Reaction of 6-Aminopyrimidin-4-ones with Diethyl Ethoxymethylenemalonate in Several Media: Synthesis of Pyrido[2,3-*d*]pyrimidines [1]

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Reactions of 6-amino-3,4-dihydro-2-methoxy-4-oxopyrimidine **1** and its 3-methyl derivative **2**, with diethyl ethoxymethylenemalonate (EMME) are discussed in this paper. These reactions have been carried out in the following media: under fusion, ethanol, sodium methoxide/methanol, sodium ethoxide:ethanol and acetic acid media. In acetic medium, mixtures of products proceeding from *C*-alkylation and *N*-alkylation were obtained, while in the remaining conditions only products of *N*-alkylation were obtained.

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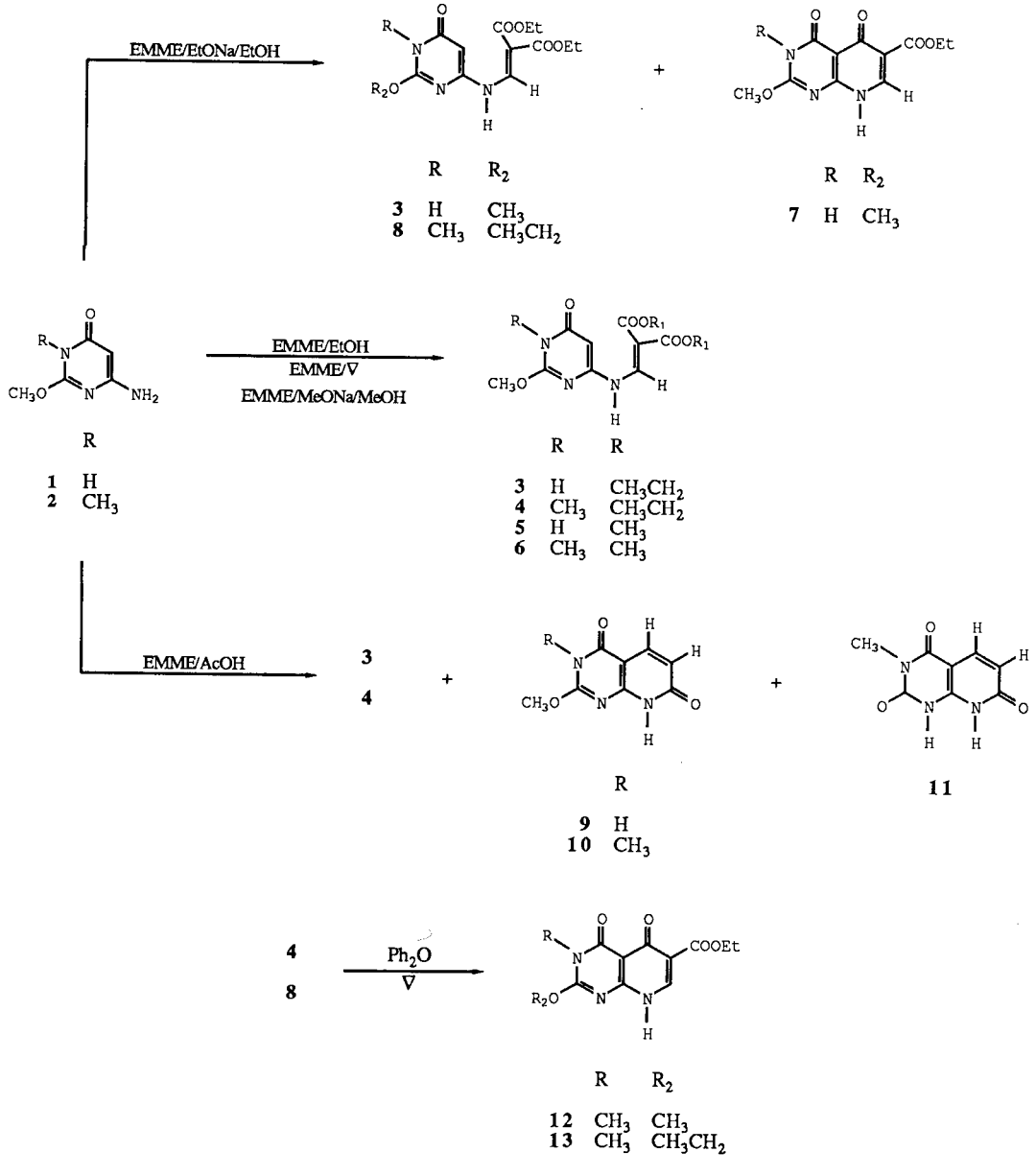
Pyrido[2,3-*d*]pyrimidines and their nucleoside derivatives have interesting biological properties [2,3]. From all the synthetic methods described in bibliography what appears to give the best results is the one using the reaction of 6-aminopyrimidines with EMME [4]. In this reaction the medium used determines the class of com-



