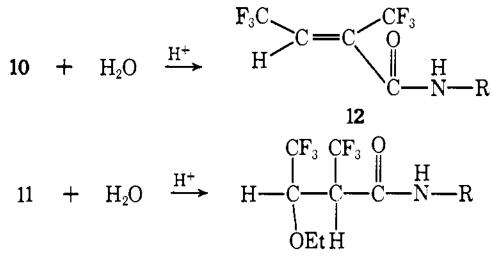
It is interesting to note that we were able to reduce the double bond of the 2:1 adducts (the peak at 5.25 μ completely disappeared) while the unsaturation producing the peak at 4.80 μ remained intact. At the same time, a weak absorption at 3.25 μ appeared which may be due to cyclopropyl C–H.[16] Similarly, the amides could also be reduced with hydrogen and platinum oxide. Again only 1 mol of hydrogen was absorbed per mol of amide and the peak near 5.28 μ completely disappeared. These reductions took place with some difficulty. Using 50 psi of hydrogen, we found it best to use freshly purified material, long reaction times (2 to 3 days), and rather large amounts of catalyst.

We feel that all of the above evidence, taken together, points strongly toward structure **5** as the structure of the 2:1 adducts. However, it is the reaction of isocyanides with perfluorobutyne-2 in ethanol as solvent that provided the necessary data to make the structure assignment more conclusive.

When cyclohexylisocyanide reacts with perfluorobutyne-2 in ethanol, an exothermic reaction occurs to produce two different 1:1:1 adducts (butyne, isocyanide, and ethanol). The higher boiling compound possessed a strong absorption at 4.80 μ which can only be assigned to a ketenimine functional group in view of the fact that this compound is easily hydrolyzed to an amide which differs in chemical analysis from the 1:1:1 adduct only by the addition of a molecule of water. The position and the intensity of the 4.80 μ absorption are almost identical in this 1:1:1 adduct and the original 1:2 adduct. The low-boiling 1:1:1 adduct does not possess an absorption in the 4.0–5.5-μ region. Strong bands at 5.88 and 5.98 μ together with the loss of the ethoxy group upon hydrolysis to give an amide, indicates that this material is an imino ester. The formation of the two 1:1:1 adducts may be visualized as shown in Scheme III.[17] The hydrolysis of **10** and **11** produced two different amides. In one case (**10**) the ethoxy group is lost whereas in the other case (**11**) the ethoxy group is retained.

Scheme III





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The isolation of the 1:1:1 adducts (**10** and **11**) indicates the possible prior formation of a 1:1 intermediate (**8**) which is trapped by the protic solvent. This same intermediate may be used to explain the formation of **5**.[18]

An interesting analogy to this reaction is found in the work of Meinwald and Aue[19] on the addition of a nitrene to a normal triple bond (2-butyne). They proposed the following as a possible mechanism to explain the formation of the major observed product (**15**). Meinwald and Aue point out that the intermediate (**14**)

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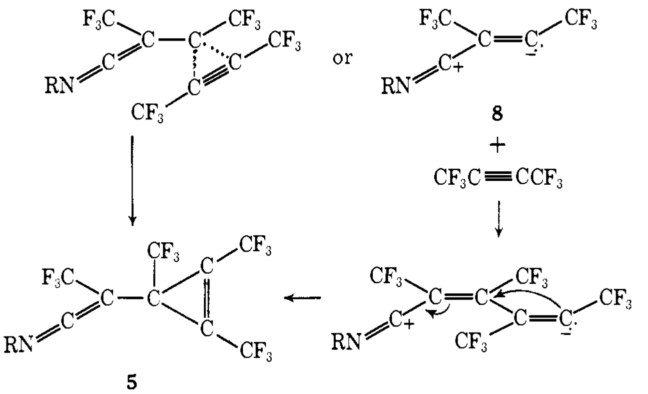
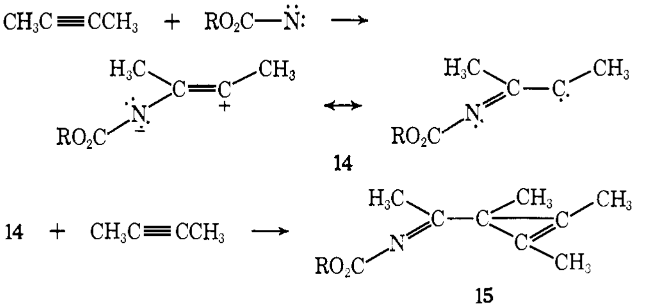
(16) H. E. Simmons, E. P. Blanchard, and H. D. Hartzler, *J. Org. Chem.*, 31, 295 (1966).

