Formation of Urea, Isourea, and Triazine Derivatives from Diisopropylcyanamide with Trifluoroacetic Anhydride and Trifluoromethanesulfonic Anhydride: Thermal Instability of Urea and Isourea Derivatives

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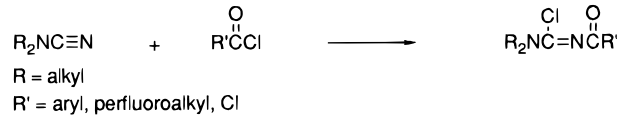
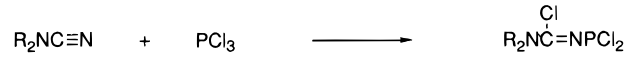
Diisopropylcyanamide reacts exothermically with trifluoroacetic anhydride to give **2**, an equilibrium mixture, in C_6D_6 solution, of 1:1 adducts, *N*,*N*-diisopropyl-*N*′,O-bis(trifluoroacetyl)isourea, **2a** (10%), and *N*,*N*-diisopropyl-*N*′,*N*′-bis(trifluoroacetyl)urea, **2c** (90%), at 27 °C. Compound **2c** is a colorless solid, mp 49−51 °C. Thermolysis of **2**, at 117 °C, shows first-order kinetics with the intital products being trifluoroacetonitrile, **4**, and diisopropylcarbamic trifluoroacetic mixed anhydride, **3**. Trifluoroacetonitrile trimerizes to 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, and **3** is thermally labile giving diisopropyltrifluoroacetamide and CO_2. In the thermolysis reaction **4** reacts with **2a** to give a small amount of 4-(diisopropylamino)-4-(trifluoroacetoxy)-2,6-bis(trifluoromethyl)-4*H*-1,3,5-oxadiazine, **7**. A related compound, 4,4-bis(diisopropylamino)-2,6-bis(trifluoromethyl)-4*H*-1,3,5-oxadiazine, **8**, is formed from **7** and **2c** going through a concentration maximum at 4000 s in the kinetic run. Compound **8** thermolytically dissociates to generate **4** and tetraisopropylurea. Compound **2** is a trifluoroacetylating agent with methanol giving methyl trifluoroacetate in 97% yield. Accompanying this reaction is a methanol displacement of diisopropylamine giving a 1.7% yield of methyl-*N*-(trifluoroacetyl)urethane. Diisopropylcyanamide also reacts exothermically with trifluoromethanesulfonic anhydride to give 2,4,6-tris(diisopropylamino)-1-(trifluoromethanesulfonyl)triazinium trifluoromethanesulfonate, **15**, in 96% yield. X-ray crystallographic structure drawing of **15** shows N1 (attached to CF_3SO_2) is pyramidal while N2, N4, and N6 (all diisopropylamino nitrogens) are sp^2-planar. A small amount of *O*-ethyl-*N*,*N*-diisopropyl-*N*′-(trifluoromethanesulfonyl)isourea was also recovered, produced by the reaction of the initially formed intermediate, *N*,*N*-diisopropyl-*N*′,O-bis(trifluoromethanesulfonyl)isourea, with ethanol contaminant in absolute ethyl ether solvent. Treatment of **15** with methanol, in the presence of K_2CO_3, gave a 90% yield of 2,4,6-tris-(diisopropylamino)-1-(trifluoromethanesulfonyl)-4-methoxy-1,4-dihydrotriazine.

Introduction

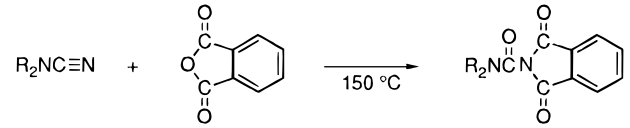
The chance observation that diisopropylcyanamide, **1**, reacted vigorously and exothermically with trifluoroacetic anhydride (TFAA) prompted the initial investigation which indicated the formation of a 1:1 adduct, **2**. Search of the literature disclosed a number of examples of dialkylcyanamides reacting with acyl chlorides with the acyl group adding to nitrogen and the chloride adding to the carbon of the cyano group, as shown in the illustration:[1−3]



Phosphorus trichloride,[4] sulfuryl chloride,[5−7] and thionyl chloride[5,7] react with dialkylcyanamides, similarly, to add chloride on the carbon and the remainder on the nitrogen of the cyano group, as demonstrated with phosphorus trichloride:



There was one reference[8] to the reaction of dialkylcyanamides with phthalic anhydride which required several hours of heating at 150 °C as opposed to the exothermic reaction of TFAA with diisopropylcyanamide, **1**, at low



temperature. Very recently a reference appeared on the reaction of trifluoromethanesulfonic anhydride (triflic anhydride) with dimethylcyanamide[9] which proceeded

[⊗] Abstract published in *Advance ACS Abstracts,* December 1, 1997.

(1) Bredereck, K.; Richter, R. *Chem. Ber.* **1966**, *99*, 2454−2460.
(2) Lebedev, V. N.; Yurechko, V. V.; Vishnyakova, T. P. *Zh. Vses. Khim. Ova.* **1981**, *26*, 465−466.
(3) Tocker, S. Ger. Offen. 2708024, 1977; *Chem. Abstr.* **1977**, *87*, 201591p.
(4) Shevchenko, V. I.; Pisanenko, N. P.; Kosinskaya, I. M. *Zh. Obshch. Khim.* **1978**, *48*, 1179.
(5) Markovskii, L. N.; Shermolovich, Yu. G.; Shevchenko, V. I. *Zh. Org. Khim.* **1973**, *9*, 633−634.
(6) Schindler, N. *Chem. Ber.* **1973**, *106*, 56−61.
(7) Markovskii, L. N.; Shermolovich, Yu. G.; Nuzhdina, Yu. A.; Shevchenko, V. I. *Zh. Org. Khim.* **1974**, *10*, 1000−1006.
(8) (a) Grigat, E. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 949−963 (see p 955). (b) Grigat, E.; Pütter, R. Ger. Offen. 1936127, 1971; *Chem. Abstr.* **1971**, *74*, 87642k.
(9) Martinez, A. G.; Fernandez, A. H.; Jimenez, F. M.; Ruiz, P. M.; Subramanian, L. R. *Synlett* **1995**, 161−162.

