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Ethyl Esters of Malonanilic Acids. Synthesis and Pyrolysis

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Abstract: The pyrolysis under 170-220°C or boiling in DMF of malonanilic acids ethyl esters (2) is accompanied by formation of malonic acids symmetric dianilides (7) with high yields. A possible mechanism for this transformation has been suggested.

INTRODUCTION

Ethyl esters of malonanilic acids are valuable semi-products in the synthesis of numerous aromatic[1] and heterocyclic[2] compounds with wide spectrum of biological activity.

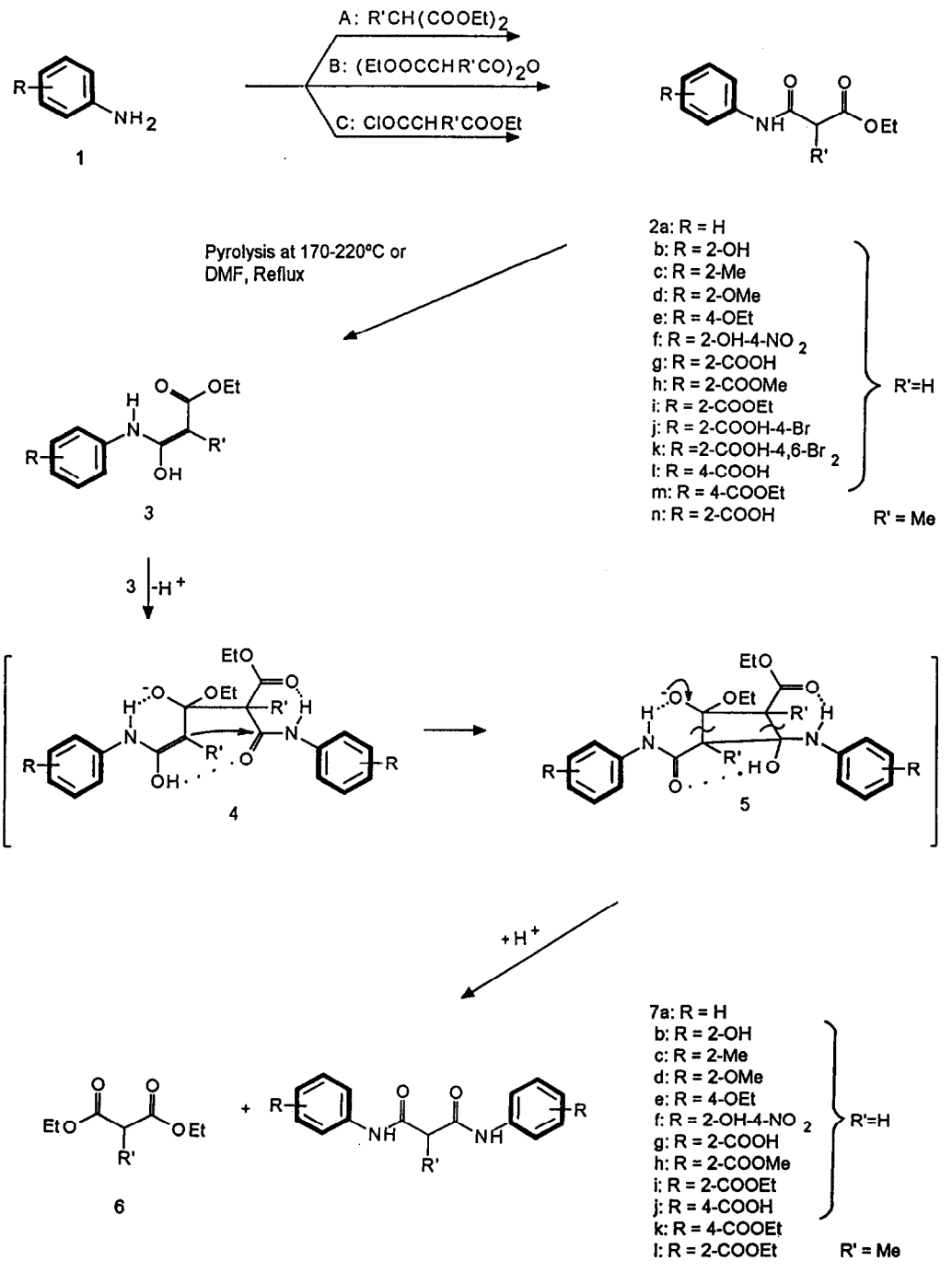
At present while obtaining these substances arylamines are subjected to interact with various malonic acids derivatives, e.g. chlorides[3,4] or anhydrides[1f,4] of malonic acids monoethyl esters, but the most frequent interaction is the most available and cheapest diethyl malonates[1a,b;5]. However, acylation of aromatic amines by diethyl malonates both in equimolar ratio and in the excess of the later is practically always accompanied with undesired side-reaction, i.e. the formation of malonic acids symmetric dianilides. Previously[4] we've made an effort to explain this fact due to more marked electrophilic properties of ethoxycarbonyl group of malonanilic acids ethyl esters as compared to diethyl malonate. These properties were caused by electron density shift to benzene ring which results in easier amidation of these compounds than that of malonic ester.

