6-in. Vigreux column gave 3.0 g. (20%) of α-acetoxy-α-methylitaconic anhydride (XV), b.p. 113–114° (1.3 mm.), $n^{25}D$ 1.4725.

Anal. Calcd. for $C_8H_8O_5$: C, 52.17; H, 4.35. Found: C, 52.60; H, 4.70.

Dimethylmaleic Anhydride (XIV).—At the rate of 1 ml. per min., a solution of 3.0 g. of α-acetoxy-α-methylitaconic anhydride (XV) in 10 ml. of ether was added to the Vycor pyrolysis tube heated at 545°. Distillation of the ether and acetic acid from the pyrolysate, followed by titration of the acid, showed that 46% of the theoretical amount of acetic acid had been liberated. Distillation of the residue through a 6-in. Vigreux column gave a liquid, b.p. 58–65° (1.3 mm.), which solidified in the condenser. Recrystallization of this solid from a benzene–petroleum ether mixture gave 0.33 g. (16%) of dimethylmaleic anhydride (XIV), m.p. 95–96° (reported[15] m.p. 96°). A mixed melting point determination with an authentic sample of dimethylmaleic anhydride (XIV) showed no depression.

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[15] W. Roser, *Ber.*, **15**, 1319 (1882).

Fluorocarbon Nitrogen Compounds. IX. The Reaction of Nitriles with Carboxylic Acids[1]

WILLIAM S. DURRELL,[2] JOHN A. YOUNG, AND RICHARD D. DRESDNER

Departments of Chemistry and Chemical Engineering, University of Florida, Gainesville, Florida

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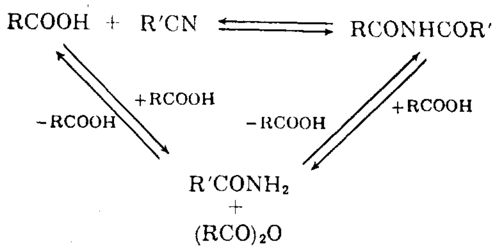
Equilibria and relative reaction rates in the reactions of acetic and trifluoroacetic acids with aceto- and trifluoroacetonitrile are described. The position of equilibrium between imide and the acid–nitrile pair is thought to be related to the respective amounts of resonance stabilization possible in the reactants and in the product. Differences in reaction rates of the various pairs, either alone or catalyzed by acid or base, may be explained by a concerted mechanism.

The most recent studies of the reaction of an organic acid with a nitrile are those of Wiley and Guerrant[3] and Davidson and Skovronek.[4a,b] The former reported equilibrium yields of about 40% diamide in the reactions of phenyl- and *p*-nitrophenylacetic acids with their respective nitriles. Davidson and Skovronek observed that various nitriles and acids reacted at elevated temperatures to give not only the diamides but also the corresponding anhydride and amide, due to the interlocking equilibria shown below.



(1)

The present paper deals with the effects of substituting a trifluoromethyl group for methyl in either the acid, the nitrile, or both, giving a total of four acid–nitrile systems. In contrast to the results of Davidson and Skovronek,[4a] we did not detect the presence of the anhydride–amide pair in any of these four systems,[5] so that the equilibria of equation 1 reduced to that shown in equation 2. Consequently, relationships in the present work could be investigated by approaching equilibrium from opposite directions; that is, either by reaction of nitrile with acid or by disproportionation of imide at the same temperature. Results obtained in this way are given in Table I, the equilibrium conversion being taken as that point which was attained irrespective of approach direction.

$$\mathrm{RCOOH + R'CN \rightleftharpoons RCONHCOR'} \qquad (2)$$

TABLE I

EQUILIBRIA IN THE SYSTEM

$\mathrm{RCOOH + R'CN \rightleftharpoons RCONHCOR'}$

R	R′	% Imide at equilibrium
CH_3	CF_3	97
CF_3	CF_3	96
CF_3	CH_3	72
CH_3	CH_3	60

$$\mathrm{RCOOH + R'CN \rightleftharpoons RCONHCOR' \rightleftharpoons R'COOH + RCN} \qquad (3)$$

