yellow precipitate was separated. The precipitate was filtered, washed with water, and dried in vacuo to yield crude product (1.9 g). The product was purified by preparative TLC to obtain 1.6 g of 6 (yield 80%).

Rate of Addition Reaction of Ethanol to the Compound 2. The reaction was started when ethanolic potassium hydroxide was added to a benzene solution of 2 and the absorbance at 615 nm at 21 °C was followed. Because of the presence of excess ethanol, a pseudo-first-order rate constant (k_{obsd}) was calculated by the equation $k_{obsd} = (2.303/t)(\log A_0/A)$, where A is absorbance at time t, and A_0 is that of time $t = 0$. Plots of $\log A_0 - \log A$ vs. time t gave good straight lines.

Acknowledgment. The authors are grateful to professor Toshio Goto, Nagoya University, for the gift of 2-ethoxy-2*H*- and 4-ethoxy-4*H*-2,4,5-triphenylimidazole. The authors wish to thank Dr. Toshiyuki Nakajima, National Institute of Radioactive Science, for ESR measurements and Mrs. Kyoko Ushiki, Gunma University, for her assistant in some of the UV spectra measurements.

Supplementary Material Available. NMR spectra of compounds 5 and 7 (6 pages). Ordering information is given on any current masthead page.

Registry No.—1, 4051-59-6; 2, 6117-27-7; 4, 49629-44-9; 5, 68827-60-1; 6, 68827-62-3; 7a, 68827-61-2; ethanol, 64-17-5.

References and Notes

(1) U. Mayer, H. Baumgärtel, and H. Zimmermann, *Angew. Chem.*, **78**, 303 (1966).
(2) Y. Sakaino, K. Maeda, and T. Hayashi, *Nippon Kagaku Kaishi*, 100 (1972).
(3) Y. Sakaino, H. Kakisawa, K. Arita, K. Kouno, and H. Morishima, *Tetrahedron*, **29**, 1185 (1973).
(4) The addition reaction in a neutral benzene–ethanol (1:1) solution required several days to obtain a minor amount of 5 while the reaction proceeded rapidly in the presence of a catalytic amount of a base. The rate became more rapid the higher the concentration of potassium hydroxide. KOH: 5×10^{-4} mol/L, $k = 4 \times 10^{-3}$ L/(mol s); 7×10^{-4} mol/L, $k = 12.1 \times 10^{-3}$ L/(mol s) (k is rate constant at 21 °C). The solvent deuterium isotope effect on the rate constant (k^{EtOH}/k^{EtOD}) for the base-catalyzed addition of ethanol to 2 was found to be about 7.3.
(5) Y. Sakaino, H. Kakisawa, and T. Kusumi, *Heterocycles*, **12**, 953 (1975).
(6) H. Tanino, T. Kondo, K. Okada, and T. Goto, *Bull. Chem. Soc. Jpn.*, **45**, 1474 (1972).
(7) Y. Sakaino and H. Kakisawa, in preparation.
(8) K. Maeda and T. Hayashi, *Bull. Chem. Soc. Jpn.*, **43**, 429 (1970).

Reactions of Phthalic Anhydride with 2-Amino Alcohols[1]

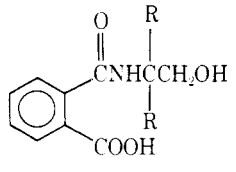
Zeno W. Wicks, Jr.,* and Gang-Fung Chen

Polymers and Coatings Department, North Dakota State University, Fargo, North Dakota 58105

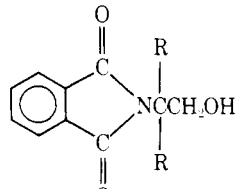
Received October 20, 1978

Depending on conditions, equimolar amounts of phthalic anhydride and 2-amino-2-methyl-1-propanol react to form amide 1-AMP, imide 2-AMP, and/or ester 3-AMP. Amide 1-AMP undergoes an acyl shift to ester 3-AMP, apparently representing the first example of an *N*- to *O*-acyl shift in the absence of strong acid. In contrast, phthalic anhydride and 2-aminoethanol yield only amide 1-AE or imide 2-AE. No acyl shift of amide 1-AE to ester 3-AE was detected. Oxazolines 6-AE and 6-AMP hydrolyze to esters 3-AE and 3-AMP when recrystallized from 95% EtOH. Our results disprove earlier claims of rearrangement to the eight-membered ring lactam–lactone compound 7, which appears to remain unknown.