RESULTS AND DISCUSSION

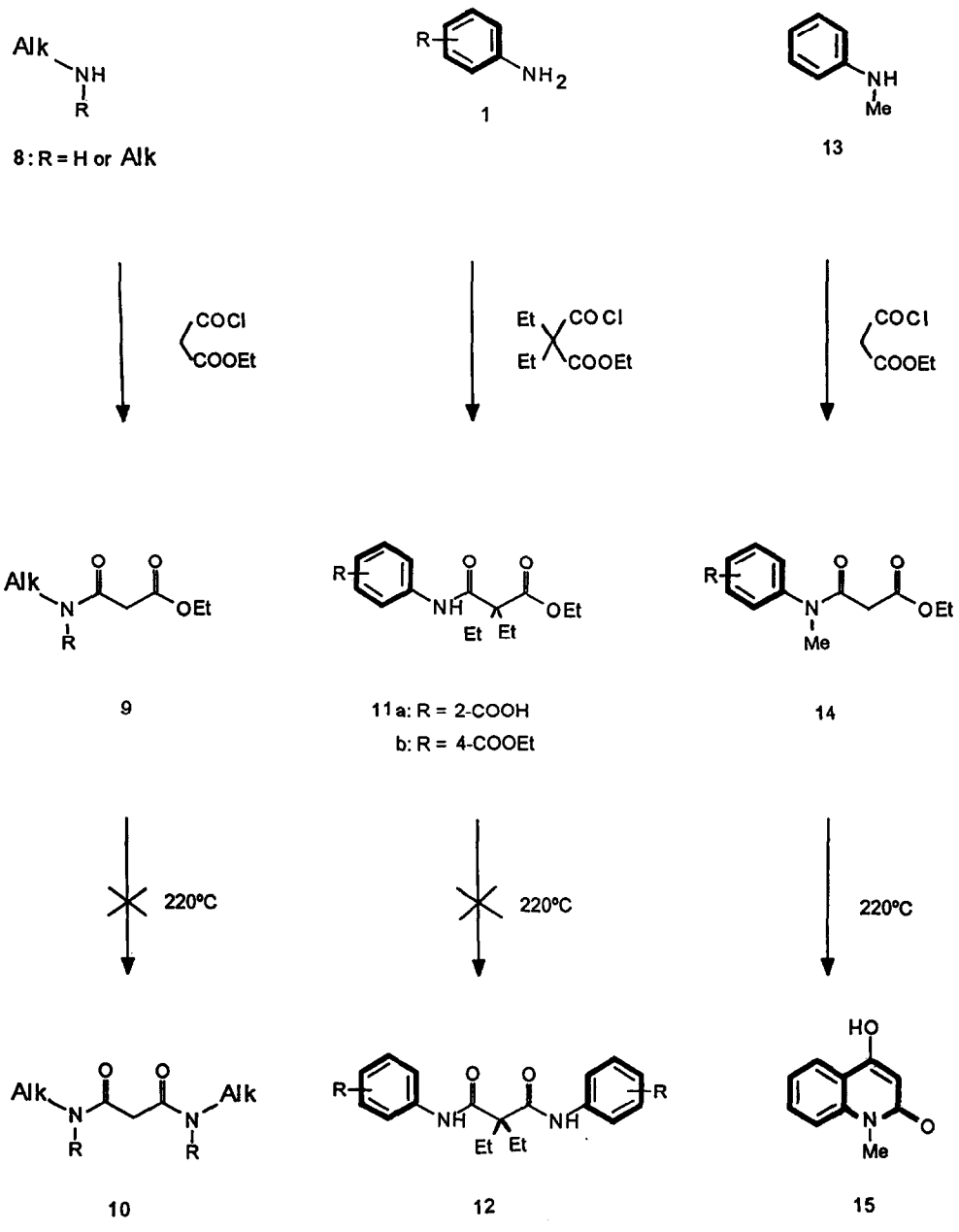
The results of our research given below allow to conclude that the mechanism of the formation of malonic acids symmetric dianilides may be also somehow different.

