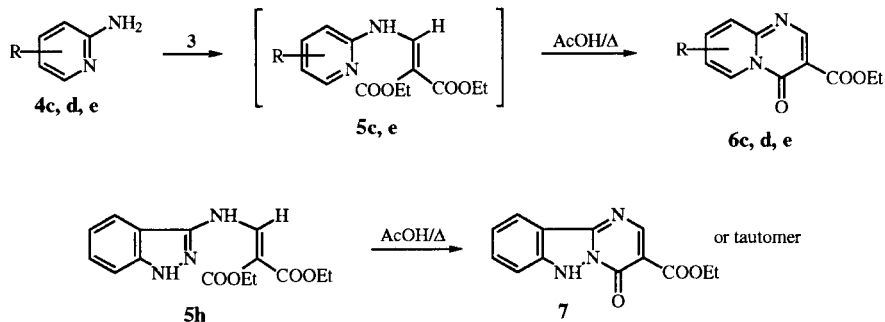


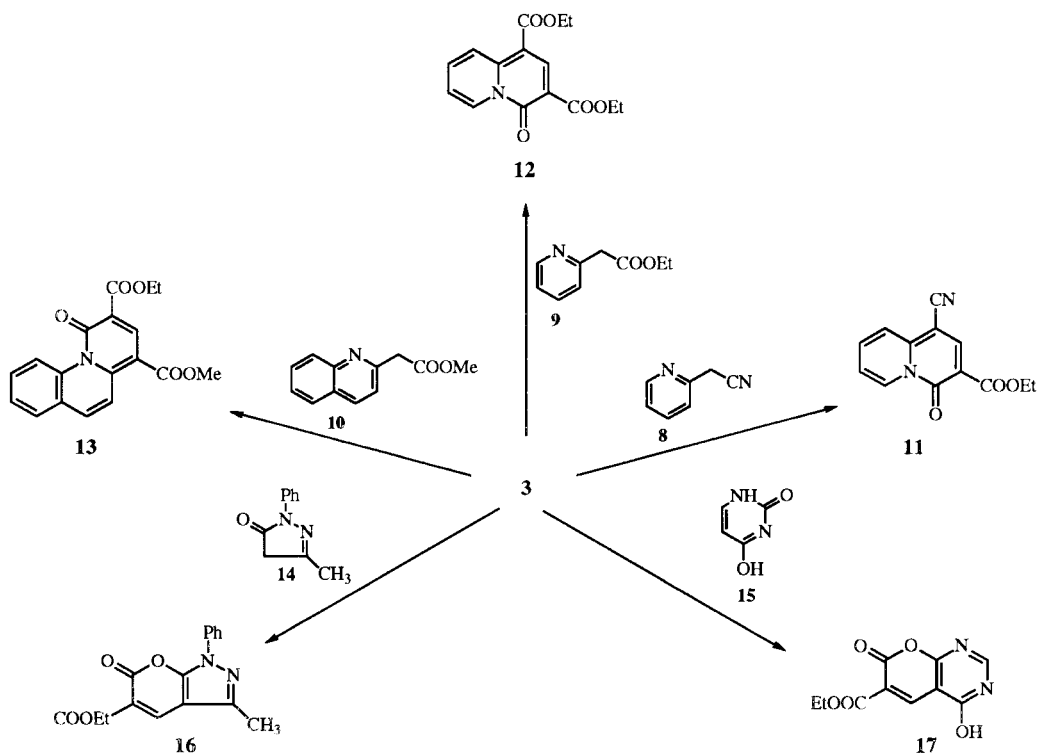
Scheme 3



quinolizine (**11**), 1,3-(diethoxycarbonyl)-4-oxo-4*H*-quinolizine (**12**), and 2-ethoxycarbonyl-3-methoxycarbonyl-4-oxo-4*H*-benzo[*c*]quinolizine (**13**), were formed, respectively. Furthermore, also heterocyclic compounds with a methylene or potential methylene group incorporated in the cyclic system, such as 3-methyl-1-phenylpyrazol-4(5*H*)-one (**14**) and uracil (**15**), react in acetic acid to give fused pyranones, 5-ethoxycarbonyl-3-methyl-1-phenyl-6-oxo-1(6*H*)-pyrano[2,3-*c*]pyrazole (**16**) and 6-ethoxycarbonyl-4-hydroxy-7-oxo-7*H*-pyrano[2,3-*d*]pyrimidine (**17**), respectively (Scheme 4).

