

Oxidation of Cyclohexane with Cobalt(III) Acetate.—A total of 23.7 g (285 mmol) of cyclohexane and 130 ml of 0.27 M cobalt(III) acetate in acetic acid were stirred under nitrogen atmosphere for 3 days at 70° until Co(III) ions were consumed. The mixture was cooled, diluted with water, saturated with NaCl, and extracted with ethyl ether. The organic layer was washed with water, dried with MgSO₄, and concentrated in a rotary evaporator to a volume of ~2 ml. Analysis by vpc identified the following products in order of their appearance on the chromatogram (10 ft × 0.25 in., 10% Carbowax 20M column at 90°): bicyclohexyl (1.8 wt %), cyclohexanone (trace), cyclohexyl acetate (35.4), cyclohexanol (trace), cyclohexylidene diacetate (14.0), and 2-acetoxycyclohexanone (48.8). On the basis of stoichiometry, 4 mol of Co(III) required/mol of cyclohexylidene diacetate, 2 mol/mol of cyclohexyl acetate, and 6 mol/mol of 2-acetoxycyclohexanone, the products accounted for ~69% of the oxidant consumed. The aqueous layer also contained small quantities of cyclohexanone and cyclohexanol which were not determined as well as open-chain products of cyclohexane on the basis of nmr, but their structures have not been established with certainty. Conversion of cyclohexane was ~1.6%. Major products were also identified by their fragmentation patterns (vpc-mass spectrum).

Competitive Rate Study.—Competitive oxidations on mixtures of substrates were done under conditions earlier described.¹⁰

Initial concentration of each substrate was held at a low value (~1.0 M) to minimize possible solvent effects. After the initiation period was over, reaction was allowed to proceed for 5 min. Initial charge and the pentane extract of the final mixture were analyzed directly by vpc for the disappearance of starting hydrocarbons. Analyses were carried out by vpc using 20 ft × 1/8 in., 20% Carbowax 20M column (Hewlett-Packard 7620A research chromatograph, TC detector), and chlorobenzene or *o*-dichlorobenzene as internal standard. Peak areas were electronically measured. All reactivities were related to toluene using eq 4

$$\frac{k_a}{k_b} = \frac{\log ([A]_f/[A]_i)}{\log ([B]_f/[B]_i)} \quad (4)$$

where [A] and [B] refer to concentrations of the two substrates before and after the reaction in weight per cent.

Competitive oxidations with cobaltic salts alone were carried out in sealed ampoules under nitrogen atmosphere.

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Registry No.—Cobalt(III) ion, 7440-48-4; cobalt(III) acetate, 917-69-1.

Cleavage of Saturated Fatty Acid Amides by Anhydrous Hydrogen Fluoride-Boron Trifluoride

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N-n-Butylamides of long-chain, unbranched carboxylic acids undergo degradation, isomerization, and (in part) dimerization of the fragments when treated at 0–5° with liquid hydrogen fluoride saturated with boron trifluoride. The compounds studied were the *N-n*-butylamides of undecanoic, myristic, palmitic, and stearic acid. Two major classes of products were obtained: (1) saturated, branched *N-n*-butylamides and (2) saturated, branched *N,N'*-di-*n*-butyldiamides. The ratio of the former to the latter is 2:1. The products from *N-n*-butylundecanamide consist mainly of the following *N-n*-butylamides (relative proportions): 5-methylhexanamide (12.9%), 6-methylheptanamide (25.6%), 5-methylheptanamide (18.5%), 7-methyloctanamide (14.5%), and 6-methyloctanamide (6.5%). The branched diamides are predominantly of chain length C₁₂–C₁₅ (acid moiety). Similar results are obtained with *N-n*-butylmyristamide, *N-n*-butylpalmitamide, and *N-n*-butylstearamide when treated under the indicated reaction conditions; however, *N-n*-butylamides of acid moiety chain length shorter than C₁₀ (e.g., the *N*-alkyloctanamide) are not affected. The probable mechanism of the reaction is discussed, and it is concluded that the inductive effect of the protonated amide group is important in determining the product distribution.

