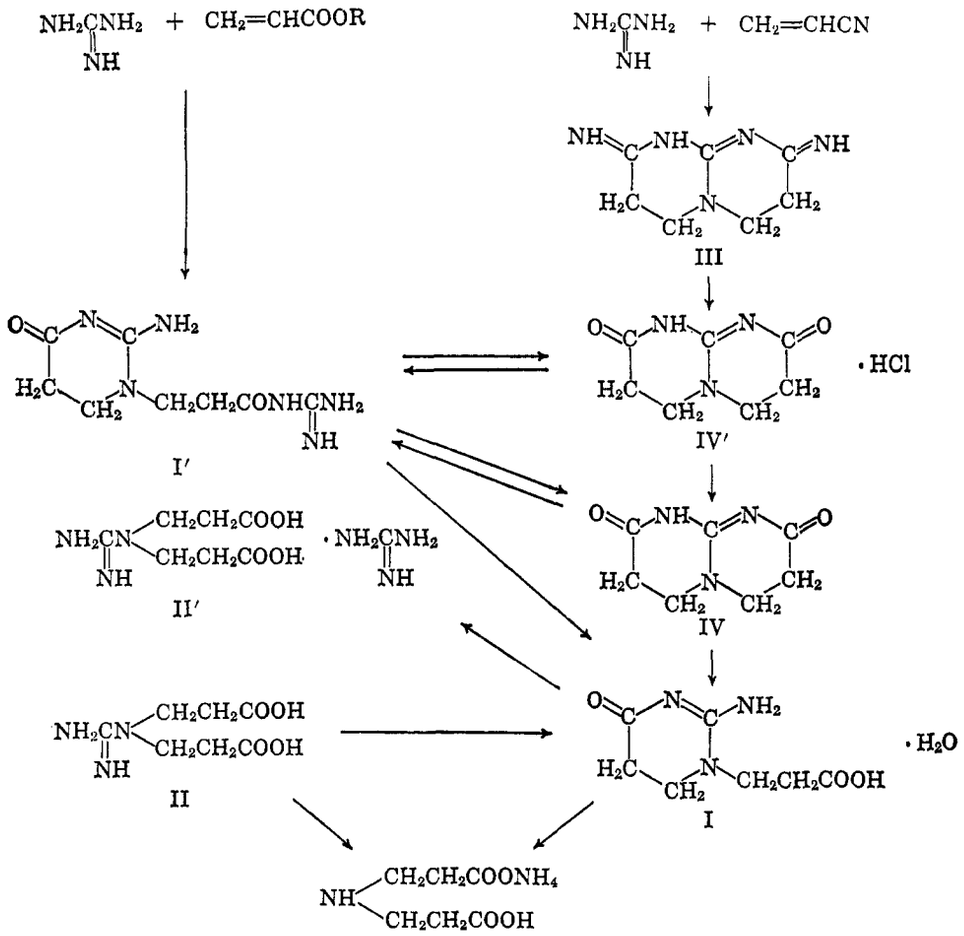
CHART I



worked up the same as in the above experiment to obtain 2.2 g (71%) of monoammonium salt of 3,3′-iminodipropionic acid.

Conversion of I′ into IV′.—A solution of 11.3 g (0.05 mol) of I′ dissolved in 17 ml of 6 *N* hydrochloric acid (0.1 mol) was allowed to stand for 3 hr to obtain 8.3 g (82%) of IV′ which melted at 299–303° dec after purification.

Conversion of the Hydrochloride of I′ into IV.—A solution of 4.0 g of the hydrochloride of I′ (prepared in ethanol) in 200 ml of ethanol was refluxed for 3 hr and concentrated at reduced pressure to obtain 1.6 g (63%) of IV which melted at 229° after recrystallization.