The malonic esters pyrolysis[6] is known to be accompanied with ethoxycarbonyl group decomposition. However, the corresponding dianilides (7) can be synthesized with high yields by boiling in DMF or by heating of previously obtained malonanilic acids ethyl esters (2) to 170-220°C without any solvent irrespective of substituents in aromatic ring. It has been experimentally determined that the necessary condition of their formation was the presence of proton in amide function and at least one proton in methylene group of malonic acid. This fact allows to suggest that the reaction includes intermolecular interaction stage of enolic forms (3) where carbonyl atom of carbon in ester group being as electrophile and carbon atom of methylene group of

Scheme 1


A: R'CH(COOEt)2
B: (EtOOCCHR'CO)2O
C: ClOCCHR'COOEt
1
2a: R = H
b: R = 2-OH
c: R = 2-Me
d: R = 2-OMe
e: R = 4-OEt
f: R = 2-OH-4-NO2
g: R = 2-COOH
h: R = 2-COOMe
i: R = 2-COOEt
j: R = 2-COOH-4-Br
k: R =2-COOH-4,6-Br2
l: R = 4-COOH
m: R = 4-COOEt
n: R = 2-COOH
R'=H
R' = Me
Pyrolysis at 170-220°C or
DMF, Reflux
3
-H+
4
5
+H+
6
7a: R = H
b: R = 2-OH
c: R = 2-Me
d: R = 2-OMe
e: R = 4-OEt
f: R = 2-OH-4-NO2
g: R = 2-COOH
h: R = 2-COOMe
i: R = 2-COOEt
j: R = 4-COOH
k: R = 4-COOEt
l: R = 2-COOEt
R'=H
R' = Me

Scheme 2


Alk
NH
R
8: R = H or Alk
R
NH2
1
NH
Me
13
COCl
COOEt
Et
CO Cl
Et
COOEt
COCl
COOEt
Alk
N
R
O
O
OEt
9
R
NH
O
O
OEt
Et Et
11a: R = 2-COOH
b: R = 4-COOEt
R
N
Me
O
O
OEt
14
220°C
220°C
220°C
Alk
N
R
O
O
N
R
Alk
10
R
NH
O
O
NH
R
Et Et
12
HO
N
Me
O
15

malonic acid as nucleophile.

The continuation of the reaction is likely to pass through 4-member cyclic transition state **(5)** and lead to diethyl malonates **(6)** and dianilides **(7)** in the end (Scheme 1).

The indirect confirmation of enol **(3)** presence in this reaction is that there are no changes in ethyl esters of malonic acid alkyl (or dialkyl) amides **(9)** under the same conditions as well as in monoesters anilides of dialkyl-substituted malonic acids **(11)** while ethyl ester of N-methylmalonanilic acid **(14)** closes the ring in 1-methyl-2-oxo-4-hydroxyquinoline **(15)** (Scheme 2).

The reaction mechanism can be hardly explained by the ability of malonic acid derivatives to form stable carbanions because in the case of 2-carbalkoxyanilides **(2h,i)** it would be inevitably accompanied by intramolecular cyclization according to Dieckmann condensation[1b,7]. Radicals are unlikely to form since the reaction appeared to be non-sensitive to the action of inhibitors of radical processes, in particular hydroquinone.

As a results of these investigations the acylation of arylamines by equimolar quantity of diethyl malonate in suitable solvent or without it under the temperature of the reaction mixture being not higher than 160°C can be recommended as an available method of the synthesis of malonanilic acids ethyl esters. If it's impossible to use diethyl malonate as a acylating agent in such conditions more electrophilic reagents should be used such as chlorides or anhydrides of malonic acids monoethyl esters.