pounds obtained [5].

We are concerned with the synthesis of pyrido[2,3-*d*]-pyrimidines not only because of its potential antitumor [6] and antibacterial [7] properties but also because they can be used in the synthesis of nucleoside homologues of sangyvamicine and tubercidine.

Condensation of **1** and **2** with double molar amounts of EMME at 165-170° afforded the corresponding *N*-alkylated products **3** and **4**. The same products were obtained by refluxing **1** and **2** with EMME using ethanol as the solvent. The highest yields were obtained in this case.

Treatment of **1** and **2** with double molar amounts of EMME and a molar amount of sodium methoxide in methanol, provides selective *N*-alkylation; besides this, a transesterification [8] of the carboxyethyl functions takes place, the last yielding **5** and **6** respectively. The substitution of ethoxy groups for the methoxy group could be substantiated by means of ^{1}H-nmr and ^{13}C-nmr.

When the base employed is sodium ethoxide in ethanol, the isolated products are different depending on the starting compounds (**1** or **2**). Whereas **1** yields **3**, (as their main product) and **7**, compound **2** allowed us to obtain **8**, whose lone structural difference with **4** is the substitution of C_2-OEt for C_2-OMe, which was revealed by spectroscopic methods.

The formation of **7** should proceed to the **3** which could ɔe explained by the fact that the ethoxide medium can avour the loss of the N-3 proton in compound **3**, this esulting in a net charge on the pyrimidine ring and mak-ng possible the side chain cyclization to the pyridone by lectrophilic attack to some of the ester functions.

In addition to the *N*-alkylation products **3** and **4**, *C*-lkylation compounds **9** and **10** were also obtained when he reaction was carried out in refluxing acetic acid nedium. Formation of **3** and **4** in the reaction under liscussion shows that this is not regioselective (contrary to which occurs in other cases [5]) for compounds **1** and **2**, since we obtained at the same time products resulting from *N*-alkylation with a subsequent decarboxylation which yields **9** and **10**. Compound **11** is obtained from **10** by the loss of the -CH_3 group of the C-2 atom of the pyrimidine ring. This is a consequence of the acidic conditions [9] of the reaction.

Finally, the thermal cyclizations of **4** and **8** were carried out in refluxing diphenyl ether, giving of **12** and **13** respectively.

EXPERIMENTAL

Melting points were determined in a Melting Point Apparatus Gallenkamp and are uncorrected. Proton nuclear magnetic resonance spectra were recorded with a Hitachi Perkin-Elmer R-600 and a Bruker AM-300 spectrometers using tetramethylsilane as internal standard. Chemical shifts were expressed in δ values. The following abbreviations were used: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad. Carbon-13 nuclear magnetic resonance spectra were recorded with a Bruker AM-300 spectrometer. Ultraviolet spectra were recorded with a Perkin-Elmer Lambda 5 spectrophotometer. Infrared spectra were recorded with a Beckman 4250 spectrophotometer (potassium bromide pellets). The analysis of C, H and N have been performed in the "Servicios Técnicos de la Universidad de Granada" using a Perkin-Elmer 240C equipment. Mass spectra were recorded with a Hewlett-Packard A-5988 spectrometer. Thin layer chromatography (tlc) was run on silica gel Merck 60G, using ethyl acetate-dichloromethane (4:1) as eluent. Finally column chromatography was done on Kieselgel 60 silica gel (70-230 mesh) using the solvent systems indicated in each case.

