Anal. Calcd for $C_{11}H_{21}NS$: C, 66.27; H, 10.62; N, 7.03. Found: C, 66.03; H, 10.51; N, 7.11.

Nmr and ir ($\nu_{C=N}$ at 1595 cm^{-1}) spectra supported its structure.

Reaction of *t*-Butyl Isocyanide (4) with Benzenethiol (8).—A mixture of 0.55 g (5 mmol) of **8** and 0.42 g (5 mmol) of **4** was heated in the presence of 1.7 mg (0.01 mmol) of AIBN at 80° for 2 hr. Distillation gave 0.65 g (67%) of phenyl N-*t*-butylthiothioformimidate: bp 99–101° (3 mm), $n^{25}D$ 1.5514.

Anal. Calcd for $C_{11}N_{15}NS$: C, 68.34; H, 7.82. Found: C, 68.22; H, 7.95.

The structure was further confirmed by nmr and ir ($\nu_{C=N}$ at 1597 cm^{-1}) spectra.

Reaction of *t*-Butyl Isocyanide (4) with Ethanethiol (7).—Similarly, the **4**–**7** reaction by AIBN was carried out at 35° for 4 hr, which gave ethyl N-*t*-butylthioformimidate: bp 75–76° (70 mm), $n^{25}D$ 1.4654.

Anal. Calcd for $C_7H_{15}NS$: C, 57.90; H, 10.34. Found: C, 57.60; H, 10.20.

Dependency of the Molar Ratio of 14/13 on the Concentration of 2-Propanethiol (12).—A series of five reactions was carried out, in which the initial concentration of 2-propanethiol was varied. A typical run was as follows. A mixture of 0.43 g (5.6 mmol) of **12** and 1.34 g (12.4 mmol) of **5** (concentration of **12**, 2.8 mol/l.) was heated without radical initiator at 100° for 20 min. The total conversion for **12** was 8% and the molar ratio of **14/13** was determined to be 0.48 by glpc analysis.

Reactions of *t*-Butyl Isocyanide (4) with α-Toluenethiol (9).—The radical reaction of **4** with **9** by AIBN at 80° gave 93% *t*-butyl isothiocyanate and 96% toluene.

To a mixture of 1.24 g (10 mmol) of **9** and 1.00 g (12 mmol) of **4** was added 8.0 mg (0.1 mmol) of cupric oxide as a catalyst. The reaction system soon became homogeneous at room temperature. When the reaction mixture was heated at 100° for 2.0 hr, 91% of **9** disappeared. Benzyl N-*t*-butylthioformimidate was isolated by preparative glpc, $n^{25}D$ 1.5435.

Anal. Calcd for $C_{12}H_{17}NS$: C, 69.51; H, 8.26; N, 6.76. Found: C, 69.78; H, 8.37; N, 6.52.

Reaction of Cyclohexyl Isocyanide (5) with 2-Methyl-2-propanethiol (11) in the Presence of Cupric Oxide and *p*-Benzoquinone.—A mixture of 0.63 g (7 mmol) of **11**, 0.54 g (5 mmol) of **5**, 8 mg (0.1 mmol) of cupric oxide, and 55 mg (0.5 mmol) of *p*-benzoquinone was refluxed at 90° for 3 hr. By glpc analysis of the reaction mixture, *t*-butyl N-cyclohexylthioformimidate[3] (64%) and **13** (6%) were formed.

Registry No.—*sec*-Butyl N-cyclohexylthioformimidate, 24058-23-9; phenyl N-*t*-butylthioformimidate, 24058-24-0; ethyl-N-*t*-butylthioformimidate, 24058-25-1; benzyl N-*t*-butylthioformimidate, 24058-26-2; **4**, 630-18-2; **5**, 931-53-3; **6**, 100-47-0; **7**, 75-08-1; **8**, 108-98-5; **9**, 100-53-8; **10**, 513-53-1; **11**, 75-66-1.

Peroxide–Metal Ion Oxidations. II. A Convenient Synthesis of Imides

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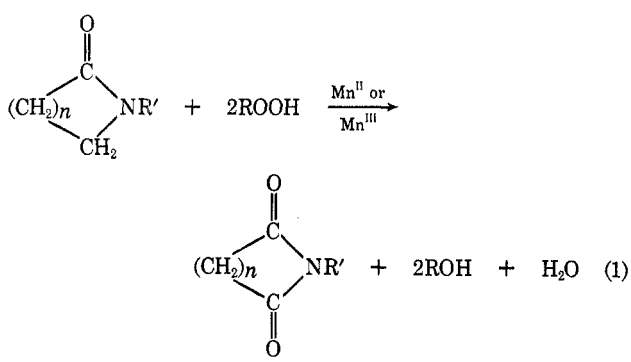
A novel and highly selective oxidation of lactams and N-alkylamides to the corresponding imides has been developed. The oxidant consists of a hydroperoxide or a peroxy acid in combination with a catalytic amount of a manganese(II) or -(III) salt. The extremely mild reaction represents the first convenient method for synthesizing many imides, including adipimide, a polymer intermediate which had previously been preparable only in low yields. The synthetic scope of the oxidation and its limitations are discussed.