EXPERIMENTAL SECTION

All melting points are uncorrected. ^{1}H NMR spectra were recorded at 100 MHz on a Bruker WP-100 SY spectrometer in DMSO-d_6 or $CDCl_3$ using tetramethylsilane as an internal standard (0.00 ppm), and chemical shifts are expressed as δ values. Coupling constants (J) are given in hertz. Elemental analyses for all new compounds were in satisfactory agreement with the calculated values (C,H,N ± 0.3).

2-Hydroxymalonanilic acid ethyl ester (2b) (Method A). Diethyl malonate (1.52 mL, 10 mmol) and o-aminophenol (1.09 g, 10 mmol) were heated in an metal bath at 155°C for 1 h. The reaction mixture was cooled to room temperature, 15 mL water was added. The precipitate was filtered and washed with a little amount of cold water and dried (yield 1.94 g, 87%). Recrystallization from water gave colorless plates: mp 132-133°C; ^{1}H NMR (DMSO-d_6) 1.21 (3H, t, J = 7.0, CH_3), 3.58 (2H, s, $COCH_2CO$), 4.11 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 6.64-6.99 (3H, m, 4,5,6-H), 7.87 (1H, d, J = 8.0, 3-H), 9.48 (1H, s, NH), 9.84 (1H, s, OH). This spectrum is compared with lit[8].

2-Methylmalonanilic acid ethyl ester (2c) (Method B). Anhydride of malonic acid monoethyl ester [prepared from malonic acid monoethyl ester (2.64 g, 10 mmol) and N,N'-dicyclohexylcarbodiimide (2.06 g, 10 mmol) in diethyl ether] was added to a solution of o-toluidine (1.07 g, 10 mmol) in 5 mL acetone. The reaction mixture was stirred for 4 h at room temperature and 20 mL water was added. The precipitate was filtered off and recrystallized from diethyl ether; yield 1.90 g (86%), colorless needles: mp 76-77°C; ^{1}H NMR (DMSO-d_6) 1.22 (3H, t, J = 7.0, $CH_2\underline{CH_3}$), 2.21 (3H, s, Ar-$\underline{CH_3}$), 3.48 (2H, s, $COCH_2CO$), 4.12 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.08-7.29 (3H, m, 4,5,6-H), 7.40 (1H, d, J = 7.9, 3-H), 9.52 (1H, s, NH).

Malonanilic acid ethyl ester (2a) (Method C). Ethyl malonyl chloride (1.66 g, 11 mmol) was added to a solution of aniline (0.93 g, 10 mmol) and triethylamine (1.54 mL, 11 mmol) in acetone. The reaction mixture

was stirred for 4 h at room temperature and the solvent was removed in vacuo. Water (10 mL) was added to the residue and was acidified with hydrochloric acid to pH 3. 1.69 g (82%) of the product that solidified with time was obtained. Recrystallization from diethyl ether gave colorless needles: mp 38-39°C (lit.[9] mp 38-39°C); ^{1}H NMR (DMSO-d_6) 1.18 (3H, t, J = 7.0, CH_3), 3.56 (2H, s, $COCH_2CO$), 4.17 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.10 (1H, t, J =7.1, 4-H), 7.31 (2H, t, J = 8.0, 3,5-H), 7.65 (2H, d, J = 7.0, 2,6-H), 10.39 (1H, s, NH).

Other ethyl esters of malonanilic acids have been prepared by this procedure.

2-Methoxymalonanilic acid ethyl ester (2d). Yield 91%. Recrystallization from diethyl ether gave colorless prisms: mp 63-64°C (lit.[5] mp 63°C); ^{1}H NMR (DMSO-d_6) 1.23 (3H, t, J = 7.0, $CH_2\underline{CH_3}$), 3.61 (2H, s, $COCH_2CO$), 3.87 (3H, s, OCH_3), 4.14 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 6.81-7.20 (3H, m, 4,5,6-H), 8.06 (1H, d, J = 8.0, 3-H), 9.50 (1H, s, NH).