Reaction in Ethanol.

a) Two g (14 mmoles) of **1** in ethanol (40 ml) was heated under reflux to solution, then 5.6 ml (28 mmoles) of EMME was added. The reaction mixture was refluxed and stirred for 4 days. After this time, the white precipitate which formed was filtered hot and recrystallized from ethanol to afford diethyl *N*-(3,4-dihydro-2-methoxy-4-oxo-6-pyrimidinyl)aminomethylenemalonate **3**, yield 1.56 g (36%), mp 198°; ^{1}H-nmr (deuteriochloroform): 12.5 (1H, br, exchangeable with deuterium oxide, N(1)-H), 10.9 (1H, d, J = 12 Hz, C(6)-NH, exchangeable with deuterium oxide), 8.9 (1H, d, J = 12 Hz, NH-C*H*, with deuterium oxide s), 5.5 (1H, s, C(5)-H), 4.2 (4H, m, COOC*H*$_2$-CH$_3$), 4.0 (3H, s, CH$_3$-O), 1.4 (6H, dt, COOCH$_2$-C*H*$_3$); ^{13}C-nmr (deuteriochloroform): 168.2, 167.0 (*C*OOEt), 165.1 (C-4), 158.3 (C-2), 157.4 (C-6), 89.2 (C-5), 55.6 (CH$_3$-O), 148.6 (*C*H=NH), 98.4 (=*C*(COOET)$_2$), 65.0, 60.6 (-*C*H$_2$-CH$_3$), 14.3, 14.2 (CH$_2$-*C*H$_3$); ir: 3.450 (N-H), 3.100 (C-H), 1.740 (C=O), 1.690 (C=O), 1660 (C=C), 1620, 1590 (C=N, C=C); ms: m/z 311 (65%) M$^+$; uv (methanol): λ max (nm) (ϵ) 216 (10,000), 269 (11,000), 318 (38,500).

Anal. Calcd. for $C_{14}H_{19}N_3O_6$: C, 51.69; H, 5.88; N, 12.92. Found: C, 51.50; H, 5.85; N, 12.97.

b) Compound **2** (3.1 g, 20 mmoles) in ethanol (100 ml) was heated under reflux to solution, then 8.0 ml (40 mmoles) of EMME was added. The reaction mixture was refluxed and stirred for one day. After this time the mixture was evaporated to dryness and the residue was refluxed with 100 ml of diethyl ether for 3 hours and then the hot suspension was filtered. The clear filtrate afforded a white solid which was identified as diethyl *N*-(3,4-dihydro-2-methoxy-3-methyl-4-oxo-6-pyrimidinyl)aminomethylenemalonate **4** yield 1.40 g (22%), mp 138-139°; ^{1}H-nmr (deuteriochloroform): 10.8 (1H, d, br, J = 14 Hz, exchangeable with deuterium oxide, C(6)-N*H*-CH=), 8.9 (1H, d, J = 14 Hz, with deuterium oxide s, NH-C*H*=), 5.6 (1H, s, C(5)-H), 4.2 (4H, m, COO-C*H*$_2$-CH$_3$), 4.0 (3H, s, CH$_3$-O), 3.4 (3H, s, N(3)-CH$_3$), 1.4 (6H, dt, COO-CH$_2$-C*H*$_3$); ^{13}C-nmr (deuteriochloroform): 168.2, 165.3 (*C*OOEt), 163.4 (C-4), 157.5 (C-2), 154.1 (C-6), 89.0 (C-5), 56.0 (*C*H$_3$-O), 27.7 (*C*H$_3$-N(3)), 149.0 (-*C*H=C(COOEt)$_2$), 97.6 (-CH=*C*(COOEt)$_2$), 60.8, 60.4 (COO-*C*H$_2$-CH$_3$)$_2$, 14.2, 14.1 (COO-CH$_2$-*C*H$_3$)$_2$; ir: 3440 (N-H), 3090 (C-H), 1725 (C=O), 1690 (C=O), 1660 (C=C), 1630, 1530 (C=N, C=C); ms: m/z 325 (65%) M$^+$; uv (methanol): λ max (nm) (ϵ) 216 (10,000), 269 (11,000), 318 (38,400).

Anal. Calcd. for $C_{14}H_{19}N_3O_6$: C, 51.69; H, 5.88; N, 12.92; Found: C, 51.50; H, 5.85; N, 12.97.