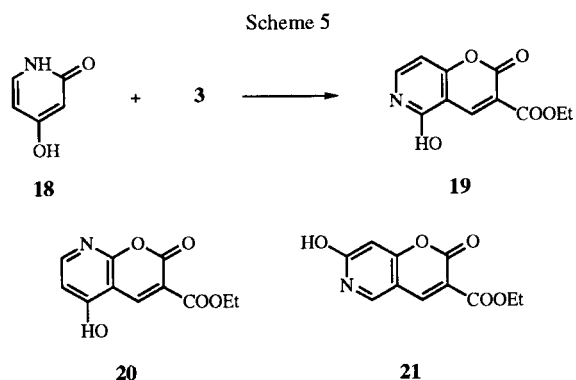
dependent on the initial attack of the reagent either at position 3 or 5, and further cyclization to adjacent hydroxy group attached either at position 2 or 4. On the basis of the magnitude of the coupling constant, $J = 7.0$ Hz, between two protons at $\delta = 6.32$ ppm and $\delta = 7.75$ ppm, characteristic for ortho protons, the structure **21** was eliminated. The chemical shifts for these two protons are characteristic for structure **19**, and are in agreement with those found in other derivatives of this system [7], while the pyridine protons of the isomeric structure **20** would appear at around $\delta = 7.5$ ppm and

Scheme 4

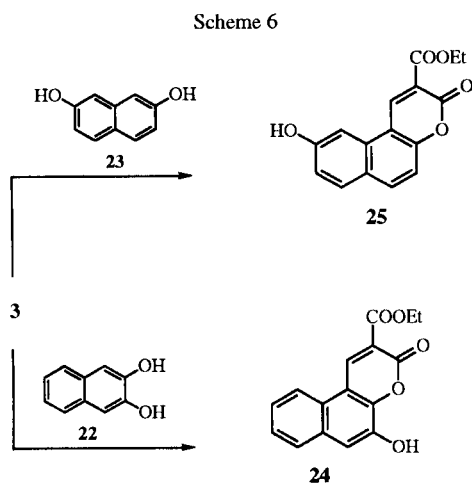


In the case of 4-hydroxypyridin-2(1*H*)-one (**18**) three isomeric structure **19**, **20**, and **21** can be formed,

$\delta = 8.5$ ppm, as shown in some other derivatives of this system [8] (Scheme 5).



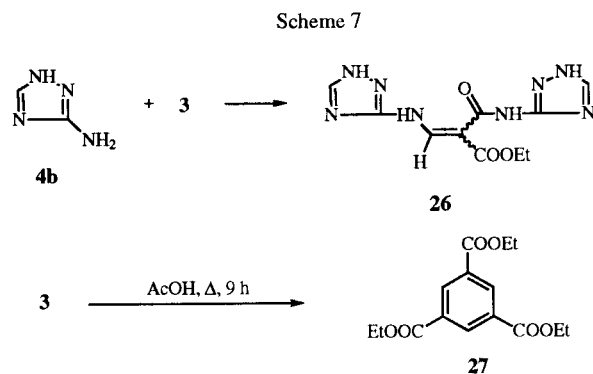
Compound **3** reacts also with dihydroxynaphthalenes, such as 2,3-dihydroxy **22** and 2,7-dihydroxynaphthalene (**23**) at position 1, in boiling acetic acid, to give 2-ethoxycarbonyl-5-hydroxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran (**24**) and 2-ethoxycarbonyl-9-hydroxy-3-oxo-3*H*-naphtho[2,1-*b*]pyran (**25**), respectively (Scheme 6).