When R and R′ are different, equation 2 is no longer completely valid, since the mixed imide can disproportionate to give both acids and both nitriles, according to equation 3 and if reaction rates of the two acid–nitrile pairs are greatly different, the initial "equilibium" conversion may not be that which would result from thermodynamic considerations. Thus, with the acetic acid–trifluoroacetonitrile pair, the fast reaction of acetic acid with trifluoroacetonitrile is able to go nearly to completion, but eventually the slower reverse action leading to the more energetically stable pair takes control. The apparent ultimate composition of the reaction mixture, presumably dictated by thermodynamic properties, is 72% mixed imide, the remainder being trifluoroacetic acid and acetonitrile. The yield of 97% given in Table I therefore represents only the "equilib-

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[1] Taken from the Ph.D. dissertation of W. S. Durrell, University of Florida, 1961. Presented in part at the 140th National Meeting of the American Chemical Society, Chicago, Ill., September 3–8, 1961. This work was supported by the Army Research Office and this paper may be used in whole or in part for any purposes of the U. S. Government. For the preceding paper in this series, see *J. Am. Chem. Soc.*, **84**, 2105 (1962).

[2] Present address, Peninsular ChemResearch, Inc., Gainesville, Fla.

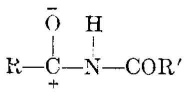
[3] R. H. Wiley and W. B. Guerrant, *J. Am. Chem. Soc.*, **71**, 981 (1949).

[4a] D. Davidson and H. Skovronek, *ibid.*, **80**, 376 (1958). (4b) Davidson's most recent work [R. N. Ring, J. G. Sharefkin, and D. Davidson, *J. Org. Chem.*, **27**, 2428 (1962)], which has appeared in print since submission of this paper, leads to mechanistic conclusions essentially in accord with these presented here. Both papers were originally given at the 140th National Meeting of the American Chemical Society, September, 1961.

[5] This discrepancy is explained by the fact that an excess of free acid was used by the authors cited. It can be seen from the diagram above that presenee of excess acid would force the total equilibrium toward the amide–anhydride pair.

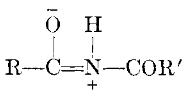
rium" of the fast reaction, but for our intended purposes this is the proper measurement.[6]

The positions of equilibrium for the various reactant pairs of Table I can be related to the relative amounts of resonance stabilization in the compounds involved. Canonical forms of an imide or of an acid can be written, as shown below, in which the formal positive charge occasioned by carbonyl polarization can be shifted to neighboring atoms, but no forms analogous to II can be written for the polarized nitrile structure $\mathrm{R\overset{+}{C}{=}\overset{-}{N}}$.



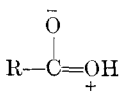
$\mathrm{R{-}\underset{+}{\overset{\overset{\bar{O}}{|}}{C}}{-}\overset{\overset{H}{|}}{N}{-}COR'}$

I



$\mathrm{R{-}\overset{\overset{\bar{O}}{|}}{C}{=}\underset{+}{\overset{\overset{H}{|}}{N}}{-}COR'}$

II

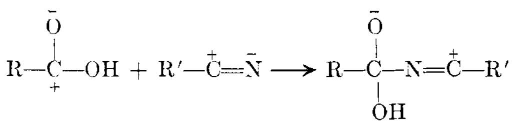


$\mathrm{R{-}\overset{\overset{\bar{O}}{|}}{C}{=}\underset{+}{O}H}$

III

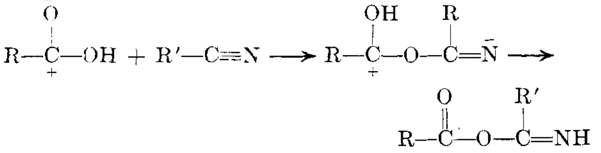
When R = CH_3, the energies of both nitrile and imide are lowered by inductive and hyperconjugative effects. When R = CF_3, however, the electron-withdrawing effect of the CF_3 group can be relieved to a greater extent in the imide than in the nitrile, if structures of type II make any appreciable contribution. It follows from such energy considerations that in the reaction acid + nitrile → imide, the equilibrium would be shifted to the right by *fluorine or other electron-withdrawing substituents* in the nitrile. The effect is similar in direction but smaller in magnitude for substitution in the R group of the acid, presumably because of the relatively greater stabilization afforded the CF_3-substituted imide, through the contribution of II, over that available to trifluoroacetic acid through III, the difference being due to the greater effectiveness of nitrogen in donating electrons.