Reaction by Fusion.

a) Compound **1** (1.1 g, 7 mmoles) was heated with 2.8 ml (14 mmoles) of EMME at an oil bath temperature of 165-170° for 3

hours. The melt was cooled and refluxed with 50 ml of chloroform for 15 minutes and filtered. This process was repeated twice. The chloroform solution was evaporated to dryness and the remaining solid was crystallized from ethanol. The compound obtained was identified as **3**, yield 0.55 g (25%), mp 196-197°.

b) One g (6.4 moles) of **2** was heated with 1.3 ml (12.8 mmoles) of EMME at an oil bath temperature 165-170° for 2 hours. The melt was cooled and refluxed with 50 ml of diethyl ether for 4 hours. The suspension was filtered and the clear solution obtained was treated with charcoal, filtered and kept at 5° overnight. The white precipitate which formed was filtered, washed with diethyl ether and identified as **4**, yield 0.39 g (38%), mp 138°.

Reaction in Sodium Methoxide/Methanol.

a) To 25 ml of methanol containing 0.16 g (7 mmoles) of sodium 1.06 g (7 mmoles) of **1** and 3.0 ml (14 mmoles) of EMME was added. The solution obtained was refluxed for 24 hours. The separated precipitate was removed by filtration. The mother liquors were evaporated under reduced pressure and the syrupy residue was dissolved in the minimal amount of water, neutralized with acetic acid and the resulting solid was crystallized from ethanol-chloroform and identified as dimethyl *N*-(3,4-dihydro-2-methoxy-4-oxo-6-pyrimidinyl)aminomethylenemalonate **5**, yield 0.63 g (32%), mp 230° dec; ^{1}H-nmr (deuteriochloroform): 10.6 (1H, d, br, J = 12 Hz, exchangeable with deuterium oxide; C(6)-N*H*-), 8.9 (1H, d, J = 12 Hz, NH-C*H*=, with deuterium oxide s), 5.5 (1H, s, C(5)-H), 4.0 (3H, s, CH_3-O), 3.8 (6H, s, $(COOCH_3)_2$; ^{13}C-nmr (deuteriochloroform): 165.5 (C-4), 158.3 (C-2), 157.2 (C-6), 89.6 (C-5), 168.7, 166.6 (*C*OOMe), 149.1 (-*C*H=C(COOMe)$_2$), 97.8 (-CH=*C*(COOMe)$_2$), 55.8 (CH_3-O), 53.1, 52.8 (=C(COO*C*H$_3$)$_2$); ir: 3400 (N-H), 1730 (C=O), 1680 (C=O), 1660 (C=O), 1610, 1580 (C=N, C=C); ms: m/z 283 (90%) M$^+$; uv (methanol): λ max (nm) (ε) 216 (9,200), 267 (8,900), 320 (16,300).

Anal. Calcd. for $C_{11}H_{13}N_3O_6$: C, 46.64; H, 4.63; N, 14.84. Found: C, 46.44; H, 4.47; N, 14.59.

b) To 50 ml of methanol containing 0.34 g (15 mmoles) of sodium, 2.33 g (15 mmoles) of **2** and 6 ml (30 mmoles) of EMME were added. The solution was refluxed for 24 hours, and the precipitate formed was removed by filtration. The mother liquors were evaporated under reduced pressure and the syrupy residue was dissolved in the minimal amount of water, neutralized with acetic acid and the resulting solid was crystallized from water and identified as dimethyl *N*-(3,4-dihydro-3-methyl-2-methoxy-4-oxo-6-pyrimidinyl)aminomethylenemalonate **6**, yield 1.1 g (24%), mp 161°; ^{1}H-nmr (deuteriochloroform): 10.7 (1H, d, br, J = 13 Hz, exchangeable with deuterium oxide, C(6)-N*H*-), 8.7 (1H, d, J = 13 Hz, with deuterium oxide s, C(6)-NH-C*H*=), 5.5 (1H, s, C(5)-H), 4.0 (3H, s, CH_3-O), 3.7 (6H, s, $(COOCH_3)_2$), 3.7 (3H, s, CH_3-N); ^{13}C-nmr (deuteriochloroform): 168.4, 165.4 (*C*OOMe), 163.2 (C-4), 157.4 (C-2), 154.0 (C-6), 89.2 (C-5), 56.0 (*C*H$_3$-O), 27.6 (*C*H$_3$-N), 61.8, 51.7 (COO*C*H$_3$)$_2$, 96.7 (CH=*C*(COOMe)$_2$, 149.1 (NH-*C*H=); ir: 3280 (N-H), 3085 (C-H), 1730 (C=O), 1690 (C=O), 1670 (C=C), 1630, 1560 (C=N, C=C); ms, m/z: 297 (99%) M$^+$; uv (methanol): λ max (nm) (ε) 216 (10,600), 269 (11,400), 318 (18,500).

