be associated with the nature of the enaminone and the selection of the alkylating agent, the basic catalyst, and the solvent.

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(4) As to some of the variations in photochemical behavior observed in the present work (e.g., C–C vs. C–N coupling), a reviewer has suggested the possibility that they are due to solvent effects. In our experiments, all the photochemical reactions have been conducted in the presence of an excess of triethylamine, and, except in the case of **7**, **26a**, and **26b**, acetonitrile has been used as such or with dioxane as the solvent. The selection of the solvent has depended on the solubility of the substrates. Thus these photolyses should be regarded to have been conducted essentially in the same solvent system. Although a solvent effect has not been ruled out, we feel that the differences in the course of the cyclizations are due to structural differences in the substrates and not variations in solvent composition.

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Structures and Chromotropic Properties of 1,4-Bis(4,5-diphenylimidazol-2-yl)benzene Derivatives

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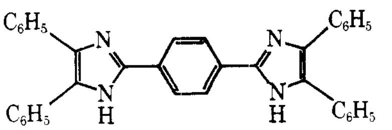
Received July 11, 1978

Three new imidazolyl derivatives (**5–7**) were prepared by ferricyanide oxidation of 1,4-bis(4,5-diphenylimidazol-2-yl)benzene (**1**). Base-catalyzed addition of ethanol to 3,6-bis(4,5-diphenyl-2*H*-imidazol-2-idene)-1,4-cyclohexadiene also afforded the compound **5**. The structure of diethoxy compound (**6**) was assigned 1,4-bis[4,4′-diethoxy-4,5-diphenyl-2(4*H*)-imidazolyl]benzene. The compound **7** was determined to be a dimer of the 4-ethoxyimidazolyl radical **10** produced by oxidation of **5**. Irradiation of **5** with UV light results in the formation of the starting quinonoid compound **2**, as indicated by its deep blue color. Diethoxy compound **6** was not affected by the light. Dimeric compound **7** shows chromotropism caused by radical dissociation of the dimer during irradiation, heating, or grinding.

Zimmermann and co-workers prepared 3,6-bis(4,5-diphenylimidazol-2-yden)-1,4-cyclohexadiene (**2**) by bromine oxidation of the sodium salt of 1,4-bis(4,5-diphenylimidazoly-2-yl)benzene (**1**).[1] We also obtained the same quinonoid compound **2** by lead dioxide oxidation of **1** or ferricyanide oxidation of the potassium salt of **1** and reported that the quinonoid compound **2** isomerizes on heating to a biradical (**3**), which reverses to the original quinone (**2**) on cooling.[2]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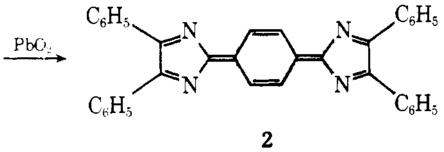
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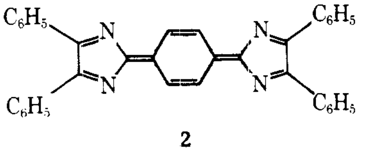
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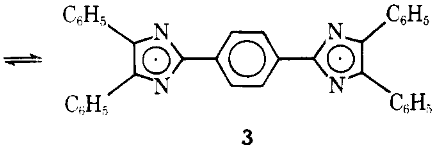
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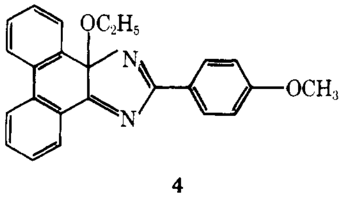
Whereas ferricyanide oxidation of bis(imidazolyl)benzene **1** in dioxane had afforded the quinonoid compound **2** as sole product, the same oxidation in an ethanolic potassium hydroxide solution gave a complex mixture, from which three new compounds were obtained. These compounds showed remarkable photo- and thermochromisms. We wish to report the results of structural and chromotropic studies on these compounds.

Results and Discussion

When an aqueous potassium ferricyanide solution was added to bis(imidazolyl)benzene **1** in an ethanolic potassium hydroxide solution at 5 °C, a purple color appeared at first, and a pale yellow precipitate gradually separated. The precipitate showed many spots on TLC, and three new compounds, **5**, **6**, and **7**, were isolated in a pure state. Although this reaction afforded **5** and **7** as the major products besides a minor amount of **6**, the same reaction carried out in an oxygen atmosphere yielded compound **6** as a main product.