Two reasonable mechanisms can be written for the nitrile–acid reaction. In the first the nucleophilic nitrogen atom of the nitrile attacks the electrophilic carbon and imide formation occurs in subsequent rapid steps. *A priori*, acid catalysis should increase the rate through protonation of the carbonyl, if the organic acid can compete successfully with the nitrile for the proton.



$$\mathrm{R{-}\underset{+}{\overset{\overset{\bar{O}}{|}}{C}}{-}OH + R'{-}\overset{+}{C}{\equiv}\overset{-}{N} \longrightarrow R{-}\underset{\underset{OH}{|}}{\overset{\overset{\bar{O}}{|}}{C}}{-}N{=}\overset{+}{C}{-}R'} \qquad (4)$$

The second mechanism postulates nucleophilic attack of carbonyl oxygen on the carbon atom of the nitrile, with subsequent rearrangement of isoimide to imide. In this mechanism, catalysis by both acid and base would be expected, the first through protonation of the nitrile, increasing its electrophilicity, and the second through loss of a proton from the acid, increasing its nucleophilicity.



$$\mathrm{R{-}\underset{+}{\overset{\overset{\bar{O}}{|}}{C}}{-}OH + R'{-}C{\equiv}N \longrightarrow R{-}\underset{+}{\overset{\overset{OH}{|}}{C}}{-}O{-}\overset{\overset{R}{|}}{C}{=}\overset{-}{N} \longrightarrow R{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{R'}{|}}{C}{=}NH} \qquad (5)$$

The relative rates of reaction for the four acid–nitrile pairs are given in Table II.

TABLE II

RELATIVE REACTION RATES IN THE SYSTEM

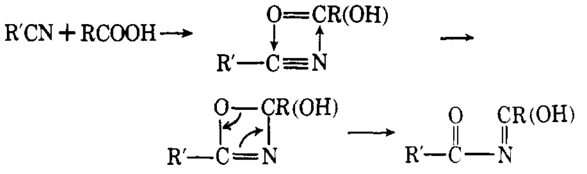
$RCOOH + R'CN \longrightarrow RCONHCOR'$[a]

R	R′	No catalyst	Acid catalyst (H_2SO_4)	Base (metal acetate)
CH_3	CF_3	1	3.3	3.3
CF_3	CH_3	0.6	1.2	0.6–0.7
CF_3	CF_3	.3	5.0	2.5
CH_3	CH_3	.012	0.036	0.012

[a] Calculated from the number of hours at 150° necessary for 50% conversion to imide. Raw data are given in the Experimental.

The data of Table II are not wholly explicable in terms of either mechanism alone. Equation 4 does not predict base catalysis, but such catalysis is found in the trifluoroacetonitrile systems. On the other hand, equation 5 predicts base catalysis for both systems, but it is observed actually only with trifluoroacetonitrile. The uncatalyzed and acid-catalyzed rates, however, can be rationalized by either mechanism.

In view of the polarizability of the multiple bonds in the two reacting species, which can lead to the development of both an electrophilic and nucleophilic center in each molecule (particularly on passing into a transition state), it seems reasonable that a concerted mechanism might be written which in effect merges the two mechanisms as shown in equation 6. The last structure tautomerizes to the imide.



(6)

This mechanism is in accord with all the known facts of the acid–nitrile reaction and also with the facile interconversions shown in the three-way equilibria of equation 1. Indeed, the mechanisms shown in equations 4 and 5 can be considered as limiting cases of equation 6 in which the new C—N and C—O bonds are not represented as forming simultaneously.

Davidson has found the isoimide mechanism, which he favored previously,[4a] to be inadequate for explaining exchange reactions between acids and N,N-disubstituted amides.[4b] The concept of concerted reaction through a four-membered intermediate such as that shown in equation 6 or implied in ref. 4b removes this difficulty.