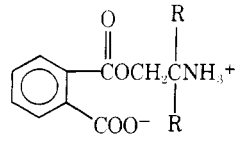
Phthalic anhydride (PA) has been reported[2] to react exothermally with 2-aminoethanol (AE) at room temperature. Without isolating the product (presumably amide 1-AE), the reaction mixture was heated to yield the (2-hydroxyethyl)-



1-AE, R = H
1-AMP, R = CH_3



2-AE, R = H
2-AMP, R = CH_3



3-AE, R = H
3-AMP, R = CH_3

phthalimide (2-AE). In attempting to synthesize amide 1-AMP and imide 2-AMP by reaction of PA with 2-amino-2-methyl-1-propanol (AMP), we find marked differences in reactions of the two amino alcohols.

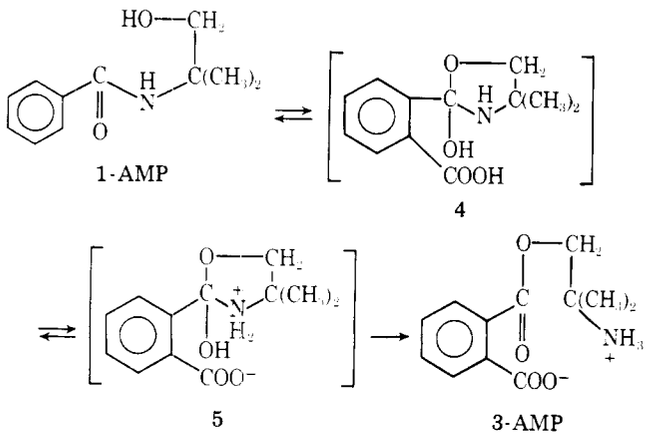
Results and Discussion

The product of reaction of equimolar amounts of PA with AE at room temperature in acetonitrile was found to be amide 1-AE. As reported,[2] when PA and AE react in refluxing benzene, imide 2-AE is formed. In contrast, in acetonitrile at room temperature or in refluxing benzene, PA reacts with AMP to give mixtures of amide 1-AMP and ester 3-AMP. When reacted in gently refluxing toluene, only ester 3-AMP is obtained. Reaction in refluxing xylene was required to obtain imide 2-AMP. It was found that amide 1-AMP rearranges to ester 3-AMP when a suspension is refluxed in benzene or more rapidly by refluxing a solution in acetonitrile. However, when amide 1-AE is refluxed in benzene it does not rearrange to ester 3-AE, and when a solution in acetonitrile is refluxed imide 2-AE is formed.

Many (2-hydroxyalkyl)amides have been shown to undergo acyl shifts to form 2-aminoalkyl ester hydrochlorides in the presence of stoichiometric amounts of HCl.[3] This appears to be the first report of an acyl shift in the absence of a strong acid. We propose that the shift is facilitated by the neighboring carboxylic acid group as shown in Scheme I. The proposed mechanism is analogous to one proposed by Welsh[3e] for rearrangement of (2-hydroxyalkyl)benzamides. Protonation of N in the tetrahedral intermediate 4 is proposed to enhance the leaving tendency of this group. Furthermore, the reverse reaction is restricted by the lower solubility of ester 3-AMP