Elemental analysis and the mass spectrum (*m/e* 558) of compound **5** gave the molecular formula $C_{34}H_{30}N_4O$, indicating the incorporation of one ethoxy group into compound **2**. The NMR spectrum of **5** exhibited a triplet at 1.22 (J = 7 Hz) for the methyl protons and a multiplet (XY part of A_3XY spectrum) centered at 3.45 ppm for the methylene protons.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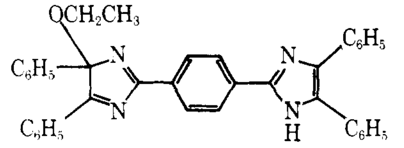
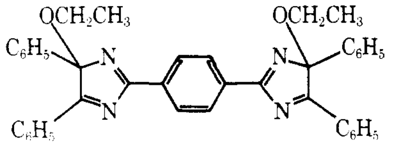
This observation showed the ethoxy group is bonded to a chiral center. The nonequivalence of the methylene protons in an ethoxy group was previously observed with an ethoxyphenanthroimidazole (**4**).[3]



5

The protons of the *p*-phenylene group bonded to the 2-position of the 4*H*-imidazole ring showed the characteristic A_2B_2 pattern at 8.05 and 8.5 ppm (J = 8 Hz). The chemical shift values of these protons are consistent with that reported in the literature[3] for similar systems. From these spectral properties the structure **5** was deduced for the oxidation product. This structure was reported by an independent synthesis; addition of a catalytic amount of potassium hydroxide to the deep blue benzene–ethanol solution of the quinonoid compound **2** afforded a yellow product, which was identical with the compound **5**.[4]

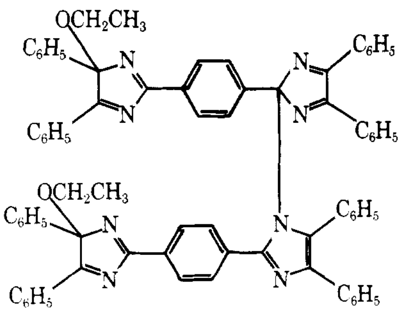
The elemental analysis and the mass spectrum of compound **6** gave molecular formula $C_{40}H_{34}N_4O_2$, which indicated the incorporation of two ethoxy groups during the ferricyanide oxidation. The NMR signals of these two ethoxy groups appeared coincidentally at 1.25 and 3.5 ppm. The aromatic protons of the central phenylene group were found downfield at 8.7 ppm as a singlet. The coincidence of two ethoxy signals and the equivalence of the four aromatic protons show that compound **6** has a symmetrical structure. The nonequivalence of the methylene protons of the ethoxy groups and the downfield resonance of the four aromatic protons of the central phenylene group showed that the ethoxy groups were incorporated at C-4 of the imidazolyl groups consistent with the structure **6**.



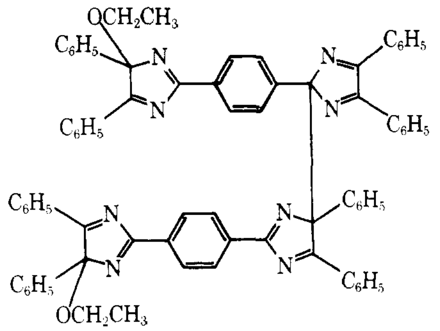
6

Molecular weight determination and combustion analysis revealed that the third compound **7**, $(C_{38}H_{29}N_4O)_2$, corresponds to dehydrodimer of the ethoxyimidazole **5**. The NMR spectrum exhibited the presence of two ethoxy groups in different environments (two methyl signals appeared at 1.10 and 1.08 ppm in C_6D_6). Two A_2B_2 signals at 8.52, 7.48 (J = 7 Hz) and 8.24, 7.45 (J = 7 Hz) were assigned to the protons of two para disubstituted phenylene groups. These spectral properties suggested that the compound has an unsymmetrical structure such as **7a**, **7b**, or **7c**. Two possible structures, **7b** and **7c**, were excluded by analyses of the NMR patterns of the two 1,4-disubstituted phenylene groups. The central phenylene groups in the assumed structures, **7b** and **7c**, bear three 4*H*-4-substituted imidazolyl groups and one 2*H*- or 1*H*-imidazolyl group, respectively. As described for the compound **5**, ortho protons of aromatic group bonded to the 2-position of 4*H*-4-substituted imidazolyl-2-benzene were found to be strongly deshielded and to appear at 8 ppm or more downfield.[5,6] Since only four protons were detected at as far downfield at 8 ppm, structures **7b** and **7c** can be excluded and **7a** is left as the only possible structure for the oxidation product. The NMR multiplets observed at 7.65 (4 H) were assigned to the ortho protons of phenyl groups bonded to the 4-position of 4*H*-4-ethoxyimidazolyl groups.