Conversion of IV and IV′ into I′.—To a solution of 0.6 g (0.01 mol) of free guanidine in 50 ml of methanol was added 1.7 g (0.01 mol) of IV [or 1.0 g (0.005 mol) of IV′] dissolved in 200 ml of methanol and the solution was allowed to stand for 3 hr at room temperature to obtain 2.1 g (93%) [or 0.9 g (80%)] of I′ which melted at 250° dec after purification.

Conversion of I′ into I.—A solution of 11.3 g (0.05 mol) of I′ dissolved in 100 ml of water containing 8.5 ml of 6 *N* hydrochloric acid (0.05 mol) was boiled for 3 hr and concentrated at reduced pressure to obtain 6.9 g (68%) of I which melted at 190° after recrystallization.

Conversion of I into II′.—To a solution of 0.6 g (0.01 mol) of free guanidine in 10 ml of water was added 2.0 g (0.01 mol) of I and the solution was boiled for 1 hr. The resulting solution was worked up the same as in the preparation of II′ from I′: yield 2.4 g (92%); mp 176° after recrystallization.

Conversion of II into I.—A solution of 2.0 g of II in 50 ml of water was boiled for 3 hr and evaporated to dryness to obtain 1.8 g (90%) of I which melted at 190° after recrystallization.

Registry No.—I, 16675-75-5; I picrate, 16675-76-6; I′, 16675-77-7; II, 16675-32-4; II picrate, 16675-78-8; II′, 16675-79-9; III, 16675-80-2; IV, 16675-81-3; IV picrate, 16675-82-4; IV′, 16675-31-3; monoammonium salt of 3,3′-iminodipropionic acid, 16675-33-5; acrylonitrile, 107-13-1; guanidine, 113-00-8; dimethylformamide, 68-12-2.

Acknowledgment.—This investigation was promoted by a grant from Nippon (Japan) Carbide Industries, Inc., for which the authors wish to express their deep appreciation. The authors also wish to thank Professor Masaki Ohta of the same institute for his helpful discussions. Our thanks are also extended to the staff of the microanalytical services in the Laboratory of Organic Chemistry of this institute for the microanalyses.

Cyclizations of Substituted N-(Purin-6-yl)-2-aminoethanol System[1]

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The current interest [2–6] in the internal cyclization of suitably substituted 6-aminopurine derivatives (Ia, Ib,

(1) Presented in part at the 2nd Annual Great Lakes Regional Meeting of the American Chemical Society, Milwaukee, Wis., June 1968.

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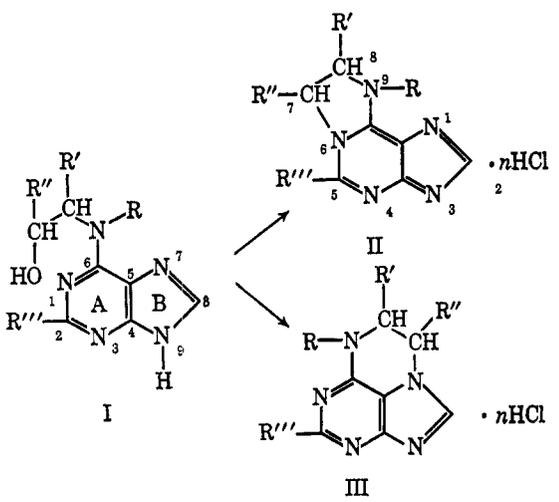
Ic) encouraged us to report our findings in this area. Compounds Id–h were used to determine if the direction of cyclization of I could be modified by changing the electrophilic center and the electron density at the nucleophilic center (Scheme I). The pendent alcohol function was varied from primary, Id, to secondary, If, to benzylic secondary, Ig, with the expectation of changing the relative rate of reaction[7] and the nature of the attacking electrophile.[7] The purine ring system, especially ring A, was made less electronegative by the introduction of a chlorine atom at the 2 position.[8] This can be seen from the pK_a values of alcohols Id (3.80) and Ie (1.82).

