Pyrolysis of Esters. XXIV. 2,3-Dicarboxy-1,3-butadiene[1,2]

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2,3-Dicarboxy-1,3-butadiene was prepared in a five-step synthesis from biacetyl in which the key step was the pyrolysis of a diacetate. The diene–diacid was characterized by analysis and infrared and ultraviolet spectra and its dimethyl ester was converted to a solid Diels–Alder adduct. The pyrolysis was complicated by an anomolous reduction to give partially reduced products. In the pyrolysis of diacetoxydimethylsuccinic anhydride, dimethylmaleic anhydride was isolated as a major product.

In an over-all program to produce a series of cyclic dienes[5,6] and bisdienes for the preparation of Diels–Alder polymers,[7] dienes with substituents in the 2,3-positions were of interest.[8] 2,3-Dicarboxy-1,3-butadiene (I) was of particular interest because it could be used to prepare a cyclic diene with anhydride ring, which on polymerization and subsequent hydrolysis could give a noncyclic all-*cis* polymer. The diene I on esterification with a glycol could give a cyclic bisdiene for use in a Diels–Alder polymerization.

In a series of patents, Prill[9] described the pyrolysis of α,α'-dimethyldiacetoxysuccinonitrile (IV) to give the related 2,3-dicyano-1,3-butadiene (III), but the description of the reaction was very brief and the preparation of IV was omitted. For these reasons the pyrolysis described by Prill was repeated. The addition of liquid hydrogen cyanide to biacetyl gave the key intermediate biacetyldicyanohydrin (II) in a 99% yield. Attempts to prepare the diacetate IV by acetylation with acetic anhydride gave very poor yields; in fact, the main product (43% yield) of this reaction was instead 3-acetoxy-3-cyano-2-butanone (V), which was characterized by analysis and conversion to a solid 2,4-dinitrophenylhydrazone. Treatment of II with acetyl chloride, however, gave a 72% yield of the α,α'-dimethyldiacetoxysuccinonitrile (IV). Pyrolysis of IV under the conditions described by Prill gave a 10% yield of 2,3-dicyano-1,3-butadiene (III) and a 15% yield of the monoacetate VI.

Hydrolysis of the dicyanohydrin II with concentrated hydrochloric acid, followed by esterification of the resulting hydroxyacid, gave a 45% yield of dimethyl α,α'-dimethyltartrate (VII), which in turn was acetylated with acetyl chloride to give an 80% yield of the diacetyltartrate VIII. Pyrolysis of the molten ester VIII at 490° over glass helices gave a 23% yield of impure 2,3-dicarbomethoxy-1,3-butadiene (IX) and a 33% yield of the intermediate olefin acetate X. Attempts to purify the diene IX by distillation failed since the impurity, which had a higher hydrogen content than IX (presumably dimethyl dimethylmaleate), had a boiling point quite close to that of IX. However, the diene–diester IX was characterized by conversion to a solid Diels–Alder adduct XI by treatment with maleic anhydride. Hydrolysis of the crude IX with dilute sodium hydroxide, followed by acidification, gave the 2,3-dicarboxy-1,3-butadiene (I). The structure of the diene was indicated by its analysis and ultraviolet and infrared spectra. Because of the three cross-conjugated systems, very little interaction is noted between the carboxyl groups.

An alternative synthesis of I failed because of an even greater amount of anomalous reduction during pyrolysis. Thus the dicyanohydrin II was hydrolyzed in a 50% yield to the diacid XII, which in turn gave a 23% yield of dimethyldiacetyltartaric anhydride (XIII) upon treatment with acetic anhydride. Pyrolysis of an acetone solution of XIII at 440° over glass helices, under conditions such that 30% of 2 molar equivalents of acetic acid was liberated, gave a 20% yield of α-acetoxy-α-methylitaconic anhydride (XV). Separate pyrolysis of XV at 545° under conditions such that 46% of the theoretical amount of acetic acid was liberated gave a 16% yield of dimethylmaleic anhydride (XIV) as the only isolable product. Pyrolysis of XIII under more vigorous conditions gave a lower yield of dimethylmaleic anhydride (XIV) plus a large quantity of gaseous products. This anomalous reaction can be rationalized by the assumption that the olefin acetate XV which is formed can undergo cleavage into a fairly stable free radical plus an acetoxy radical. This radical, which is stabilized by resonance with a double bond as well as with the carboxy group, might abstract a hydrogen atom to give the dimethylmaleic anhydride (XIV) or add to XV as well as any diene that was formed. A similar anomalous reaction[10] was noted in the pyrolysis of a cyclohexadienylmethyl acetate to give 3-methylenecyclohexene, toluene, and bibenzyl.

