TABLE II
MASS SPECTRAL ANALYSIS OF OXYGEN GAS

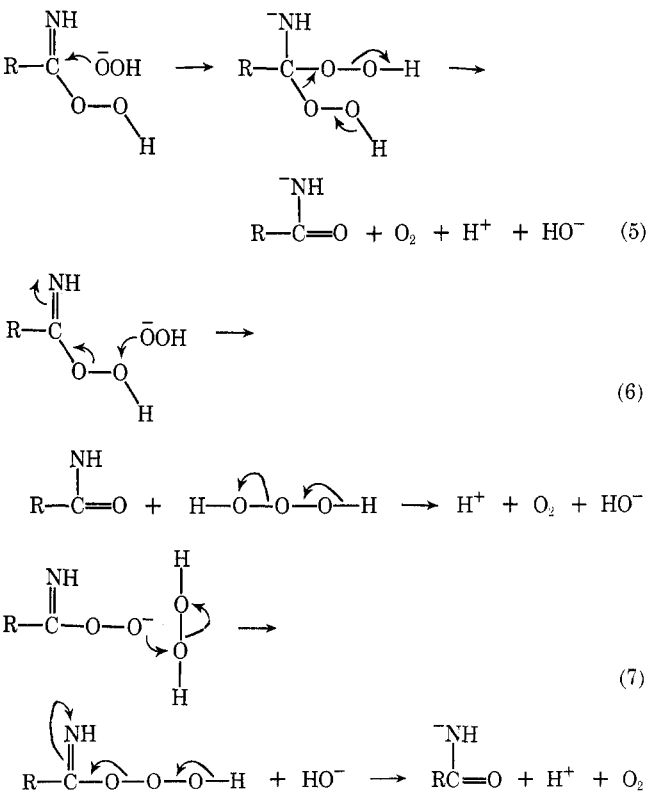
	Mole fractions		
	$^{32}O_2$	$^{34}O_2$	$^{36}O_2$
H_2O_2[a]	0.826	0.014	0.160
Reaction[b]	0.834	0.037	0.129

$$\text{Per cent unscrambled} = \frac{0.129}{0.160} \times 100 = 81\%$$

[a] Oxygen liberated by oxidation with Ce(IV) in 20% H_2SO_4 at 25°.[12] [b] In 0.1 M phosphate buffer containing 1×10^{-3} M EDTA at pH 7.4 in deionized water; T = 50–52°.

oxycarboxylic acids may decompose simultaneously *via* two distinctly different paths: (1) involving nucleophilic attack by the peroxy acid anion upon the carbonyl carbon of the peroxy acid (no scrambling) and (2) involving nucleophilic attack of the peroxy acid anion upon the outer oxygen of the peroxy acid (scrambling). For example, peroxyacetic acid decomposes 83% *via* path 1 and 17% *via* path 2.[11] When the carbonyl site is sterically hindered, as in the case of peroxypivalic acid, the results are reversed, 24% *via* path 1 and 76% *via* path 2.[13]

Because of the similarity in structure between I and peroxycarboxylic acids, we suggest that the fast step of the reaction can best be described by eq 5–7. Equation 5 predicts no scrambling, eq 7 predicts complete scrambling, and eq 6 predicts 50% scrambling. Edwards' work with peroxycarboxylic acids indicates that the transition states for paths 1 and 2 must be of similar energy; however, sp^2 carbon is the preferred site for attack.[14] In our case, since scrambling occurs, either eq 6 or eq 7 or both must be operative. We therefore conclude that eq 5 accounts for the major portion of the oxygen produced at pH 7.4. Under these conditions, if scrambling occurs only by eq 6, eq 5 will account for 62% of the reaction. If scrambling occurs only by eq 7, eq 5 will account for 81% of the reaction. Since the pK_a values of the peroxycarboximidic acid is probably in the vicinity of 8 (by analogy with peroxycarboxylic acids),[15] we expect that eq 7 will increase in importance at the expense of eq 5 and 6 at higher pH values. However, the complexity of the reaction at higher pH values, *vide ante*, would make the interpretation of double-labeling experiments in carbonate buffer or in sodium hydroxide solutions equivocal.



(5)

(6)

(7)

(14) The anion of hydrogen peroxide is an extremely powerful nucleophile toward the sp^2 carbon.[3]

Experimental Section

Kinetics were followed by monitoring the rate of loss of H_2O_2 by iodometric titration in the usual manner. A Warburg apparatus was used in those experiments for which the product of oxygen was followed.