A convenient synthesis of imides has been developed, using a novel and particularly mild oxidation procedure.[1] Lactams or N-alkylamides treated with a hydroperoxide or a peroxy acid in the presence of a metal ion catalyst such as manganese(II) produced the corresponding imides in excellent yield. The oxidation has proved to be quite general, proceeding under mild conditions to provide imides, many of which have previously been preparable only in poor yields. The general reaction and apparent stoichiometry are indicated below.



Metal ion interactions with hydroperoxides and peroxy acids are well known[2,3] and have been used to synthetic advantage in the past. Kharasch, Kochi, and their respective groups prepared 2-alken-1-yl esters and unsymmetrical peroxides by copper(I)-catalyzed treatment of olefins with peroxy esters and hydroperoxides, respectively.[4] More recently, primary amines have been converted to oximes,[5] tertiary amines to amine oxides,[6] and sulfides to sulfoxides and sulfones[7] by peroxide–metal ion oxidants. These latter reactions are characterized by oxidative transformations at the heteroatom.

The oxidation of amides to imides, a two-electron transformation at the position adjacent to the heteroatom, has been accomplished in low yield by autoxidation[8] and by treatment with ruthenium tetroxide[9] and persulfates.[10] The procedure which we describe offers several advantages, the most significant being ease of operation, high selectivity, and generally satisfactory

(1) For a preliminary report on the oxidation system, see A. R. Doumaux, Jr., J. E. McKeon, and D. J. Trecker, *J. Amer. Chem. Soc.*, **91**, 3992 (1969).

(2) A. G. Davies, "Organic Peroxides," Butterworth and Co. (Publishers) Ltd., London, 1961, Chapters 12 and 13.

(3) E. G. E. Hawkins, "Organic Peroxides, Their Formation and Reactions," D. Van Nostrand Co., Inc., Princeton, N. J., 1961, Chapters 1, 3, and 7.

(4) M. S. Kharasch and A. Fono, *J. Org. Chem.*, **24**, 606 (1959), and references therein. J. K. Kochi, *J. Amer. Chem. Soc.*, **83**, 3162 (1961); **84**, 774, 2121, 3271 (1962).

(5) L. Jarkovsky and J. Pasek, *Chem. Prum.*, **16**, 591 (1966); Belgium Patent 668,811 (1966).

(6) U. S. Patent 3,274,252 (1966); L. Kuhnen, *Chem. Ber.*, **99**, 3384 (1966); M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **33**, 588 (1968).

(7) L. Kuhnen, *Angew. Chem. Int. Ed. Engl.*, **5**, 893 (1966).

(8) A. Rieche and W. Schön, *Chem. Ber.*, **99**, 3238 (1966); M. V. Lock and B. F. Sagar, *J. Chem. Soc., B*, 690 (1966); B. F. Sagar, *ibid.*, 428, 1047 (1967).

(9) British Patent 900,107 (1962).

(10) H. L. Needles and R. E. Whitfield, *J. Org. Chem.*, **31**, 341 (1966).

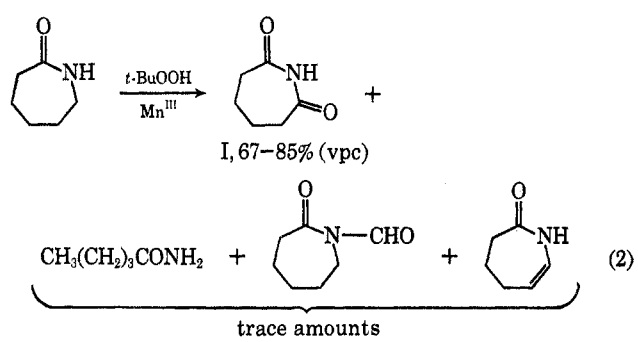
TABLE I

t-BUTYL HYDROPEROXIDE OXIDATION OF ε-CAPROLACTAM

Catalyst	t-BuOOH/ lactam mole ratio	t-BuOOH/ metal mole ratio	Reaction time, hr	% conversion of Lactam	% conversion of t-BuOOH	% yield of imide based on Lactam	% yield of imide based on t-BuOOH
Cobalt(II) naphthenate	1.03	182	64	21.8	50.8	23.7	10.9
Cobalt(II) naphthenate	1.13	200	136	21.2	100.0	44.6	16.7
$Mn(acac)_2$	1.13	200	136	38.7	56.1	44.5	54.2
$Mn(acac)_3$	1.13	200	136	28.6	54.6	78.0	72.1
$Mn(acac)_3$	1.03	182	64	20.6	28.1	80.5	89.0
$Mn(acac)_3$	1.13	357	144	23.9	31.0	76.8	52.2
$Mn(acac)_3$	2.03	355	96	18.5	67.8	84.5	48.9

yields. A typical procedure consists of simply mixing the lactam and a twofold molar excess of hydroperoxide, adding a trace of manganese(III) acetylacetonate, and stirring at room temperature for several days. When a peroxy acid is used as the oxidant, it is added dropwise to a stirred solution of lactam and the metal ion catalyst in ethyl acetate at 0–10°.