Polymers from this interesting diene will be reported separately.

Experimental[11]

Biacetyldicyanohydrin (II).—To 100 ml. of liquid hydrogen cyanide at 0° was added dropwise with occasional shaking a few drops of a saturated potassium carbonate solution, followed by 43 g. (0.5 mole) of biacetyl. After the reaction mixture was shaken to disperse any yellow color which peristed and to dislodge the crusted solid which had begun to form, the contents of the flask was poured into a large evaporating dish to remove the excess hydrogen cyanide by evaporation. The resulting solid was collected on a filter and washed with chloroform to give 70 g. (99%) of biacetyldicyanohydrin (II), m.p. 109–110° (reported[12] m.p. 110° dec.].

A modification of the above procedure, in which the biacetyl was added with vigorous stirring to refluxing liquid hydrogen

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[1] Previous paper in this series, *J. Org. Chem.*, **27**, 3088 (1962).

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[3] Office of Naval Research Fellow, 1951–1955.

[4] Office of Naval Research Fellow, 1955–1957; Goodyear Tire and Rubber Fellow, 1957; and Dunlop Research Fellow, 1957–1958.

[5] W. J. Bailey and H. R. Golden, *J. Am. Chem. Soc.*, **76**, 5418 (1954).

[6] W. J. Bailey and C. E. Knox, *J. Org. Chem.*, **25**, 511 (1960).

[7] W. J. Bailey, J. Economy, and M. E. Hermes, *ibid.*, **27**, 3295 (1962).

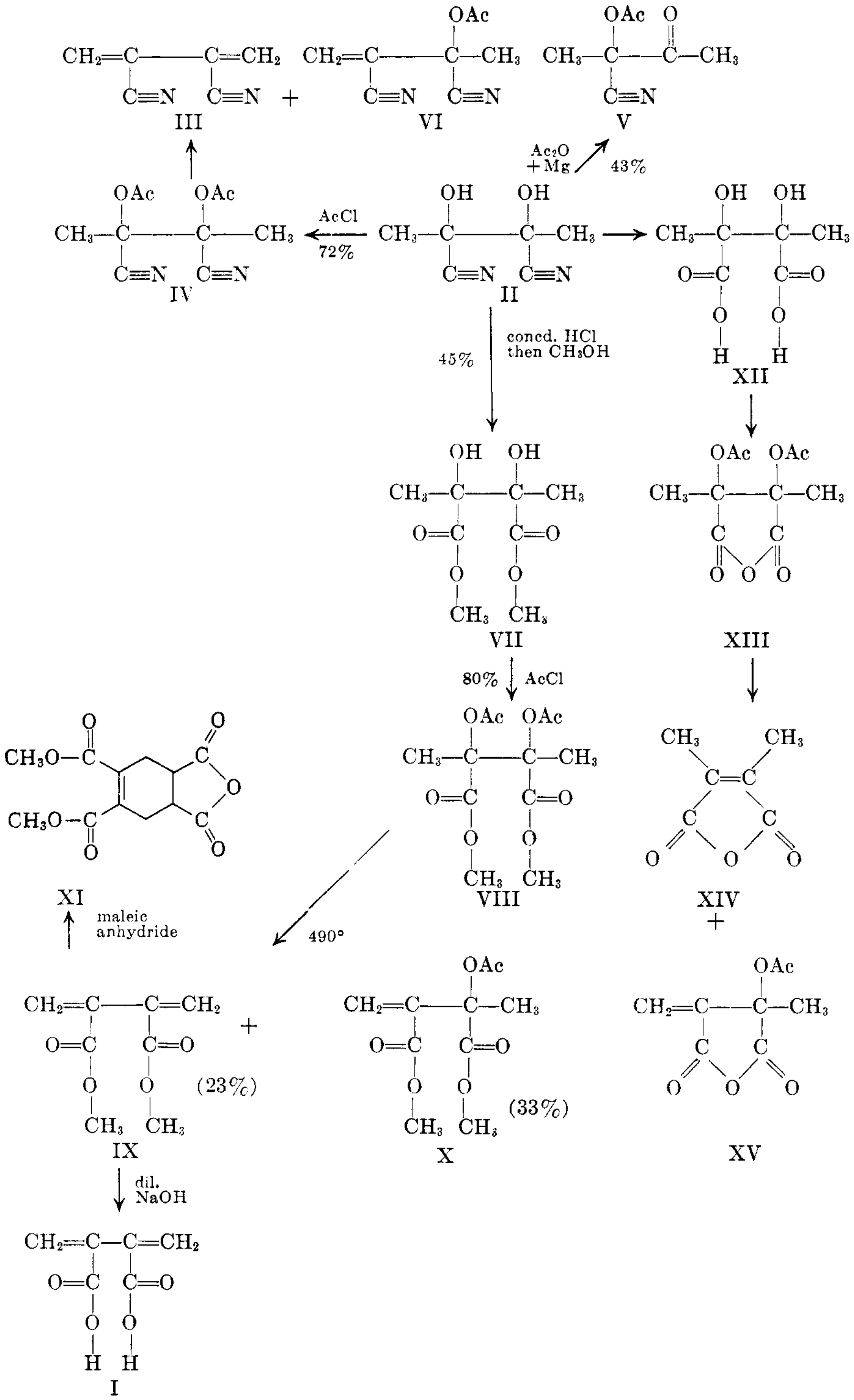
[8] W. J. Bailey, W. G. Carpenter, and M. E. Hermes, *ibid.*, **27**, 1975 (1962).