Anal. Calcd. for $C_{12}H_{15}N_3O_6$: C, 48.48; H, 5.09; N, 14.14. Found: C, 48.15; H, 4.91; N, 13.99.

Reaction in Sodium Ethoxide/Ethanol.

a) To 50 ml of ethanol containing 0.32 g (14 mmoles) of sodium, 2.0 g (14 mmoles) of **1** and 5.6 ml (28 mmoles) of EMME were added. The solution obtained was refluxed for 48 hours. After this time, two products were detected by tlc. The precipitate formed was removed by filtration. The mother liquors were treated in the same manner as in the case of the reaction with sodium methoxide/methanol, obtaining 0.86 g of **3**.

The solid obtained, in the first filtration, was dissolved in the minimal amount of water, neutralized with acetic acid and the precipitate was filtered. This solid was fractioned by column chromatography using dichloromethane-diethyl ether (1:1) solution as eluent. The order of elution was the following: 0.75 g of **3** and 6-carbethoxy-3,4,5,8-tetrahydro-2-methoxy-4,5-dioxopyrido-[2,3-*d*]pyrimidine **7**, yield 0.50 g (14%); mp 230-232°; ^{1}H-nmr (DMSO-d$_6$): 12.6 (2H, s, br, exchangeable with deuterium oxide, N(3)-H, N(8)-H), 8.5 (1H, s, C(7)-H), 4.3 (2H, cp, J = 7.2 Hz, COOC*H*$_2$-CH$_3$), 4.0 (3H, s, C*H*$_3$-O), 1.3 (3H, t, J = 7.2 Hz, COOCH$_2$-C*H*$_3$); ^{13}C-nmr (DMSO-d$_6$): 159.6 (C-2), 160.4 (C-4), 97.5 (C-4a), 159.8 (C-5), 115.7 (C-6), 141.0 (C-7), 157 (C-8a), 163.4 (*C*OOEt), 60.1 (COO*C*H$_2$-), 10.1 (COOCH$_2$-*C*H$_3$), 55.5 (*C*H$_3$-O); ir: 3400 (N-H), 1710 (C=O), 1640 (C=O), 1600, 1560 (C=N, C=C); ms, m/z: 265 (40%) M$^+$; uv (methanol): λ max (nm) (ε) 218 (12,200), 246 (7,000), 281 (5,900), 338 (12,000).

Anal. Calcd. for $C_{11}H_{11}N_3O_5$: C, 49.85; H, 4.18; N, 15.85. Found: C, 48.93; H, 4.10; N, 15.60.

b) To 50 ml of ethanol containing 0.34 g (15 mmoles) of sodium, 2.33 g (15 mmoles) of **2** and 6.0 ml (30 mmoles) of EMME were added. The solution obtained was refluxed for 2 hours (at this time no starting product was detected by tlc). The reaction mixture was kept at 4° overnight and the resulting solid was filtered, recrystallized from diethyl ether and identified as diethyl *N*-(2-ethoxy-3,4-dihydro-3-methyl-4-oxo-6-pyrimidinyl)-aminomethylenemalonate **8**, yield 1.9 g (38%), mp 122°; ^{1}H-nmr (deuteriochloroform): 10.8 (1H, d, br, J = 13 Hz, exchangeable with deuterium oxide, C(6)-N*H*-), 8.8 (1H, d, J = 13 Hz, with deuterium oxide s, -NH-C*H*=), 5.6 (1H, s, C(5)-H), 4.3 (6H, m, -C*H*$_2$-O), 3.4 (3H, s, CH$_3$-N(3)), 1.3 (9H, m, C*H*$_3$-CH$_2$-O-); ^{13}C-nmr (deuteriochloroform); 163.5 (C-4), 157 (C-2), 154.3 (C-6), 88.9 (C-5), 27.7 (*C*H$_3$-N(3)), 148.8 (NH-*C*H=), 97.5 (CH=*C*(COOEt)$_2$), 65.6 (CH$_3$-*C*H$_2$-O-C(2)), 60.8, 60.4 (CH$_3$-*C*H$_2$-OCO-), 14.2 (*C*H$_3$-CH$_2$-O); ir: 3250 (N-H), 3090 (C-H), 1725 (C=O), 1690 (C=O), 1650 (C=C), 1630, 1560 (C=N, C=C); ms, m/z: 339 (26%) M$^+$; uv (methanol): λ max (nm) (ε) 217 (10,200), 269 (10,900), 318 (37,000).