0022-3263/79/1944-1244$01.00/0

Scheme I

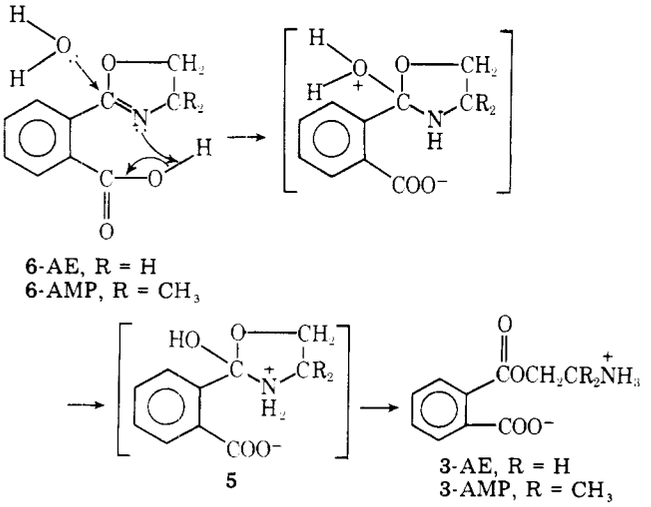


and stabilization of the product as the zwitterion. Reasenberg and Goldberg[3c] report that acyl shifts occur more readily if the carbon adjacent to the nitrogen has two substituents but provide no explanation. However, it is well known that *gem*-dimethyl groups facilitate ring closure reactions.[4] Formation of cyclic intermediate **4** may be facilitated by the methyl groups. Absence of methyl groups in amide **1**-AE decreases the ease of formation of a corresponding cyclic intermediate and hence would make rearrangement to ester **3**-AE more difficult. Since imide **2**-AE forms under such mild conditions, attempts to force rearrangement of amide **1**-AE to ester **3**-AE lead instead to formation of imide **2**-AE. Attempts to effect the acyl shift by the standard HCl procedure[3] resulted in hydrolysis to phthalic acid and AE.

Both imides **2**-AE and **2**-AMP were found to saponify so easily that they could be titrated as monofunctional acids by continuing addition of base until the drifting end point stabilized. Substituted phthalimides have been saponified by refluxing 5 min in alcoholic KOH.[5] However, titration at room temperature has not been reported. The 2-hydroxy group may increase the ease of saponification.

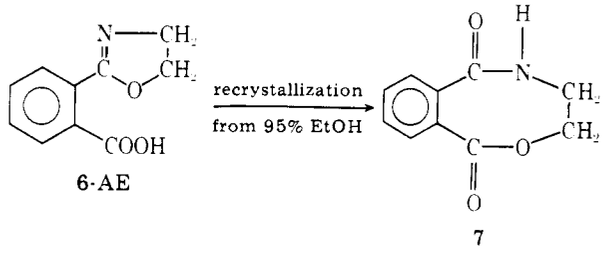
Conditions for reacting PA with AE or AMP to form oxazolines were not found. Oxazoline **6**-AMP was synthesized by the procedure for making oxazoline **6**-AE.[6,7] The structure was confirmed by titration, IR, NMR, and elemental analysis. It could be recrystallized from dry 1-propanol; however, recrystallization from 95% EtOH led to hydrolysis to form ester **3**-AMP. Most oxazolines are quite resistant to hydrolysis.[8] For example, Goldberg[9] found that refluxing in H_2O for 20 h was required to hydrolyze 2-phenyloxazoline to *N*-(2-hydroxyethyl)benzamide. The anchimeric effect on hydrolysis of many

Scheme II



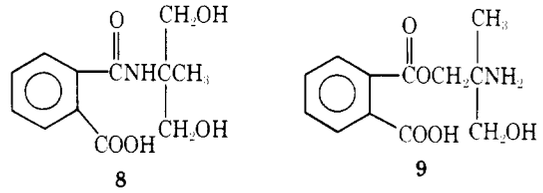
phthalic acid derivatives is well known.[10] A possible mechanism for the hydrolysis is represented by Scheme II.

Hasan[7] reported that oxazoline **6**-AE rearranged to 4,5-dihydro-1*H*-2,5-benzoxazoline-1,6(3*H*)-dione (**7**) on recrystallization from 95% EtOH. However, we find that the product is not **7**, but rather is ester **3**-AE. The elemental analysis reported by Hasan is consistent with **3**-AE, $C_{10}H_{11}NO_4$, not **7**, $C_{10}H_9NO_3$. The analysis was attributed to a hydrate of **7**,