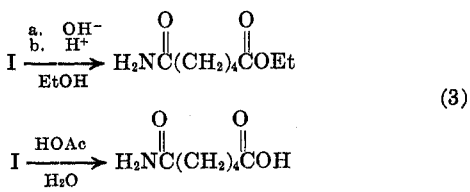
Oxidation of ε-Caprolactam.—*t*-Butyl hydroperoxide–manganese(III) treatment of ε-caprolactam provided a useful synthesis of adipimide (I). Adipimide has been prepared previously in low yields by other routes[11] and is a compound of interest as a polymer intermediate.[12] Several coproducts formed in lesser amounts were also identified (eq 2). Table I records the conversions and



(2)

yields achieved under a variety of reaction conditions. Most of the transition metal ions studied provided some reactivity, but manganese(II) or (III) was clearly the catalyst of choice.

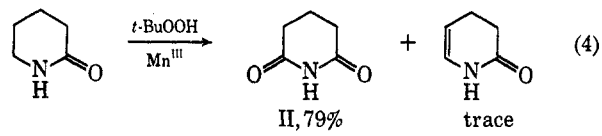
Much shorter reaction times were possible when peracetic acid was used as the oxidant. With manganous dichloride as the catalyst, 33–38% isolated yields of adipimide were obtained after 32 hr at 0°. Vpc analyses indicated yields approaching 60%, but isolation difficulties amplified by the reactivity of I resulted in diminished actual yields. Adipimide was found to be extremely susceptible to ring opening from nucleophilic reagents, forming adipamic acid derivatives with ease (see Experimental Section). This was found to be especially true in the presence of acetic acid (formed



(3)

when peracetic acid was used as the oxidant), adipamic acid being formed in high yield (eq 3).

2-Piperidone and Derivatives.—Both hydroperoxides and peroxy acids reacted smoothly with 2-piperidone, giving rise to glutarimide (II) with high selectivity.



(4)

Isolated yields of 54–72% were routinely achieved from peracetic acid treatment. The effectiveness of various metal ion catalysts is recorded in Table II.

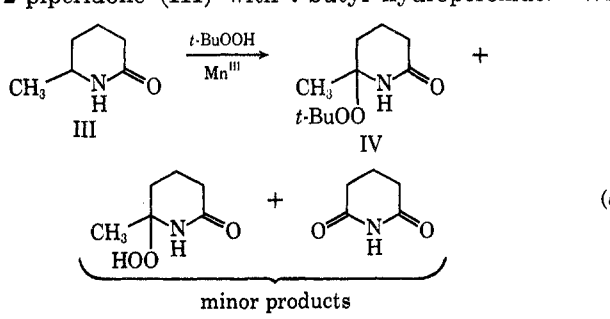
TABLE II

EFFECT OF METAL ION CATALYSTS[a] ON THE PERACETIC ACID OXIDATION OF 2-PIPERIDONE[b]

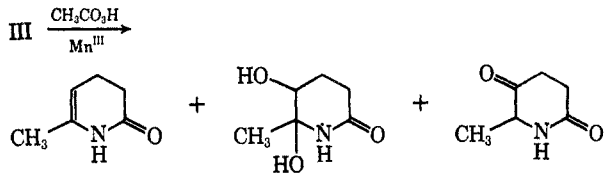
Metal salt[c]	% conversion into II based on 2-piperidone
None	5.0
$Mn(acac)_3$	72.0
$Mn(OAc)_2$	59.8
$MnCl_2$	78.3
$Fe(acac)_3$	23.1
$Co(acac)_3$	35.2
$CoCl_2$	26.3
$Co(acac)_2$	53.1

[a] $VO(acac)_2$, $Cr(acac)_3$, $Cu(O_2CC_6H_5)_2$, $Zn(acac)_2$, $Zr(acac)_4$, $Mo(CO)_6$, $RuCl_3$, $RhCl_3$, $PdCl_2$, $(NH_4)_2WO_4$, NH_4ReO_4, $OsCl_3$, $IrCl_3$, $IrCl_4$, H_2PtCl_6, $HgCl_2$ $Tl(OAc)_3$, $Pb(OAc)_2$, and $Ce(acac)_3$. $Ni(acac)_2$ caused an explosion. The concentration of peracetic acid was too high. All reactions using peracetic acid should be tested for peroxide concentration during the reaction. [b] 0.1 *M* 2-piperidone; 0.2 *M* in peracetic acid; reaction in ethyl acetate at room temperature. [c] 10^{-3} *M* in metal salt.

Of considerable interest was the reaction of 6-methyl-2-piperidone (III) with *t*-butyl hydroperoxide. With



(5)

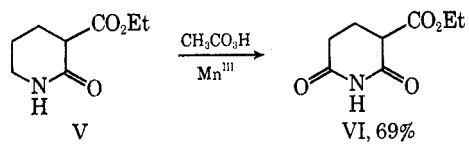


(11) E. N. Zil'berman, *Zh. Obshch. Khim.*, **25**, 2127 (1955); **30**, 596(1960). H. K. Hall, Jr., and A. K. Schneider, *J. Amer. Chem. Soc.*, **80**, 6409 (1958). N. Tokura, R. Tada, and K. Yokoyama, *Bull. Chem. Soc. Jap.*, **34**, 1812 (1961).