Anal. Calcd. for $C_{15}H_{21}N_3O_6$: N, 53.09; H, 6.24; N, 12.38. Found: C, 54.41; H, 6.12; N, 12.53.

Reaction in Acetic Acid.

a) One g (7 mmoles) of **1** and 1.5 ml (7.7 mmoles) of EMME were refluxed 24 hours in glacial acetic acid (10 ml). After this time, two products were detected by tlc. The hot separated precipitate was removed by filtration, digested in ethanol-water and identified as 4,7-dioxo-2-methoxy-3,4,7,8-tetrahydropyrido-[2,3-*d*]pyrimidine **9**, yield 0.91 g (68%), mp 300°; ^{1}H-nmr (DMSO-d$_6$): 12.0 (1H, s, br, exchangeable with deuterium oxide, N(8)-H), 7.9 (1H, d, J = 10 Hz, C(5)-H), 6.2 (1H, d, J = 10 Hz, C(6)-H, 4.0 (3H, s, CH$_3$-O); ^{13}C-nmr (DMSO-d$_6$): 158.0 (C-2), 163.4 (C-4), 97.8 (C-4a), 136.1 (C-5), 116.2 (C-6), 160.4 (C-7), 155.0 (C-8a), 55.1 (*C*H$_3$-O); ir: 3400 (N-H), 3100 (C-H), 1680-1610 (C=O; C=N), 1575 (C=C); ms: m/z 193 (90%) M$^+$; uv (methanol): λ max (nm) (ε) 219 (20,900), 281 (15,200), 314 (16,900), 327 (12,400).

Anal. Calcd. for $C_8H_7N_3O_3$: C, 49.74; H, 3.65; N, 21.76. Found: C, 49.94; H, 3.48; N, 21.79.

The mother liquors were evaporated to dryness under reduced pressure by adding methanol and evaporating several times. The residue was refluxed with 100 ml of diethyl ether for 1 hour and the clear solution obtained kept at 5° overnight. The formed precipitate was filtered, washed with cool diethyl ether and identified as **3** (0.14 g).

b) Two g (13 mmoles) of **2** and 2.9 ml (14.3 mmoles) of EMME were refluxed for 24 hours in glacial acetic acid (20 ml). After this time, complex mixture was detected by tlc. The hot suspension was filtered. The reaction mixture was kept at 5° overnight. The formed precipitate was filtered, recrystallized from acetic acid and identified as 1,2,3,4,7,8-hexahydro-3-methyl-2,4,7-trioxopyrido[2,3-*d*]pyrimidine **11**, yield 0.35 g (13%), mp 265°; ^{1}H-nmr (DMSO-d_6): 8.6 (1H, d, J = 8 Hz, C(5)-H), 6.6 (1H, d, J = 8 Hz, C(6)-H), 3.4 (3H, s, CH_3-N); ir: 3080 (C-H), 1710-1670 (C=O), 1630, 1550 (C=N, C=C); ms: m/z 193 (100%) M$^+$.

Anal. Calcd. for $C_8H_7N_3O_3$: C, 49.74; H, 3.65; N, 21.76. Found: C, 49.80; H, 3.70; N, 22.00.