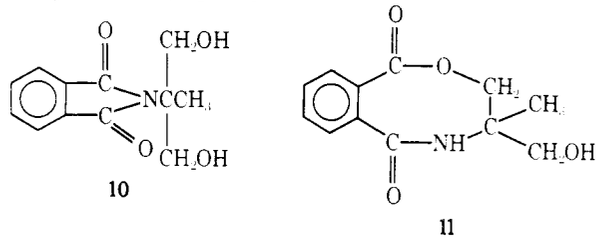


"$C_{10}H_9O_3N{\cdot}H_2O$". NMR in Me_2SO-d_6 shows a peak at δ 7.8–7.5 as Hasan reported and attributed to the aromatic protons. On closer examination, the peak is seen to be superimposed on a broad absorption from δ 8.6–6.2. The total number of protons over this range integrates at seven, accounting for the aromatic and NH_3 protons. NMR in CF_3COOH[11] clearly separates the three protons of $-{}^+NH_3$ at δ 7.65–6.5 from four aromatic protons at δ 8.2–7.65. The acid and amine equivalent weights correspond to structure **3**-AE rather than **7**. While Hasan reports that the molecular weight by mass spectrometry corresponds to $C_{10}H_9NO_3$, this ion could result from loss of H_2O from a $C_{10}H_{11}NO_4$ ion. Since oxazoline **6**-AE can be recrystallized unchanged from absolute EtOH, as shown by Körmendy[6] and confirmed here, the change in 95% EtOH is not just a thermal effect.

Sprung[12] reported that the reaction product of PA with 2-amino-2-methyl-1,3-propanediol was the half-amide **8**.



However, his titration data are consistent with a mixture of **8** and half-ester **9**, in line with our results with AMP. At higher temperature an equivalent of water was evolved; Sprung considered two possible structures for the product, imide **10** and dihydrobenzoxazocinedione derivative **11**. Although the compound yielded a dibenzoyl derivative on reaction with benzoyl chloride, Sprung decided on structure **11** since an



acetic anhydride–pyridine determination of hydroxy equivalent weight indicated the presence of one hydroxyl group. Based on our finding that imides **2**-AE and **2**-AMP saponify readily, it would be expected that imide **10** would saponify during the titration when determining hydroxy equivalent weight. Therefore, we conclude that the compound was imide **10** since failure to consider saponification would lead to the conclusion that there was one instead of two hydroxyl groups. Thus, as far as we can determine, there has been no substantiated synthesis of 4,5-dihydro-1*H*-2,5-benzoxazocine-1,6(3*H*)-dione or its derivatives.

Experimental Section

Nonaqueous titrations for amine equivalent weight were done following the method of Fritz.[13] Acid equivalent weights were determined in DMF with 0.1 N aqueous NaOH. NMR spectra were obtained using an EM-390 90-MHz NMR spectrometer. IR spectra were obtained using a Perkin-Elmer Model 137 IR spectrophotometer. PA was reagent grade from Fisher Scientific, AE was reagent grade from Sigma Chemical Co., and AMP was from IMC Chemical Group, Inc. Elemental analyses were run by Chemalytics, Inc., Tempe, Ariz.

Reactions of Phthalic Anhydride with 2-Aminoethanol (AE). A solution of 12.2 g (0.2 mol) of AE in 50 mL of acetonitrile was added to a solution of 29.6 g (0.2 mol) of PA in 250 mL of acetonitrile while cooling to keep the temperature below 30 °C. Filtration gave 38.5 g (92%) of 2-[[(2-hydroxyethyl)amino]carbonyl]benzoic acid (amide **1**-AE). Recrystallized from MeOH–ether, it had mp 123–125.5 °C with an acid equivalent weight, IR, and NMR appropriate for amide **1**-AE. A melting point of 113 °C for this amide prepared by hydrolysis of imide **2**-AE has been reported.[7] Duplication of this procedure gave amide **1**-AE with mp 122–124 °C.

Reaction of the same amounts of AE and PA in refluxing benzene gave an 80% yield of 2-(2-hydroxyethyl)-1*H*-isoindole-1,3(2*H*)-dione (imide **2**-AE). After recrystallization from H_2O, it had mp 124.5–127 °C (lit.[2] mp 123–126 °C). Titration gave an acid equivalent weight of 188 (calcd 191, assuming saponification to amide **1**-AE) at the end of a drifting end point and showed the absence of amine. IR and NMR were appropriate for imide **2**-AE.