(17) A *cis* or *trans* configuration is possible in both **8** and **10**. The apparent small coupling constant between the two CF_3 groups (J = 3 cps) seems to favor a *trans* configuration for **10** which, in turn, implies that **8** is perhaps transoid but these conclusions are tentative. *Cf.* J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 2, Pergamon Press, Oxford, England, 1966, pp 912–913.

(18) We have attempted to alter the course of this reaction by employing solvents of different polarity. We hoped that the ylide **8** would undergo a 1,3 cycloaddition to hexafluorobutyne-2 in the more polar solvents to produce the imino cyclopentadienone, **3**. Thus far, however, the only 2:1 adducts which have been isolated correspond to structure **5**.

(19) J. Meinwald and D. H. Aue, *J. Am. Chem. Soc.*, **88**, 2849 (1966).





may have predominant carbene or carbonium ion character. In an analogous situation, we wonder if the proposed 1:1 intermediate in our reaction (**8**) has predominate *carbene* or *carbanion* character. Or, perhaps, we could describe the intermediate as a *nucleophilic carbene*. This brings up the interesting question as to the existence of such a species, and the methods of detection of such a species.

First, it should be pointed out that these intermediates (**8**) should possess more carbene character than the isocyanides. In the isocyanides, the charge-separated structure is about three times as important as the "carbene" structure.[20] In the case of intermediate **8**, the charge separated form should be relatively less important since the extent of charge separation is greater.

We have made some attempts to trap intermediate **8** with other than protic solvents. Some of the trapping agents employed were cyclohexene, 4-octyne, 3-hexyne, diphenylacetylene, and diethylmaleate. We have not yet been able to trap **8** with any of these compounds but we are investigating this aspect further.

Experimental Section

N-Cyclohexyl-3-perfluoromethyl-3-(1,2,3-*tris*(perfluoromethylcyclopropenyl))ketenimine. A 500-ml Parr pressure bottle containing 10.9 g (0.10 mol) of cyclohexylisocyanide and 200 ml of dichloromethane was cooled in a Dry Ice–acetone bath. Using a gas delivery tube, 32.4 g (0.20 mol) of perfluorobutyne-2 was condensed into the Parr bottle. The bottle was then stoppered and shaken on a Parr apparatus for 4 hr at room temperature. The pressure rapidly increased to 35 psi and after about 2 hr decreased to 10 psi. The solvent was removed under vacuum, and the brown viscous residue was distilled yielding 12.6 g (29%) of a light yellow liquid, bp 50–51° (0.7 mm). Similar yields were obtained when different solvents were employed: acetone (57%), cyclohexene (43%), propionitrile (30%). Triethylamine as solvent gave only a viscous polymeric material.

A redistillation of the yellow liquid afforded an analytical sample: bp 33–35° (0.1 mm); $\lambda_{\max}^{\text{neat}}$ 3.36 and 3.46 (CH), 4.80 (-N=C=C<), 5.26 μ (strained >C=C<), and 7.5–9.0 μ (-CF$_3$). The ^{19}F nmr spectrum in CCl$_4$ displayed peaks in the ratio of 1:2:1 at 3226 (octet), 3433 (complex), and 3988 Hz (complex) using CFCl$_3$ as an internal standard. The ^{1}H nmr showed a broad diffuse peak centered at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.67.

Anal. Calcd for C$_{15}$H$_{11}$NF$_{12}$: C, 41.57; H, 2.54; N, 3.23; F, 52.66. Found: C, 42.04; H, 2.38; N, 3.51; F, 52.09.

N-Phenyl-3-perfluoromethyl-3-(1,2,3-*tris*(perfluoromethylcyclopropenyl))ketenimine. Similar to the above procedure, 10.3 g (0.10 mol) of phenylisocyanide, 200 ml of dichloromethane, and 20.0 g (0.12 mol) of perfluorobutyne-2 were shaken overnight in the Parr vessel. Removal of the solvent under vacuum, and distillation of the residue yielded 7.7 g (33% based on the butyne) of a clear yellow liquid, bp 37–40° (0.5 mm). A large amount of blood red polymeric material remained in the pot. Redistillation of the yellow liquid afforded an analytical sample: bp 35–37° (0.25 mm); $\lambda_{\max}^{\text{neat}}$ 4.85 (>C=C=N-), 5.25 (strained >C=C<), and 7.5–9.0 μ (-CF)$_3$. The ^{19}F nmr spectrum in CCl$_4$ displayed peaks in the ratio of 1:2:1 at the following positions (CFCl$_3$ as internal standard); 3221 (octet), 3431 (complex), and 3987 H$_z$ (complex). The ^{1}H nmr showed a single sharp peak at $\delta_{\text{TMS}}^{\text{CCl}_4}$ 7.67.