[9] E. J. Prill, U. S. Patent 2,446,167 (1948); 2,480,961 (1949).

[10] W. J. Bailey, R. Barclay, Jr., and R. A. Baylouny, *J. Org. Chem.*, **27**, 1951 (1962).

[11] The authors are grateful to Dr. Mary Aldridge and Mrs Kathryn Baylouny for the microanalyses.

[12] von R. Fittig, C. Daimler, and H. Keller, *Ann.*, **249**, 208 (1888).



cyanide, was faster and easier to control but gave slightly lower yields (70%).

α,α'-**Dimethyldiacetoxysuccinonitrile** (IV).—To a solution of 98.5 g. (0.704 mole) of biacetyldicyanohydrin (II) in 300 ml. of chloroform was added, at once, 300 ml. of acetyl chloride. After the mixture had been heated under reflux with stirring for 2 days, the cold mixture was filtered. The resulting solid was recrystallized from glacial acetic acid to yield 76 g. of IV, m.p. 170–172°. Concentration of the filtrate by evaporation gave an additional 37 g. for a total yield of 113 g. (72%). Recrystallizations from a chloroform–petroleum ether mixture and then ether produced an analytically pure sample of α,α'-dimethyldiacetoxysuccinonitrile (IV), m.p. 172–173°.

Anal. Calcd. for $C_{10}H_{12}N_2O_4$: C, 53.56; H, 5.40; N, 12.50. Found: C, 53.55; H, 5.13; N, 12.67.

2,3-Dicyano-1,3-butadiene (III).—By the general procedure of Prill[9] but with the apparatus used in these laboratories,[13] 24 g. of α,α'-dimethyldiacetoxysuccinonitrile (IV) was pyrolyzed. Distillation of the pyrolysate through a 6-in., helix-packed column gave 1.0 g. (10%) of 2,3-dicyano-1,3-butadiene (III), b.p. 54° (2.5 mm.) [reported[9] b.p. 80° (8 mm.)], and 2.6 g. (15%) of 2,3-dicyano-2-acetoxy-1-butene (VI), b.p. 94° (1.4 mm.) [reported[9] b.p. 88–89° (1.0 mm.)].