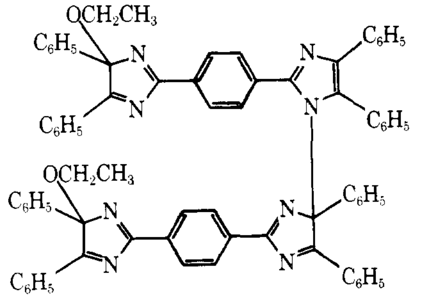
The UV spectrum of **7** showed an absorption maximum at 280 nm (log ε = 4.73). The UV spectrum of a 1:1:1 mixture of **5**, **8**, and **9** closely resembled that of **7** except for a peak at 385 nm. The 385 nm absorption band in the spectrum of **5** has been assigned to the intramolecular charge-transfer band,[7] whereas this charge-transfer interaction in the dimer **7** is inhibited by a twist of two imidazolyl planes.



7a

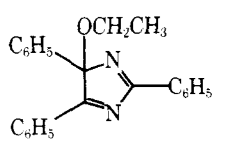


7b



7c

The unsymmetrical dimer **7** was first prepared by ferricyanide oxidation of the bis(imidazole) **1** in ethanolic potassium hydroxide solution. The same compound could be prepared by oxidation of the ethoxyimidazole **5** with ferricyanide in dioxane or lead dioxide in benzene. On addition of lead dioxide to the compound **5** in benzene, the color of the solution turned to green and the color gradually lightened to afford the dimer **7**. The green solution showed the characteristic absorption spectrum of a bis(imidazolyl) radical **10** (vide infra). These observations suggested the oxidation process from **1** to **7**; ferricyanide oxidation of the starting material **1** afforded at first the quinonoid compound **2**, which gave, through a base-catalyzed addition of ethanol, the mono ethoxy compound **5**; further oxidation of the latter resulted in the formation of the dimer **7** via the radical intermediate **10**. The diethoxy com-



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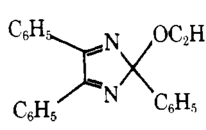

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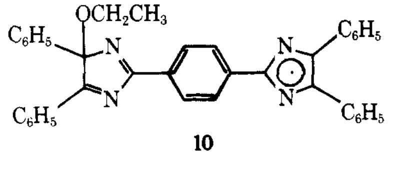
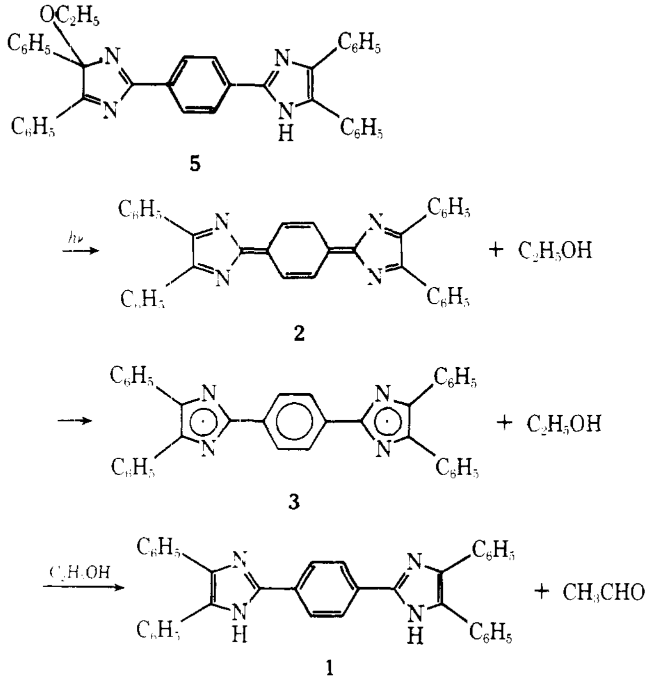


10

pound **6** was considered to be produced by combination of radical intermediate **10** and ethanol or by heterolytic substitution of ethanol onto the dimer **7**.

The color of the benzene solution of the monoethoxy compound **5** turned blue on exposure to the sun or a mercury lamp. The blue solution showed the characteristic absorption spectrum of the quinonoid compound **2**.[2] From the briefly irradiated solution ethanol was detected, but prolonged irradiation of the solution brought formation of acetaldehyde and bis(imidazolyl)benzene **1**. The formation of these compounds was probably due to hydrogen abstraction from ethanol by the biradical **3**.