Doubly labeled $H_2{}^{18,18}O_2$ was prepared by passing ^{18}O enriched H_2O (98 atom % ^{18}O, Miles-Yeda Ltd., Lot No. 18W97U) through an electric discharge tube.[16] The product $H_2{}^{18,18}O_2$ was rinsed from the cold traps with normal 30% H_2O_2 (Mallinkrodt, Lot WPBP) such that the resulting peroxide solution had an isotopic enrichment of 16 atom % of ^{18}O.

The *p*-cyanobenzoic acid (Aldrich Chemical Co., Lot No. 070671) was recrystallized twice from deionized water and treated with decolorizing charcoal. Deionized water was obtained by passing distilled water through a Barnsted mixed-bed ion exchange column. The mono- and dibasic potassium phosphate salts and the mono- and dibasic sodium carbonate salts used for buffer solutions were reagent grade. The disodium salt of EDTA was obtained from Eastman Organic Chemicals (Lot 681 A).

The reaction of the nitrile with hydrogen peroxide was carried out at 50–52°. Gas samples were collected at 2-hr intervals at a pressure of approximately 200 Torr at room temperature. Mass spectrometric analyses were performed on a Hitachi Perkin-Elmer RMU-6D instrument.

Registry No.—Hydrogen peroxide, 7722-84-1; *p*-cyanobenzoic acid, 619-65-8.

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(15) J. F. Goodman, P. Robson, and E. R. Wilson, *Trans. Faraday Soc.*, **86**, 1846 (1962).

(16) R. E. Ball, J. O. Edwards, and P. Jones, *J. Inorg. Nucl. Chem.*, **28**, 2458 (1966).

Nitrile Synthesis *via* the Acid–Nitrile Exchange Reaction

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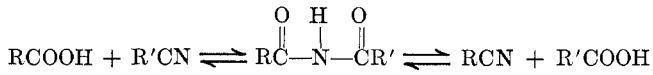
Organic nitriles traditionally have been synthesized from the corresponding carboxylic acids by ultimate dehydration of the amide. Occasionally, the acid–nitrile exchange reaction has been used to accomplish direct conversion of carboxylic acids to nitriles by reaction with acetonitrile at high temperatures.[1,2] Apparently

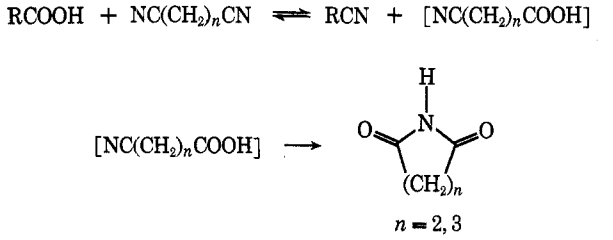
(1) D. J. Loder, U. S. Patent 2,377,795 (1945).

(2) French Patent 1,525,498 (1968).

an equilibrium exists which proceeds through an imide addition product, the equilibrium being displaced toward the side of the weaker carboxylic acid.[3]



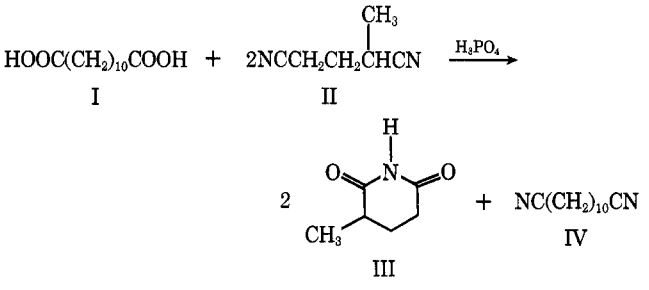
We have found that replacing acetonitrile with short-chain dinitriles (specifically succinonitrile, glutaronitrile, and α-methylglutaronitrile) provides two distinct advantages in the use of this reaction as a synthetic method. First, the use of pressure equipment to reach the required high temperatures (150–300°) is avoided. Second, distinct improvements in yield of product nitrile, especially for aliphatic systems, have been realized due to the fact that the once-exchanged short-chain cyano acid undergoes an internal cyclic imide formation, removing it from the equilibrium and thus driving the reaction to completion.



