DOI 10.1515/hc-2012-0053 — Heterocycl. Commun. 2013; 19(1): 57–63

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Melamine-formaldehyde resin supported H^+-catalyzed three-component synthesis of 1,8-dioxo-decahydroacridine derivatives in water and under solvent-free conditions

Abstract: A convenient and practical synthesis of 1,8-dioxo-decahydroacridine derivatives using various aldehydes, 5,5-dimethyl-1,3-cyclohexanedione and thiourea in water, was successfully carried out in the presence of melamine-formaldehyde resin supported H^+ (MFRH) as a catalyst. Under solvent-free conditions, rapid and efficient synthesis of 1,8-dioxo-decahydroacridine and *N*-substituted 1,8-dioxo-decahydroacridine derivatives could also be achieved using ammonium acetate and aromatic amines as the nitrogen source.

Keywords: 1,8-dioxo-decahydroacridines; heterogeneous catalyst; melamine-formaldehyde; three-component reaction; thiourea.

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Introduction

The 1,4-dihydropyridine derivatives are important compounds because of their pharmacological properties such as vasodilatory, bronchodilatory, antiatherosclerotic, anticancer, antidiabetic [1–4], and platelet antiaggregative activity. Alzheimer's disease and cardiovascular diseases including hypertension [5–8] are also targeted by this class of compounds. Acridine-1,8-diones and their derivatives are polyfunctionalized 1,4-dihydropyridines. They have been shown to have very high lasing efficiencies [9], important photophysical and electrochemical properties [10], and are useful photoinitiators [11].

A straightforward procedure for the synthesis of acridine-1,8-diones involves a three-component cyclocondensation between dimedone and aldehydes in the presence of nitrogen source such as urea [12], ammonium bicarbonate [13], ammonium acetate on basic alumina [14], ammonium hydroxide [15], hydroxylamine [16], methylamine [17], or substituted anilines [18].

Several methods have been reported for preparation of 1,4-dihydropyridines in ionic liquids [19], under microwave irradiation [20], and in the presence of triethylbenzylammonium chloride [21], *p*-dodecylbenzenesulfonic acid [22], proline [23], amberlyst 15 [24], and ammonium chloride or $Zn(OAc)_2{\cdot}2H_2O$ [25].

Green chemistry is conducted best without any solvent or in water. There are many advantages of solvent-free reactions including reduced pollution, low costs, and simplicity. Also, water as the reaction medium is generally considered as an inexpensive, safe, and environmentally benign alternative to organic solvents. Owing to the low solubility of common organic compounds in water, the use of water as solvent often makes the purification of products easy by simple filtration or extraction [26].

The application of heterogeneous catalysts to carry out various organic transformations is of great importance in organic synthesis. These catalysts can conveniently be handled and removed from the reaction mixture, making the experimental procedure simple and eco-friendly. The catalyst should have high catalytic activity under solvent-free conditions [27]. In continuation of our studies [28–31] on the application of heterogeneous solid catalysts in organic synthesis, in this report we explored the catalytic activity of melamine-formaldehyde resin supported H^+ (MFRH) as a highly efficient heterogeneous acid catalyst toward the synthesis of 1,8-dioxo-decahydroacridine derivatives.

Results and discussion

MFRH was readily prepared by small-portion addition of melamine-formaldehyde resin to sulfuric acid (60%) while keeping the temperature below 0°C with stirring for 72 h. The solid product was filtered and washed with acetone. The resin was kept at 80°C for 10 h in an oven to furnish MFRH as a free-flowing powder. This white heterogeneous, solid acid is fairly stable on storage. The structure and acidity of this heterogeneous MFRH catalyst was characterized using the back-titration method and FT-IR spectrometry. The back-titration method is considered as an effective technique for evaluation of the percentage of acidified melamine-formaldehyde resin. To characterize the resin by the back-titration method, briefly, 0.01 g of the catalyst was suspended in excess amount of NaOH (0.01 M, 10 mL), after sonication of the media at frequency to ~500 kHz for 30 min, and then the resin was centrifuged and the solution was titrated with HCl (0.05 M). According to this method, the weight percentage of the acidic group was evaluated to be ~0.004% (0.039 mmol/g). When both melamine-formaldehyde and protonated melamine-formaldehyde resins were separately sonicated in 5.00 mL H_2O, a significant pH change from 6.93 to 4.52 was observed for the acid-treated melamine-formaldehyde resin, which is in good agreement with the results obtained from the back-titration method. For further confirmation of the protonation of the nitrogen atoms in the