(12) U. S. Patent 3,033,831 (1962); Netherlands Patent 6,516,904 (1966); O. Wichterle, J. Stehlíček, T. Kodaira, and J. Šebenda, *Polym. Lett.*, **5**, 931 (1967).

only one available carbon–hydrogen bond at the reactive site, oxidation proceeded to give the stable 6-*t*-butylperoxy derivative (IV) as the major product. A considerably more complex reaction occurred with peracetic acid, giving rise to numerous products of secondary oxidation, including 6-methyl-3,4-dihydro-2-pyridone and 6-methyl-5,6-dihydroxy-2-piperidone.

The remarkable selectivity of the peroxide–manganese ion system was illustrated convincingly with 3-carbethoxy-2-piperidone (V), a compound with three distinct reactive sites. As before, oxidation proceeded solely at the nitrogen-adjacent methylene group to give VI as the only isolable product.



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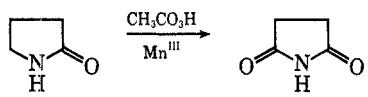
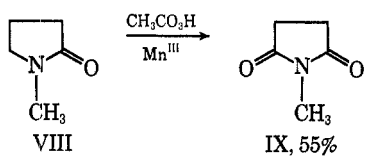
2-Pyrrolidone and Derivatives.—Near-quantitative yields based on consumed 2-pyrrolidone, were achieved for the *t*-butyl hydroperoxide preparation of succinimide (VII). However, a very sluggish reaction rate—92 hr was required to convert 11% of the lactam—made peroxy acid treatment the preferred synthetic route. Reaction with peracetic acid–manganese(III) provided a 64% isolable yield of VII in a 16-hr reaction period. Replacement of the amide hydrogen with a methyl group (VIII) did not impede the oxidation, with attack



(7)



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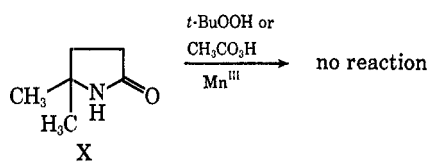
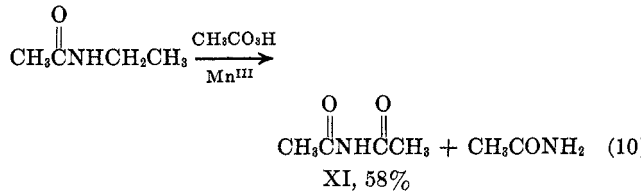


(9)

still occurring at the methylene group adjacent to the amide nitrogen (eq 8). A control experiment showed that succinimide was inert to further oxidation under normal reaction conditions. Starting material was recovered quantitatively.

Monomethyl substitution at the 5 position provided the 5-*t*-butylperoxy product from treatment with *t*-butyl hydroperoxide. Here, however, unlike IV, the unsymmetrical peroxide was unstable and product isolation in pure form was not possible. 5,5-Dimethyl substitution (X) rendered the lactam completely inert to both hydroperoxide and peroxyacid oxidation. The next lower lactam homolog, β-propiolactam, examined as its N-phenyl derivative, was also unreactive to oxidation with peracetic acid.

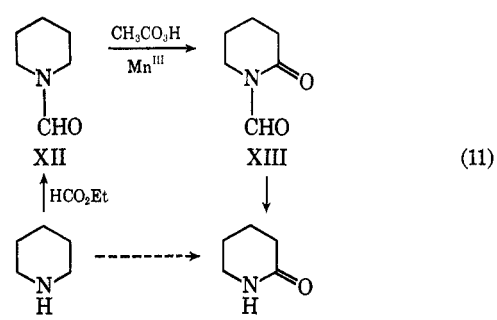
Oxidation of N-Alkylamides.—Linear N-alkylamides possessing a methylene adjacent to the amide nitrogen responded readily to peracetic acid–manganese(III) oxidation but reacted sluggishly when treated with hydroperoxide and manganese; competing reactions



(10)

occurred instead. Peracetic acid oxidized N-ethylacetamide to diacetamide (XI) and a small amount of acetamide. Similar reaction with *t*-butyl hydroperoxide gave rise to a host of products.

Ring-containing amides and compounds disubstituted at the nitrogen-adjacent position were found to be generally inert. Thus, N-acetylpiperidine, N-acetylpyrrolidine, N-cyclohexylbenzamide, and N-cyclohexylacetamide were recovered unreacted from normal oxidation treatment. An exception was N-formylpiperidine (XII), which was converted into N-formyl-2-piperidone (XIII). The ease of reversible N-formyl-



(11)

ation in such systems suggests that this route may be useful for converting cyclic amines into lactams.