$n = 2, 3$

Although the reaction proceeds uncatalyzed, there are apparent advantages in adding 0.5–1.0 wt % of compounds such as sulfonic, sulfuric, or phosphoric acids or their various salts.

We have used this method for the synthesis of aliphatic dinitriles. Reaction of 1,12-dodecanedioic acid (I) with 2 molar equiv of α-methylglutaronitrile (II) afforded a 98% recovered yield of α-methylglutarimide (III) and a 97% recovered yield of 1,12-dodecanedinitrile (IV). Azelaonitrile similarly was prepared in 87% recovered yield from azelaic acid.



Conversion of I into IV also was accomplished in high yield by refluxing with 2 molar equiv of glutaronitrile or succinonitrile. The products glutarimide, mp 158–159°, and succinimide, mp 126–127°, were purified by recrystallization from chloroform and characterized by infrared, proton magnetic resonance, and elemental analyses.

Experimental Section

A typical reaction involved refluxing (*ca.* 285°) a mixture of 1150 g (5.0 mol) of dodecanedioic acid (I) and 1150 g (10.65 mol) of α-methylglutaronitrile (II) containing 11.6 g of 85% H_3PO_4 for 18 hr. The resulting black solution was cooled and vacuum distilled to give 1246 g (98% of theoretical) of tan solid α-methylglutarimide (III), bp 137° (7 mm), and 929.7 g (97% of theoretical) of yellow liquid dodecanedinitrile (IV), bp 193° (8 mm). Aqueous NaOH washing and redistillation afforded colorless liquid IV, mp 21–22°.

Anal. Calcd for $C_{12}H_{20}N_2$: C, 75.00; H, 10.42; N, 14.58. Found: C, 74.95; H, 10.52; N, 14.54.

Redistillation and recrystallization from 1:1 benzene–cyclohexane afforded white, crystalline III, mp 98.5–99°.

Anal. Calcd for $C_6H_9NO_2$: C, 56.69; H, 7.09; N, 11.02. Found: C, 56.44; H, 7.14; N, 11.00.

Proton magnetic resonance and infrared spectra of III were consistent with the proposed cyclic imide structure.

Registry No.—I, 693-23-2; III, 29553-51-3; IV, 4543-66-2.

(3) F. Becke and T. F. Burger, *Justus Liebigs Ann. Chem.*, **716**, 78 (1968).

Ionization Scheme for the *N*,*N*-Di(carboxymethyl)anilines

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It is well known that aliphatic amino acids exist in aqueous media in the form of dipolar molecules (zwitterions). In fact, the equilibrium between the neutral form and the dipolar form favors the dipolar form by a factor of several tens of thousands.[1] However, if the basicity of the nitrogen is reduced by interaction with an aromatic ring, then the neutral form and dipolar form can have comparable stabilities in aqueous media. For example, the *o*-, *m*-, and *p*-aminobenzoic acids have dipolar molecule–neutral molecule ratios of 0.2, 2.5, and 0.17.[2] Infrared work in D_2O and D_2O–dioxane mixtures[3] demonstrated that the three pyridinecarboxylic acids existed largely as dipolar molecules in aqueous media, but the neutral form was present to a nonnegligible extent.

The purpose of this work was to decide whether or not dipolar molecules or ions were important species in the ionization scheme of the *N*,*N*-di(carboxymethyl)anilines. Two complementary studies on five of these acids (unsubstituted and the para-substituted chloro, fluoro, methyl, and methoxy acids) led to the conclusion that dipolar molecules or ions are not involved to any appreciable extent in the ionization scheme of these acids.

The ionization scheme is presented in Scheme I. It can be seen that H_2A and HA^- can both exist in either a dipolar form or a neutral form, *i.e.*, protonated or nonprotonated on the nitrogen. H_3A^+ represents the fully protonated species. Since thermodynamics does not discriminate between the possible forms, the three experimental p*K*'s which completely describe the ionization scheme for any one acid are actually composite p*K*'s. However, using nonthermodynamic experiments and reasoning, it has been possible to demonstrate

(1) J. P. Greenstein and M. Winitz, "Chemistry of the Amino Acids," Vol. 1, Wiley, New York, N. Y., 1961, p 447.

(2) J. J. Christensen, D. P. Wrathall, R. M. Izatt, and D. O. Tolman, *J. Phys. Chem.*, **71**, 3001 (1967).

(3) J. F. Wojcik and T. H. Stock, *ibid.*, **73**, 2153 (1969).