Anal. Calcd for C$_{15}$H$_5$NF$_{12}$: C, 42.15; H, 1.17; N, 3.28; F, 53.40. Found: C, 41.52, 41.39; H, 1.21; N, 3.28; F, 54.19, 53.46.

N-*t*-Butyl-3-perfluoromethyl-3-(1,2,3-tris(perfluoromethylcyclopropenyl))ketenimine. Similar to the above procedure, 6.23 g (0.075 mol) of *t*-butylisocyanide, 100 ml of dichloromethane, and 24.3 g (0.15 mol) of perfluorobutyne-2 were shaken overnight in the Parr vessel at room temperature. Removal of the solvent under vacuum and distillation of the residue yielded 10.67 g (35%) of a light yellow liquid, bp 34–35° (2.5 mm). Redistillation of this material afforded an analytical sample: $\lambda_{\max}^{\text{neat}}$ 4.80 (-N=C=C<), 5.26 (strained >C=C<), and 7.5–9.0 μ (-CF$_3$).

Anal. Calcd for C$_{13}$H$_9$NF$_{12}$: C, 38.33; H, 2.21; N, 3.44; F, 56.02. Found: C, 38.58; H, 2.45; N, 3.22; F, 56.19.

N-Cyclohexyl-α-perfluoromethyl-α-(1,2,3-*tris*(perfluoromethylcyclopropenyl))acetamide. The 1:2 molar adduct of cyclohexylisocyanide and perfluorobutyne-2 was hydrolyzed to the amide in quantitative yield by vigorously shaking 1.0 g of the ketenimine with 10 ml of 50% sulfuric acid in a tightly stoppered vial. A white hydrophobic solid separated out almost immediately. Recrystallization of this material from benzene afforded an analytical sample: small white needles, mp 130–131°; $\lambda_{\max}^{\text{CHCl}_3}$ 2.88 (NH), 5.28 (strained >C=C<), 5.90 (>C=O), and 7.5–9.0 μ (CF$_3$). The ^{19}F nmr in CDCl$_3$ displayed four rather broad peaks of equal area at 3373, 3383, 3724, and 3968 Hz above CFCl$_3$. The ^{1}H nmr displayed broad diffuse peaks in the cyclohexyl region ($\delta_{\text{TMS}}^{\text{CDCl}_3}$ 1.7) and a quartet at δ 3.63 with a coupling constant of 8 cps.

Anal. Calcd for C$_{15}$H$_{13}$NOF$_{12}$: C, 39.91; H, 2.88; N, 3.10; F, 50.55. Found: C, 39.86; H, 2.74; N, 3.07; F, 50.72.

N-Phenyl-α-perfluoromethyl-α-(1,2,3-*tris*(perfluoromethylcyclopropenyl))acetamide. The 1:2 molar adduct of phenylisocyanide and perfluorobutyne-2 was hydrolyzed to the amide in quantitative yield by vigorously shaking 1.0 g of the ketenimine with 10 ml of 50% sulfuric acid in a tightly stoppered vial. The white hydrophobic solid that separated out was recrystallized three times from benzene to afford an analytical sample: small white needles, mp 120–122°; $\lambda_{\max}^{\text{CHCl}_3}$ 2.90 (NH), 5.28 (strained >C=C<), 5.85 (>C=O), and 7.5–9.04 μ (-CF$_3$). The ^{19}F nmr in CDCl$_3$ displayed four rather broad peaks of equal area at 3366, 3380, 3703, and 3966 Hz above CFCl$_3$. The ^{1}H nmr gave a complex pattern in the phenyl region (δ 7.3) and a quartet at $\delta_{\text{TMS}}^{\text{CDCl}_3}$ 3.87 where J = 8 cps.

Anal. Calcd for C$_{15}$H$_7$NOF$_{12}$: C, 40.45; H, 1.57; N, 3.15; F, 51.24. Found: C, 40.57; H, 1.56; N, 3.17; F, 51.26.

N-Cyclohexyl-3-perfluoromethyl-3-(1,2,3-*tris*(perfluoromethylcyclopropyl))ketenimine. The 1:2 molar adduct of cyclohexylisocyanide and perfluorobutyne-2 was reduced only by using rather large amounts of catalyst and somewhat extended reaction times.