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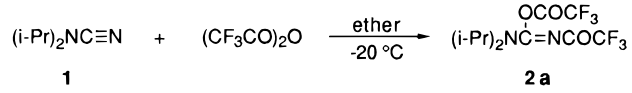
quite differently from the reaction of triflic anhydride with **1** in the present work.

Research discussed in this work includes reaction of **1** with TFAA to give **2**, kinetics of the thermolysis of **2**, reactions of the thermolysis fragments of **2**, and **2** as a trifluoroacetylating agent with methanol. In addition, the quite different reaction of **1** with triflic anhydride will be discussed.

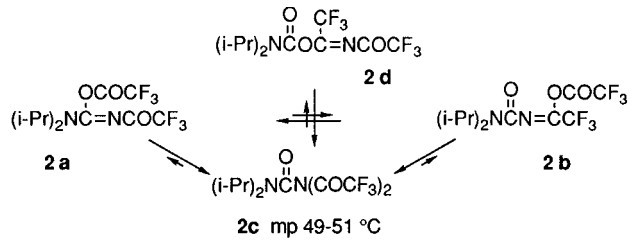
Discussion and Results

Reaction of Diisopropylcyanamide with Trifluoroacetic Anhydride. Diisopropylcyanamide, **1**, reacts exothermically with trifluoroacetic anhydride in ether to give a high yield (98%) of a 1:1 adduct, **2**. The reaction presumably proceeds by addition of TFAA to the nitrile triple bond, similar to the way acyl chloride adds to dialkylcyanamides[1−3] (with the acyl group on the nitrogen and the chloride on the carbon), to give *N*,*N*-diisopropyl-*N*′,O-bis(trifluoroacetyl)isourea, **2a**, which rearranges



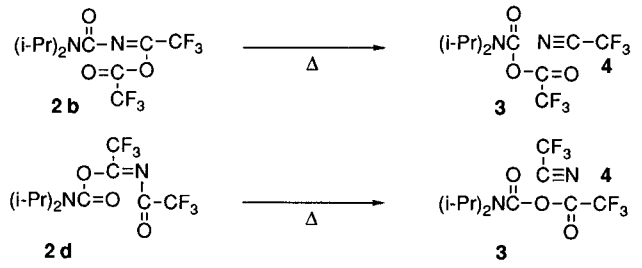
largely to *N*,*N*-diisopropyl-*N*′,*N*′-bis(trifluoroacetyl)urea, **2c**, by O → N acyl group migration.

Phthalic anhydride adds to dialkylcyanamide in a similar way, rearranging to give a phthalimide derivative.[8] *N*,*N*-Diisopropyl-*N*′-[2,2,2-trifluoro-1-(trifluoroacetoxy)ethylidene]urea, **2b**, and *N*-trifluoroacetyl *O*-(*N*′,*N*′-diisopropylcarbamyl)trifluoroacetimidate, **2d**, also could be formed by the appropriate acyl group migrations. The



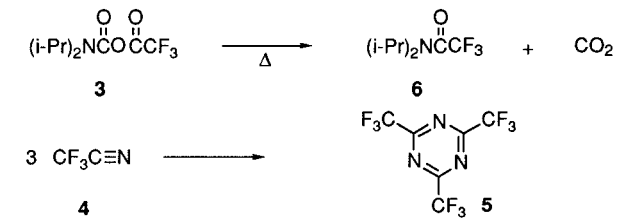
reaction product **2**, according to NMR in C_6D_6 solution, consists of **2c** as the principal component, along with about 10% of an isomeric material, which could be either **2a**, **2b**, or **2d**, all of which have nonequivalent CF_3 groups. Because the N → O migrating acyl group of **2c**, seemingly, would prefer the more electron-rich oxygen of the diisopropylcarbamyl group to the oxygen of a trifluoroacetyl group, compound **2a** could represent the 10% isomeric material. Conceivably, low concentrations of **2b** and/or **2d**, undetectable by NMR, could also exist. In the course of kinetic analysis of the thermal decomposition of **2**, a dynamic equilibrium between **2c** and **2a** was observed. Compound **2c** exists as a colorless solid, mp 49−51 °C. The structure of the solid was not determined directly, but considering the structural symmetry of **2c** versus that of the other isomers, **2c** would probably be higher melting and, therefore, is considered the structure.

Thermolysis of 2. Thermal decomposition of **2** leads, initially, to dissociation into two fragments: diisopropylcarbamic trifluoroacetic mixed anhydride, **3**, and trifluoroacetonitrile, **4**. Isomeric structures **2b**,**d** would seem to readily accommodate the thermal fragmentation, while **2a**,**c** would not. Equilibrium concentrations of **2b** and/or **2d**, at 27 °C, may be small and undetectable by NMR

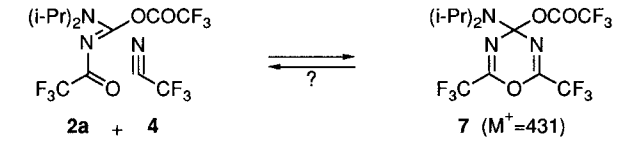


but may be present in sufficient concentration, particularly at higher temperature (117 °C), to account for the thermolysis. As mentioned later, the equilibrium concentration of **2a** probably more than triples going from 27 to 117 °C.

The mixed anhydride **3** is also thermally labile and can expel CO_2 to give diisopropyltrifluoroacetamide, **6**.[10] Trifluoroacetonitrile, **4**, trimerizes to give 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, **5**.[11] Monomeric **4** is never detected by NMR in the thermolysis products of **2**, even when conducted in sealed NMR tubes.