4-Ethoxymalonanilic acid ethyl ester (2e). Yield 89%. Colorless plates: mp 88-90°C (from diethyl ether); ^{1}H NMR (DMSO-d_6) 1.20 (3H, t, J = 7.0, $COOCH_2\underline{CH_3}$), 1.30 (3H, t, J = 7.0, $OCH_2\underline{CH_3}$), 3.40 (2H, s, $COCH_2CO$), 3.98 (2H, q, J = 7.0, $O\underline{CH_2}CH_3$), 4.10 (2H, q, J = 7.0, $COO\underline{CH_2}CH_3$), 6.86 (2H, dd, J = 8.9, 2.1, 2,6-H), 7.47 (2H, dd, J = 8.9, 2.1, 3,5-H), 10.01 (1H, s, NH).

2-Hydroxy-4-nitromalonanilic acid ethyl ester (2f). Yield 96%. Light yellow needles: mp 204-206°C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.22 (3H, t, J = 7.0, CH_3), 3.70 (2H, s, $COCH_2CO$), 4.16 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.70 (1H, s, 3-H), 7.76 (1H, dd, J = 8.9, 2.9, 6-H), 8.38 (1H, dt, J = 8.9, 1.0, 5-H), 9.92 (1H, s, NH), 11.12 (exchange, 1H, s, OH).

2-Carboxymalonanilic acid ethyl ester (2g). Yield 92%. Colorless needles: mp 104-105°C (from water); ^{1}H NMR (DMSO-d_6) 1.21 (3H, t, J = 7.0, CH_3), 3.59 (2H, s, $COCH_2CO$), 4.14 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.19 (1H, td, J = 7.1, 1.3, 4-H), 7.60 (1H, td, J = 8.0, 2.0, 5-H), 8.0 (1H, dd, J = 7.5, 1.4, 6-H), 8.42 (1H, dd, J = 8.0, 1.0, 3-H), 11.24 (1H, s, NH), 13.64 (broad, 1H, s, COOH).

2-Carbomethoxymalonanilic acid ethyl ester (2h). Yield 83%. Colorless needles: mp 37-38° C (from diethyl ether); ^{1}H NMR (DMSO-d_6) 1.20 (3H, t, J = 7.0, $CH_2\underline{CH_3}$), 3.69 (2H, s, $COCH_2CO$), 3.96 (3H, s, OCH_3), 4.27 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.21 (1H, td, J = 7.9, 2.0, 4-H), 7.62 (1H,td, J = 7.0, 1.9, 5-H), 7.94 (1H, dd, J = 7.9, 1.9, 6-H), 8.28 (1H, d, J = 8.0, 3-H), 11.26 (1H, s, NH).

2-Carboethoxymalonanilic acid ethyl ester (2i). Yield 94%. Colorless needles: mp 53-54°C (from diethyl ether); ^{1}H NMR (DMSO-d_6) 1.21 (3H, t, J = 7.0, $CH_2COOCH_2\underline{CH_3}$), 1.32 (3H, t, J = 7.0, Ar-$COOCH_2\underline{CH_3}$), 3.59 (2H, s, $COCH_2CO$), 4.14 (2H, q, J = 7.0, $CH_2COO\underline{CH_2}CH_3$), 4.33 (2H, q, J = 7.0, Ar-$COO\underline{CH_2}CH_3$), 7.20 (1H, td, J = 7.8, 2.0, 4-H), 7.60 (1H, td, J = 7.0, 2.0, 5-H), 7.92 (1H, dd, J = 7.8, 1.8, 6-H), 8.24 (1H, d, J = 8.0, 3-H), 10.80 (1H, s, NH).

2-Carboxy-4-bromomalonanilic acid ethyl ester (2j). Yield 95%. Colorless needles: mp 138-140°C (from ethanol/water); ^{1}H NMR (DMSO-d_6) 1.22 (3H, t, J = 7.0, CH_3), 3.60 (2H, s, $COCH_2CO$), 4.14 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.81 (1H, dd, J = 8.9, 2.4, 5-H), 8.05 (1H, d, ^{4}J = 2.2, 3-H), 8.38 (1H, d, J = 8.3, 6-H), 11.18 (1H, s, NH), 13.40 (broad, 1H, s, COOH).