Upon exposure to the sun light or a xenon lamp, a light yellow benzene solution of the dimer **7** quickly turned to green, and the color reverted to the original color when placed in the dark at room temperature. The light yellow benzene solution of **7** showed no ESR signals, but the green solution showed marked ESR signals, whose intensities gradually decreased on standing in the dark. The rate of decrease of the signals obeyed the second-order rate law. Neither acetaldehyde nor reduced imidazolyl compound was detected from the irradiated solution even after prolonged irradiation. A mechanism for the photochromism of the dimer **7** was considered to be a reversible dissociation of the dimer to a radical **10**. A light yellow benzene solution of **7** prepared in a dark place showed an absorption maximum at 280 nm, but a green solution obtained by irradiation showed new absorption maxima at 345, 410, 432, 483, 575, 613, and 670 nm. The absorbances of these bands decreased in a dark place, and the absorption at 280 nm recovered. An isosbestic point was found at 323 nm. The new absorption bands were assigned to those of radical **10**. The degree of photodissociation of the dimer in benzene ($c = 1 \times 10^{-5}$ mol/L, light source 280 nm, 150 μW) was estimated to be 0.2 from the change of absorbance at 280 nm. The rate constant of recombination of the radical was evaluated using a second-order equation with the rate of decrease of absorbance at 432 nm being 12 L/(mol s), and the activation energy 8.1 kcal/mol. The higher activation energy for the dimerization of radical **10** than that of the lophyl radical **11** (7.8 kcal/mol) is due to the extended conjugation in the former radical **10**.

On heating over 80 °C, the light yellow color of a mixture of dimer **7** and naphthalene turned green, and the color intensity increased with the rise in temperature. On cooling in the dark, the color returned to initial yellow. The phenomenon exhibited that the dimer **7** also possesses a reversible thermochromic property.

The dimer **7** changed to green on grinding the crystals in a mortar, and the original color was recovered after a long time, demonstrating a piezochromic property.

Experimental Section

UV spectra were recorded on a Hitachi EPS-3T spectrophotometer with a Komatsu CTE and CTR Coolnics circulater, and IR spectra were measured on a Hitachi EPI-S2 spectrophotometer. NMR spectra were recorded on a JEOL-MH-100 and Hitachi R-24B instruments with tetramethylsilane as internal standard and mass spectra on a JES-ME-3X spectrometer. Molecular weight was determined on Hitachi molecular weight apparatus Model 115.

1,4-Bis(4,5-diphenylimidazol-2-yl)benzene (1) was synthesized by the same method as reported previously.[2]

3,6-Bis(4,5-diphenylimidazol-2-idene)-2,5-cyclohexadiene (2). A cold 20% solution of potassium ferricyanide (400 mL) was dropped during 2 h into a suspension of **1** (2 g) in dioxane (100 mL) containing an aqueous solution of potassium hydroxide (6%, 50 mL). The mixture was maintained between 5 and 7 °C and was stirred by bubbling in a stream of nitrogen. A deep purple precipitate separated. The precipitate was collected, washed with water, and dried. The crude product (1.9 g) was dissolved in benzene, the solution was filtered to remove undissolved substance (**1**), and the filtrate was concentrated; addition of a small amount of hexane to the concentrated filtrate gave **2** as fine deep greenish blue prisms. Melting point and IR spectrum of the product were identical with those of an authentic sample which had been prepared by PbO_2 oxidation of **1**.[2]

Preparation of 2[4-(4-Ethoxy-4,5-diphenyl-4*H*-imidazol-2-yl)phenyl]-4,5-diphenylimidazole (5) and the Dimer 7. A cold aqueous solution of potassium ferricyanide (5%, 200 mL) was dropped during 1 h into a solution of **1** (1 g) in 99% ethanol (100 mL) containing potassium hydroxide (6 g). The mixture was maintained between 5 and 10 °C and was stirred by bubbling in a nitrogen stream. A greenish light yellow precipitate was formed. The precipitate was collected, washed with water, and dried. The crude product (1 g) was subjected to silica gel TLC (developing solvent; benzene (10) and ethyl acetate (1)) to give **5** (142 mg), **7** (630 mg), and **6** (94 mg). Compounds **5** and **7** were crystallized from ethanol–water and **6** was recrystallized from benzene–hexane **5**: mp (double melting points) 167 and 248 °C, yellow prisms. Anal. Calcd for $C_{38}H_{30}N_4O{\cdot}H_2O$: C, 79.13; H, 5.60; N, 9.71. Found: C, 79.16; H, 5.43; N, 9.72. MS Calcd for $C_{38}H_{30}N_4O$: 558.2416. Found: *m/e* 558.245 (M^+). NMR ($CDCl_3$) δ 1.22 (t, 3 H, J = 7 Hz), 3.45 (m, 2 H), 7.2, 7.7 (m, 18 H), 8.25 (m, 2 H), 8.05 (d, 2 H, J = 8 Hz), 8.5 (d, 2 H, J = 8 Hz). **7**: NMR ($CDCl_3$ + C_6D_6 (1:1)) 1.13 (brt, 6 H), 3.3 (m, 4 H), 7.45 (d, 2 H, J = 7 Hz), 8.24 (d, 2 H, J = 7 Hz), 7.84 (d, 2 H, J = 7 Hz), 8.52 (d, 2 H, J = 8 Hz). Anal. Calcd for $(C_{38}H_{29}N_4O)_2{\cdot}H_2O$: C, 80.53; H, 5.35; N, 9.89. Found: C, 80.45; H, 5.35; N, 9.89. Molecular weight Calcd for $(C_{38}H_{29}N_4O)_2$: 1114. Found: 1218 (in methanol).