During these investigations, we observed, that by the heating of 3-amino-1,2,4-triazole (**4b**) with the compound **3** in acetic acid, in the presence of catalytic amounts of hydrobromic acid (36%), under reflux for seven hours, one of the ester groups was transformed to give ethyl 3-[(1,2,4-triazolyl-3)amino]-2-[(1,2,4-triazolyl-3)carbamoyl]propenoate (**26**) in 34% yield. No attempts were made in order to establish the orientation around the double bond.

The reagent **3** is thermally unstable. By heating in acetic acid under reflux for nine hours 1,3,5-triethoxycarbonylbenzene (**27**) was formed in 11% yield. This compound was always found as an impurity present in the reaction mixtures when longer heating was required (Scheme 7).

The structures of all new compounds were determined on the basis of elemental analyses for C, H, and N, and ¹H nmr spectra.



EXPERIMENTAL

Melting points were taken on a Kofler micro hot stage. The ¹H nmr spectra were obtained on a Varian EM 360 L spectrometer, ir spectra on a Perkin-Elmer 1310 instrument, and microanalyses for C, H and N on Perkin-Elmer Analyser 2400.

Diethyl *N,N*-dimethylaminomethylenemalonate (**3**) was prepared according to the procedure described in the literature [5].

Diethyl *N*-(Isoxazolyl-3)aminomethylenemalonate (**5a**).

3-Aminoisoxazole (**4a**, 216 mg, 0.0026 mole) and diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 1.376 g, 0.0064 mole) were dissolved in acetic acid (3 ml) and the solution was allowed to stand at room temperature for one day. Then one half of the solvent was evaporated *in vacuo* and the mixture was allowed to stand at 5° for 24 hours. The precipitate was collected by filtration to give **5a** in 32% yield, mp 62-63° (from ethanol/water); ¹H nmr (deuteriochloroform): δ 1.30 (3H, t, CH₃CH₂), 1.33 (3H, t, CH₃CH₂), 4.22 (2H, q, CH₂CH₃), 4.26 (2H, q, CH₂CH₃), 6.25 (1H, d, H_{4'}), 8.32 (1H, d, H_{5'}), 8.49 (1H, d, CHNH), 10.87 (1H, br d, NHCH), J_{CH₃CH₂} = 7.0 Hz, J_{H_{4'}H_{5'}} = 2.0 Hz, J_{NHCH} = 13.0 Hz.

Anal. Calcd. for C₁₁H₁₄N₂O₅: C, 51.97; H, 5.55; N, 11.02. Found: C, 52.74; H, 5.64; N, 11.04.

In the same manner the following compounds were prepared:

Diethyl *N*-(3-Methylpyridinyl-2)aminomethylenemalonate (**5c**).

This compound was prepared from 2-amino-3-methylpyridine (**4c**, 1.000 g, 0.0093 mole) and diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 2.000 g, 0.0128 mole) by heating at 70° for 16 hours to give **5c** in 35% yield, mp 64-65° (from ethanol/water), lit [9] mp 61-62°; ¹H nmr (deuteriochloroform): δ 1.23 (3H, t, CH₃CH₂), 1.26 (3H, t, CH₃CH₂), 2.28 (3H, s, 3'-Me), 4.17 (2H, q, CH₂CH₃), 4.20 (2H, q, CH₂CH₃), 7.09 (1H, t, H_{5'}), 7.70 (1H, dd, H_{4'}), 8.22 (1H, dd, H_{6'}), 9.10 (1H, d, CHNH), 11.00 (1H, br d, NHCH), J_{CH₃CH₂} = 7.0 Hz, J_{H_{4'}H_{5'}} = 5.0 Hz, J_{H_{5'}H_{6'}} = 5.0 Hz, J_{H_{4'}H_{6'}} = 2.0 Hz, J_{NHCH} = 13.0 Hz.

Anal. Calcd. for C₁₄H₁₈N₂O₄: C, 60.42; H, 6.52; N, 10.07. Found: C, 60.66; H, 6.42; N, 10.46.