Acid-catalyzed isomerization and degradation reactions of saturated hydrocarbons have been extensively studied because of their practical importance in the petroleum industry.² This work has led to an understanding of certain fundamental aspects of these reactions and has also revealed interesting transformations such as the isomerization of *endo*-trimethylenenorbornane to adamantane.³ Recently, new reactions in superacid media, such as direct alkylation and nitration of alkanes, have been explained as occurring by the intervention of pentacoordinated carbonium ions,^{4,5} a development that has spurred additional interest in

this field. However, there have been only scattered studies on the transformations of fatty acid derivatives under strongly acidic conditions.^{6–9} The investigation of these reactions is rendered more complex by the presence of the carbonyl group; important questions about the effect of the functional group on the reactivity of C–C and C–H bonds in other parts of the molecule need to be answered. We report here the cleavage reactions of secondary aliphatic amides in the acidic medium hydrofluoric acid-boron trifluoride (HF-BF₃).

Results

In a typical experiment, one of the *N-n*-butylamides **1a-1g** (0.006 mol) was dissolved in 12 ml of liquid HF at 0–5° followed by saturation of the solution with

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(2) H. Pines and N. E. Hoffman in "The Friedel Crafts and Related Reactions," Vol. 2, part 2, George Olah, Ed., Interscience, New York, N. Y., 1964, Chapter 23.

(3) P. v. R. Schleyer and M. M. Donaldson, *J. Amer. Chem. Soc.*, **82**, 4645 (1960).

(4) (a) G. A. Olah, Y. Halpern, J. Shen, and Y. K. Mo, *J. Amer. Chem. Soc.*, **93**, 1251 (1971); (b) G. A. Olah and J. A. Olah, *J. Amer. Chem. Soc.*, **93**, 1257 (1971); (c) G. A. Olah and H. C. Lin, *J. Amer. Chem. Soc.*, **93**, 1259 (1971).

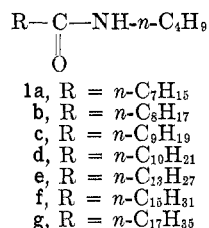
(5) G. A. Olah, Morley Medal Lecture, Cleveland Section of American Chemical Society, Dec 9, 1970.

(6) P. Blanchard, R. Perron, and M. Auffret, *Bull. Soc. Chim. Fr.*, **60**, 1194 (1968).

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anhydrous BF₃. After standing at this temperature for 30 min, the reaction was quenched with water, and the organic products (70–90% by wt) were isolated and identified.

In each case where reaction was observed, the major products were (1) mixtures of saturated branched *N*-*n*-butylamides having chain lengths shorter than the starting amide (see Table I) and (2) mixtures of

TABLE I
MONOAMIDE PRODUCTS FROM THE REACTION
OF SECONDARY AMIDES WITH HF-BF₃

$$\text{RCNH}-n\text{-C}_4\text{H}_9 \xrightarrow{\text{HF-BF}_3} \text{R}'\text{CNH}-n\text{-C}_4\text{H}_9$$

Monoamide products, R'	Relative yields of monoamide products from starting amides ^c		
	1d, R = <i>n</i> - C ₁₀ H ₂₂	1e, R = <i>n</i> - C ₁₃ H ₂₇	1f, R = <i>n</i> - C ₁₅ H ₃₂
2, (CH ₃) ₂ CH(CH ₂) ₃ -	12.9	17.3	9.7
3, CH ₃ (CH ₂) ₅ -	0.4	0.2	0.2
4, (CH ₃) ₂ CH(CH ₂) ₄ -	25.6	25.8	22.3
5, CH ₃ CH ₂ C(CH ₃)H(CH ₂) ₃ -	18.5	17.6	14.5
6, CH ₃ (CH ₂) ₆ -	1.3	1.4	0.8
7, (CH ₃) ₂ CH(CH ₂) ₅ -	14.5	11.4	12.7
8, CH ₃ CH ₂ C(CH ₃)H(CH ₂) ₄ -	6.5	4.7	5.3
9, CH ₃ (CH ₂) ₇ -	2.3	2.5	2.3
10, (CH ₃) ₂ CH(CH ₂) ₆ -	3.6	2.9	6.2
11, CH ₃ CH ₂ C(CH ₃)H(CH ₂) ₅ -	1.9	1.1	2.7
12, CH ₃ (CH ₂) ₈ -	1.9	0.9	1.7
Others	10.7 ^a	14.2 ^b	21.5 ^c

^a These are comprised of ten branched amides of unknown structure; each component is less than 2.1% of the total monoamides. ^b These are comprised of branched amides, 6.8% of which are unknowns of chain length C₁₀ or less, and 7.1% are C₁₁ and C₁₂ branched amides. ^c These are comprised of branched amides of which 3.6% are unknowns of chain length C₁₀ or less, and the remaining 17.9% are C₁₁ and C₁₂ branched amides.