A Parr bottle was charged with 110 ml of absolute ethanol, 10.1 g of the cyclohexylketenimine, and 0.35 g of PtO$_2$ and shaken under 50 psi of hydrogen for 36 hr. The catalyst was filtered off, and the solvent was removed at 35° using a rotary evaporator. Distillation of the residue yielded 8.0 g (80%) of a pale yellow liquid, bp 60–70° (0.50–1.0 mm). This material contained no peak in the strained >C=C< region (5.0–6.0 μ) while a strong absorption was still present in the ketenimine region (4.8 μ). The pale yellow liquid was distilled twice more and a center cut afforded an analytical sample: bp 44–45° (0.25 mm); $\lambda_{\max}^{\text{neat}}$ 4.80 (-N=C=C<) and 7.5–9.0 μ (CF$_3$). The ^{19}F nmr displayed four peaks of approximately equal area at 3138 (triplet), 3432 (complex), 3610 (doublet), and 3860 Hz (complex). The ^{1}H nmr displayed a broad diffuse peak in

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(20) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p 270.

the cyclohexyl region (δ_{TMS}^{neat} 1.47) and two additional ill-defined peaks at 2.73 and 3.74 ppm.[21]

Anal. Calcd for $C_{15}H_{13}NF_{12}$: C, 41.37; H, 3.02; N, 3.22; F, 52.40. Found: C, 41.03; H, 3.00; N, 3.12; F, 53.01.

N-Cyclohexyl-α-perfluoromethyl-α-(1,2,3-*tris*(perfluoromethylcyclopropyl))acetamide. The cyclohexylamide obtained by hydrolysis of the ketenimine was reduced by shaking 5.0 g of the freshly recrystallized amide, 150 ml of absolute ethanol, and 0.30 g of PtO_2 under 50 psi of hydrogen for 4 days at room temperature. The catalyst was filtered off and the solvent removed using a rotary evaporator. The residue was recrystallized from benzene to yield 1.77 g (35%) of fine white fluffy needles. A second recrystallization from benzene afforded an analytical sample: mp 154–155° subl; $\lambda_{max}^{CHCl_3}$ 2.90 (NH), 5.95 (>C=O), and 7.5–9.0 μ (CF_3); no absorption in the 5.0–5.9 μ region (strained >C=C<).

Anal. Calcd for $C_{15}H_{15}NOF_{12}$: C, 39.74; H, 3.31; N, 3.09; F, 50.33. Found: C, 39.69; H, 3.23; N, 3.09; F, 50.30.

Reaction of Cyclohexylisocyanide, Perfluorobutyne-2, and Ethanol. A 500-ml Parr bottle in a Dry Ice–acetone bath was charged with 100 ml of absolute ethanol, 10.9 g (0.10 mol) of cyclohexylisocyanide, and 40.5 g (0.25 mol) of perfluorobutyne-2. The bottle was placed on the shaker and allowed to warm to room temperature. The pressure rose to 60 psi very rapidly as an exothermic reaction took place. The bottle was shaken overnight by which time the pressure had dropped to 5 psi. The solvent was removed from the yellow solution using a rotary evaporator. The solvent fraction contained a fairly large amount of a fluoro compound as determined by infrared. This was probably the addition product of ethanol to perfluorobutyne-2, $CF_3CH{=}CCF_3OEt$ (bp 72–73°).[22]

The orange liquid residue was then fractionally distilled. An early cut consisting of 10.57 g (bp 25–40° (0.1 mm)) and a late cut consisting of 12.02 g (bp 45–55° (0.1 mm)) were collected. The low-boiling cut possessed a strong peak at 5.98 μ (>C=N–) and little absorption in the 4.5–5.0-μ region (–N=C=C<) while the reverse was true for the high-boiling fraction. (The high-boiling fraction possessed a very strong peak at 4.80 μ.)

The low-boiling cut was redistilled and a fraction boiling at 29–30° (0.1 mm) afforded an analytical sample of **1,2-bis(perfluoromethyl)-3-ethoxy-3-(N-cyclohexylimino)propene (10)**, an imino ester; λ_{max}^{neat} 3.36 (CH), 5.88 and 5.98 (conjugated >C=N–), and 7.5–9.0 μ (–CF_3). The ^{19}F nmr spectrum ($CFCl_3$) displayed two signals of equal area: 3156 (two complex doublets, with *J* values of 4 and 14 cps) and 3540 Hz (broadened triplet, *J* = 3 cps). The ^{1}H nmr spectrum (TMS) showed the triplet (1.27 ppm) quartet (4.17 ppm) pattern of the ethoxy group. The triplet at 1.27 ppm was well defined but superimposed on the cyclohexyl hydrogens. A broad ill-defined peak at 2.96 ppm and a poorly resolved signal at 6.34 ppm (pair of doublets) each representing one proton also appeared in the spectrum.