Reactions of Phthalic Anhydride with 2-Amino-2-methyl-1-propanol (AMP). PA (29.6 g, 0.2 mol) and AMP (17.8 g, 0.2 mol) in 150 mL of toluene were refluxed for 5 hr. No water was evolved. A 90% yield of mono(2-amino-2-methyl-1-propyl) ester of benzene-1,2-dicarboxylic acid (ester **3**-AMP) was collected by filtration of the cooled reaction. Melting point after recrystallization from MeOH was 192–194 °C: acid equivalent weight 239; amine equivalent weight 236 (calcd 237); IR ν_{max} (KBr) 3200–2500, 2150, 1725, 1625, 1550 cm^{-1}; NMR (Me_2SO-d_6) δ 7.7–7.3 (m, 4 H), 4.3 (s, 2 H), 1.35 (s, 6 H); NMR (CF_3COOH) δ 8.2–7.7 (m, 4 H), 7.3–6.7 (s, 3 H), 4.65 (s, 2 H), 1.68 (s, 6 H). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.76; H, 6.33; N, 5.91. Found: C, 60.71; H, 6.24; N, 5.74. The same product resulted from refluxing PA and AMP in acetonitrile for 1.5 h.

A solution of 17.8 g (0.2 mol) of AMP in 50 mL of acetonitrile was added dropwise to a solution of 29.6 g (0.2 mol) of PA in 500 mL of acetonitrile while maintaining the temperature at 4–15 °C. After 1 week in a refrigerator, 24 g of solid was formed: acid equivalent weight 230, amine equivalent weight 479, corresponding to approximately 50% amide **1**-AMP and 50% ester **3**-AMP. When the reaction was carried out in refluxing benzene for 0.5 h, 91% of product was obtained. Based on acid and amine equivalent weights, it was approximately 33% amide **1**-AMP and 67% ester **3**-AMP.

Refluxing the same amounts of PA and AMP in 150 mL of xylene for 3 h led to evolution of 0.2 mol of H_2O. Dilution with 500 mL of hexane gave a viscous liquid (after removing solvent under vacuum, 20.6 g). The supernatant liquid was decanted, and after standing overnight 13 g of 2-(1,1-dimethyl-2-hydroxyethyl)-1*H*-isoindole-1,3(2*H*)-dione (imide **2**-AMP) was obtained. Recrystallization from MeOH–hexane gave mp 66–69 °C: IR ν_{max} (KBr) 3500, 2950, 1780, 1700, 1625, 1475, 1040 cm^{-1}; NMR (Me_2SO-d_6) δ 7.8 (s, 4 H), 5.5–4.7 (s, 1 H), 3.8 (s, 2 H), 1.63 (s, 6 H), addition of D_2O eliminated the peak from OH at δ 5.5–4.7. Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.94; N, 6.39. Found: C, 66.10; H, 5.79; N, 5.97. Acid equivalent weight after waiting for the drifting end point was 218 (calculated, assuming saponification to amide **1**-AMP, 219). Based on titration, IR, and NMR, the viscous liquid contained a substantial fraction of imide as well as other products possibly including low molecular weight oligomers and oxazoline **6**-AMP.

2-[[(1,1-Dimethyl-2-hydroxyethyl)amino]carbonyl]benzoic Acid (1-AMP). Since amide **1**-AMP could not be isolated from reaction of AMP and PA, it was synthesized by hydrolysis of imide **2**-AMP. Imide **2**-AMP (2.8 g) was dissolved in 10 mL of 10% aqueous NaOH at room temperature. After filtration, the solution was neutralized to pH 2 with HCl at 0 °C; 1.7 g of 2-[[(1,1-dimethyl-2-hydroxyethyl)amino]carbonyl]benzoic acid (amide **1**-AMP) was obtained. Recrystallization from MeOH–ether gave crystals with mp 144–147 °C: acid equivalent weight 237 (calcd 237); IR ν_{max} (KBr) 3350, 3200, 2900, 1700, 1640, 1540, 1040 cm^{-1}; NMR (Me_2SO-d_6) δ 7.8–6.3 (m, 7 H), 3.5 (s, 2 H), 1.3 (s, 6 H). Anal. Calcd for $C_{12}H_{15}NO_4$: C, 60.76; H, 6.33; N, 5.91. Found: C, 60.87; H, 6.55; N, 5.88.