saturated branched *N,N'*-di-*n*-butyldiamides (see Table II). A complex mixture of branched γ -lactones

TABLE II
DIAMIDE PRODUCTS FROM THE REACTION
OF SECONDARY AMIDES WITH HF-BF₃

$$\text{RCNHBu} \xrightarrow{\text{HF-BF}_3} \text{BuNHC}(\text{C}_n\text{H}_{2n})\text{CNHBu}$$

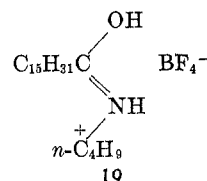
Saturated diamide products ^{a,b}	Yields of diamide products from starting amides		
	1d, R = <i>n</i> -C ₁₀ H ₂₁	1e, R = <i>n</i> -C ₁₃ H ₂₇	1f, R = <i>n</i> -C ₁₅ H ₃₁
13, <i>n</i> = 9	1.7	3.6	0.8
14, <i>n</i> = 10	9.8	11.0	6.1
15, <i>n</i> = 11	26.2	28.7	21.9
16, <i>n</i> = 12	30.9	31.8	31.8
17, <i>n</i> = 13	16.0	15.1	21.1
18, <i>n</i> = 14	0	0	7.4
Others	15.4	9.8	10.9

^a Bu = *n*-C₄H₉. ^b Only branched diamides were observed. The exact branching patterns have not been established.

(2–4%) and hydrocarbon polymers (10–20%) was also isolated.^{10,11} The monoamides and diamides were isolated in amounts that accounted for 96–98% of the carbonyl-containing fragments, and the ratio of monoamides to diamides was generally about 2:1. The products were identified by conversion of the monoamides into the corresponding methyl esters 2e–12e and comparison of their glpc retention times, mass spectra, and ir spectra to those of authentic samples.

The chain length of the starting amide does not greatly affect the production distribution in cases where reaction is observed apart from small proportions of products branched at positions more remote from the functional group. However, there is no reaction under our conditions when the starting amide acid chain contains fewer than ten carbon atoms. Thus, *n*-butylnonanamide (1b) is recovered unchanged and *n*-butyldecanamide (1c) undergoes only partial reaction in 30 min at 0°. Also, no reaction is observed unless trace amounts of unsaturated material are present. For example, olefin-free *N*-*n*-butylundecanamide (1d) is inert until a little methyl oleate is added as a promoter. We further checked our conclusions regarding the lack of reactivity of the shorter chain length amides by doing runs with mixtures of amides. When *N*-*n*-butyloctanamide (1a) and *N*-*n*-butylundecanamide (1d) were mixed and the reaction was carried out as usual, the latter was completely consumed, while the former remained unchanged.

The results described here¹² may be compared with the isolation of stable amide hydrofluoroborates under similar conditions. The hydrofluoroborate 19 can be



isolated when *N*-*n*-butylpalmitamide, 1f (0.01 mol), is dissolved in 4 ml of liquid hydrogen fluoride followed by saturation with boron trifluoride.¹³ However, if 0.01 mol of 1f is dissolved in even a larger excess of hydrogen fluoride, and the solution is then saturated with boron trifluoride, the cleavage reaction is observed. Thus, by varying the amount of hydrogen fluoride saturated with BF₃, and therefore the ratio of BF₃ to amide, one of the two results may be selected. We have observed that an amide hydrofluoroborate such as 19 also undergoes the cleavage reaction (when subjected to the conditions of our experiments with 1d–1f) to give product distribution similar to that obtained from free amide starting material. It therefore seems likely that the first step in the reaction is formation of the amide hydrofluoroborate.

(10) Yields were determined by assuming an average chain length of C₈ for monoamide products and an average chain length of C₁₄ for diamide products. This average is based on the actual product distribution (Tables I and II).

(11) In certain cases (1f, 1g) mixtures of hydrocarbon monomers were also isolated.

(12) Similar results were obtained using *N*-methyl- and *N*-*tert*-butylamides. Stearamide and *N,N*-dimethylstearamide also undergo fragmentation in HF-BF₃.