The concerted mechanism also furnishes a useful rationalization of the nitrile synthesis reported recently by Pomeroy and Craig,[7] in which O,N-bis(trifluoroacetyl)hydroxylamine reacts with aldehydes in the presence of pyridine to give the corresponding nitriles in high yield. A possible mechanism for this reaction is as follows.

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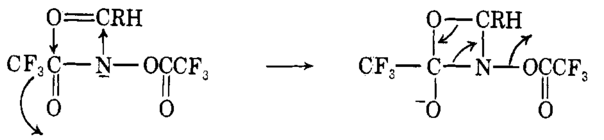
(6) Since both nitriles and both acids can be formed from the mixed imide, it follows that the two diamides $(RCO)_2NH$ and $(R'CO)_2NH$ should also be found. When an equimolar mixture of trifluoroacetic acid and acetonitrile was heated for eight hours at 200°, both diamides were detected, in addition to a 50% yield of the mixed imide $CF_3CONHCOCH_3$; however, under these severe conditions considerable decomposition occurred. Since the methyl-substituted compounds were the more severely affected, a reaction controlled purely thermodynamically by the equilibria of equation 3 could not be completely attained.

(7) J. H. Pomeroy and C. A. Craig, *J. Am. Chem. Soc.*, **81**, 6340 (1959).

$$CF_3CONHOCOCF_3 \xrightarrow[-H^+]{\text{pyridine}} CF_3CO\bar{N}OCOCF_3 \qquad (7)$$



$$\xrightarrow[-H^+]{\text{pyridine}} RCN + 2CF_3COO^- \qquad (8)$$

The strong inductive effect of the trifluoromethyl groups is vital to this synthesis in three ways. First, the acidity of the diacylhydroxylamine is increased so that a proton can be removed from the —NH— group by pyridine. Secondly, the electrophilicity of the carbonyl group attached to nitrogen is increased sufficiently to allow participation of the carbonyl carbon in the reaction. Finally, the decreased basicity of the trifluoroacetate anion increases its effectiveness as a leaving group.

Experimental

One-gram samples of an equimolar solution of the acid and the nitrile were heated in weighed sealed glass ampoules at 150 and 200° in an oil bath whose temperature was regulated to ±0.5°. Conversion to imide was followed by two different methods, depending on the nitrile being used. With acetonitrile, the unchanged acid and nitrile were evaporated under vacuum and the ampoule reweighed. The volatile fraction was also analyzed by vapor phase chromatography on Dow Corning 550 oil-Haloport column, which separated acetic acid, acetonitrile, and acetic anhydride readily. None of the last was detected at any time. The nonvolatile imide residue was shown in infrared examination to contain no more than trace amounts of impurities except after long periods at 150° or shorter periods at 200°. The accuracy of the method was also checked by repeating one run on a larger scale, in which the conversion estimated by the small scale run was 68% and that obtained by actual distillation and isolation of products was 69%. With trifluoroacetonitrile, the reaction was conveniently followed by measuring the change in vapor pressure of the trifluoroacetonitrile in a calibrated volume before and after reaction since the boiling point of this compound was at least 130° lower than any other component. Because of its volatility, this nitrile was added to the acid by vacuum transfer during makeup of samples. Reaction times (hours) and conversions to imide (%) are given below.

Acetic Acid–Acetonitrile.—Uncatalyzed reaction at 150°: 48, 17.5; 108, 27; 156, 45; 204, 50; 318, 60. With 5% (by weight) sulfuric acid: 24, 30; 54, 45; 70.5, 52. With 5% sodium acetate: 54, 22; 132, 38.

Disproportionation of Diacetamide.—Uncatalyzed at 150°: 48, 96; 108, 90; 156, 89; 204, 87, the last two samples being partially decomposed. With 5% sulfuric acid: 54, 84; 132, badly decomposed. With 5% sodium acetate: 54, 94; 132, 90.

Trifluoroacetic Acid–Acetonitrile.—Uncatalyzed reaction at 50°: 2, 43; 6, 59; 8, 69; 24, 43 (partial decomposition). With 5% sulfuric acid: 0.92, 33; 3.2, 60. With 5% potassium trifluoroacetate: 0.92, 30; 3.2, 48.