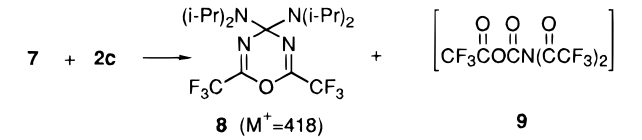


Reactions of Thermolysis Fragments. In the thermolysis reaction mixture some additional compounds have been detected by NMR and GC−MS. One is a compound with a mass of 431 which could be formed by the reaction of **4** with **2a** to give 4-(diisopropylamino)-4-(trifluoroacetoxy)-2,6-bis(trifluoromethyl)-4*H*-1,3,5-oxadiazine, **7**. It is consumed in the thermolysis reaction



by reverse reaction and/or by conversion to **8** since it is reduced to very low concentration in the reaction mixture in the 9 half-lives thermolysis experiment with **2**.

Another compound detected by NMR and GC−MS is one with a mass of 418. 4,4-Bis(diisopropylamino)-2,6-bis(trifluoromethyl)-4*H*-1,3,5-oxadiazine, **8**, is suggested for the structure. The trifluoroacetoxy group of **7** could be replaced by a diisopropylamino group from **2c** to give **8**. The other product, *N*,*N*-bis(trifluoroacetyl)carbamic



trifluoroacetic mixed anhydride, **9**, was never detected. In the kinetic run at 117 °C the concentration of **8** reaches

(10) Robson, J. H.; Reinhart, J. *J. Am. Chem. Soc.* **1955**, *77*, 498−499.

(11) Pyrolysis of pentafluoropropionamidine gives 2,4,6-tris(pentafluoroethyl)-1,3,5-triazine, presumably passing through the monomeric R_fCN. Reilly, W. L.; Brown, H. C. *J. Org. Chem.* **1957**, *22*, 698−699.

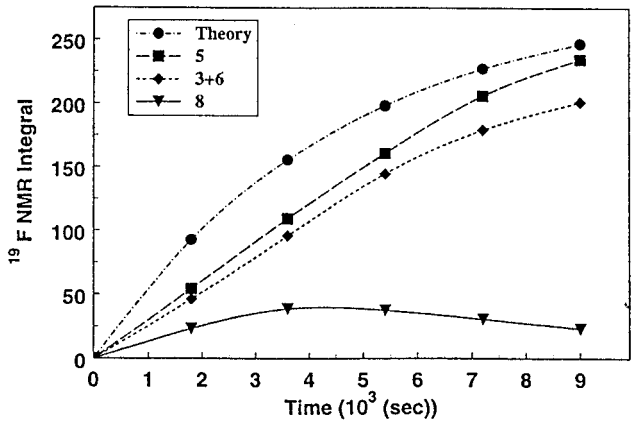
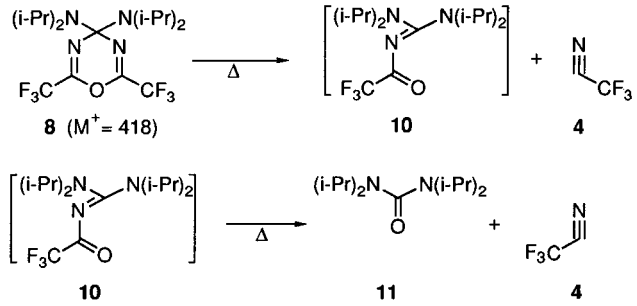


Figure 1. Plot of concentration versus time of principal thermolysis products of **2** at 117 °C plus a calculated plot (theory) for a thermolysis product.[13]

a maximum at about 4000 s (Figure 1). In the 9 half-lives thermolysis experiment with **2** there is still 6.3% of **8**. There is 0.75% of tetraisopropylurea, **11**,[12] suggesting that some of the thermal decompostion reaction of **8** could proceed as indicated. There was never any *N*″-(trifluoroacetyl)-*N*,*N*,*N*′,*N*′-tetraisopropylguanidine, **10**, detected. Monomeric **4** was never detected and would have been incorporated in the trimer **5**.

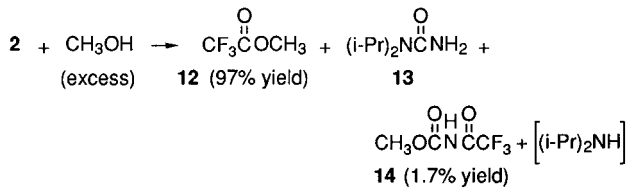


Kinetics of Thermolysis of 2. Kinetic analysis of the thermolysis of **2** in C_6D_6 at 117 °C shows it to follow first-order kinetics, $k = 2.15 \times 10^{-4}$ s^{-1}. While a major part of **2** is consumed by fragmentation to **3** and **4**, there is a reaction occurring between **2a** and the fragmentation product **4**. Nevertheless, the plot of log [**2a**+**2c**] (^{19}F NMR integral) versus time gives a good straight line, $r^2 = 0.9983$. The concentration (^{19}F NMR integral) versus time plots of products **5**, **3**+**6**, and **8** are shown in Figure 1 along with the theoretical (theory) plot[13] of a first-order fragmentation product. The plot of **5**, in the beginning, lags behind the theory plot, because some of **4** (precursor to **5**) is reacting with **2a** to give **7** (which largely converts to **8**), but after about 3 half-lives **5** approaches to 95% of the theoretical value. The belated concentration increase of **5** derives from the thermal decomposition of **8**, which generates the **5** precursor, **4**. The plot of **8** goes through a maximum at about 4000 s. Also, the ^{19}F NMR integral plot of **3**+**6**, the other half of the thermal fragmentation process of **2**, similarly lags behind the theory plot because the concentration of **2** is being decreased by reaction of **2a** with **4**. At 3 half-lives the ^{19}F NMR integral plot of **3**+**6** is 81% of the theoretical value.