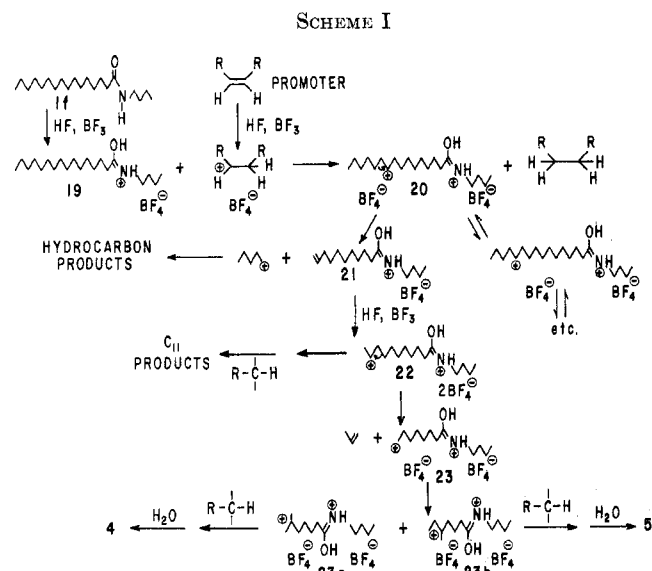
(13) S. S. Hecht and E. S. Rothman, *J. Org. Chem.*, **38**, 395 (1973).

Discussion

In considering a rational explanation for these reactions, it is necessary to account for several facts of special significance. The first of these is the predominance of products having chain lengths (acid moiety) in the range of C₇-C₁₀, regardless of the alkyl chain length of the starting amide. Monoamides shorter than C₇ are not found in the final product mixtures and the C₁₁-C₁₂ fractions from **1e** and **1f** are relatively small.

A second important feature is the virtual exclusion of straight-chain products which comprise, on the average, only 5.4% of the monoamide fraction. Unbranched compounds are not present to any significant extent in the diamide mixtures. Also, the selectivity in branching patterns is remarkable, particularly in the case of the C₇ product where *N-n*-butylisooheptanamide (**2**) is formed to the complete exclusion of the anteisoamide. The monoamide product mixtures of longer chain lengths become increasingly complex; the C₁₀ amides include three unknowns (4.5% of total monoamides) in addition to the iso-, anteiso-, and straight chain products. The decreased reactivity of short-chain amides is another special feature of the reaction.

A formal scheme accounting for monoamide products from *N-n*-butylpalmitamide (**1f**) is presented in Scheme I. The first steps are protonation of **1f** to give amide



salt **19** and protonation of the trace olefin to give the promoter carbenium ion. Hydride abstraction from **19** by the promoter generates a new carbenium ion **20**. The positive charge on carbon in this intermediate can migrate *via* hydride shifts to other positions along the alkyl chain. There is ample precedent for this equilibration.^{8,9,14,15} At positions closer to the carbonyl than C-5, the inductive effect of the strongly electron-attracting amide salt functionality apparently begins to deter carbenium ion formation. More evidence for this is presented later. There are several reaction pathways open to a typical intermediate such as **20**, but the most important one for purposes of this dis-

ussion is cleavage to give an amide and a hydrocarbon fragment as indicated.¹⁶ The hydrocarbon fragment gives rise to polymeric material. The unsaturated amide fragment **21** may be protonated to give a new carbenium ion **22** which can undergo either further cleavage to an intermediate formally represented as **23**,¹⁷ or rearrangement and hydride abstraction to give C₁₁ products. The unstable ion **23** rearranges to the tertiary carbenium ions **23a** and **23b**, corresponding to the observed products **4** and **5**.¹⁸ This generalized pathway leading to the same results may be written for other typical intermediates related to **20**.

An important aspect of this picture is the apparent lack of stability of intermediates in which the positive charge would be localized at C-4, C-3, or C-2 of the amide salt alkyl chain. Evidence for this is provided by the exclusive formation of *N-n*-butylisooheptanamide (**2**) as the C₇ product. By contrast, both the iso and anteiso C₈ amides **4** and **5** are observed in good yield. Rearrangement of a C₇ amide fragment (related to **23**) to *N-n*-butylanteisoheptanamide requires location of positive charge at C-4. The absence of this product indicates the probable difficulty of such a process. The isolation of traces of γ -lactones may reflect a certain number of cases in which C-4 carbenium ions were involved.¹⁹ The high yield of the C₈ products **4** and **5** indicates the relative ease of carbenium ion formation at C-5 and C-6.