Diethyl *N*-(3-Hydroxypyridinyl-2)aminomethylenemalonate (**5e**).

This compound was prepared from 2-amino-3-hydroxypyridine (**4e**, 600 mg, 0.0055 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 1.376 g, 0.0064 mole) by heating

at 60° for 8 hours, to give **5e** in 30% yield, mp 179-185° (from ethanol); ¹H nmr (deuteriochloroform): δ 1.33 (3H, t, CH₃CH₂), 1.36 (3H, t, CH₃CH₂), 4.35 (2H, q, CH₂CH₃), 4.39 (2H, q, CH₂CH₃), 7.00 (1H, t, H_{5'}), 7.30 (1H, dd, H_{4'}), 7.39 (1H, s, OH), 8.06 (1H, dd, H_{6'}), 9.40 (1H, d, CHNH), 11.63 (1H, br d, NHCH), J_{CH₃CH₂} = 7.0 Hz, J_{H_{4'}H_{5'}} = 5.0 Hz, J_{H_{5'}H_{6'}} = 5.0 Hz, J_{H_{4'}H_{6'}} = 2.0 Hz, J_{NHCH} = 13.0 Hz.

Anal. Calcd. for C₁₃H₁₆N₂O₅: C, 55.71; H, 5.75; N, 10.00. Found: C, 56.00; H, 5.67; N, 10.27.

Diethyl *N*-(6-Chloropyridazinyl-3)aminomethylenemalonate (**5f**).

This compound was prepared from 3-amino-6-chloropyridazine (**4f**, 300 mg, 0.0026 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 1.376 g, 0.0064 mole) under reflux for 7 hours to give **5f** in 13% yield, mp 164-166° (from ethanol/water), lit [10] mp 169°; ¹H nmr (deuteriochloroform): δ 1.30 (3H, t, CH₃CH₂), 1.35 (3H, t, CH₃CH₂), 4.26 (2H, q, CH₂CH₃), 4.31 (2H, q, CH₂CH₃), 7.10 (1H, s, H_{4'}), 7.49 (1H, d, H_{5'}), 9.18 (1H, d, CHNH), 11.44 (1H, br d, NHCH), J_{CH₃CH₂} = 7.0 Hz, J_{H_{4'}H_{5'}} = 9.0 Hz, J_{NHCH} = 13.0 Hz.

Anal. Calcd. for C₁₂H₁₄ClN₃O₄: C, 48.09; H, 4.71; N, 14.02. Found C, 48.41; H, 4.62; N, 13.98.

Diethyl *N*-(Pyrimidinyl-2)aminomethylenemalonate (**5g**).

This compound was prepared from 2-aminopyrimidine (**4g**, 400 mg, 0.0042 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 1.376 g, 0.0064 mole) by heating at 100° for 8 hours to give **5g** in 56% yield, mp 114-116° (from ethanol/water), lit [11] mp 113°; ¹H nmr (deuteriochloroform): δ 1.31 (3H, t, CH₃CH₂), 1.35 (3H, t, CH₃CH₂), 4.29 (2H, q, CH₂CH₃), 4.34 (2H, q, CH₂CH₃), 7.00 (1H, t, H_{5'}), 8.58 (2H, d, H_{4'} and H_{6'}), 9.12 (1H, d, CHNH), 11.00 (1H, br d, NHCH), J_{CH₃CH₂} = 7.0 Hz, J_{H_{4'}H_{5'}} = J_{H_{5'}H_{6'}} = 5.0 Hz, J_{NHCH} = 13.0 Hz.

Anal. Calcd. for C₁₂H₁₅N₃O₄: C, 54.33; H, 5.70; N, 15.84. Found: C, 54.63; H, 5.63; N, 15.65.

Diethyl *N*-(Indazolyl-3)aminomethylenemalonate (**5h**).