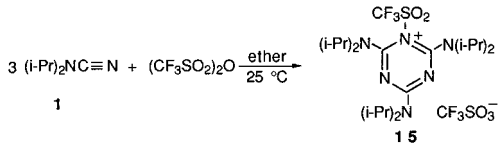
(12) Barton, D. H. R.; Elliott, J. D.; Gero, S. D. *J. Chem. Soc., Perkin Trans. 1* **1982**, 2085−2090.

(13) Theoretical plot: $y = 1/2\{[\mathbf{2}]_0 - [\mathbf{2}]_t\}$, or $y = 1/2(10^{2.761} - 10^{2.761-9.351\times10^{-5}t})$, where $y = {}^{19}$F NMR integral and $t = 0$−9000 s.

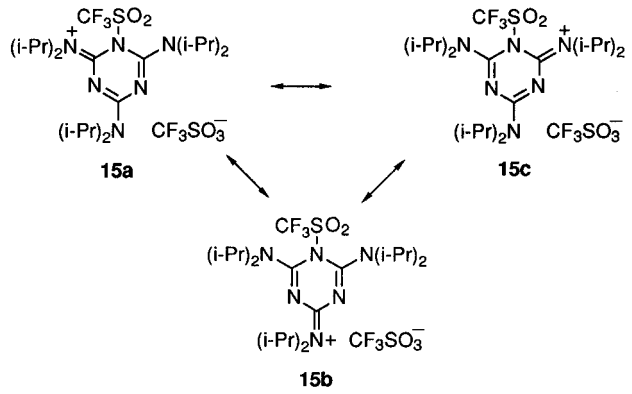
Reaction of 2 with Methanol. Equilibrium mixture, **2a**+**2c**, reacts with methanol as a trifluoroacetylating agent giving a 97% yield (^{19}F NMR) of methyl trifluoroacetate, **12**, along with *N*,*N*-diisopropylurea, **13**.[14] In addition there is a 1.7% yield of methyl-*N*-(trifluoroacetyl)urethane, **14**.[15] The fate of the displaced diisopropylamine was not determined. Reaction of **2** with an alcohol is quite different from the reaction of the triflic anhydride−dimethylcyanamide addition product, *N*,*N*-dimethyl-*N*′,*N*′-bis(trifluoromethanesulfonyl)urea, with alcohol as reported in ref 9. This latter compound, with ethanol, gives *N*,*N*-dimethyl-*O*-ethyl-*N*′-(trifluoromethanesulfonyl)isourea and, presumably, triflic acid.[9]



Reaction of Diisopropylcyanamide with Trifluoromethanesulfonic Anhydride (Triflic Anhydride). Triflic anhydride was chosen as another acid anhydride to react with **1**. It reacts exothermically with **1** in ether to give a high yield (96%) of isolated, very pure 2,4,6-tris(diisopropylamino)-1-(trifluoromethanesulfonyl)triazinium trifluoromethanesulfonate, **15**, which is a white



solid that endures normal laboratory handling without noticeable reaction with atmospheric moisture. An X-ray crystallographic structure drawing of the cation of **15** is shown in Figure 2.[16] There are several consistent structural cues that point to the structure being best represented by the three-part hybrid **15a**−**c**. The only



nitrogen atom which is significantly nonplanar is N1, with average bond angles of 115.1°. The three bonds of

(14) van der Zand, M. K. H. M. *Recl. Trav. Chim. Pays-Bas* **1889**, *8*, 221−247.

(15) Boiko, V. I.; Samari, L. I. *Ukr. Khim. Zh.* **1992**, *58*, 797−798.

(16) Crystals of **15** belong to monoclinic space group $P2_1$. Crystal data: $a = 10.181(2)$, $b = 15.393(2)$, $c = 11.238(2)$ Å; $\beta = 109.47(2)°$, $Z = 2$, $D_x = 1.322$ mg mm^{-3}; $R = 0.0554$, $R_{2w} = 0.1557$ for 2126 unique observed [$I > 2\sigma(I)$] reflections. The authors have deposited X-ray crystallographic data for the structure of compound **15** with the Cambridge Crystallographic Data Center. The data can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

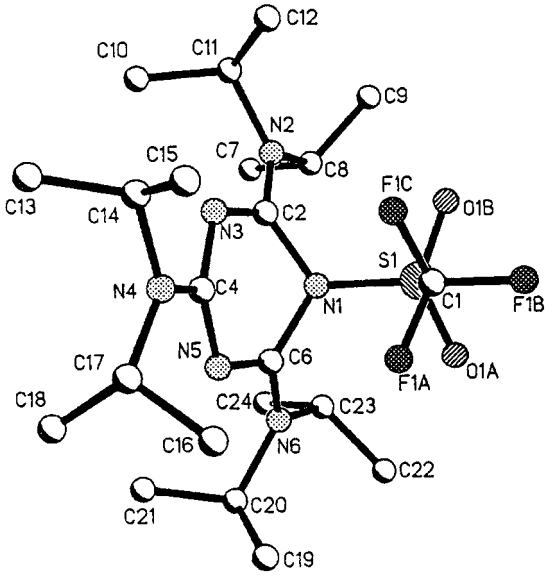
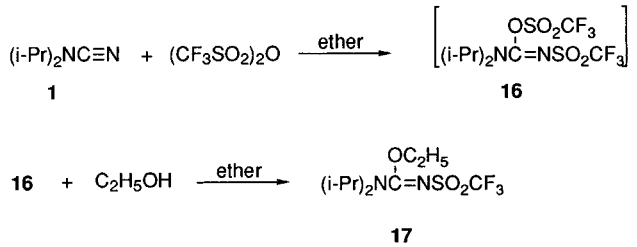


Figure 2. Drawing of the structure observed in the crystal for the cation of **15**.[16] The nitrogen atom N1 is pyramidal, with its three bond angles averaging 115.1°; nitrogen atoms N2, N4, and N6 are essentially planar; each displays average bond angles of 119.9°. The hydrogen atoms are omitted for visibility.