The predominance of monoamide products having chain length C₇ through C₉ results from the resistance of intermediates such as **23a** and **23b** to further cleavage. These carbenium ions have positive charge localized at the C-6 and C-5 positions. Further cleavage would involve placing a positive charge at the C-3 or C-4 positions, which appears to be energetically unfavorable because of the inductive effect of the amide salt group. By contrast, the intermediate **22** can undergo fragmentation to **23** without experiencing this effect.²⁰

The dimeric amides probably result from alkylation of an unsaturated amide with an amide carbenium ion. The predominance of C₁₃ and C₁₄ diamides may reflect the fact that the C₆ and C₇ carbenium ion fragments have fewer avenues of stabilization available to them.

We have followed the development of products from the reaction of *N-n*-butylstearamide (**1g**) with hydrogen fluoride-boron trifluoride. The eventual product distribution for **1g** is similar to those outlined for **1d-f**. In the early stages of the reaction, a random distribution of product monoamides was observed, indicating initial cleavage from a variety of inter-

(16) Rearrangement of **20a** may precede cleavage, but for simplicity we consider an unrearranged intermediate. Also cleavage to a charged amide fragment and an olefin is possible, but the eventual result is the same.

(17) The actual intermediacy of a primary carbenium ion is an open question. Certain nonclassical ions corresponding to **23** are possible. Also **22** may undergo direct fragmentation to two olefinic molecules.

(18) See D. A. McCaulay, *J. Amer. Chem. Soc.*, **81**, 6437 (1959), for a discussion of the mechanism of isomerization of hydrocarbons under conditions similar to ours.

(19) Only a small fraction of this mixture could have arisen from ring closure of the precursor to *N-n*-butylanteisoheptanamide. Ring closure to lactonic products could also proceed through attack on a Δ^4 double bond.

(20) See ref 15 where the same trend is observed in the Friedel-Crafts reactions of alkanolic acids. The pK_a values for H₃N⁺(CH₂)_xCO₂H show small increases in acidity over the unsubstituted acids for x = 4 and x = 3, and much greater effects at x = 2, 1. The relative contributions of inductive vs. field effects in our experiments is not known.

(14) M. F. Ansell, B. E. Grimwood, and T. M. Kafka, *J. Chem. Soc. C*, 1802 (1967).

(15) M. F. Ansell and G. F. Whitfield, *J. Chem. Soc. C*, 1098 (1971).

mediates resembling **20**. As the reaction proceeded, the relative amounts of C₇-C₉ amides gradually increased, a result in agreement with the inhibition of further cleavage of species such as **23a** and **23b**. The fact that diamides were observed only after the accumulation of the shorter chain length monoamides indicates that they are probably secondary products.²¹

The lack of reactivity of *n*-butyloctanamide (**1a**) and *n*-butylnonanamide (**1b**) under our conditions probably reflects difficulty in the initial hydride abstraction step. If hydride abstraction were to take place, one might expect at least some isomerization of the starting amide; this is not observed. It seems unlikely that the inductive effect of the amide salt group would play an important role at C-7 or C-8. Other features may be involved in this bimolecular reaction; for example, the approach of the promoter carbenium ion may be hindered by the repulsion of the amide salt positive charge.

From our results, we conclude that the inductive effect of the amide salt functionality is important in determining the eventual product distribution when secondary amides **1d-f** are allowed to undergo the acid-catalyzed cleavage reaction. This conclusion leads to the possibility that reactions of this kind might be controlled to give only prescribed products by judicious placement of suitable electronegative groups.

Experimental Section

Equipment.—Melting points (uncorrected) were determined on a Kofler hot stage. Infrared spectra were measured on a Perkin-Elmer²² Model 457 grating spectrophotometer. Nmr spectra were recorded on a Jeolco C-60H²³ high-resolution nmr spectrometer. Mass spectra were determined with a Du Pont Model 21-492 mass spectrometer. Combined gas chromatographic-mass spectrometric analyses were obtained using this instrument coupled to a Varian Aerograph gas chromatograph via a jet type separator; data were collected with the aid of a Digital Equipment Corporation PDP-12 computer. Routine gas chromatographic runs were conducted with a Hewlett-Packard Model 5750 research chromatograph equipped with a thermal conductivity detector and the following columns: column A (6 ft × 1/4 in. 25% diethylene glycol adipate-3% phosphoric acid on 60-80 Chromosorb A), column B (30 ft × 1/8 in. 15% Carbowax on 45-60 Chrom W), column C (6 ft × 1/4 in. 15% OV-1 on 60-80 WAW DMCS).