Thermal Rearrangement of Amide 1-AMP and Ester 3-AMP. A suspension of 4.05 g of **1**-AMP was refluxed in 20 mL of benzene for 1.5 h. No water was evolved. After cooling and filtering, 3.6 g of product with mp 139–143 °C was obtained: acid equivalent weight 236, amine equivalent weight 1723, corresponding to 86% amide **1**-AMP and 14% ester **3**-AMP. After refluxing in benzene for 16.5 h, 48% of amide **1**-AMP had rearranged to ester **3**-AMP. When a solution of 3.1 g of amide **1**-AMP was refluxed in 20 mL of acetonitrile for 16.5 h, 2.85 g of ester **3**-AMP, mp 190–193 °C, was obtained: acid equivalent weight 235; amine equivalent weight 236.

When 3.1 g of ester **3**-AMP was refluxed in 20 mL of benzene for 16.5 h, the product (3 g) was found to have mp 190–192 °C, acid equivalent weight 235, and amine equivalent weight 236, and IR showed no change. Similar results were obtained by refluxing in toluene for 38 h and in acetonitrile for 16.5 h.

Attempted Rearrangement of Amide 1-AE. A suspension of 9 g of amide **1**-AE was refluxed in 150 mL of benzene until the first indication of water evolution was observed, 5 h. On filtration, 7.45 g of product (82.8%) was recovered (mp 121–122.5 °C), acid equivalent weight 205 (calcd 209). At the very end of the titration the end point drifted, indicating the presence of a small amount of imide **3**-AE. No ester was formed as indicated by the absence of a significant amount of amine by titration. IR was identical with starting material.

When 2 g of amide **1**-AE was refluxed in 30 mL of acetonitrile for 5 h, a small amount of viscous liquid separated on cooling. A total of 1.2 g of white crystals, mp 122.5–125 °C, was obtained by concentrating the solution. IR was the same as for imide **2**-AE, and the acid equivalent weight was 192 after waiting for the drifting end point (calculated for imide **2**-AE, assuming saponification to amide **1**-AE, 191). No amine could be detected by titration.

2-(4,5-Dihydro-4,4-dimethyl-2-oxazolyl)benzoic Acid (6-AMP). The procedure for 2-(bromoethyl)phthalimide[14] was modified to make (2-bromo-1,1-dimethylethyl)phthalimide. The product had mp 58–59 °C. Without purification, it was warmed in 10% aqueous NaOH. Acidification (to pH 5 with HCl) of the filtered solution at 0 °C gave 14.1 g of white crystals: mp 175.5–177.5 °C; acid equivalent weight 216; amine equivalent weight 219 (calcd 219); IR ν_{max} (KBr) 3400, 2900, 2450, 1700, 1660, 1560 cm^{-1}; NMR (Me_2SO-d_6) δ 7.8–7.4 (m, 4 H), 4.0 (s, 2 H), 1.25 (s, 6 H). Anal. Calcd for $C_{12}H_{13}NO_3$: C, 65.75; H, 5.94; N, 6.39. Found: C, 65.79; H, 5.90; N, 6.07.

When **6**-AMP was recrystallized twice from 95% EtOH, the melting point increased to 192–194 °C. Acid equivalent weight, 235, amine equivalent weight, 236, IR, NMR, and elemental analysis were identical with ester **3**-AMP.

When **6**-AMP was recrystallized from dry 1-propanol, the product had mp 173–176 °C: acid equivalent weight 222; amine equivalent weight 223; IR was unchanged; NMR (Me_2SO-d_6) showed a small $-CH_2-$ peak at δ 4.3 in addition to the major oxazoline $-CH_2-$ peak at δ 4.0. Thus, there had been a small degree of hydrolysis, but the oxazoline did not rearrange due to heat.

Recrystallization of Oxazoline 6-AE. When 5 g of oxazoline **6**-AE was recrystallized from 35 mL of 95% EtOH, 2.6 g of crystals was obtained; after a second recrystallization from 95% EtOH, the melting point was 143–147 °C: acid equivalent weight 204; amine equivalent weight 209 (calcd for $C_9H_{11}NO_4$, 209); IR ν_{max} (KBr) 3300–2250, 2100, 1750, 1640, 1540 cm^{-1}; NMR (Me_2SO-d_6) δ 8.6–6.2 (m, 7 H), 4.55–4.38 (t, 2 H), 3.25–2.1 (t, 2 H); NMR (CF_3COOH) δ 8.2–7.65 (m, 4 H), 7.65–6.5 (s, 3 H), 5.0–4.75 (t, 2 H), 3.95–3.6 (m, 2 H). Anal. Calcd for $C_{10}H_{11}NO_4$: C, 57.42; H, 5.26; N, 6.70. Found: C, 57.19; H, 5.44; N, 6.68. The product was ester **3**-AE.