This compound was prepared from 3-aminoindazole (**4h**, 400 mg, 0.003 mole) and diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 1.376 g, 0.0064 mole) was allowed to stand at 20° for 24 hours to give **5h** in 49% yield, mp 167-169° (from ethanol), lit [12] mp 153-156°; ¹H nmr (deuteriochloroform): δ 1.33 (3H, t, CH₃CH₂), 1.39 (3H, t, CH₃CH₂), 4.29 (2H, q, CH₂CH₃), 4.35 (2H, q, CH₂CH₃), 7.00-7.80 (4H, m, Ar), 8.97 (1H, d, CHNH), 10.26 (1H, broad peak, H_{1'}), 11.44 (1H, br d, NHCH), J_{CH₃CH₂} = 7.0 Hz, J_{NHCH} = 13.0 Hz.

Anal. Calcd. for C₁₅H₁₇N₃O₄: C, 59.40; H, 5.65; N, 13.85. Found: C, 59.49; H, 5.53; N, 13.89.

3-Ethoxycarbonyl-9-methyl-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**6c**).

A mixture of diethyl *N*-(3-methylpyridinyl-2)aminomethylenemalonate (**5c**, 300 mg, 0.0011 mole) and acetic acid (3 ml) was heated under reflux for 2 hours, the solvent was evaporated *in vacuo* and the solid residue recrystallized from ethyl acetate to give **6c** in 60% yield, mp 153-155° (from ethyl acetate), lit [9] mp 149-150°; ¹H nmr (deuteriochloroform): δ 1.40 (3H, t, CH₃CH₂), 2.68 (3H, s, 9-Me), 4.43 (2H, q, CH₂CH₃), 7.24 (1H, dd, H₇), 7.81 (1H, dd, H₈), 9.00 (1H, s, H₂), 9.20 (1H, dd, H₆), J_{CH₃CH₂} = 7.0 Hz, J_{H₆H₇} = 7.0 Hz, J_{H₆H₈} = 1.0 Hz, J_{H₇H₈} = 7.0 Hz.

Anal. Calcd. for C₁₂H₁₂N₂O₃: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.11; H, 4.94; N, 12.21.

3-Ethoxycarbonyl-8-methyl-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**6d**).

A mixture of 2-amino-4-methylpyridine (**4d**, 540 mg, 0.005 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for 90 minutes, two thirds of the solvent evaporated *in vacuo* and cooled. The precipitate was collected by filtration and washed with water and diethyl ether to give **6d** in 35% yield, mp 165-169° (from toluene), lit [13] mp 171-172°; ¹H nmr (deuteriochloroform): δ 1.42 (3H, t, CH₃CH₂), 2.59 (3H, s, 8-Me), 4.46 (2H, q, CH₂CH₃), 7.20 (1H, br d, H₇), 7.61 (1H, br s, H₉), 9.08 (1H, s, H₂), 9.22 (1H, br d, H₆), J_{CH₃CH₂} = 7.0 Hz, J_{H₆H₇} = 7.0 Hz.

Anal. Calcd. for C₁₂H₁₂N₂O₃: C, 62.06; H, 5.21; N, 12.06. Found: C, 62.16; H, 5.10; N, 11.94.

3-Ethoxycarbonyl-9-hydroxy-4-oxo-4*H*-pyrido[1,2-*a*]pyrimidine (**6e**).

A mixture of diethyl *N*-(3-methylpyridinyl-2)aminomethylenemalonate (**5e**, 200 mg, 0.0007 mole) and acetic acid (3 ml) was heated under reflux for 8 hours. Then the reaction mixture was cooled and some water was added. The precipitate was collected by filtration and washed with water and diethyl ether to give **6e** in 78% yield, mp 171-173° (from ethanol); ¹H nmr (deuteriochloroform): δ 1.41 (3H, t, CH₃CH₂), 4.44 (2H, q, CH₂CH₃), 6.95-7.55 (3H, m, H₇, H₈ and OH), 8.80 (1H, dd, H₆), 8.99 (1H, s, H₂), J_{CH₃CH₂} = 7.0 Hz, J_{H₆H₇} = 7.0 Hz, J_{H₆H₈} = 2.0 Hz, J_{H₇H₈} = 7.0 Hz.