Discussion

Regarding mechanism, several pathways are consonant with the observed results. A detailed study of the oxidation mechanism is underway, and the results will be presented in a subsequent publication. However, several observations bear mention at this time. First, the high degree of selectivity at the nitrogen-adjacent site makes it clear that the oxidation may not involve strictly free radicals[13a]—this in spite of the fact that conventional transition metal ion (*e.g.*, Co^{II}, Mn^{II}) interactions with hydroperoxides and peroxyacids are known to produce such species.[2,3] This apparent inconsistency may be resolved if one postulates the formation of a metal ion–carbonyl or –nitrogen complex which precedes oxidation and establishes a template that controls the direction of subsequent attack. Amide–transition metal complexes have been well documented.[13b] Bonding between the amide and the metal ion appears to occur through the carbonyl oxygen.[13b] Finally, the isolation of IV from the hydroperoxide treatment of III suggests that such

(13) (a) Radical abstraction has been observed at *both* the nitrogen-adjacent and the carbonyl-adjacent methylenes of lactams: G. I. Nikishin and R. I. Mustafaev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1832 (1964); D. Elad and J. Sinnreich, *Chem. Ind.* (London), 768 (1965). (b) W. E. Bull, S. K. Madan, and J. E. Willis, *Inorg. Chem.*, **2**, 303 (1963); S. K. Madan and H. H. Denk, *J. Inorg. Nucl. Chem.*, **29**, 1669 (1967); R. J. Niedzielski and G. Znider, *Can. J. Chem.*, **43**, 2618 (1965); Y. Saito, H. Iwasaki, Y. Wawata, and A. Masuko, *Chem. Abstr.*, **67**, 371143 (1967).

peroxides (and perhaps the corresponding peroxy esters) are intermediates, albeit unstable ones, in the oxidation sequence of the corresponding unsubstituted lactams.

Experimental Section

General Procedure. Hydroperoxide Oxidation.—The lactam was dissolved in up to a twofold molar excess of *t*-butyl hydroperoxide (Matheson Coleman and Bell, 69–70% assay in *t*-butyl alcohol) and then treated with a manganese salt (usually 0.5–1.0% of the lactam). The resulting solution was stirred magnetically at room temperature for 3–6 days. At the end of that time the unreacted hydroperoxide was determined by conventional iodide/thiosulfate analysis.[14]

General Procedure. Peroxy Acid Oxidation.—The lactam and manganese salt (0.5–1.0% of the lactam) were dissolved in ethyl acetate (with added acetic acid if necessary to obtain homogeneity) and placed in a reaction flask equipped with dropping funnel, condenser, thermometer, magnetic stirrer, and external brine-cooled jacket. A twofold molar excess of peracetic acid (Union Carbide Corp., 25% assay in ethyl acetate) was then added at a rate sufficient to maintain a reaction temperature of 0–10°. After addition was complete, stirring was continued, generally overnight, or until an iodide test for peracid was negative.[14]

Oxidation of ε-Caprolactam.—In a typical hydroperoxide oxidation, ε-caprolactam (213 g, 1.89 mol), manganic acetylacetonate (3.8 g, 1.1×10^{-2} mol), and 69.1% by weight *t*-butyl hydroperoxide (500 g, containing 3.84 mol of hydroperoxide) were stirred together at room temperature for 96 hr. Analysis of caprolactam and adipimide (I) was carried out by vpc, employing a 10-ft 5% Carbowax 20M on Chromosorb G column at 170° and dibutyl adipate as an internal standard. Work-up consisted of filtration to remove a dark precipitate, presumably spent catalyst, and then *in vacuo* distillation. After removal of the unreacted hydroperoxide and *t*-butyl alcohol, several large fractions were taken (bp 85–90° at 0.025 mm) which contained caprolactam, I, and five minor coproducts. Separation of I was accomplished by continuously extracting the distillate in a Soxhlet extractor with refluxing 35–37° boiling petroleum ether. Essentially pure I was recovered from the thimble after extracting a 124-g sample for 113 hr. The material melted at 100–101° and was spectroscopically (ir, nmr) identical with an authentic sample.[11]

In a typical peroxy acid oxidation, ε-caprolactam (282.5 g, 2.5 mol) and manganese chloride (*ca.* 10^{-5} mol in 10 ml of ethyl acetate) in ethyl acetate (200 ml) were treated dropwise with peracetic acid (1500 g of 25%, 4.9 mol), with the temperature being maintained at 0–10°. After stirring overnight, the reaction mixture was filtered and the filtrate was evaporated *in vacuo* to a red oil. Trituration with isopropyl alcohol and subsequent cooling gave I as a white crystalline solid (120 g, 0.94 mol, 37.6% yield).

Several minor coproducts obtained from a forerun distillation fraction (bp 65–68° at 0.1 mm) of a large-scale synthesis run (H_2O_2) were isolated by preparative-scale vpc (12 ft × 1/4 in. Al, 5% Carbowax 20M on Chromosorb G, DMCS-treated and acid washed, 175°). Valeramide was identified by comparison of melting point and spectra (ir, nmr) with those of an authentic sample. N-Formyl-ε-caprolactam was similarly compared with an independently synthesized sample.[15] Also identified was 1-[H]-7-oxo-4,5-dihydroazepine: ir (neat) 3125 (NH) and 1665 cm^{-1} (C=O); uv (MeOH) λ_{max} 236 mμ (ϵ_{max} 6240); nmr ($CDCl_3$) δ 1.91 (m, 2, ring CH_2), 2.21 (m, 2, $-C=CHCH_2-$), 2.57 (m, 2, $-CH_2CO-$), 4.98 (m, 1, $-C=CHCH_2-$), 5.76 (m, 1, $-NHCH=CH$), and 8.15 (s, 1, NH).