Materials.—Commercial grade BF₃ and HF were used directly. The *N*-*n*-butylamides, **1a-e**, were prepared by reaction of *n*-butylamine with the appropriate acid chloride. The amides, **1f-g**, were prepared via the method of Jordan and Port.²³ The amides **1a**, **1c**, and **1g** had physical properties in agreement with the reported values.²³⁻²⁵ Amides **1b**, **1d**, **1e**, and **1f** which have not been reported previously, gave the expected ir and nmr spectral properties and elemental analyses were in accord with expected values. Boiling or melting points are as follows: **1b** (R = *n*-C₈H₁₇), bp 115° (0.2 mm); **1d** (R = *n*-C₁₀H₂₁), mp 47-47.2°; **1e** (R = *n*-C₁₃H₂₇), mp 66-67°; **1f** (R = *n*-C₁₅H₃₁), mp 75-76°.

Reaction of *N*-*n*-Butylamides **1a-g with HF-BF₃.**—All HF reactions were performed in a graduated polyethylene bottle with an inlet tube for attachment to HF and BF₃ cylinders and an exit tube protected by calcium sulfate. The usual precau-

tions to maintain dryness were taken. Appropriate safety precautions should be taken to avoid toxicity and severe burns in the handling of HF.

The procedure described here for *n*-butylpalmitamide (**1f**) is identical with that used for all other amides. The amide, **1f** (1.83 g, 0.006 mol), and 1 drop of methyl oleate were dissolved in liquid HF (12 ml) at 0-5°, and BF₃ was bubbled in for 6 min at a moderate rate, or until excess BF₃ was visible in the exit tube. The resulting solution was allowed to stand at 0-5° for 30 min. During this time, a small upper layer appeared.²⁶ The reaction was terminated by cautious dropwise addition of H₂O (15 ml). Extraction (CH₂Cl₂), combination of organic layers, drying (Na₂SO₄), and evaporation of solvent gave an oil, 1.34 g.

Analysis of Products from **1f.**—The oil obtained from the reaction of **1f** with HF-BF₃ was chromatographed on a column of dry Florisil (45 × 4 cm) with sequential elution by CH₂Cl₂, Et₂O, and MeOH to give the following fractions: fraction A (30 mg), fraction B (40 mg), fraction C (610 mg), fraction D (380 mg). These fractions were each examined and had the following spectral and chromatographic properties.

Fraction A (polymeric hydrocarbons; elution with CH₂Cl₂): ir (film) 3000-2800, 1450, 1380 cm⁻¹; nmr (CDCl₃) δ 2.5-0.5 (m); glpc (column C, 70-300°, programmed temperature rise 2°/min), no peaks other than solvent.

Fraction B (γ-lactones, elution with CH₂Cl₂): ir (CHCl₃) 3000-2850, 1760 (lactone carbonyl), 1460 cm⁻¹; nmr (CDCl₃) δ 2.56 (m, -CH₂C(O)=O), 2.1-0.6 ppm (m); mass spectrum *m/e* a series of peaks 99 (4-methyl γ-butyrolactone fragment), 113, 127, 141, 155, 169, etc.; glpc (column C, 50-300°, 4°/min), a complex mixture of at least 20 components eluting between 135-210°.

Fraction C (monoamides, elution with Et₂O): ir (CHCl₃) 3455, 3000-2850, 1660, 1460 cm⁻¹; nmr (CDCl₃) δ 6.02 (1 H, broad s, -NH), δ 3.30 (2 H, q, -C(=O)NHCH₂CH₂-), 2.21 (2 H, t, CH₂CH₂C(=O)N-), 1.80-0.7 (22 H, m); glpc (column A, 200°), peak 1 (rel retention time 1.00), peak 2 (1.44), peak 3 (2.02), peak 4 (2.76), peak 5 (3.84); mass spectrum *m/e* (rel intensity of peak 1, 185 (10), molecular ion, 170 (15), 142 (20), 128 (18), 115 (100), peak 2, 199 (15), mol ion, 184 (20), 128 (50), 115 (100); peak 3, 213 (5), molecular ion, 128 (25), 115 (100); peak 4, 227 (5), molecular ion, 128 (30), 115 (100). These spectra are characteristic of saturated *n*-butylamides corresponding to the C₇-C₁₀ acids, respectively (peak 5-C₁₁). However, comparison of retention times with those of straight-chain *n*-butylamides indicates branching; e.g., relative retention time of *n*-butyloctanamide on column A at 200° = 1.72.