Anal. Calcd. for C₁₁H₁₀N₂O₄: C, 56.41; H, 4.30; N, 11.96. Found: C, 56.70; H, 4.13; N, 11.90.

3-Ethoxycarbonyl-4-oxo-4(6*H*)-pyrimido[1,2-*b*]indazole (**7**).

A mixture of diethyl *N*-(indazolyl-3)aminomethylenemalonate (**5h**, 303 mg, 0.001 mole) and acetic acid (5 ml) was heated under reflux for 6 hours, cooled and the precipitate collected by filtration to give **7** in 31% yield, mp 280-310° dec (from DMSO/water), lit [12] mp 315°; ¹H nmr (deuteriochloroform) δ 1.08 (3H, t, CH₃CH₂), 4.16 (2H, q, CH₂CH₃), 7.10-8.10 (4H, m, H₇, H₈, H₉ and H₁₀), 8.83 (1H, s, H₂), J_{CH₃CH₂} = 7.0 Hz.

Anal. Calcd. for C₁₃H₁₁N₃O₃: C, 60.70; H, 4.31; N, 16.33. Found: C, 60.94; H, 4.19; N, 16.54.

1-Cyano-3-ethoxycarbonyl-4-oxo-4*H*-quinolizine (**11**).

A solution of ethyl 2-pyridylacetate (**8**, 500 mg, 0.0042 mole) and diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) in acetic acid (5 ml) was allowed to stand at room temperature for 10 days, the precipitate collected by filtration and washed with water and diethyl ether to give **11** in 84% yield, mp 179-181° (from ethanol), lit [14] mp 174°; ¹H nmr (deuteriochloroform): δ 1.39 (3H, t, CH₃CH₂), 4.42 (2H, q, CH₂CH₃), 7.46 (1H, m, H₇), 8.05 (2H, m, H₈ and H₉), 8.73 (1H, s, H₂), 9.55 (1H, dd, H₆), J_{CH₃CH₂} = 7.0 Hz, J_{H₆H₇} = 7.0 Hz, J_{H₆H₈} = 1.5 Hz.

Anal. Calcd. for C₁₃H₁₀N₂O₃: C, 64.46; H, 4.16; N, 11.56. Found C, 64.78; H, 3.96; N, 11.75.

1,3-Diethoxycarbonyl-4-oxo-4*H*-quinolizine (**12**).

A mixture of ethyl 2-pyridylacetate (**9**, 800 mg, 0.0049 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated at 60° for 5 hours, cooled, the precipitate collected by filtration and washed with water and

diethyl ether to give **12** in 64% yield, mp 127-128° (from ethanol), lit [15] mp 131-132°; ¹H nmr (deuteriochloroform): δ 1.43 (6H, t, CH₃CH₂), 4.38 (2H, q, CH₂CH₃), 4.42 (2H, q, CH₂CH₃), 7.35 (1H, ddd, H₇), 7.90 (1H, ddd, H₈), 9.20 (1H, s, H₂), 9.50 (2H, dd, H₆ and H₉), J_{CH₃CH₂} = 7.0 Hz, J_{H₆H₇} = 8.0 Hz, J_{H₆H₈} = 2.0 Hz, J_{H₇H₈} = 6.0 Hz, J_{H₈H₉} = 8.0 Hz.

Anal. Calcd. for C₁₅H₁₅NO₅: C, 62.28; H, 5.23; N, 4.84. Found: C, 62.50; H, 5.08; N, 5.21.

2-Ethoxycarbonyl-3-methoxycarbonyl-1-oxo-1*H*-benz[*c*]quinoxaline **13**.