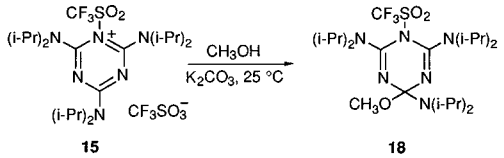
N1 are all quite long indicating full single-bond character. The CN bonds are 1.458 and 1.464 Å, typical single-bond values, and the NS bond at 1.674 Å matches single NS bonds found in the X-ray crystallographic structural database. Atoms N2, N4, and N6 are sp^2-planar; each of them has the same average bond angle, 119.9°. The CN bonds along the N2···N4 and N4···N6 pathways range from 1.309 to 1.386 Å; thus, all fall in the aromatic single/double-hybrid-bond category.

Triflic anhydride reacts quite differently with **1** compared to TFAA (which gives the 1:1 adduct **2**), and compared to **1**, dimethylcyanamide reacts quite differently with triflic anhydride, as recently reported.[9] Literature NMR data were consistent with *N*,*N*-dimethyl-*N*′,*N*′-bis(trifluoromethanesulfonyl)urea as the structure of their isolated, 1:1, adduct.[9]

Besides **15** there was a small amount of *O*-ethyl-*N*,*N*-diisopropyl-*N*′-(trifluoromethanesulfonyl)isourea, **17**, isolated. The initially formed intermediate **16** reacts with C_2H_5OH, contaminant in the absolute ether, to give **17**. This parallels the literature-reported reaction of *N*,*N*-dimethyl-*N*′,*O*-bis(trifluoromethanesulfonyl)isourea with ethanol.[9]



Reaction of 15 with Methanol. Compound **15** is stable to exposure to moisture in laboratory air and at least to brief solution in pure methanol. In methanol, in the presence of K_2CO_3, methoxide adds in the 4-position of **15** to give a 90% yield of 2,4,6-tris(diisopropylamino)-1-(trifluoromethanesulfonyl)-4-methoxy-1,4-dihydrotriazine, **18**. In the ^1H NMR spectrum of **18** the



methyl and methine protons of the isopropyl groups are not well-resolved but integrate satisfactorily for the required number. The methoxide proton peak is clearly evident at δ 3.24.

Conclusion

Trifluoroacetic anhydride adds to **1** to give **2** which, in C_6D_6 solution, is an equilibrium mixture of a 10% concentration of the initial adduct **2a** with 90% rearranged **2c** at 27 °C as evidenced by ^1H and ^{19}F NMR. Compound **2c** is a colorless solid, mp 49−51 °C. Thermolysis of **2** at 117 °C shows first-order kinetics. The initial thermolysis products are **3** and **4**. Compound **3** is thermally unstable and fragments to **6** and CO_2, and **4** trimerizes to **5**. In the thermolysis reaction mixture **4** reacts with **2a** to give an adduct, **7**, of mass 431. A related compound, **8**, of mass 418 is formed from **7** and **2c** in the thermolysis going through a concentration maximum at 4000 s in the kinetic run at 117 °C (see Figure 1). The formation of **8** consumes **4** (**5** precursor) which causes the plot of **5** to initally lag behind the theoretical plot but to largely recover after 3 half-lives as concentration of **8** thermolytically decreases with release of **4**. Similarly, formation of **8** consumes **2** which causes the **3**+**6** plot to lag behind the theoretical plot. With methanol, **2** is a trifluoroacetylating agent giving a 97% yield of methyl trifluoroacetate. In addition methanol displaces diisopropylamine from **2** to give 1.7% of methyl-*N*-(trifluoroacetyl)urethane, **14**. Triflic anhydride reacts with **1** in quite a different way to give a 96% yield of **15**, a triazine derivative. Ethanol contaminant in the absolute ether solvent trapped intermediate 1:1 adduct **16** as *O*-ethylisourea derivative **17**. Compound **15** reacts with methanol in the presence of K_2CO_3 to give a 90% yield of 2,4,6-tris(diisopropylamino)-1-(trifluoromethanesulfonyl)-4-methoxy-1,4-dihydrotriazine, **18**.

Experimental Section

Melting points were determined on a Mel-Temp II apparatus and are uncorrected. GC−MS analyses were performed on a Hewlett-Packard 5890 Series II gas chromatograph, with a temperature-programmed 30-m Restek XTI-5 column, helium gas, and a 250 °C injection port temperature, connected to a Fisons TS-250 Tribrid high-resolution mass spectrometer, 70 eV ionization energy.

Reaction of Diisopropylcyanamide, 1, with Trifluoroacetic Anhydride. Trifluoroacetic anhydride, 23.1 g (0.110 mol), dissolved in 25 mL of anhydrous ether was added, with stirring, to 12.6 g (0.100 mol) of diisopropylcyanamide, **1**, dissolved in 25 mL of anhydrous ether at −20 ± 5 °C, protected from atmospheric moisture. When addition was complete the reaction mixture was warmed to 25 °C and volatiles were removed under reduced pressure (1 mm/25 °C) to give 33.0 g (98% yield) of a liquid 1:1 addition product, **2**. Chilling and scratching induced crystallization. Recrystallization from hexane (1 g of **2** to 2 mL of hexane) gave colorless crystals of **2c**, mp 49−51 °C. Filtration was done in a drybox, dewpoint = −109 °C. NMR analyses were run on solutions prepared from the crystalline material in the drybox using carefully dried equipment and solvent. NMR spectra for **2c**: ^1H NMR (400 MHz, C_6D_6/TMS, 27 °C) δ 0.62 [d, J = 6.6 Hz (2 CH_3)], 1.21 [d, J = 6.8 Hz (2 CH_3)], 2.84 [septet, J = 6.8 Hz (CH)],