The mother liquors were evaporated to dryness under reduced pressure by adding methanol and evaporating several times. The residue was refluxed with 100 ml of diethyl ether for 1 hour and then filtered. The solid obtained was fractioned by column chromatography on silica gel using hexane-diethyl ether (1:1) solution as eluent. The order of elution was: 0.6 g of **4** and 3,4,7,8-tetrahydro-2-methoxy-3-methyl-2,4,7-trioxopyrido[2,3-*d*]-pyrimidine **10**, yield 0.15 g (5%), mp 227°; ^{1}H-nmr (deuteriochloroform): 11.2 (1H, s, br, exchangeable with deuterium oxide), N(8)-H), 8.5 (1H, d, J = 10 Hz, C(5)-H), 6.5 (1H, d, J = 10 Hz, C(6)-H), 4.2 (3H, s, CH_3-O), 3.5 (3H, s, CH_3-N); ir: 3180 (N-H), 1690-1630 (C=O, C=N), 158 (C=C).

Anal. Calcd. for $C_9H_9N_3O_3$: C, 52.17; H, 4.38; N, 20.28. Found: C, 52.01; H, 4.52; N, 19.98.

From the diethyl ether soluble portion several crops of 0.61 g of **4** were isolated.

Cyclization in Diphenyl Ether.

a) One g (3 mmoles) of **4** was added to 6 ml of boiling diphenyl ether. The mixture was heated to reflux for 1 hour, cooled, and diluted with 30 ml of diethyl ether. The precipitate was collected, washed with diethyl ether and recrystallized from ethanol/chloroform. This compound was identified as 6-carbethoxy-3,4,5,8-tetrahydro-2-methoxy-3-methyl-4,5-dioxopyrido[2,3-*d*]pyrimidine **12**, yield 0.50 g (60%), mp 206-207°; ^{1}H-nmr (deuteriochloroform); 15.3 (1H, s, br, exchangeable with deuterium oxide, N(8)-H), 8.6 (1H, s, C(7)-H), 4.4 (2H, m, COO-C*H*$_2$-), 3.9 (3H, s, CH_3-O), 3.4 (3H, s, CH_3-N), 1.4 (3H, t, $COOCH_2$-C*H*$_3$); ^{13}C-nmr (deuteriochloroform): 156.4 (C-2), 161.7 (C-4), 97.1 (C-4a), 171.8 (C-5), 106.5 (C-6), 150.6 (C-7), 156.0 (C-8a), 168.0 (*C*OOEt), 40.3 *C*H$_3$-O), 27.4 (*C*H$_3$-N), 62.0 (COO-*C*H$_2$-), 14.3 ($COOCH_2$-*C*H$_3$); ir: 3060 (C-H), 1700 (C=O), 1635 (C=O, C=N), 1580 (C=C); ms, m/z: 279 (16%) M$^+$; uv: λ max (nm) (ε): 231 (16,600), 254 (31,200), 288 (13,900), 327 (3,800).

Anal. Calcd. for $C_{12}H_{13}N_3O_5$: C, 51.61; H, 4.69; N, 15.05. Found: C, 51.48; H, 4.49; N, 15.59.

b) Compound **8** (0.4 g, 1.2 mmoles) was added to 3 ml of boiling diphenyl ether. The mixture was refluxed for 1 hour, cooled and diluted with 10 ml of diethyl ether. The precipitate was collected, washed with diethyl ether and recrystallized from ethanol. This compound was identified as 6-carbethoxy-2-ethoxy-3,4,5,8-tetrahydro-3-methyl-4,5-dioxopyrido[2,3-*d*]pyrimidine **13**, yield 0.26 g (74%), mp 209-211°; ^{1}H-nmr (DMSO-d_6): 12 (1H, s, br, exchangeable with deuterium oxide, N(8)-H), 9.0 (1H, s, C(7)-H), 4.3 (4H, m, COO-CH_2-CH_3), 3.2 (3H, s, CH_3-N), 1.4 (t, COO-CH_2-C*H*$_3$); ir: 3050 (C-H), 1690 (C=O), 1630 (C=O, C=N, C=C); ms: m/z 293 (46%) M$^+$; uv: λ max (nm) (ε) 234 (19,700), 254 (32,100), 288 (14,100), 324 (3,900).

Anal. Calcd. for $C_{13}H_{15}N_3O_5$: C, 53.24; H, 5.15; N, 14.33. Found: C, 53.20; H, 4.94; N, 14.70.

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