Fraction D (diamides, elution with MeOH): ir (CHCl₃) 3455, 3000-2850, 1660, 1460 cm⁻¹; nmr (CDCl₃) δ 5.95 (2 H, broad s, -C(=O)NH-), 3.30 (4 H, q, -C(=O)NHCH₂CH₂-), 2.20 (4 H, t, -CH₂CH₂C(=O)NH-), 1.9-0.8 (34 H, m); glpc (column A, 200°), no peaks visible.

Hydrolysis of Monoamides (Fraction C) and Identification of Products.—The monoamide mixture (610 mg) was added to ethylene glycol (14 ml) and 4 *M* aqueous KOH (2 ml). The mixture was stirred and allowed to reflux for 48 hr. After cooling, it was poured into H₂O (50 ml) and extracted (Et₂O) to give a neutral fraction which contained no extractable material. The aqueous phase was acidified (aqueous HCl) and extracted (Et₂O). The ethereal layers were dried (Na₂SO₄) and concentrated giving 440 mg of acids (100%). The acids were converted into methyl esters with CH₃N₂ and analyzed by glpc (column B, 70-150°, 2°/min) and by combined glpc-ms techniques (same column) giving the following results in peak number (rel retention time, percentage, molecular ion, compound no.): 1 (1.00, 9.7, 144, **2e**), 2 (1.12, 0.2, 144, **3e**), 3 (1.43, 22.3, 158, **4e**), 4 (1.47, 14.5, 158, **5e**), 5 (1.54, 1.6, 172, unknown), 6 (1.57, 0.8, 158, **6e**), 7 (1.73, 12.7, 172, **7e**), 8 (1.76, 5.3, 172, **8e**), 9 (1.82, 1.6, 186, unknown), 10 (1.86, 2.3, 172, **9e**), 11 (1.99, 2.0, 186, unknown), 12 (2.04, 6.2, 186, **10e**), 13 (2.06, 2.7, 186, **11e**), 14 (2.13, 4.1, 200, unknown), 15 (2.19, 1.7, 186, **12e**), 16 (2.33, 9.0, 200, unknown), 17 (2.38, 3.1, 200, unknown). Each component gave rise to characteristic mass spectral peaks for methyl esters of saturated acids (base peak, *m/e* 74). In each case where identifications have been made, the mass spectra and ir spectra (obtained by trapping) were identical with those of authentic samples. The un-

(21) See ref 6 and 18 in which dimers are thought to be the precursors of monomeric cleavage products.

(22) Reference to brand or firm name does not constitute endorsement by the U. S. Department of Agriculture over others of a similar nature not mentioned.

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(26) This additional layer was observed with **1f** and **1g** but not with the other amides. In one case, this material was isolated by transfer to a separatory funnel and recovery of 20 mg of an extremely complex mixture of saturated and unsaturated hydrocarbons.

known components from reactions of amides other than 1f were the same ones as listed above, with slight variations in percentages. Analysis by glpc was also performed using column C (50–300°, 2°/min) and no additional components were observed.

Hydrolysis of Diamides (Fraction D).—The diamides (380 mg) were hydrolyzed to the corresponding diacids by exactly the same procedure used for hydrolysis of fraction C. This gave diacids (230 mg, 92%) which were esterified with CH_2N_2 and analyzed by glpc (column C, 150–300°; 2°/min) and by combined glpc–mass spectrometry giving the following results in peak number (rel retention time, percentage, number of corresponding diamide in text): 1 (1.00, 0.8, 13), 2 (1.26, 6.1, 14), 3 (1.51, 21.9, 15), 4 (1.61, 6.6, 16), 5 (1.77, 25.2, 16), 6 (1.85, 8.7, 17), 7 (2.00, 12.4, 17), 8 (2.09, 7.4, 18), 9 (2.24, 4.9), 10 (2.32, 3.0), 11 (2.55, 1.2). Typical of the mass spectra obtained in this series and characteris-

tic of diesters is that observed from peak 3: m/e (rel intensity) 241 (10) ($M - 31$), 199 (25); 167 (25), 126 (40), 112 (84), 98 (84), 74 (82), 55 (100). The other peaks simply gave rise to homologous spectra. Branching was firmly established by comparison of retention times to those of authentic straight-chain diesters, for example, dimethyl tridecanedioate, rel retention time 1.66, compared to 1.51 for 15.