Anal. Calcd for C_6H_9ON: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.03; H, 8.49; N, 12.32.

Ring Opening of Adipimide.—Adipimide (1.0 g) was stirred into a solution of sodium hydroxide (2.0 g) in absolute ethanol (50 ml). The precipitate formed (10–15 min) was collected by filtration and washed with *n*-heptane: ir (KBr) 3230 (NH_2), 1645 (CO), 1572 and 1422 cm^{-1} (CO_2^-). Esterification was accomplished by treatment with gaseous HCl in absolute alcohol. After removal of the precipitated NaCl by filtration, the solution was evaporated to dryness. The crystals which remained were washed with acetone, and the acetone wash was evaporated to dryness. Thus obtained, the product was washed with *n*-hexane and collected by filtration: mp 74°; nmr (CD_3COCD_3) δ 1.22 (t, 3, CH_3CH_2), 1.63 (m, 4, $-CH_2-$), 2.27 (m, 4, CH_2CO), 4.14 (q, 2, CH_2CH_3), 6.2 (s, 2, NH_2); ir (KBr) 3260 (NH), 1720 (ester CO), 1668 (amide CO), 1638 cm^{-1}.

Anal. Calcd for $C_8H_{15}O_3N$: C, 55.47; H, 8.73; N, 8.09. Found: C, 55.28; H, 8.56; N, 8.01.

Oxidation of 2-Piperidone.—A solution of 2-piperidone (95 g, 0.96 mol), manganic acetylacetonate (1.0 g), and 68.8% *t*-butyl hydroperoxide (200 g, containing 1.53 mol of hydroperoxide) was stirred for 96 hr. Analysis by vpc (12 ft × 1/4 in. Al, 5% Carbowax 20M on Chromosorb G, 175°), employing dibutyl adipate as an internal standard, showed unreacted valerolactam (0.582 mol, 39.4% conversion), II (0.299 mol, 79.2% based on consumed lactam), and a small amount of 3,4-dihydro-2-pyridone. Fractional distillation provided II (bp 72.5–73 at 0.1 mm), which after several washings with 35–37° boiling petroleum ether, melted at 145–146°[16] and was spectroscopically (ir, nmr) identical with an authentic sample. 3,4-Dihydro-2-pyridone was isolated by careful redistillation of early fractions: bp 72.5–73° at 0.1 mm; mp 27°; ir 3215 (NH), 1682 (amide C=O), 1635 cm^{-1} (C=C); nmr ($CDCl_3$) δ 2.42 (m, 4, ring $-CH_2-$), 5.11 (m, 1, $-C=CHCH_2$), 6.17 (q, 1, J = 7.5 Hz, J' = 5 Hz, $HNCH=C$), 8.83 (s, 1, NH).

Anal. Calcd for C_5H_7ON: C, 61.83; H, 7.26; N, 14.43; parent mass, 97. Found: C, 61.55; H, 7.49; N, 14.50; parent mass, 97.

By the general procedure described above, peracetic acid (64 g, 25%, 0.2 mol) treatment of 2-piperidone (9.9 g, 0.1 mol) and manganic acetylacetonate in ethyl acetate (50 ml) provided II (in 72% yield), recovered by solvent evaporation and recrystallization from ethanol.

Oxidation of 6-Methyl-2-piperidone with *t*-Butyl Hydroperoxide.—A solution of 6-methyl-2-piperidone (28.25 g, 0.25 mol), *t*-butyl hydroperoxide (74.25 g, 0.50 mol), and manganic acetylacetonate (0.5 g, 1.4×10^{-3} mol) was stirred at room temperature for 144 hr. The reaction mixture was then filtered, and the filtrate was evaporated *in vacuo* to give a pale yellow solid. Three recrystallizations from isopropyl alcohol–hexane provided material (9.0 g) which melted at 118.6–121.6°: nmr ($CDCl_3$) δ 1.20 (s, 9, CH_3C), 1.48 (s, 3, CH_3C), 1.78 (m, 4, $-CH_2-$), 2.30 (m, 2, CH_2CO), 6.65 (s, 1, NH); ir (KBr) 3450, 3200, 2980, 1650 (C=O), 1465, 1450, 1410, 1280, 1217, 1194, 1135, 1107, 966, 923, 891, 876 (OO), 833 cm^{-1}. The structure was thus identified as 6-methyl-6-*t*-butylperoxy-2-piperidone (IV).

Anal. Calcd for $C_{10}H_{19}O_3N$: C, 59.67; H, 9.52; N, 6.96. Found: C, 59.65; H, 9.54; N, 7.00.

The insoluble brown residue from which the original reaction material was filtered was slurried with chloroform, filtered, and then dissolved in boiling isopropyl alcohol and refiltered while hot. Cooling afforded a white crystalline solid (1.1 g) which, when recrystallized from isopropyl alcohol, melted (dec) at 142.7°: ir (KBr) 3450 (OH), 3200 (NH), 1650 cm^{-1} (NHCO); nmr (pyridine-d_5) δ 1.66 (s, 3, CH_3C), 2.0–1.3 (m, 4, CH_2), 2.35 (m, 2, CH_2CO). The structure was thus identified as 6-methyl-6-hydroperoxy-2-piperidone.