SCHEME I



I II III

a, R = R′ = R″ = R‴ = H; n = 1
b, R = $HOCH_2CH_2$; R′ = R″ = R‴ = H; n = 1
c, R = CH_3CH_2; R′ = R″ = R‴ = H; n = 1
d, R = R″ = R‴ = H; R′ = CH_3CH_2; n = 2
e, R = R″ = H; R′ = CH_3CH_2; R‴ = Cl; n = 1
f, R = R′ = R‴ = H; R″ = CH_3; n = 2
g, R = R′ = R‴ = H; R″ = C_6H_5; n = 2
h, R = R′ = H; R″ = C_6H_5; R‴ = Cl; n = 1

Alcohols Id–h were prepared from 6-chloropurine (IV) and 2,6-dichloropurine (V) in fair to good yields according to standard techniques available in the literature.[9–12] The displacement of the 6-chloro group in V in preference to the 2-chloro group was anticipated on the basis of their known relative reactivities.[8,13]

When primary alcohols Id and Ie and secondary benzylic alcohols Ig and Ih were treated with thionyl chloride under the described conditions (see Experimental Section), the only products isolated were 8-ethyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine dihydrochloride (IId), 5-chloro-8-ethyl-7,8-dihydro-9H-imidazo[2,1-*i*]-purine hydrochloride (IIe), 7-phenyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine dihydrochloride (IIg), and 5-chloro-7-phenyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine hydrochloride (IIh). The conversion of IIh into IIg *via* hydrogenolysis proved that the direction of cyclization was the same and substantiated the displacement of the 6-chloro group. Although the conversion of IIe into IId was not attempted, the similarities in physical properties indicated that they had cyclized in the same direction. The ultraviolet absorption correlation of Leonard, *et al.*,[14] and the dissociation constants[3,5,15,16] of all the products are consistent with cyclization occurring at N-1.

The reaction of N-(purin-6-yl)-1-amino-2-propanol (If) with thionyl chloride was studied at 79, 50, 25, and −70°. The only product isolated from the high-temperature reaction was 7-methyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine dihydrochloride (IIf). The spectral and paper chromatographic data of the isolated crude solids from the other reactions indicated that IIf was the major product.

Our results indicate that the direction of cyclization is not dependent upon temperature, nature of the electrophile, or the basicity of the nucleophile. These results can be rationalized on the basis of (1) the much greater nucleophilicity of N-1 compared with N-7, (2) the greater probability of forming a five-membered heterocyclic ring,[17,18] or (3) a combination of these effects.

Experimental Section[19]

N-(Purin-6-yl)-2-aminobutanol (Id).—To a 500-ml, one-necked, round-bottom flask equipped with a condenser were added 6-chloropurine (30 g, 0.195 mol), 2-amino-1-butanol (34.5 g, 0.39 mol, 36.8 ml), and water (200 ml). The mixture was heated at reflux temperature for 3 hr and then reduced under vacuum to a dark, viscous liquid. The oily liquid was triturated with water (170 ml) to yield crude Id (22.2 g, 55%), mp 198–201°. Crystallization from water after decolorization with charcoal gave pure Id (17.9 g, 45%), mp 165–167°. The trituration filtrate was decolorized with charcoal and reduced in volume to give solids which were crystallized from water to yield pure Id (2.2 g, 5.5%), mp 200.5–204°. Mixture melting points of the low- and high-melting forms (50:50 and 90:10 ratios) were 199–204.5 and 200–203°, respectively. The infrared spectra were identical.

An analytical sample, mp 203–206°, was prepared from water from a mixture of the two forms and had the following properties: pK_a 3.80, 10.0; ir (KBr), 3.0, 3.2, 9.2, and 9.7 μ; uv max (H_2O, pH 1.0) 273.5 mμ (ε 17,050), (pH 10) 273.0 (15,850).