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Registry No.—1b, 24928-30-1; 1d, 41328-62-5; 1e, 41328-72-7; 1f, 41328-73-8; 1g, 4219-50-5; HF-BF₃, 16872-11-0.

Conversion of a Saturated to an Unsaturated Acid by Pyridine *N*-Oxide^{1a-c}

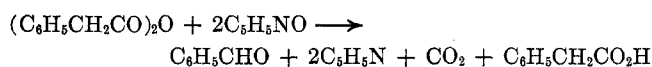
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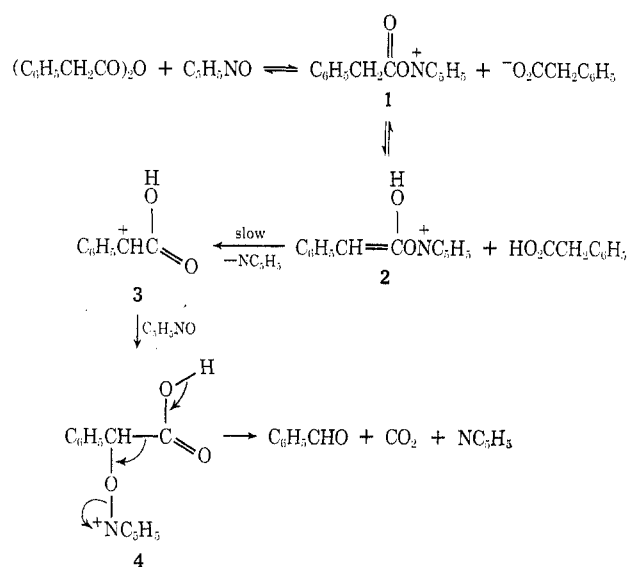
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Oxidation of 2,3-diphenylpropanoic acid by pyridine *N*-oxide in the presence of acetic anhydride yields the normal decarboxylative oxidation product deoxybenzoin (7, 25%) in addition to the *cis* and *trans* isomers of 2,3-diphenylpropenoic acid (8, 20%) and 2-acetoxy-2,3-diphenylpropanoic acid (9, 43%). The production of 8 and 9 is taken as further evidence that a key intermediate bearing a cationic site α to a carboxyl function (in this case 6) is involved in such reactions. The mass spectral fragmentation pattern of methyl 2,3-diphenylpropenoate is discussed in terms of a 1,3-methoxy migration in the parent radical cation.

Certain carboxylic acid anhydrides which possess an acidic α hydrogen atom may be oxidatively decarboxylated by aromatic amine oxides.²⁻⁵ For example, the oxidation of phenylacetic anhydride by pyridine *N*-oxide produces benzaldehyde and proceeds according to the following stoichiometry.



In the presence of acetic anhydride, the corresponding carboxylic acid is readily oxidized in a similar manner.^{2b,5} The first step in the reaction is thought²⁻⁵ to involve reversible acylation of the *N*-oxide to give cation 1. Deuterium isotope effect studies⁶ and the requirement for an α hydrogen atom^{2b,3c,5} suggest the reversible formation of an enol species 2 prior to the rate-determining step in which 2 is attacked in an $\text{S}_{\text{N}}1'$ manner⁷ by a second *N*-oxide molecule to yield the *N*-(α -carboxybenzyloxy)pyridinium ion 4. In the latter step, the reactive electrophilic species 3 would be an



intermediate.⁸ Decarboxylative fragmentation of 4 with loss of pyridine would then lead to the major observed products. The scheme is consistent with the kinetics observed by Koenig.⁴ Some such electrophilic intermediate has been trapped by acetic acid and by pyridine, each utilized as a solvent.⁵ In the present paper, we present additional evidence for a cationic intermediate of type 3 in the oxidation of carboxylic acids by pyridine *N*-oxide.

Although one of the most characteristic reactions of carbocations is the loss of an adjacent proton to yield

(8) The conjugate base of 3, which is the open form of an α -lactone,⁹ appeared as a reasonable intermediate at one time,⁸ but Rüchardt¹⁰ has reported experiments, which have been confirmed by Koenig,¹⁰ indicating that the behavior of a related α -lactone is unaffected by the presence of pyridine *N*-oxide.

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