Anal. Calcd for $C_6H_{11}O_3N$: C, 49.64; H, 7.64; N, 9.65. Found: C, 49.87; H, 7.83; N, 9.41.

Oxidation of 6-Methyl-2-piperidone with Peracetic Acid.—Peracetic acid (64.0 g, 25%, 0.2 mol) was added dropwise to a solution of 6-methyl-2-piperidone (11.3 g, 0.1 mol), manganic acetylacetonate (50 mg), ethyl acetate (50 ml), and acetic acid (50 ml). After stirring for 3 days (−10°) the solution was filtered giving a white crystalline product, 6-methyl-5,6-dihydroxy-2-piperidone: mp 131–133° (recrystallization from acetonitrile raised the melting point to 138.5–142°); nmr (D_2O) δ 1.80 (s, 3, CH_3-), 2.23 (m, 2, CH_2), 2.70 (m, 2, CH_2CO), 4.1 (m, 1, CHO) (the multiplets at 4.1 and 2.33 were coupled as shown by a spin-decoupling experiment); ir (KBr) 3200 (broad, NH, OH), 1660, 1645 (amide C=O), 1087 cm^{-1} (CO).

Anal. Calcd for $C_6H_{11}O_3N$: C, 49.64; H, 7.64; N, 9.65. Found: C, 49.80; H, 7.74; N, 9.94.

The filtrate was evaporated under reduced pressure to a red oil, then distilled *in vacuo* into two fractions. Fraction 1, bp 125–130° at 2 mm, was identified as a mixture of 6-methyl-4,5-

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dihydro-2-pyridone and glutarimide. Purification of 6-methyl-4,5-dihydro-2-pyridone was accomplished by preparative vpc (1/4 in. × 12 ft Al, 5% Versamide on Chromosorb G, DMCS treated, acid washed, 175°, 120 cc/mm He, retention time 11.2 min): mp 113–115°; nmr ($CDCl_3$) δ 1.81 (s, 3, CH_3C=), 2.34 (m, 4, $-CH_2-$), 4.78 (m, 1, -CH=C-), 8.5 (broad singlet, 1, NH); ir (KBr) 3150 (NH), 1670 (amide CO), 1239, 1179, 918, 813, 762, 663 cm^{-1}.

Anal. Calcd for C_6H_9ON: C, 64.84; H, 8.16; N, 12.60. Found: C, 64.80; H, 8.46; N, 12.80.

Fraction 2, bp 130–160° at 2 mm, was recrystallized from isopropyl alcohol–*n*-hexane: mp 143–145°; nmr ($CDCl_3$) δ 1.40 (d, 3, CH_3CH), 2.67 (s, 4, CH_2CO), 3.98 (q, 1, $CHCH_3$), 7.76 (broad singlet, 1, NH); ir (KBr) 3200 (NH), 1725 (C=O), 1670 cm^{-1} (amide C=O).

Anal. Calcd for $C_6H_9O_2N$: C, 56.68; H, 7.14; N, 11.02. Found: C, 56.79; H, 6.97; N, 10.79.

This compound was identified as 6-methyl-5-oxo-2-piperidone.

Oxidation of 3-Carbethoxy-2-piperidone.—Peracetic acid (32 g, 25%, 0.1 mol), 3-carbethoxy-2-piperidone (8.55 g, 0.05 mol), and manganic acetylacetonate (50 mg) were allowed to react in the usual manner. Evaporation under vacuum afforded VI as a white solid (6.4 g, 69% yield) which, after two recrystallizations from ethanol, had mp 74–76°; ir (KBr) 3100 (hydrogen bonded NH), 1745 (ester C=O), 1708 (sh), 1690 cm^{-1} (imide C=O); nmr ($CDCl_3$), δ 1.29 (t, 3, CH_3CH_2-), 2.24 (m, 2, $-CH_2-$CH–), 2.66 (m, 2, CH_2CO), 3.6 (t, 1, $-CHCH_2$), 4.27 (q, 2, CH_2CH_3).

Anal. Calcd for $C_8H_{11}O_4N$: C, 51.88; H, 5.99; N, 7.56. Found: C, 51.60; H, 5.81; N, 7.32.

Oxidation of 2-Pyrrolidone.—Peracetic acid (64 g, 25%, 0.2 mol) treatment of 2-pyrrolidone (8.5 g, 0.1 mol) and manganic acetylacetonate (50 mg) in ethyl acetate (50 ml) was carried out in the usual manner. Filtration and evaporation provided succinimide (5.7 g, 63.7% yield) as a white crystalline material whose melting point (124°, ethanol recrystallization) and infrared spectrum were identical with those of an authentic sample.

Oxidation of N-Methyl-2-pyrrolidone.—Peracetic acid (64 g, 25%, 0.2 mol), N-methyl-2-pyrrolidone (9.9 g, 0.1 mol), and manganic acetylacetonate (50 mg) in ethyl acetate (50 ml) were allowed to react in the usual manner. Work-up afforded N-methylsuccinimide (6.25 g, 55.3% yield), mp 64°.[17] The structure was verified by infrared comparison with an authentic sample.