2-Carboxy-4,6-dibromomalonanilic acid ethyl ester (2k). Yield 96%. Colorless needles: mp 176-178°

C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.20 (3H, t, J = 7.0, CH_3), 3.43 (2H, s, $COCH_2CO$), 4.12 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.87 (1H, d, J = 2.3, 5-H), 8.16 (1H, d, J = 2.3, 3-H), 10.05 (1H, s, NH), 13.42 (broad, 1H, s, COOH).

4-Carboxymalonanilic acid ethyl ester (2l). Yield 95%. Colorless needles: mp 205-207°C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.21 (3H, t, J = 7.0, CH_3), 3.50 (2H, s, $COCH_2CO$), 4.14 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.67 (2H, d, J = 8.5, 2,6-H), 7.91 (2H, d, J = 8.5, 3,5-H), 10.49 (1H, s, NH), 12.74 (broad, 1H, s, COOH).

4-Carboethoxymalonanilic acid ethyl ester (2m). Yield 97%. Colorless needles: mp 100-101°C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.22 (3H, t, J = 7.0, $CH_2COOCH_2\underline{CH_3}$), 1.32 (3H, t, J = 7.0, Ar-$COOCH_2\underline{CH_3}$), 3.52 (2H, s, $COCH_2CO$), 4.19 (4H, m, J = 7.0, $\underline{CH_2}CH_3$ x 2), 7.72 (2H, d, J = 8.5, 2,6-H), 7.96 (2H, d, J = 8.5, 3,5-H), 10.52 (1H, s, NH).

2-Carboxyanilide monoethyl ester of methylmalonic acid (2n). Yield 93%. Colorless needles: mp 120-122°C (from ethanol); ^{1}H NMR ($CDCl_3$) 1.30 (3H, t, J = 7.0, $CH_2\underline{CH_3}$), 1.57 (3H, d, J = 7.0, $CH\underline{CH_3}$), 3.58 (1H, q, J = 7.0, COCHCO), 4.27 (2H, q, J = 7.0, $\underline{CH_2}CH_3$), 7.15 (1H, td, J = 7.9, 1.2, 4-H), 7.62 (1H, td, J = 8.2, 2.0, 5-H), 8.16 (1H, dd, J = 7.9, 1.9, 6-H), 8.50 (broad, 1H, s, COOH), 8.74 (1H, d, J = 8.0, 3-H), 11.25 (1H, s, NH).

General Procedure for the Preparation of 7a-l from malonanilic acids ethyl esters 2. The corresponding ethyl ester **(2)** was heated in an metal bath at 170-220°C for 1 h (or boiled in DMF for 5 h). The reaction mixture was cooled to room temperature (or the solvent removed in vacuo) and the residue was triturated with diethyl ether. Filtration with suction and recrystallization from suitable solvent gave final dianilide **(7)**. The filtrate was evaporated and the corresponding diethyl malonate **(6)** was obtained. Diethyl malonates **(6)** yields have not been determined.

N,N'-Dianilide of malonic acid (7a). Yield 86%. Colorless needles: mp 225-227°C (from ethanol) (lit.[9] mp 225°C); ^{1}H NMR (DMSO-d_6) 3.61 (2H, s, CH_2), 7.09 (2H, t, J = 7.0, 4,4'-H), 7.32 (4H, t, J = 7.9, 3,5,3',5'-H), 7.63 (4H, d, J = 7.0, 2,6,2',6'-H), 10.17 (2H, s, NH x 2).

N,N'-Di-2-hydroxyanilide of malonic acid (7b). Yield 89%. Colorless crystalls: mp 231-233°C (from DMF); ^{1}H NMR (DMSO-d_6) 3.65 (2H, s, CH_2), 6.78-7.04(6H, m, 4,5,6,4',5',6'-H), 7.88 (2H, d, J = 8.0, 3,3'-H), 9.55 (2H, s), 9.72 (2H, s).

N,N'-Di-2-methylanilide of malonic acid (7c). Yield 92%. Colorless needles: mp 190-191°C (from ethanol); ^{1}H NMR (DMSO-d_6) 2.24 (6H, s, CH_3 x 2), 3.50 (2H, s, CH_2), 7.10-7.30 (6H, m, 4,5,6,4',5',6'-H), 7.44 (2H, d, J = 8.0, 3,3'-H), 9.54 (2H, s, NH x 2).