3.43 [septet, $J = 6.6$ Hz (CH)]; ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −70.11 (s, 2 CF_3). NMR spectra for **2a**: ^{1}H NMR (400 MHz, C_6D_6/TMS, 27 °C) δ 0.72 [d, $J = 6.8$ Hz (2 CH_3)], 0.85 [d, $J = 6.8$ Hz (2 CH_3)], 3.33 [septet, $J = 6.8$ Hz (2 CH)]; ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −73.81 (s, CF_3), −72.50 (s, CF_3). The ^{1}H and ^{19}F NMR spectra obtained show that **2** consists of *N*,*N*-diisopropyl-*N*′,*N*′-bis(trifluoroacetyl)-urea, **2c**, as the predominant component (90%), with a single ^{19}F signal (equivalent CF_3 groups), and about a 10% concentration of *N*,*N*-diisopropyl-*N*′,*O*-bis(trifluoroacetyl)isourea, **2a**, which shows two equivalent (by integration) ^{19}F signals (nonequivalent CF_3 groups). As demonstrated later, **2** is an equilibrating mixture of **2c**,**a**. **2**: MS (*m*/*z*) 336 (M^+), 321 (100), 279, 267, 236, 210, 165, 154, 140, 128, 113, 97, 86, 70, 58. Anal. Calcd for $C_{11}H_{14}F_6N_2O_3$: C, 39.29; H, 4.20; N, 8.33. Found: C, 39.49; H, 4.15; N, 8.37. The reaction product is very reactive toward atmospheric moisture, and the solid, **2c**, within minutes becomes a colorless liquid when exposed to laboratory air (30% relative humidity).

Thermolysis of 2. Sixty-six grams (0.20 mol) of **2** was heated in a distillation flask (condenser cooled to 0 °C) at 97 °C at 162 Torr for 2 h and then at 110 °C for 30 min. There was 16.4 g of distillate, bp 47−90 °C. Combining this with 4.7 g, recovered from the dry ice−acetone trap, and redistillation gave 14.6 g (77% yield), bp 92−102 °C/700 Torr (lit.[11] bp 95−96 °C), of 2,4,6-tris(trifluoromethyl)-1,3,5-triazine, **5**:[11] ^{19}F NMR (188 MHz, $CDCl_3$/$CFCl_3$, 27 °C) δ −70.04 (s, CF_3); ^{13}C NMR (100 MHz, $CDCl_3$/TMS, 27 °C) δ 117.7 [q, $J = 276$ Hz (CF_3)], 168.2 [q, $J = 42$ Hz (C, ring)]; MS (*m*/*z*) 285 (M^+), 266, 190, 121, 76, 69 (100).

Distillation of the distillation residue, from recovery of **5**, gave 31.7 g (80% yield) of *N*,*N*-diisopropyltrifluoroacetamide, **6**: bp 85−90 °C/50 Torr, mp 49−52 °C (lit.[10] mp 52−52.5 °C).

Another thermolysis of **2** was observed when a CH_2Cl_2 solution of **2** was injected into the 250 °C injection port of the GC−MS instrument. The GC plot indicated about 40% of **2** passed through unchanged [MS (*m*/*z*) 336 (M^+)], 55% of the plot consisted of **3** (from loss of CF_3CN from **2**) [MS (*m*/*z*) 241 (M^+)], and 5% consisted of **6** (from loss of CO_2 from **3**) [MS (*m*/*z*) 197 (M^+)]. Compound **5** was not detected in the GC plot because it exited too close to the solvent front.

Kinetics of Thermolysis of 2. A 0.216 M solution of **2** in C_6D_6, prepared in a drybox and sealed in a 5-mm NMR tube, was heated at 117 ± 1 °C over successive 30-min (1800-s) intervals and thermally quenched, and concentration changes of **2c**,**a**, **5**, **3**, **6**, and **8** were determined, relative to an internal standard of $C_6H_5CF_3$, by ^{19}F NMR integration. A least-squares plot of log of ^{19}F NMR integration values of **2** (**2c**+**2a**) versus time gave $\log y = -9.351 \times 10^{-5}x + 2.761$, $r^2 = 0.9983$. The reaction rate constant, at 117 °C, for thermolysis of **2**, is $k = 2.15 \times 10^{-4}$ s^{-1}. The concentrations (^{19}F NMR integrals) of **5**, **3**+**6**, and **8**, plotted against time, are shown in Figure 1.

A significant observation, in this kinetic run, was that the concentration of **2a**, in the thermally quenched sample at 1800 s, was 26% of the concentration of **2**. This indicates that at 117 °C the equilibrium concentration of **2a** shifts to something greater than 26% (greater, because of some time delay between thermal quenching and ^{19}F NMR analysis) and is kinetically slow in returning to the 10% equilibrium concentration at 27 °C. After the sample stands at 27 °C for several hours (minimum time not determined) the **2a** value returns to 10% of **2**. Similar results were observed when the other quenched samples were analyzed. It was also observed that a sample of **2** in C_6D_6 in a sealed NMR tube stored at −10 °C for an extended period, then thawed and an ^{19}F NMR quickly run, had a 6% concentration of **2a**.

Thermolysis of 2 for 9 Half-Lives at 117 ° C. A 0.119 M solution of **2** along with $C_6H_5CF_3$ in C_6D_6 in a sealed 5-mm NMR tube was placed in a 117 °C bath for 8 h. ^{19}F NMR analysis of the reaction mixture gave the following yields based on the starting amount of **2**: **2**, 0.0%; **5**, 79%; **3**, 55%; **6**, 35%; **8**, 6.3%. GC−MS analysis of the reaction mixture, using uncalibrated response of the GC, gave the following yields based on the sum of the components detected: **2**, 0.0%; **3**, 56%; **6**, 32%; **7**, 1.4%; $M^+ = 316$ (unidentified), 2.4%; **8**, 7.1%; *N*,*N*,*N*′,*N*′-tetraisopropylurea, **11**,[12] 0.75%.