A mixture of methyl 2-quinolylacetate (**10**, 90%, 700 mg, 0.0036 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (3 ml) was heated at 60° for 10 hours. Then one half of the solvent was evaporated *in vacuo*, some water and ethanol was added and the mixture was left at 5° for several days. The precipitate was collected by filtration and washed with water and diethyl ether to give **13** in 22% yield, mp 146-148° (from ethanol); ¹H nmr (deuteriochloroform): δ 1.41 (3H, t, CH₃CH₂), 3.95 (3H, s, OMe), 4.45 (2H, q, CH₂CH₃), 7.65 (4H, m, H₅, H₇, H₈ and H₉), 8.91 (1H, s, H₃), 9.02 (1H, d, H₆), 9.39 (1H, m, H₁₀), J_{CH₃CH₂} = 7.0 Hz, J_{H₅H₆} = 6.0 Hz.

Anal. Calcd. for C₁₈H₁₅NO₅: C, 66.45; H, 4.65; N, 4.31. Found: C, 66.52; H, 4.48; N, 4.71.

5-Ethoxycarbonyl-3-methyl-1-phenyl-6-oxo-1(6*H*)-pyrano[2,3-*c*]pyrazole (**16**).

A mixture of 3-methyl-1-phenyl-4(5*H*)-pyrazolone (**14**, 500 mg, 0.0029 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for one hour. The reaction mixture was then cooled, some water was added, the precipitate collected by filtration and washed with water and diethyl ether to give **17** in 82% yield, mp 148-168° (from ethanol); ¹H nmr (deuteriochloroform): δ 1.37 (3H, t, CH₃CH₂), 2.45 (3H, s, 3-Me), 4.39 (2H, q, CH₂CH₃), 7.20-8.10 (5H, m, Ph), 8.60 (1H, s, H₄), J_{CH₃CH₂} = 7.0 Hz.

Anal. Calcd. for C₁₆H₁₄N₂O₄: C, 64.43; H, 4.73; N, 9.39. Found: C, 64.79; H, 4.68; N, 9.25.

6-Ethoxycarbonyl-4-hydroxy-7-oxo-7*H*-pyrano[2,3-*d*]pyrimidine (**17**).

A mixture of 4,6-dihydroxypyrimidine (**15**, 450 mg, 0.004 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for 3 hours. The reaction mixture was then cooled, three quarters of the solvent were evaporated *in vacuo*, some water was added, the precipitate collected by filtration and washed with water and diethyl ether to give **17** in 53% yield, mp 213-215° (from ethanol), lit [16] mp 210-213°; ¹H nmr (DMSO-*d*₆): δ 1.31 (3H, t, CH₃CH₂), 4.29 (2H, q, CH₂CH₃), 8.55 (1H, s, H₅), 8.56 (1H, s, H₂), J_{CH₃CH₂} = 7.0 Hz.

Anal. Calcd. for C₁₀H₈N₂O₅: C, 50.86; H, 3.41; N, 11.86. Found: C, 51.20; H, 3.33; N, 11.59.

3-Ethoxycarbonyl-5-hydroxy-2-oxo-2*H*-pyrano[4,3-*b*]pyridine (**19**).

A mixture of 2,4-dihydroxypyridine (**18**, 350 mg, 0.0032 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for 45 minutes, cooled, and the precipitate collected by filtration and washed with water and diethyl ether to give **19** in 94% yield, mp 245-265° dec (from ethanol); ¹H nmr (DMSO-*d*₆): δ 1.30 (3H, t,

CH₃CH₂), 4.21 (2H, q, CH₂CH₃), 6.32 (1H, d, H₈), 7.75 (1H, d, H₇), 8.51 (1H, s, H₄), 13.15 (1H, br s, OH), J_{CH₃CH₂} = 7.0 Hz, J_{H₇H₈} = 7.0 Hz.

Anal. Calcd. for C₁₁H₉NO₅: C, 56.18; H, 3.86; N, 5.95. Found: C, 56.27; H, 3.74; N, 6.12.

2-Ethoxycarbonyl-5-hydroxy-3-oxo-3*H*-naphtho[2,1-*b*]pyrane (**24**).