1,4-Bis(4-ethoxy-4,5-diphenyl-4*H*-imidazol-2-yl)benzene (6) was prepared from **1** by a method similar to that used for the preparation of **5** and **7**, employing 20% aqueous solution of potassium ferricyanide (400 mL), maintained at about 20 °C and stirred by a stream of oxygen. Recrystallization from benzene–hexane afforded colorless prisms: yield 80%; mp (double melting points) 192 and 257 °C; NMR ($CDCl_3$) δ 1.25 (t, 6 H, J = 7 Hz), 3.10, 3.75 (m, 4 H), 7.20, 7.55 (m, 16 H), 8.25 (dd, 4 H, J = 7.2 Hz), 8.7 (s, 4 H). Anal. Calcd for $C_{40}H_{34}N_4O_2$: C, 79.70; H, 5.70; N, 9.30. Found: C, 79.89; H, 5.72; N, 8.80. MS: *m/e* calcd for $C_{40}H_{34}N_4O_2$: 602.2679. Found: 602.264.

Addition Reaction of Ethanol to Compound 2. To a solution of **2** (1 g) in benzene (300 mL) was added ethanolic potassium hydroxide (1 N, 100 mL) and the mixture was stirred for 30 min at room temperature. The deep blue color of **2** turned to reddish yellow. The solution was washed with water and was evaporated to dryness in vacuo, and a residue was subjected to silica gel TLC (benzene–ethyl acetate 10:1). A main yellow band was eluted by ethyl acetate to yield the compound **5** (0.85 g). Four other minor unstable compounds were found, but these compounds could not be obtained in a pure state.

Oxidation of 5. (a) Lead Dioxide Oxidation. A mixture of **5** (300 mg), lead dioxide (10 g), and sodium sulfate (5 g) in benzene (100 mL) was stirred for 12 h and then filtered. The filtrate was evaporated and the residue was subjected to purification by preparative TLC (benzene–ethyl acetate 10:1) to obtain 200 mg of **7**.

(b) Ferricyanide Oxidation. To a solution of **4** (2 g) in dioxane (50 mL) containing aqueous potassium hydroxide (1 N, 300 mL), aqueous potassium ferricyanide (20%, 400 mL) was dropped under ice cooling at 5–10 °C in a period of 2 h. After addition of cold water (400 mL), the mixture was stirred for an additional 1 h. A greenish 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 $k_{\text{obsd}} = (2.303/t)(\log A_0/A)$, 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.

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(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 ($k^{\text{EtOH}}/k^{\text{EtOD}}$) for the base-catalyzed addition of ethanol to **2** was found to be about 7.3.

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

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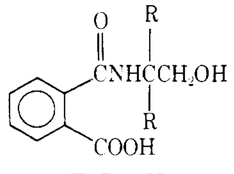
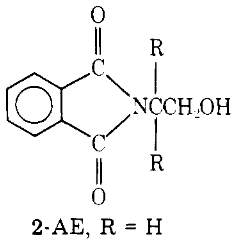
Depending on conditions, equimolar amounts of phthalic anhydride and 2-amino-2-methyl-1-propanol react to form amide **1**-AMP, imide **2**-AMP, and/or ester **3**-AMP. Amide **1**-AMP undergoes an acyl shift to ester **3**-AMP, apparently representing the first example of an *N*- to *O*-acyl shift in 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)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.



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



2-AE, R = H
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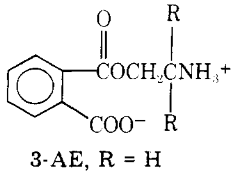

3-AE, R = H
3-AMP, R = CH_3

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

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