Hydrolysis Product of Diisopropylcarbamic Trifluoroacetic Anhydride, 3. (This was an attempt to prepare and isolate **3**, but instead the hydrolysis product, diisopropylammonium trifluoroacetate, was obtained.) Diisopropylcarbamyl chloride, 1.64 g (0.0100 mol), dissolved in 25 mL of acetonitrile was added to 2.43 g (0.0110 mol) of silver trifluoroacetate dissolved in 25 mL of acetonitrile and stirred for 30 min at 25 °C. Silver chloride, 1.43 g (0.0100 mol), was filtered off, and volatiles were removed from the filtrate on the rotary evaporator to leave 2.0 g (95% yield) of diisopropylammonium trifluoroacetate. Recrystallization from hexane gave 1.2 g: mp 122−123 °C; ^{1}H NMR (400 MHz, C_6D_6/TMS, 27 °C) δ 0.94 [d, $J = 6.5$ Hz (4 CH_3)], 2.65 [septet, $J = 6.3$ Hz (2 CH)]; ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −73.81 (s, CF_3); MS (*m*/*z*) (solid probe, 70 eV) 114, 101, 97, 95, 86 (100), 69 (90), 58, 51. Anal. Calcd for $C_8H_{16}NF_3O_2$: C, 44.64; H, 7.49; N, 6.51. Found: C, 44.56; H, 7.51; N, 6.45.

Preparation of Diisopropylcarbamic Trifluoroacetic Mixed Anhydride, 3. In a drybox, dew point −111 °C, 16.7 mg (0.102 mmol) of diisopropylcarbamyl chloride dissolved in 0.7 mL of dry C_6D_6 was added to 22.7 mg (0.103 mmol) of silver trifluoroacetate dissolved in 0.3 mL of dry C_6D_6 and thoroughly mixed. Silver chloride was filtered off, and the filtrate was sealed in a dried 5-mm NMR tube. ^{1}H and ^{19}F NMR and GC−MS were run on the filtrate. ^{1}H NMR showed, by integration, that 94% of the product was **3**, 4.6% was the previously described hydrolysis product, diisopropylammonium trifluoroacetate, and there was 1.6% of **6** (thermolysis product of **3**). The ^{1}H NMR spectrum of **3** shows a multiplet at δ 3.33 for the isopropyl methines which is due to a 6.8-Hz overlap of the septets of the two methine protons: ^{1}H NMR (400 MHz, C_6D_6/TMS, 27 °C) δ 0.68 [d, $J = 6.8$ Hz (2 CH_3)], 0.98 [d, $J = 6.8$ Hz (2 CH_3)], 3.33 [septet, $J = 6.8$ Hz (CH)], 3.34 [septet, $J = 6.8$ Hz (CH)]; ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −73.89 (s, CF_3); MS (*m*/*z*) 241 (M^+), 226, 141, 128, 97, 86, 84, 70 (100), 69, 58, 56.

4-(Diisopropylamino)-4-(trifluoroacetoxy)-2,6-bis(trifluoromethyl)-4*H*-1,3,5-oxadiazine, 7.[17] In the thermolysis reaction mixture of **2**, **7** was detected by NMR and GC−MS: ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −73.54 (s, 2 CF_3), −73.25 (s CF_3); MS (*m*/*z*) 431 (M^+), 416, 331, 318, 303, 274, 260, 249, 234, 187, 165, 140, 128, 112, 97, 84, 70, 69 (100), 58.

4,4-Bis(diisopropylamino)-2,6-bis(trifluoromethyl)-4*H*-1,3,5-oxadiazine, 8.[17] Compound **8** was detected in the thermolysis reaction mixture of **2** by NMR and GC−MS. It reached maximum concentration at about 4000 s in the 117 °C kinetic thermolysis run (see Figure 1): ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −73.76 (s, 2 CF_3); MS (*m*/*z*) 418 (M^+), 349, 318, 276, 234, 128, 100, 86 (100), 70, 58.

Reaction of 2 with Methanol. In a drybox, 16.6 mg (0.0494 mmol) of compound **2** was dissolved in 0.5 mL of dry C_6D_6 and treated with 30 μL (0.74 mmol) of CH_3OH and 1 drop of $CF_3C_6H_5$ ^{19}F NMR standard. The reaction mixture was analyzed by ^{19}F NMR and GC−MS. ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) integration showed a 97% yield of $CF_3CO_2CH_3$, **12**, δ −73.50 (s, CF_3), and a 1.7% yield of methyl-*N*-(trifluoroacetyl)urethane, **14**,[15] δ −74.58 (s, CF_3). GC−MS showed a trace of unknown material, MS (*m*/*z*) 224 (M^+). **14**:[15] 1.7% yield; MS (*m*/*z*) 171 (M^+), 140, 112, 102, 97, 69 (100), 57, 58. *N*,*N*-Diisopropylurea **13**:[14] 95% yield; ^{1}H NMR (400 MHz, C_6D_6/TMS, 27 °C) δ 1.03 [d, $J = 6.8$ Hz (4 CH_3)], 3.46 [septet, $J = 6.8$ Hz (2 CH)], 4.90 (s, NH_2); MS (*m*/*z*) 144 (M^+), 129, 101, 86 (100), 70, 58.

Preparation of 2,4,6-Tris(diisopropylamino)-1-(trifluoromethanesulfonyl)triazinium Trifluoromethanesulfonate, 15. Triflic anhydride, 5.64 g (0.0200 mol), dissolved in

(17) Compounds **7** and **8** were not isolated (except GC−MS), and no elemental analyses were obtained. The structures were deduced from mass spectral data, mass spectral cracking patterns, and synthetic components available in the thermolysis reaction mixture. Thermolysis products **4** and **11** are consistent with structure **8**. ^{19}F NMR data, obtained from the thermolysis reaction mixtures, are compatible with the structures.