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(19) The melting points were determined with a Fisher-Johns melting point apparatus or a Thomas–Hoover capillary melting point apparatus and are corrected. The microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill., or by our analytical department. The infrared spectra were determined on either a Perkin-Elmer Infracord or a Perkin-Elmer Model 521 spectrophotometer. The ultraviolet spectra were determined in aqueous solutions using a Beckman DK-2A ratio recording spectrophotometer. The nuclear magnetic resonance spectra were determined in deuterium oxide with tetramethylsilane as an external standard at 60 Mc/sec on a Varian Associates A-60 spectrometer at Simon Research Laboratory, Elgin, Ill., by Dr. W. Simon. pK_a values were obtained spectroscopically by our analytical department. Chromatograms were developed by the ascending technique with Whatman No. 1 paper. The solvent systems employed were A, *n*-butyl alcohol–acetic acid–water (4:1:1); B, isopropyl alcohol–acetic acid–water (69:1:30); C, dimethylacetamide-concentrated ammonium hydroxide–isopropyl alcohol (25:10:65); and D, 5% aqueous ammonium sulfate–isopropyl alcohol (95:5).

Anal. Calcd for $C_9H_{13}N_5O$: C, 51.8; H, 6.31; N, 33.6. Found: C, 51.8; H, 6.31; N, 33.4.

N-(2-Chloropurin-6-yl)-2-aminobutanol (Ie).—The general procedure followed in preparation of Id was used. Crude Ie (25.8 g, 100%), mp 194.5–196.5°, prepared from 2,6-dichloropurine (19.5 g, 0.104 mol), was dissolved in hot aqueous sodium hydroxide, decolorized with charcoal, and acidified to pH 6, and the precipitated solids, after cooling, were isolated to yield pure Ie (22 g, 85%), mp 210–212°. An analytical sample, mp 217–218.5°, was prepared by this same base–acid cycle and had the following properties: pK_a 1.82, 9.35; ir (KBr), 2.9 (OH), 3.0 (N–H), 7.3 (CH_3), and 9.6 μ; uv max (H_2O, pH 1) 277.5 mμ (ϵ 15,750), (pH 10) 277.5 (16,200).

Anal. Calcd for $C_9H_{12}ClN_5O$: C, 44.75; H, 5.01; N, 29.00; Cl, 14.7. Found: C, 44.70; H, 5.31; N, 29.00; Cl, 14.5.

N-(Purin-6-yl)-2-amino-1-phenylethanol (Ig).—To a 500-ml, one-necked, round-bottom flask equipped with condenser was added 6-chloropurine (10.3 g, 0.066 mol), 2-amino-1-phenylethanol (9.0 g, 0.066 mol), sodium carbonate (3.5 g, 0.033 mol), sodium hydroxide (1 pellet), and water (120 ml). The mixture was heated at reflux for 3 hr and then cooled overnight. The precipitated white solids were isolated, washed with water, and dried to yield Ig (12.1 g, 72%), mp 254–255°. The filtrate was heated for an additional 2 hr to yield impure Ig (1.8 g, 10.7%), mp 255.5–260°. An analytical sample, mp 256–257°, was prepared by crystallization from isopropyl alcohol and had the following spectral properties: ir (KBr), 2.95 (OH), 9.1, 9.4, 9.7, 13.1, and 14.3 μ; uv max (H_2O, pH 1.0) 275.0 mμ (ϵ 17,600), (pH 10) 271.0 (17,300).

Anal. Calcd for $C_{13}H_{13}N_5O$: C, 61.16; H, 5.13; N, 27.4. Found: C, 61.30; H, 5.36; N, 27.2.

N-(2-Chloropurin-6-yl)-2-amino-1-phenylethanol (Ih).—The general procedure followed in preparation of Ig was used. Crude Ih (20.1 g, 88%), mp 240–247°, prepared from 2,6-dichloropurine (15.0 g, 0.079 mol), on crystallization from a concentrated isopropyl alcohol solution afforded a higher melting form, mp 249–252°, while crystallization from a dilute isopropyl alcohol solution gave a lower melting form, mp 235–238°. Paper chromatography of the two forms in solvent systems A, B, and C and their infrared spectra showed them to be identical. The analytical sample, mp 235–238°, had the following spectral properties: ir (KBr), 3.1, 3.3, 9.2, 9.4, 9.7, 13.2, and 14.2 μ; uv max (H_2O, pH 1) 276.5 mμ (ϵ 16,250), (pH 10) 271.0 (17,520).