N,N'-Di-2-methoxyanilide of malonic acid (7d). Yield 96%. Colorless needles: mp 159-160°C (from ethanol) (lit.[5] mp 159.5°C); ^{1}H NMR (DMSO-d_6) 3.63 (2H, s, CH_2), 3.89 (6H, s, OCH_3 x 2), 6.84-7.22 (6H, m, 4,5,6,4',5',6'-H), 8.08 (2H, d, J = 8.0, 3,3'-H), 9.51 (2H, s, NH x 2).

N,N'-Di-4-ethoxyanilide of malonic acid (7e). Yield 97%. Colorless plates: mp 228-229°C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.31 (6H, t, J = 7.0, CH_3 x 2), 3.42 (2H, s, $COCH_2CO$), 4.00 (4H, q, J = 7.0, $\underline{CH_2}CH_3$ x 2), 6.87 (4H, d, J = 8.9, 2,6,2',6'-H), 7.48 (4H, d, J = 8.9, 3,5,3',5'-H), 10.03 (2H, s, NH x 2).

N,N'-Di-2-hydroxy-4-nitroanilide of malonic acid (7f). Yield 96%. Light yellow crystalls: mp 250-252°C (from dioxane); ^{1}H NMR (DMSO-d_6) 3.90 (2H, s, CH_2), 7.70 (2H, s, 3,3'-H), 7.77 (2H, dd, J = 8.9, 2.0, 6,6'-H), 8.35 (2H, dd, J = 8.9, 1.1, 5,5'-H), 10.05 (2H, s, NH x 2), 11.13 (exchange, broad, 2H, s, OH x 2).

N,N'-Di-2-carboxyanilide of malonic acid (7g). Yield 98%. Colorless needles: mp 242-244°C (from dioxane) (lit.[10] mp 240-245°C); ^{1}H NMR (DMSO-d_6) 3.69 (2H, s, CH_2), 7.19 (2H, td, J = 8.0, 1.2, 4,4'-H), 7.63 (2H, td, J = 8.0, 1.8, 5,5'-H), 7.99 (2H, dd, J = 8.0, 1.8, 6,6'-H), 8.46 (2H, d, J = 8.0, 3,3'-H), 11.33 (2H, s, NH x 2), 13.66 (broad, 2H, s, COOH x 2).

N,N'-Di-2-carbomethoxyanilide of malonic acid (7h). Yield 91%. Colorless needles: mp 149-150°C (from dioxane); ^{1}H NMR (DMSO-d_6) 3.61 (2H, s, $COCH_2CO$), 3,84 (6H, s, OCH_3 x 2), 7.24 (2H, td, J = 7.2, 1.3, 4,4'-H), 7.62 (2H, td, J = 7.0, 2.0, 5,5'-H), 7.91 (2H, dd, J = 7.5, 2.0, 6,6'-H), 8.23 (2H, dd, J = 8.0, 1.0, 3,3'-H), 10.85 (2H, s, NH x 2).

N,N'-Di-2-carboethoxyanilide of malonic acid (7i). Yield 93%. Colorless needles: mp 139-140°C (from dioxane); ^{1}H NMR (DMSO-d_6) 1.32 (6H, t, J = 7.0, CH_3 x 2), 3.69 (2H, s, $COCH_2CO$), 4.32 (4H, q, J =7.0, $\underline{CH_2}CH_3$ x 2), 7.22 (2H, td, J = 7.1, 1.2, 4,4'-H), 7.64 (2H, td, J = 7.0, 2.0, 5,5'-H), 7.93 (2H, dd, J = 7.5, 2.0, 6,6'-H), 8.26 (2H, d, J = 8.0, 3,3'-H), 10.88 (2H, s, NH x 2).

N,N'-Di-4-carboxyanilide of malonic acid (7j). Yield 98%. Colorless needles: mp 286-288°C (from DMF); ^{1}H NMR (DMSO-d_6) 3.58 (2H, s, CH_2), 7.73 (4H, d, J = 8.5, 2,6,2',6'-H), 7.92 (4H, d, J = 8.5, 3,5,3',5'-H), 10.59 (2H, s, NH x 2), 12,72 (2H, s, COOH x 2).