Acknowledgments. We would like to thank the IMC Corporation, Chemical Group, for financial support of this research. The advice and suggestions of Dr. S. Peter Pappas are gratefully acknowledged.

Registry No.—1-AE, 58509-24-3; **2**-AE, 3891-07-4; **3**-AE, 69177-70-4; **6**-AE, 1445-70-1; **1**-AMP, 69177-71-5; **2**-AMP, 4490-74-8; **3**-AMP, 69177-72-6; **6**-AMP, 68365-12-8; PA, 85-44-9; AE, 141-43-5; AMP, 124-68-5; (2-bromo-1,1-dimethylethyl)phthalimide, 31792-17-3.

References and Notes

(1) Taken from the M.S. Thesis of G.-F. Chen; presented in part at the 18th Annual North Dakota State University Coatings Symposium, Fargo, North Dakota, June 1978.
(2) H. Wenker, *J. Am. Chem. Soc.*, **59**, 422 (1937).
(3) (a) T. Immediata and A. R. Day, *J. Org. Chem.*, **5**, 512 (1940); (b) A. C. Cope et al., *J. Am. Chem. Soc.*, **66**, 1448, 1453, 1738 (1944); (c) J. R. Reasenberg and S. D. Goldberg, *ibid.*, **67**, 933 (1945); (d) A. P. Phillips and R. Batzly, *ibid.*, **69**, 200 (1947); (e) L. H. Welsh, *J. Org. Chem.*, **32**, 119 (1967).
(4) G. S. Hammond in "Steric Effects in Organic Chemistry", M. S. Newman, Ed., Wiley, New York, 1956, p 468.
(5) J. H. Speer and A. J. Hill, *J. Org. Chem.*, **2**, 139 (1937).
(6) M. Körmendy and J. Wolford, *Acta. Chim. Acad. Sci. Hung.*, **32**, 115

(1962).
(7) S. K. Hasan and S. A. Abbas, *Can. J. Chem.*, **53**, 2450 (1975).
(8) R. H. Wiley and L. L. Bennett, Jr., *Chem. Rev.*, **44**, 447 (1949).
(9) A. A. Goldberg and W. Kelley, *J. Chem. Soc.*, 1919 (1948).
(10) W. P. Jencks, "Catalysis in Chemistry and Enzymology", McGraw-Hill, New York, 1969, especially Chapter 1.
(11) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965, p 95.
(12) M. M. Sprung, *J. Am. Chem. Soc.*, **61**, 381 (1939).
(13) J. S. Fritz, "Acid-Base Titrations in Nonaqueous Solvents", The G. Frederick Smith Chemical Co., Columbus, Ohio, 1952, pp 12–13.
(14) T. O. Soine and M. R. Buchdahl, *Org. Synth.*, **32**, 18 (1952).

Synthetic Methods and Reactions. 62.[1] Transformations with Chlorotrimethylsilane/Sodium Iodide, a Convenient in Situ Iodotrimethylsilane Reagent

George A. Olah,* Subhash C. Narang, B. G. Balaram Gupta, and Ripudaman Malhotra

The Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90007

Received September 28, 1978

A new, convenient, inexpensive alternative to iodotrimethylsilane reagent is explored. A mixture of chlorotrimethylsilane/sodium iodide in acetonitrile is found to be a better reagent than iodotrimethylsilane for the cleavage of esters, lactones, carbamates, and ethers. Cleavage of esters and lactones (10 examples) occurred somewhat slower with the present system than with iodotrimethylsilane. On the other hand, ethers (7 examples) cleaved much more readily with the present system. A feasible mechanism is proposed for this disparity. Carbamates (6 examples) also underwent facile cleavage to give the corresponding amines. The general applicability of the method has been shown using various types of substrates. The facile conversion of alcohols to iodides using the present method is also reported. Conversion of alcohols to iodides is much faster with chlorotrimethylsilane/sodium iodide than with iodotrimethylsilane, and iodides are formed in excellent yield.