Anal. Calcd for $C_{13}H_{12}ClN_5O$: C, 53.89; H, 4.18; N, 24.2; Cl, 12.2. Found: C, 53.78; H, 3.97; N, 24.0; Cl, 12.2.

N-(Purin-6-yl)-1-amino-2-propanol (If).—The general procedure followed in preparation of alcohol Ig was used. Crude If (18.2 g, 41.5%), mp 214.5–219.5°, prepared from 6-chloropurine (35 g, 0.228 mol) and 1-amino-2-propanol (17.2 g, 0.23 mol), on crystallization from water gave pure If (16.6 g, 38%), mp 232.5–235.5°. Further fractionation of the filtrates afforded additional If (18.1 g, 41.0%), mp 232.5–235.5°, which had the following spectral properties: ir (KBr), 3.2, 7.25 (CH_3), and 9.3 μ; uv max (H_2O, pH 1) 272.5 mμ (ϵ 15,950), (pH 10) 273.5 (17,000). Nuclear magnetic resonance spectrum of If dissolved in deuterium oxide and treated with anhydrous hydrogen chloride showed the following peaks: δ 8.50 (s, 1, aromatic CH), 8.44 (s, 1, aromatic CH), 4.19 (m, 1, CH_2CH), 3.77 (m, 2, N-CH_2), and 1.30 ppm (d, 3, J = 6 Hz, CH–CH_3).

Anal. Calcd for $C_8H_{11}N_5O$: C, 49.73; H, 5.75; N, 36.2. Found: C, 49.70; H, 5.79; N, 36.2.

The alcohols were thoroughly dried at 90° under vacuum before use. The apparatus was flame dried, and all reactions were conducted under an atmosphere of dry nitrogen.

8-Ethyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine Dihydrochloride (IId).—To a 1-l., three-necked, round-bottom flask equipped with stirrer, reflux condenser with drying tube, gas inlet tube, and thermometer was added thionyl chloride (250 ml). Then alcohol Id (10.3 g, 0.05 mol) was added slowly to the rapidly agitated liquid, and a slight evolution of gas was noticed. The resulting mixture was heated at reflux for 18 hr, cooled in an ice bath, and then diluted with sodium-dried benzene (400 ml). The solids were isolated by filtration, washed with benzene, and dried to yield crude IId (12.3 g, 95%), mp 258–262°. A portion (6 g) of the crude product was slurried in absolute ethanol (100 ml) and treated with anhydrous hydrogen chloride to yield pure IId: mp 259–262°; pK_a 7.2; ir (KBr), 3.2–4.8 (HCl salt), 6.2, 6.7, 7.1, 7.35 (CH_3), 10.7, 12.8 μ; uv max (H_2O pH 1) 262 mμ (ϵ 13,980), (pH 7) 265 (13,050), (pH 10) 273 (15,620) and 281 (14,200); nmr (D_2O), δ 8.58 (s, 1, aromatic ring CH), 8.50 (s, 1, aromatic ring CH), 4.90–4.30 (m, 3, ring CH and CH_2), 1.80 (m, 2, J = 7 Hz, CH_2CH_3), and 0.98 ppm (t, 3, J = 7 Hz, CH_2CH_3). Paper chromatography in solvent system A showed only one product.

Anal. Calcd for $C_9H_{11}N_5 \cdot 2HCl$: C, 41.2; H, 5.00; N, 26.7. Found: C, 41.4; H, 5.08; N, 26.8.