Oxidation of N-Ethylacetamide.—A solution of N-ethylacetamide (8.7 g, 0.1 mol) and manganic acetylacetonate (50 mg) in ethyl acetate (50 ml) was treated with peracetic acid (64 g, 25%, 0.2 mol) in the usual manner. Filtration and evaporation provided an oil which, upon distillation, yielded a small amount of acetamide and diacetamide: 5.9 g (58.4%); bp 80–90° at 1.4 mm; mp 75.5–77°;[18] nmr ($CDCl_3$) δ 2.32 (s, 6, CH_3C), 9.73 (s, 1, NH). Spectral (ir, nmr) comparisons with an authentic sample verified the structure as that of diacetamide. A mixture melting point was undepressed.

Oxidation of N-Formylpiperidine.—N-Formylpiperidine (11.3 g, 0.1 mol) and manganous chloride (5×10^{-3} mol) in ethyl acetate (50 ml) were treated with-peracetic acid (120, 25%, 0.4 mol) in the usual manner. Fractional distillation gave a mixture of starting material and N-formyl-2-piperidone (bp 80–82° at 3 mm). Preparative-scale vpc (6 ft × 1/4 in. Al, 20% Tergitol N-P44 on Chromosorb W, 170°) provided pure N-formyl-2-piperidone: nmr ($CDCl_3$) δ 1.87 (m, 4, CH_2), 2.56 (m, 2, CH_2C=O), 3.60 (m, 2, $-CH_2N$), 10.43 (s, 1, CHO); ir (neat) 1720 (CHO), 1690 cm^{-1} ($-NHCO-$).

Anal. Calcd for $C_6H_9O_2N$: C, 56.68; H, 7.14. Found: C, 56.28; H, 7.28.

Registry No.—1-[H]-7-Oxo-4,5-dihydroazepine, 2228-76-4; adipamic acid ethyl ester, 1190-69-8; 3,4-dihydro-2-pyridone, 24058-44-4; 6-methyl-6-hydroperoxy-2-piperidone, 24058-46-6; 6-methyl-5,6-dihydro-2-piperidone, 24058-47-7; 6-methyl-4,5-dihydro-2-pyridone, 24058-29-5; 6-methyl-5-oxo-2-piperidone, 24058-30-8; N-formyl-2-piperidone, 24058-32-0; $Mn(acac)_2$, 14024-58-9; $Mn(acac)_3$, 14284-89-0; IV, 24058-45-5; VI, 24058-31-9.

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Fluoro Olefins. III. The Synthesis of β-Substituted 1-Chloroperfluoro Olefins[1]

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The reaction of polyfluorinated ketones with chlorofluoromethylenetriphenylphosphorane, $(C_6H_5)_3P$=CFCl, generated *in situ* from sodium dichlorofluoroacetate and triphenylphosphine, provides a general, one-step route to β-substituted 1-chloroperfluoro olefins. The β substituent can either be an aryl or alkyl group. The reaction of this ylide with several typical aldehydes and ketones was also briefly studied. The proposed mechanism for the formation of the chlorofluoromethylene ylide involves the decomposition of an intermediate phosphobetaine salt. An alternate route to the chlorofluoromethylene ylide, *via* reaction of dichlorofluoromethane with potassium *t*-butoxide and triphenylphosphine, is also presented.

Earlier reported preparations of 1-chlorofluoro olefins generally required several steps, involving Grignard reagents and zinc dehalogenations.[3–7] Reaction of the chlorofluoromethylene ylide with a carbonyl moiety offers a simple, one-step route to these olefins. Particularly, reaction with polyfluorinated ketones offers a facile synthesis of β-substituted 1-chloroperfluoro olefins.

At present, two reports other than our own[1c] have appeared in the literature which describe the chlorofluoromethylene ylide route to 1-chlorofluoro olefins. Speziale and Ratts[8] prepared 1,1-diphenyl-2-fluoroethylene *via* the following sequence.[9] The chlorofluoromethylene ylide was generated from dichlorofluoromethane, potassium *t*-butoxide, and triphenyl-

$$(C_6H_5)_3P{=}CFCl + (C_6H_5)_2C{=}O \longrightarrow (C_6H_5)_2C{=}CFCl + (C_6H_5)_3PO$$

(1) (a) Presented in part: Abstracts, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967, p 2k. (b) Taken in part from the Doctoral Dissertation of H. C. Krutzsch, The University of Iowa, Aug 1968. (c) Preliminary report: *Tetrahedron Lett.*, 71 (1968). (d) Part II: *J. Org. Chem.*, **33**, 1854 (1968).
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(6) E. D. Bergmann, *et al.*, *J. Amer. Chem. Soc.*, **79**, 4174 (1957).
(7) T. Ando, *et al.*, *Bull. Chem. Soc. Jap.*, **40**, 1275 (1967).
(8) A. J. Speziale and K. W. Ratts, *J. Amer. Chem. Soc.*, **84**, 854 (1962).
(9) We have been unable to substantiate this earlier report. In our experiments, benzophenone did not react with the fluorochloro ylide. Professor Ando[10] has also informed us that his group was also unsuccessful in duplicating this report.
(10) Professor T. Ando, private communication. We are indebted to Professor Ando for communicating some of his unpublished data to us.