20 mL of dry ether[18] was added, with stirring, to 2.52 g (0.0200 mol) of **1** dissolved in 20 mL of dry ether keeping the reaction temperature at 25 ± 5 °C. White solid began separating from the reaction mixture as soon as triflic anhydride was added. When triflic anhydride addition was completed, the white solid was filtered off, washed with two 50-mL portions of ether, and dried to give 4.22 g (96% yield) of **15**: mp 189−191 °C dec; ^{1}H NMR (400 MHz, CD_3CN/TMS, 77 °C) δ 1.35 [d, J = 6.7 Hz (2 CH_3)], 1.41 [d, J = 6.9 Hz (2 CH_3)], 1.46 [d, J = 6.4 Hz (4 CH_3)], 1.54 [d, J = 6.8 Hz (2 CH_3)], 1.59 [d, J = 6.8 Hz (2 CH_3)], 4.13 [septet, J = 6.8 Hz (2 CH)], 4.58 [broad, (2 CH)],[19] 4.68 [septet, J = 6.5 Hz (2 CH)]; ^{13}C NMR (100 MHz, CD_3CN/TMS, 77 °C) δ 19.6 (s, 4 CH_3), 21.0 (s, 2 CH_3), 21.5 (s, 2 CH_3), 21.8 (s, 2 CH_3), 22.3 (s, 2 CH_3), 51.5 (s, 2 CH), 52.0 (s, 2 CH), 57.3 (s, 2 CH), 120.7 (q, J = 325 Hz, CF_3), 122.9 (q, J = 319 Hz, CF_3), 149.7 (s, 2 C), 158.3 (s, C); ^{19}F NMR (75 MHz, $CDCl_3$/$CFCl_3$, 27 °C) δ −77.16 (s, CF_3), −66.82 (s, CF_3); MS (*m*/*z*) 511 (M^+), 447, 378, 335, 209, 100 (100), 68, 58. Anal. Calcd for $C_{23}H_{42}N_6F_6S_2O_5$: C, 41.80; H, 6.41; N, 12.72. Found: C, 41.72, 41.68; H, 6.49, 6.32; N, 12.59, 12.66.

Volatiles were removed from the ether wash filtrate, from isolation of **15**, on a rotary evaporator, and the residue was chromatographed on a silica gel column, CH_2Cl_2 solvent, to give 0.15 g of material, mp 60−64 °C. Recrystallization from *n*-hexane gave 90 mg of *O*-ethyl-*N*,*N*-diisopropyl-*N*′-(trifluoromethanesulfonyl)isourea, **17**: mp 68−69 °C; ^{1}H NMR (400 MHz, $CDCl_3$/TMS, 55 °C) δ 1.33 [d, J = 6.8 Hz (4 CH_3)], 1.45 [t, J = 7.1 Hz (CH_3)], 4.18 [broad band (2 CH)],[19] 4.61 [q, J = 7.1 Hz (CH_2)]; ^{19}F NMR (188 MHz, $CDCl_3$/$CFCl_3$, 300 K) δ −79.01 (s, CF_3). Anal. Calcd for $C_{10}H_{19}N_2F_3SO_3$: C, 39.46; H, 6.29; N, 9.21. Found: C, 39.55; H, 6.35; N, 9.22.

Reaction of 2,4,6-Tris(diisopropylamino)-1-(trifluoromethanesulfonyl)triazinium Trifluoromethanesulfonate, 15, with Methanol in the Presence of Potasium Carbonate. To 100 mL of CH_3OH containing 0.33 g of K_2CO_3·1.5H_2O (2.0 mmol) was added 0.66 g (1.0 mmol) of **15** at 25 °C. Removal of volatiles on the rotary evaporator followed by treatment of the residue with 25 mL of H_2O and 25 mL of CH_2Cl_2, separation of the CH_2Cl_2 phase, drying over $MgSO_4$, and removal of the CH_2Cl_2 on the rotary evaporator left 0.49 g (90% yield) of 2,4,6-tris(diisopropylamino)-1-(trifluoromethanesulfonyl)-4-methoxy-1,4-dihydrotriazine, **18**. Recrystallization from 30 mL of hexane gave 0.40 g of **18**, mp 151−152 °C. Another recrystallization from hexane raised the melting point to 153−154 °C: ^{1}H NMR (400 MHz, C_6D_6/TMS, 27 °C) δ 0.89−1.39 (multiplet, 12 CH_3), 3.24 (s, CH_3O), 3.70 (unresolved, 2 CH), 4.12 (unresolved, 2 CH), 4.53 (unresolved, 2 CH); ^{19}F NMR (188 MHz, C_6D_6/$CFCl_3$, 27 °C) δ −76.11 (s, CF_3); MS (*m*/*z*) 542 (M^+), 499, 473, 457, 442, 409, 358, 310 (100), 217, 184, 142, 100, 58. Anal. Calcd for $C_{23}H_{45}N_6F_3SO_3$: C, 50.90; H, 8.36; N, 15.49. Found: C, 51.09; H, 8.41; N, 15.75.

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Supporting Information Available: ^{1}H and ^{19}F NMR spectra for **3** (3 pages). This material is contained in libraries on microfiche, immediately following this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(18) Lindner, E.; von Au, G.; Eberle, H.-J. *Chem. Ber.* **1981**, *114*, 810−813. This refers to the cleavage of the cyclic ether tetrahydro-2*H*-pyran by triflic anhydride. However, in the present work diethyl ether solvent is not cleaved by triflic anhydride.

(19) The isopropyl methine proton signal, at 27 °C, was so broad as to be undetectable. At the higher temperature used, an unresolved broad band developed, indicating its position in the spectrum.