5-Chloro-8-ethyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine Hydrochloride (IIe).—The general procedure followed in preparation of IId was used. Crude IIe (9.8 g, 91%), mp >360°, prepared from chloro alcohol Ie (10 g, 0.042 mol) at 40°, was homogeneous as indicated by paper chromatography in solvent system A. An analytical sample was prepared by recrystallization from methanol: pK_a 6.7; ir (KBr), 6.3, 6.7, 6.8, 7.0, 10.5, and 13.0 μ; uv max (H_2O, pH 1) 265 mμ (ϵ 13,670), (pH 7) 272 (11,400), (pH 10) 272.5 (15,370) and 281.5 (14,370); nmr (D_2O), δ 8.63 (s, 1, aromatic CH), 5.28–4.70 (m, 3, ring CH and CH_2), 2.16 (m, 2, J = 7 Hz, CH_2CH_3), and 1.33 (t, 3, J = 7 Hz, CH_2CH_3).

Anal. Calcd for $C_9H_{10}ClN_5 \cdot HCl$: C, 41.55; H, 4.26; N, 26.9; Cl^-, 13.6. Found: C, 41.84; H, 4.28; N, 26.5; Cl^-, 13.5.

7-Phenyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine Dihydrochloride (IIg).—The general procedure followed in preparation of IId was used. Crude IIg (4.4 g, 85%), prepared from alcohol Ig (4.0 g, 0.016 mol) at 40°, was slurried in ethanol and treated with anhydrous hydrogen chloride to yield pure IIg, mp 175° dec. Paper chromatography in solvent systems A, B, C, and D indicated one component: pK_a 6.7; ir (KBr), 3.3–4.6 (HCl salt), 6.3, 6.7, 7.1, 10.7, 11.7, 13.0, and 14.3 μ; uv max (H_2O pH 1) 262 mμ (ϵ 13,650), (pH 7) 267.5 (12,100), (pH 10) 272.5 (12,800) and (1 *N* NaOH) 281.0; nmr (D_2O), δ 8.44 (s, 1, aromatic CH), 8.13 (s, 1, aromatic CH), 7.41 (s, 5, phenyl CH), 6.19 (quadruplet, 1, J_{ab} = 8 Hz, J_{ac} = 11 Hz, C_6H_5CH–CH_2), 4.61 [d, 1, J_{ca} = 11 Hz, J_{cb} = 11 Hz, C_6H_5CH–C(H)], and 4.15 ppm [quadruplet, 1, J_{ba} = 8 Hz, J_{bc} = 11 Hz, C_6H_5CH–(H)CH].

Anal. Calcd for $C_{13}H_{11}N_5 \cdot 2HCl$: C, 50.33; H, 4.23; N, 22.6; Cl, 22.9. Found: C, 50.44; H, 4.51; N, 22.6; Cl, 22.8.

5-Chloro-7-phenyl-7,8-dihydro-9H-imidazo[2,1-*i*]purine hydrochloride (IIh).—The general procedure followed in preparation of IId was used. Pure IIh (4.8 g, 100%), mp >310°, prepared from chloro alcohol Ih (4.6 g, 0.016 mol) at 40°, was homogeneous as indicated by paper chromatography in solvent systems B and C: ir (KBr), 6.7, 7.5, 10.5, 13.1, and 14.3 μ; uv max (H_2O pH 1) 266 mμ (ϵ 12,540), (pH 7) 271.5 (10,900), (pH 10) 273.5 (12,780) and 281.5 (12,380); nmr (D_2O), δ 8.34 (s, 1, aromatic CH), 7.36 (s, 5, phenyl CH), 6.22 (quadruplet, 1, J_{ab} = 5 Hz, J_{ac} = 11 Hz, C_6H_5CH–CH_2), 4.65–5.20 (m), and 4.08 [quadruplet, J_{ba} = 5 Hz, J_{bc} = 11 Hz, C_6H_5CH–(H)CH].

Anal. Calcd for $C_{13}H_{10}ClN_5 \cdot HCl$: C, 50.66; H, 3.61; N, 22.7. Found: C, 50.45; H, 3.84; N, 22.5.