N,N'-Di-4-carboethoxyanilide of malonic acid (7k). Yield 96%. Colorless needles: mp 207-208°C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.32 (6H, t, J = 7.0, CH_3 x 2), 3.58 (2H, s, $COCH_2CO$), 4.30 (4H, q, J = 7.0, $\underline{CH_2}CH_3$ x 2), 7.74 (4H, d, J = 8.5, 2,6,2',6'-H), 7.95 (4H, d, J = 8.5, 3,5,3',5'-H), 10.54 (2H, s, NH x 2).

N,N'-Di-2-carboethoxyanilide of methylmalonic acid (7l). Ethylanthranilate is acylated by methylmalonic acid monochloride monoethyl ester and 2-carboethoxyanilide monoethyl ester of methylmalonic acid obtained without isolation in pure form is treated by general procedure method. Yield 92%. Colorless needles: mp 99-101°C (from ethanol); ^{1}H NMR (DMSO-d_6) 1.30 (6H, t, J = 7.0, $CH_2\underline{CH_3}$ x 2), 1.50 (3H, d, J = 7.0, $CH\underline{CH_3}$), 3.74 (1H, q, J = 7.0, $\underline{CH}CH_3$), 4.32 (4H, q, J = 7.0, $\underline{CH_2}CH_3$ x 2), 7.21 (2H, td, J = 8.0, 1.2, 4,4'-H), 7.62 (2H, td, J = 8.2, 2.0, 5,5'-H), 7.93, dd, J = 8.0, 2.0, 6,6'-H), 8.32 (2H, d, J = 8.0, 3,3'-H), 10.97 (2H, s, NH x 2).

2-Carboxyanilide monoethyl ester of diethylmalonic acid (11a). Prepared by acylation of anthranilic acid with diethylmalonic acid monochloride monoethyl ester in the presence triethylamine in acetone. Yield 88%. Recrystallization from diethyl ether gave colorless needles: mp 116-118°C; ^{1}H NMR (DMSO-d_6) 0.65 (6H, t, J = 7.0, $C(CH_2\underline{CH_3})_2$), 1.30 (3H, t, J = 7.0, $COOCH_2\underline{CH_3}$), 1.82 (4H, q, J = 7.0, $C(\underline{CH_2}CH_3)_2$), 4.12

(2H, q, J = 7.0, $COO\underline{CH_2}CH_3$), 7.17 (1H, td, J = 8.0, 1.2, 4-H), 7.61 (1H, td, J = 8.1, 1.9, 5H), 8.15 (1H, dd, J = 8.0, 2.0, 6-H), 8.72 (1H, d, J = 8.0, 3-H), 11.26 (1H, s, NH), 13.27 (broad, 1H, s, COOH).

4-Carboethoxyanilide monoethyl ester of diethylmalonic acid (11b). Prepared by analoguously. Yield 94%. Colorless prisms: mp 50-52°C (from ethanol); ^{1}H NMR (DMSO-d_6) 0.63 (6H, t, J =7.0, $C(CH_2\underline{CH_3})_2$), 1.01 (3H, t, J = 7.0, $COOCH_2\underline{CH_3}$), 1.15 (3H, t, J = 7.0, $COOCH_2\underline{CH_3}$), 1.79 (4H, q, J = 7.0, $C(\underline{CH_2}CH_3)_2$), 4.07 (4H, m, J = 7.0, $COO\underline{CH_2}CH_3$ x 2), 7.62 (2H, d, J = 8.5, 2,6-H), 7.78 (2H, d, J = 8.5, 3,5-H), 9.56 (1H, s, NH).

1-Methyl-2-oxo-4-hydroxyquinoline (15). Prepared by acylation of N-methylaniline according to C-method. The reaction mixture was acidified with HCl and chloroform was added. The chloroform phase was dried with anhydrous calcium chloride and concentrated on a rotary evaporator. The residue was heated on a metal bath at 220°C for 2 h. Twice recrystallization from dioxane gave light yellow needles: mp 264-266°C (lit.[11] mp 265-267°C), yield 74%; ^{1}H NMR (DMSO-d_6) 3.72 (3H, s, CH_3), 5.63 (1H, s, 3-H), 7.53 (1H, t, J = 7.0, 6-H), 7.80 (1H, d, J = 8.0, 8-H), 7.92 (1H, t, J = 8.0, 7-H), 8.12 (1H, d, J =7.9, 5-H), 13.46 (1H, s, OH).

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