A mixture of 2,3-dihydroxynaphthalene (**22**, 300 mg, 0.002 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for 7 hours. The reaction mixture was then cooled, some water was added, the precipitate collected by filtration and washed with water and diethyl ether to give **24** in 27% yield, mp 213-215° (from ethanol); ¹H nmr (DMSO-*d*₆): δ 1.34 (3H, t, CH₃CH₂), 4.31 (2H, q, CH₂CH₃), 7.30 (4H, m, H₇, H₈, H₉, and H₁₀), 8.39 (1H, br s, H₆), 9.30 (1H, s, H₁), 10.71 (1H, s, OH), J_{CH₃CH₂} = 7.0 Hz.

Anal. Calcd. for C₁₆H₁₂O₅: C, 67.60; H, 4.26. Found: C, 67.45; H, 4.07.

2-Ethoxycarbonyl-9-hydroxy-3-oxo-3*H*-naphtho[2,1-*b*]pyrane (**25**).

A mixture of 2,7-dihydroxynaphthalene (**23**, 300 mg, 0.002 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for 7 hours. The reaction mixture was then cooled, some water was added, the precipitate collected by filtration and washed with water and diethyl ether to give **25** in 72% yield, mp 214-217° dec (from ethanol); ¹H nmr (DMSO-*d*₆): δ 1.37 (3H, t, CH₃CH₂), 4.31 (2H, q, CH₂CH₃), 7.17 (1H, d, H₆), 7.29 (1H, d, H₇), 7.65 (1H, d, H₁₀), 7.91 (1H, s, H₅), 8.16 (1H, dd, H₈), 9.09 (1H, s, H₁), 10.30 (1H, s, OH), J_{CH₃CH₂} = 7.0 Hz, J_{H₅H₆} = 9.0 Hz, J_{H₇H₈} = 9.0 Hz, J_{H₈H₁₀} = 2 Hz.

Anal. Calcd. for C₁₆H₁₂O₅: C, 67.60; H, 4.26. Found: C, 67.31; H, 4.00.

Ethyl 2-[(1,2,4-Triazolyl-3)carbamoyl]-3-[(1,2,4-triazolyl-3)-amino]propenoate (**26**).

A mixture of 3-amino-1,2,4-triazole (**4b**, 160 mg, 0.0019 mole), diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0032 mole), acetic acid (3 ml) and the solution of hydrogen bromide in acetic acid (33% in acetic acid, a few drops) was heated at 100° for 6 hours. Then three quarters of the solvent were evaporated *in vacuo* and the reaction mixture was cooled. The precipitate was collected by filtration and washed with water and diethyl ether to give **26** in 34% yield, mp 190-196° (from ethanol/ethyl acetate); ¹H nmr (DMSO-*d*₆): δ 1.29 (3H, t, CH₃CH₂), 4.24 (2H, q, CH₂CH₃), 7.4 (4H, br s, NH+H₂O), 7.81 (1H, s, CHNH), 8.26 (1H, s, H₅), 8.67 (1H, s, H₅), J_{CH₃CH₂} = 7.0 Hz.

Anal. Calcd. for C₁₀H₁₂N₈O₃: C, 41.10; H, 4.14; N, 38.34. Found: C, 41.08; H, 4.06; N, 38.31.

1,3,5-Triethoxycarbonylbenzene (**27**).

A mixture of diethyl *N,N*-dimethylaminomethylenemalonate (**3**, 0.0064 mole) and acetic acid (5 ml) was heated under reflux for 16 hours. Then three quarters of the solvent were evaporated *in vacuo*, cooled and some water was added. The precipitate was collected by filtration and washed with water and diethyl ether to give **27** in 11% yield, mp 130-135° (from ethanol water), lit [17] mp 133-134°; ¹H nmr (DMSO-*d*₆): δ 1.44 (3H, t, CH₃CH₂), 4.44 (2H, q, CH₂CH₃), 8.86 (1H, s, Ar), J_{CH₂CH₃} = 7.0 Hz.

Anal. Calcd. for C₁₅H₁₈O₆: C, 61.22; H, 6.16. Found: C, 61.55; H, 6.08.

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