Hydrogenolysis of IIh.—A solution of IIh (1 g, 3.25 mmol) in water (150 ml) was prepared; then 10% Pd–C (0.35 g) was added; and the mixture was treated with hydrogen (20 psi) at room temperature with shaking. Theoretical hydrogen uptake was completed in 2 hr. The catalyst was removed and paper chromatography of the filtrate, IIg and IIh, in solvent systems B and D showed the major product to be IIg with small quantity of IIh. The filtrate was reduced to dryness and the dry solid contained IIg (80%) and IIh (20%) as indicated by nuclear magnetic resonance hydrogen integral analysis. The ultraviolet spectrum had the following absorptions: (pH 1) 263.5 mμ, (pH 7) 269.0, (pH 10) 273.0 and 282.

Effect of Temperature on the Reaction of Alcohol If and Thionyl Chlorides. A. At 79°.—The general procedure followed in preparation of IId was used. Pure IIf, mp 225–226° dec (251 mg, 1.01 mmol, 89%), prepared from alcohol If (220 mg, 1.14 mmol) had, after crystallization from methanol–benzene–ethyl acetate, the following spectral properties: uv max (H_2O pH 1) 262.0 mμ (ϵ 12,300), (pH 7) 266.5 (11,030), (pH 10) 272.0 (11,900); nmr spectrum (D_2O), δ 8.64 (s, 1 aromatic CH), 8.50 (s, 1, aromatic CH), 5.32 (m, 1, CH_3CH), 4.48 (t, 1, J = 11 Hz, $CHCH_2$), 3.92 (quadruplet, 1, J = 7 and 11 Hz, $CHCH_2$), and 1.78 (d, 3, J = 7 Hz, $CHCH_3$).

Anal. Calcd for $C_8H_9N_5 \cdot 2HCl$: C, 38.72; H, 4.47; N, 28.23. Found: C, 38.56; H, 4.52; N, 28.08.

B. At 50°.—The above sequence was repeated on alcohol If (2.0 g, 0.01 mol). Paper chromatography in solvent systems A and D of the crude product (2.5 g, mp 220–223°dec, softening from 212°) showed the presence of two ultraviolet absorbing spots; the minor one could be related to the R_f value of the starting alcohol. The nmr hydrogen integral analysis of the pendent

methyl groups showed the mixture to be composed of alcohol If (≅10%) and IIf (≅90%). The spectral properties of this mixture (pK_a 7.2) were as follows: uv max (H_2O, pH 1) 263.5 mμ (ε 12,700), (pH 7) 266.0, (pH 10) 270.5 (13,200) and 280.0.

C. At 25°.—The above sequence was repeated on alcohol If (1.0 g). The nmr hydrogen integral analysis of the pendent methyl groups of the crude product (0.9 g) showed it to contain alcohol If (≅10%), IIf (≅55–60%), and a third unidentified material XI (≅30–35%). The mixture had the following element analysis: C, 38.56; H, 4.52; Cl, 25.7; Cl^-, 18.6. These results suggest that the third component (XI) contains covalently bonded chlorine.

D. At −70°.—The above sequence was repeated on alcohol If (1.0 g). The nmr analysis of the isolated crude product (0.95 g) indicated it to be composed of If (60%) and IIf (40%).

Registry No.—Id, 16958-58-0; Ie, 16958-59-1; If, 16958-60-4; Ig, 16958-61-5; Ih, 16969-36-1; IId, 16958-64-8; IIe, 16958-65-9; IIf, 16958-62-6; IIg, 16958-63-7; IIh, 16958-66-0.

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Self-Condensation of Anthranilic Acid

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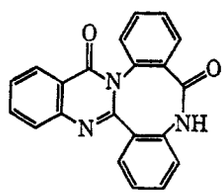
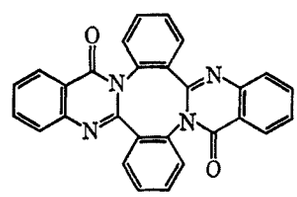
Anthranilic acid undergoes condensation with a wide variety of compounds[1,2] but its self-condensation reaction has not been reported as yet. The present communication concerns studies on the self-condensation products of anthranilic acid.