3-Acetoxy-3-cyano-2-butanone (V).—The crude reaction mixture from 86 g. (1.0 mole) of biacetyl and 200 ml. of liquid hydrogen cyanide from the evaporating dish described above was mixed with 2 l. of acetic anhydride and 120 g. (5 g.-atoms) of magnesium powder. After the mixture had been heated under reflux for 2 weeks, the cold reaction mixture was poured into ice–water. The aqueous mixture was extracted with ether in an exhaustive extractor for 48 hr. After the ether extracts were dried over anhydrous magnesium sulfate, the solvents were removed by

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[13] W. J. Bailey and J. J. Hewitt, *J. Org. Chem.*, **21**, 543 (1956).

distillation under reduced pressure and the residue was distilled through a 6-in., helix-packed column to yield 60 g. (43%) of 3-acetoxy-3-cyano-2-butanone (V), b.p. 52° (1.0 mm.), $n^{25}\text{D}$ 1.4260.

Anal. Calcd. for $C_7H_9NO_3$: C, 54.19; H, 5.85; N, 9.24. Found: C, 54.71; H, 5.86; N, 9.44.

To a solution of 2.0 g. (0.010 mole) of 2,4-dinitrophenylhydrazine containing 10 ml. of concentrated sulfuric acid, 15 ml. of water, and 50 ml. of 95% ethanol was added a solution of 4.0 g. (0.026 mole) of V in 20 ml. of 95% ethanol. After the mixture had been allowed to stand at room temperature for 30 min., the resulting precipitate was removed by filtration and recrystallized from ethanol–ethyl acetate to give 1.0 g. (30%) of yellow crystalline 3-acetoxy-3-cyano-2-butanone 2,4-dinitrophenylhydrazone, m.p. 164–166°.

Anal. Calcd. for $C_{13}H_{13}N_5O_6$: C, 46.57; H, 3.91; N, 20.89. Found: C, 46.83; H, 3.89; N, 20.80.

Dimethyl α,α′-Dimethyltartrate (VII).—After a solution of 83 g. (0.594 mole) of biacetyldicyanohydrin (II) in 500 ml. of concentrated hydrochloric acid was allowed to stand for 24 hr. at room temperature, the mixture was heated under reflux for an additional 3 hr. The cooled solution was filtered and the filtrate was evaporated to dryness on a steam bath. The residue was extracted with two 250-ml. portions of hot absolute methanol and the remaining solid removed by filtration. After 35 ml. of concentrated sulfuric acid was added to the methanolic solution, the mixture was heated under reflux for 72 hr. The cooled reaction mixture was poured into ice water and the resulting aqueous solution was made basic (pH 8) with a 20% sodium hydroxide solution. The alkaline solution was extracted first with two 500-ml. portions of ether and then with ether for 24 hr. in an exhaustive extractor. After the combined ether extracts had been dried over anhydrous potassium carbonate, the solvent was removed by distillation under reduced pressure and the residue was fractionated through a 6-in., helix-packed column to give 55 g. (45%) of dimethyl α,α-dimethyltartrate (VII), b.p. 70° (0.3 mm.). This material formed a white crystalline solid, m.p. 45–74°.

Anal. Calcd. for $C_8H_{14}O_6$: C, 46.60; H, 6.84. Found: C, 46.57; H, 6.70.

Dimethyl α,α-Dimethyldiacetyltartrate (VIII).—A mixture of 46.3 g. (0.22 mole) of dimethyl α,α-dimethyltartrate (VII) and 100 ml. of acetyl chloride was heated under reflux for 24 hr. After the cooled reaction mixture was filtered, the resulting solid was washed with 50 ml. of ether to yield 53 g. (80%) of fairly pure dimethyl α,α-dimethyldiacetyltartrate (VIII), m.p., 145–149°. This material was recrystallized twice from glacial acetic acid and washed with ether to produce an analytically pure sample, m.p. 148.5–149.5°.

Anal. Calcd. for $C_{12}H_{18}O_8$: C, 49.65; H, 6.25. Found: C, 49.84; H, 6.28.