Disproportionation of N-Acetyltrifluoroacetamide.—Uncatalyzed reaction at 150°: 2, 80.5; 6, 76; 8.2, 76; 24, 53 (partial decomposition). With 5% sulfuric acid: 1, 87; 3.3, 77 (both with some decomposition). With 5% potassium trifluoroacetate: 1, 94.

Trifluoroacetic Acid–Trifluoroacetonitrile.—Uncatalyzed reaction at 150°: 1.5, 16; 7.9. 51; 20, 84. With 5% sulfuric acid: 0.75, 77; 3, 93. With 5% potassium trifluoroacetate: 2, 79; 4.25, 91.

Disproportionation of N-Trifluoroacetyltrifluoroacetamide.—Uncatalyzed reaction at 150°: 14, 98; 30, 96. With 5% sulfuric acid: 3, 98; 5, 96.

Acetic Acid–Trifluoroacetonitrile.—Uncatalyzed reaction at 150°: 1.25, 37; 3, 64; 6, 97. With 10% sulfuric acid: 1, 73; 2, 87. With 10% sodium acetate: 1, 71; 2, 85.

Reactions at 200°.—Only approximate yields are given as decomposition was extensive. Acetic acid–acetonitrile: 24, 45; trifluoroacetic acid–acetonitrile: 8, 50; trifluoroacetic acid–trifluoroacetonitrile: 8, 50. The second of these reactions when repeated on a larger (38 g.) scale gave some $(CF_3CO)_2NH$ and $(CH_3CO)_2NH$, in addition to 18 g. (50%) of $CF_3CONHCOCH_3$.

Fluorocarbon Nitrogen Compounds. X. N,N-Difluoramines from Azoalkanes[1]

JOHN A. YOUNG AND R. D. DRESDNER

Departments of Chemistry and Chemical Engineering, University of Florida, Gainesville, Florida

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Thermal decomposition of perfluoroazoalkanes proceeds smoothly at 350–500° and radical recombination gives chain doubling without rearrangement. Decomposition in the presence of dinitrogen tetrafluoride affords good yields of fluorocarbon N,N-difluoramines while radical addition to hexafluoropropene gives a moderate yield of perfluoroheptane. Tetrasubstituted hydrazines formed by radical addition to azoalkanes display unusual thermal stability for compounds containing a nitrogen–nitrogen bond.

Although the photochemical decomposition of fluorocarbon azoalkanes, $R_FN{=}NR_F$, has been studied rather extensively,[2–5] their thermal decomposition had received no attention prior to a very recent publication by Chambers, Tullock, and Coffman.[6] Our results, which were compiled before this paper appeared, are in entire agreement with theirs; in addition, the present work extends the synthetic use of azoalkanes to the preparation of perfluoro-N,N-difluoramines.

Either photolytic or thermal decomposition of $R_FN{=}NR_F$ leads to generation of R_F radicals. These can be coupled to give $R_F{\cdot}R_F$ or added to the parent molecule to give tetrasubstituted hydrazines; either reaction can be favored by suitable choice of reaction conditions. The isolation of isomerically pure n-C_8F_{18} from decomposition of $C_4F_9N{=}NC_4F_9$ in the present work indicates that rearrangement does not occur, and since the

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[1] The authors are indebted to the U. S. Army Research Office and the National Science Foundation for financial support of this work. Reprint requests should be addressed to the senior author at the Denver Research Institute, Denver 10, Colo.

[2] G. O. Pritchard, H. O. Pritchard, H. I. Schiff, and A. F. Trotman-Dickinson, *Trans. Faraday Soc.*, **52**, 849 (1955).

[3] J. R. Dacey and D. M. Young, *J. Chem. Phys.*, **23**, 1302 (1955).

[4] A. P. Stefani, L. Herk, and M. Szwarc, *J. Am. Chem. Soc.*, **83**, 2998 (1961).

[5] A. P. Stefani, L. Herk, and M. Szwarc, *ibid.*, **83**, 4732 (1961).

[6] W. J. Chambers, C. W. Tullock, and D. D. Coffman, *ibid.*, **84**, 2337 (1962).