Anal. Calcd for $C_{13}H_{17}NOF_6$: C, 49.21; H, 5.36; N, 4.42; F, 35.96. Found: C, 49.30; H, 5.29; N, 4.65; F, 35.75.

The high-boiling cut was redistilled and a cut boiling at 61–63° (0.4 mm) afforded an analytical sample of **N-cyclohexyl-3-perfluoromethyl-3-(1-ethoxy-2,2,2-trifluoroethyl)ketenimine (11)**. The infrared spectrum displayed the following peaks: λ_{max}^{neat} 3.36 and 3.46 (CH) 4.80 (–N=C=C<) and 8.0–9.0 μ (–CF_3). The ^{19}F nmr spectrum ($CFCl_3$) displayed two signals of equal area at 3219 (doublet, *J* = 2 cps) and 4423 Hz (multiplet). The ^{1}H nmr spectrum (TMS) showed the typical ethoxy pattern (a triplet at 1.25 and a quartet at 4.05 ppm). A broad multiplet appeared at 3.63 ppm.

Anal. Calcd for $C_{13}H_{17}NOF_6$: C, 49.21; H, 5.36; N, 4.42; F, 35.96. Found: C, 49.44; H, 5.29; N, 4.25; F, 35.36.

N-Cyclohexyl-2,3-(bis(perfluoromethyl))acrylamide. To 0.942 g (0.003 mol) of the low-boiling 1:1:1 molar adduct of cyclohexylisocyanide, perfluorobutyne-2, and ethanol (the imino ester) dissolved in 10 ml of acetone was added ten drops of concentrated hydrochloric acid and then ten drops of water. The mixture was allowed to stand loosely covered until the solvent had evaporated (2 days). A white crystalline material weighing 0.75 g (80%) and melting at 80–90° was obtained. Repeated attempts at recrystallization from various solvents were unsuccessful. A sample of the original white solid (mp 80–90°) afforded an analytical sample; λ_{max}^{KBr} 3.02 (NH), 3.38 and 3.47 (CH), 3.22 (secondary amide overtone), 6.08 and 6.53 (secondary amide), and 7.5–9.0 μ (–CF_3).

Anal. Calcd for $C_{11}H_{13}NOF_6$: C, 45.67; H, 4.50; N, 4.84; F, 39.45. Found: C, 45.52; H, 4.63; N, 4.88; F, 39.16.

N-Cyclohexyl-3-ethoxy-2,3-(bis(perfluoromethyl))propionamide. To a solution of 0.500 g of the high-boiling 1:1:1 molar adduct of cyclohexylisocyanide, perfluorobutyne-2, and ethanol (the ketenimine) dissolved in 10 ml of acetone was added six drops of water and four drops of concentrated hydrochloric acid. The clear solution was heated to boiling and water was added until the solution became cloudy. Upon cooling and air evaporation of the solvent overnight, a white crystalline material was obtained in 80% yield. Recrystallization from benzene afforded an analytical sample; mp 114–117°; λ_{max}^{KBr} 2.99 (NH), 3.38 and 3.46 (CH), 3.18 (secondary amide overtone), 6.07 and 6.44 (secondary amide), and 7.5–9.0 μ (–CF_3).

Anal. Calcd for $C_{13}H_{19}NO_2F_6$: C, 46.57; H, 5.67; N, 4.18; F, 34.03. Found: C, 46.58; H, 5.76; N, 4.37; F, 33.94.

Reaction of the N-Cyclohexyl and the N-Phenyl 2:1 Adducts with Air. Small samples of these 2:1 adducts were allowed to stand in loosely covered watch glasses for 1 or 2 days. The melting points and infrared spectrum of the white crystalline solids that formed were identical with those of the amides formed by hydrolysis in 50% sulfuric acid.

The rate of hydrolysis in air was markedly dependent on the color of the 2:1 adduct. Pale yellow samples underwent air hydrolysis very rapidly (2 to 3 hr) while deeper yellow samples underwent air hydrolysis quite slowly (2 days). The spectra of the pale or deep yellow samples of the 2:1 adducts were essentially identical. Not always could the deeper yellow color be removed by redistillation.

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(21) The presence of four complex peaks in the ^{19}F nmr and the two ill-defined peaks in the proton nmr may be due to the formation of the two possible hydrogenation products, one where the two hydrogens add *cis* to the 3-CF_3 group and one where they both add *trans* to the 3-CF_3 group.

(22) R. N. Haszeldine, *J. Chem. Soc.*, 3498 (1952).