2,3-Dicarbomethoxy-1,3-butadiene (IX) **and 2,3-Dicarbomethoxy-2-acetoxy-1-butene** (X).—At the rate of 0.5 g. per min., 98 g. (0.34 mole) of molten dimethyl α,α-dimethyldiacetyltartrate (VIII), m.p. 148–149°, was passed dropwise in four portions from a 125-ml. dropping funnel wrapped with insulated resistance wire through a vertical Vycor tube packed with Pyrex helices and heated at 490°, as previously described. A clean pyrolysis tube was inserted after each portion and a slow stream of oxygen-free nitrogen was introduced at the top of the tube to minimize the effect of heavy charring during the pyrolysis. The pyrolysate, which had been collected in a side-arm flask immersed in a Dry Ice–acetone bath, was filtered to give 3.0 g. (3% recovery) of the starting diacetate VIII. Distillation of the filtrate through a 6-in., helix-packed column gave 13.5 g. (23%) of crude 2,3-dicarbomethoxy-1,3-butadiene (IX), b.p. 52–64° (1.0 mm.), $n^{25}\text{D}$ 1.4502–1.4738, and 24.2 g. (33%) of impure 2,3-dicarbomethoxy-2-acetoxy-1-butene (X), b.p. 97–106° (1.0 mm.), $n^{25}\text{D}$ 1.4638–1.4612. Redistillation of this sample of the diene mixture through a 21-in. Podbielniak column failed to remove all of the impurity. However, redistillation of the monoacetate X through the same column gave an analytically pure sample, b.p. 107–108° (1.2 mm.), $n^{25}\text{D}$ 1.4589.

Anal. Calcd. for $C_{10}H_{14}O_6$: C, 52.17; H, 6.13. Found: C, 52.47; H, 6.01.

4,5-Dicarbomethoxy-Δ⁴-tetrahydrophthalic Anhydride (XI).—A mixture of 1 g. (0.0059 mole) of the crude 2,3-dicarbomethoxy-1,3-butadiene (IX), 0.53 g. (0.0054 mole) of maleic anhydride, and 15 ml. of toluene was heated under reflux for 44 hr. After approximately half of the solvent had been removed by evaporation, the residue was cooled to yield a solid which was recrystallized from a chloroform–petroleum ether mixture to give 0.35 g. (23%) of crystalline 4,5-dicarbomethoxy-Δ^4-tetrahydrophthalic anhydride (XI), m.p. 156–157°.

Anal. Calcd. for $C_{12}H_{12}O_7$: C, 53.73; H, 4.51. Found: C, 53.73; H, 4.62.

2,3-Dicarboxy-1,3-butadiene (I).—By a modification of the method of Coes[14] for the hydrolysis of the lower alkyl esters of acrylic and methacrylic acids, 17.6 g. (0.103 mole) of crude 2,3-dicarbomethoxy-1,3-butadiene (IX), 70 ml. of 3 *N* sodium hydroxide (210 mmoles), and a crystal of 4-*tert*-butylpyrocatechol were placed in a 200-ml. flask, fitted with a reflux condenser and magnetic stirrer. After the mixture had been stirred rapidly at room temperature for 24 hr., the insoluble organic material was removed by extraction with four 30-ml. portions of ethyl ether. To the cooled aqueous phase was slowly added 35 ml. of 6 *N* sulfuric acid (210 mmoles). Upon acidification there was a slight evolution of a gas and an oil separated. The mixture was then extracted with four 30-ml. portions of ethyl ether, and the ether extracts were dried over anhydrous magnesium sulfate. After the ether had been removed by evaporation under partial vacuum and the resulting oily residue had been placed in the freezer, crystals slowly formed. The solid was removed by filtration to yield 2.78 g. (19%) of crude 2,3-dicarboxy-1,3-butadiene (I). The crude acid was placed in boiling benzene containing a crystal of 4-*tert*-butylpyrocatechol, and 1.07 g. of insoluble diacid was removed by filtration. The concentrated benzene filtrate was cooled in ice to yield an additional 0.58 g. of a white solid. Recrystallization from ethyl acetate gave an analytically pure sample of 2,3-dicarboxy-1,3-butadiene (I), m.p. 182–185° (sealed capillary).