The use of organosilicon reagents became significant during recent years in organic synthesis. New organosilicon reagents have been developed, and silylated synthons are being widely used in the activation of a substrate or in directing the reaction course in a specific manner.[2]

The high bond energy of the silicon–oxygen bond (90–110 kcal/mol) makes it thermodynamically very favorable to use a reagent with a weak Si–X bond and react it with an appropriate oxygen-containing organic molecule to form a silicon–oxygen bonded intermediate, which then can be transformed to another product in a subsequent step. One such reagent developed in our laboratories,[3–5] as well as independently by Jung,[6,7] is iodotrimethylsilane, which has gained use in the cleavage of esters,[3–6] ethers,[7] and carbamates,[8] as well as in conversion of alcohols to iodides.[9] We have also shown the usefulness of iodotrimethylsilane in the deoxygenation of sulfoxides to sulfides.[10] This reaction has since been applied to the synthesis of certain prostacyclin derivatives.[11] It has also been used in the cleavage of ketals,[12] although ethylene ketals are not cleaved cleanly.

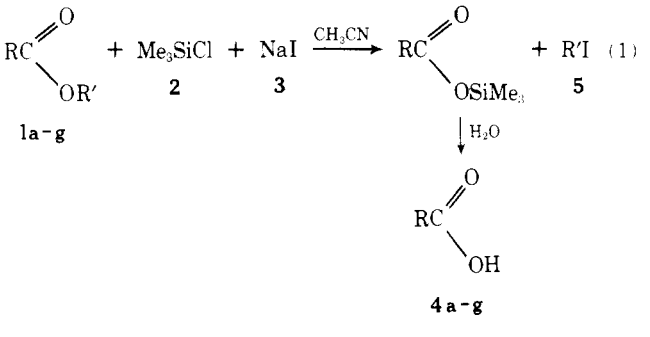
The hydrolytic susceptibility of the Si–I bond in iodotrimethylsilane could be a problem in several organic reactions containing acid sensitive compounds. In addition, iodotrimethylsilane should be prepared freshly and used under strictly anhydrous conditions, as it fumes in air and turns purple on standing, making prolonged storage undesirable. Also, it was until now a relatively expensive commercial reagent, prepared from chlorotrimethylsilane and anhydrous magnesium iodide,[13] or from phenyltrimethylsilane and iodine,[14] or from hexamethyldisiloxane/iodine/aluminum powder.[6] In each case, the reagent has to be isolated by distillation from the reaction mixture.

A comparison of the reported methods showed the phenyltrimethylsilane/iodine reagent to be most useful because iodotrimethylsilane is generated in situ.[4,5] However, under these reaction conditions, the required reaction temperature is fairly high. Also, iodine may cause side reactions, and iodobenzene can sometimes be a very inconvenient byproduct. In view of synthetic interest in iodosilane reagents, we have been interested in developing other methods to generate iodotrimethylsilane or its in situ equivalent for simplified and general use.

This led us to utilize the surprisingly simple and inexpensive alternative of chlorotrimethylsilane with sodium iodide in acetonitrile solution. When chlorotrimethylsilane is added to an acetonitrile solution of anhydrous sodium iodide, a yellow colored solution (whose spectral characteristics are similar to those of a solution obtained from iodotrimethylsilane and acetonitrile in acetone-d_6) is obtained with immediate formation of white precipitate of sodium chloride.[15]

We have, in a preliminary communication, reported our first results on the deoxygenation of sulfoxides with chlorotrimethylsilane/sodium iodide reagent.[16,17] An independent recent report by Morita et al.[18] on the cleavage of phosphonate esters with chlorotrimethylsilane/sodium iodide prompts us to report our results in full, including the cleavage of esters, lactones, carbamates, and ethers, as well as the conversion of alcohols to iodides.[19]

Cleavage of Esters and Lactones. Alkyl esters of carboxylic acids and lactones (**1**) undergo facile cleavage when the corresponding substrates are reacted with chlorotri-



0022-3263/79/1944-1247$01.00/0