Heating anthranilic acid with phosphorous pentoxide in refluxing xylene furnished[3] a compound with mp 285° as the major product together with a minor compound (yield, 2%) with mp >360°.

On the basis of its molecular formula, $C_{21}H_{13}N_3O_2$ (M^+339), spectral data [uv λ_{max}^{EtOH} 280 and 306 mμ (log ε 4.53 and 4.30) and ir λ_{max}^{Nujol} 5.9, 6.05, and 6.3 μ], and, most importantly, its mode of formation, the major compound was assigned the structure I, a trimer of anthranilic acid. This is further supported by the nmr spectrum[4] of the compound which shows all of the 13 protons in its molecule appearing as a broad multiplet between δ 7.2 and 8.0.



I



II

The minor component, mp >360°, shows spectral properties (uv, ir, and nmr) very much similar to those of I. These observations conjointly with its molecular formula, $C_{28}H_{16}N_4O_2$ (M^+440), led us to propose structure II for the compound, a tetramer of anthranilic acid. The fact that II could also be obtained by heating I with additional anthranilic acid provided final confirmation for the assigned structure of the minor component.

Experimental Section[5]

Anthranilic acid (0.5 g) in dry xylene (8 ml) was refluxed for 3 hr over phosphorous pentoxide (1.5 g). The reaction mixture after cooling was poured over crushed ice and diluted with benzene. The benzene layer was then separated and extracted with three 40-ml portions of 6 *N* hydrochloric acid. The total acidic extract was subsequently basified with ammonia and treated with three 60-ml portions of chloroform. The chloroform extract was then washed and dried. The residue upon concentration of the chloroform extract was chromatographed over alumina. Benzene–chloroform (9:1) eluate gave II (yield, 0.01 g) which crystallized from methanol as granules: mp >360°; λ_{max}^{EtOH} 280 and 306 mμ (log ε 4.26 and 4.05); λ_{max}^{Nujol} 5.95, 6.25, 6.30, and 6.40 μ; nmr 16 H (broad multiplet) between δ 7.4 and 8.05.

Anal. Calcd for $C_{28}H_{16}N_4O_2$: C, 76.36; H, 3.64; N, 12.72; O, 7.27. Found: C, 76.20; H, 3.83; N, 12.66; O, 7.50.

The chloroform eluate on removal of solvent gave I (yield, 0.30 g) crystallized from a chloroform–acetone mixture, mp 285°.

Anal. Calcd for $C_{21}H_{13}N_3O_2$: C, 74.33; H, 3.83; N, 14.15; O, 9.43. Found: C, 74.20; H, 3.51; N, 14.20; O, 9.70.

Compound I (0.65 g) mixed with anthranilic acid (0.30 g) was refluxed in dry xylene (10 ml) for 3 hr. The reaction mixture was treated as above. The basic portion in chloroform extract after concentration was chromatographed and gave II (0.09 g) together with I (0.50 g).

Registry No.—I, 17-223-74-4; II, 17-223-75-5; anthranilic acid, 118-92-3.

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(1) Wl. Baczynski and St. V. Niementowski, *Ber.*, **52**, 461 (1919).

(2) Br. Pawlewski, *ibid.*, **38**, 136 (1905).

(3) These compounds were also obtained for the first time during the synthesis of deoxyvasicinone from anthranilic acid and γ-aminobutyric acid. The major compound, designated as DVQ, was also assigned a tentative structure mainly on the basis of spectral evidence which in the present communication is being revised: A. Chatterjee and M. Ganguly, *Phytochemistry*, **7**, 307 (1968).

(4) The nmr spectra were taken in DMSO in a 60-Mc instrument with tetramethylsilane as the internal standard.

(5) Melting points were determined on a Kofler block and are uncorrected.