Anal. Calcd. for $C_6H_6O_4$: C, 50.71; H, 4.26. Found: C, 50.50; H, 4.42.

An infrared spectrum of this compound run in Nujol on a Beckman IR-5 infrared spectrophotometer supported the proposed structure with bands at 900, 910, 1290, 1608, 3150 cm.$^{-1}$, and a broad band from 1660 to 1680 cm.$^{-1}$. These bands indicate the presence of a terminal methylene, carboxyl groups, carboxyl groups, conjugated double bonds, hydroxyl group, and a carbonyl group conjugated with a double bond, respectively.

An ultraviolet absorption spectrum of a 6.56×10^{-5} *M* ethanolic solution of the diene on a Beckman DK-1 recording spectrophotometer showed neither a minimum nor a maximum above 215 mμ, but the molar extinction coefficient rose to 5590 at 215 mμ.

Dimethyldiacetyltartaric Anhydride (XIII).—By the method of Fittig, Daimler, and Keller[12] biacetyldicyanohydrin (II) was hydrolyzed with concentrated hydrochloric acid to dimethyltartaric acid (XII), m.p. 177–179° dec. (reported[12] m.p. 178–179°), in a 50% yield. After a mixture of 100 g. (0.56 mole) of XII and 800 ml. of acetic anhydride had been heated under reflux for 15 hr., the excess acetic anhydride and acetic acid were removed by distillation under reduced pressure. Since the dark sirupy residue could not be induced to crystallize, it was distilled under reduced pressure through a Claisen distilling head to give a viscous liquid, b.p. 160–180° (1.5 mm.). Toward the latter half of the distillation the distillate tended to solidify in the distilling head and the receiver. When the residue from the distillation began to decompose, the liquid in the receiver was decanted from the solid and this liquid fraction was cooled to induce crystallization. Recrystallization of the resulting solid, first from chloroform–petroleum ether and then from benzene–petroleum ether, gave 31 g. (23%) of a low melting isomer of dimethyldiacetyltartartic anhydride (XIII), m.p. 144–145°.

Anal. Calcd. for $C_{10}H_{12}O_7$: C, 49.18; H, 4.91; sapon. equiv., 61. Found: C, 49.31; H, 5.00; sapon. equiv., 59.

The solid obtained directly from the distillation was recrystallized in the manner described above to give 29 g. (21%) of a high melting isomer of dimethyldiacetyltartartic anhydride (XIII), m.p. 158–159°.

Anal. Calcd. for $C_{10}H_{12}O_7$: C, 49.18; H, 4.91; sapon. equiv., 61. Found: C, 48.91; H, 4.99; sapon. equiv., 60.

α-Acetoxy-α-methylitaconic Anhydride (XV).—At the rate of 1 ml. per. min., a solution of 20.0 g. of dimethyldiacetyltartaric anhydride (XIII) in 50 ml. of acetone was added to the Vycor pyrolysis tube heated at 440°. Distillation of the acetone and acetic acid from the pyrolysate, which had been collected in a flask cooled in a Dry Ice–acetone bath, followed by titration of the acetic acid present, indicated that 30% of 2 molar equivalents of acid had been liberated. Distillation of the residue through a

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(14) L. Coes, Jr., U. S. Patent 2,266,004 (1941).

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

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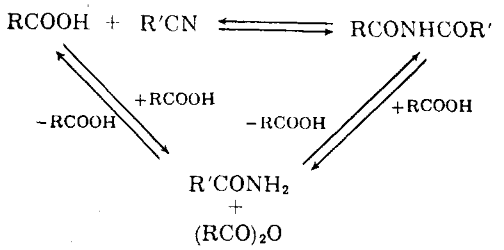
Equilibria and relative reaction rates in the reactions of acetic and trifluoroacetic acids with aceto- and trifluoroacetonitrile are described. The position of equilibrium between imide and the acid–nitrile pair is thought to be related to the respective amounts of resonance stabilization possible in 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.

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

Table I

Equilibria in the System

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

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

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

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

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).

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(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.