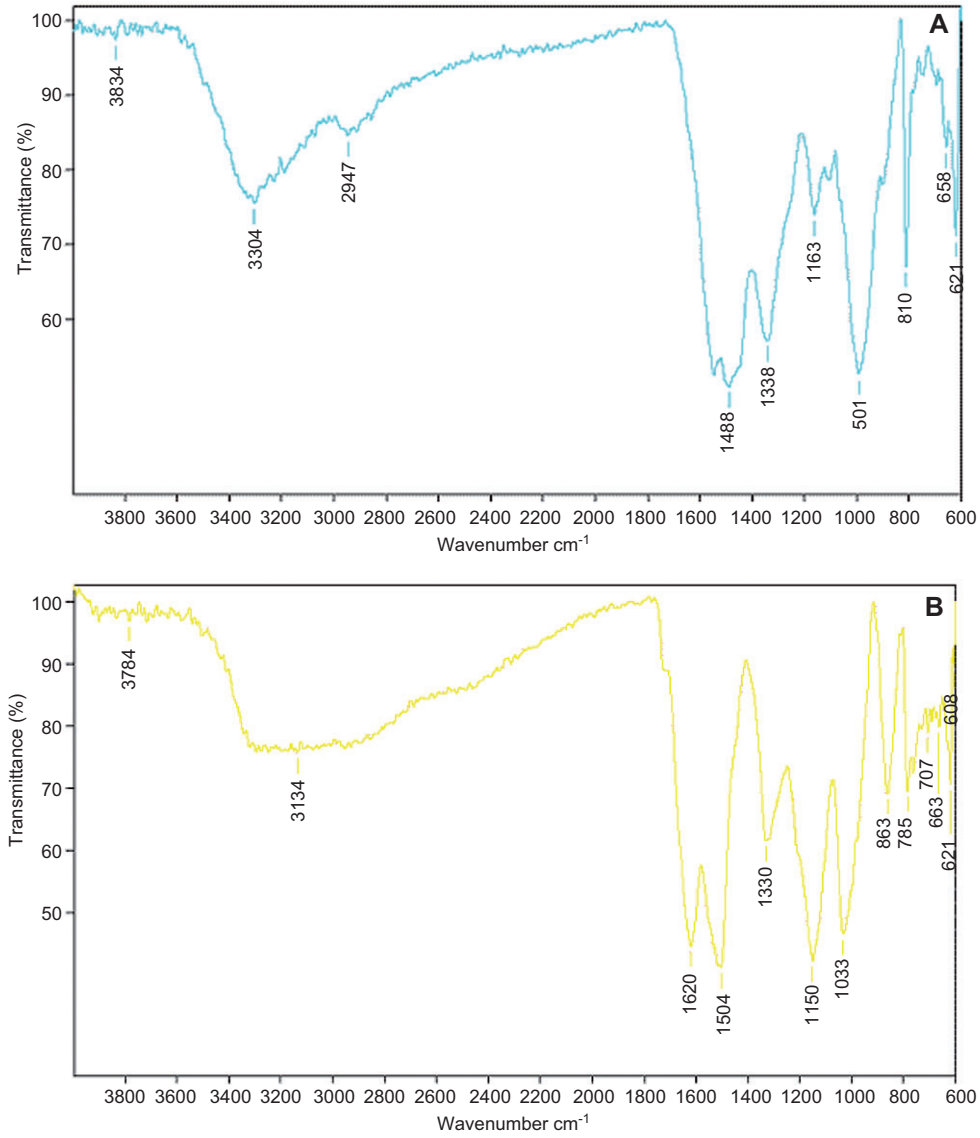


Figure 1 (A) FT-IR spectrum of melamine-formaldehyde resin (MFR); (B) FT-IR spectrum of melamine-formaldehyde resin supported H+ (MFRH).

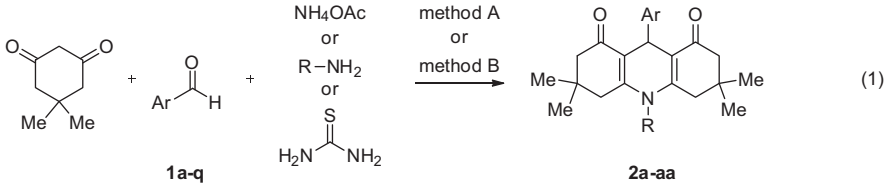
melamine-formaldehyde resin during its treatment with sulfuric acid, the resin was initially alkylated by treatment with ethyl chloride (80°C for 24 h) to form -N-CH_2CH_3 moieties. Then the modified resin was washed with methanol several times, sonicated, and finally dried inside a vacuum furnace at a temperature of 60°C before treatment with sulfuric acid. This acid-treated resin showed a very small change of pH from 6.93 to 6.89 during the back-titration process. This result clearly points out to the involvement of nitrogen atoms in the protonation process.

The FT-IR spectrophotometry was used for further characterization of the protonated melamine-formaldehyde resin. As shown in Figure 1A and B, there is a significant shift of the peak at 3304 cm^{-1} (Figure 1A) to 3134 cm^{-1} (Figure 1B) accompanied by broadening. These features can be considered as an additional indication for the protonation of nitrogen and formation of NH^+. In addition, the presence of strong peaks positioned at 1561 cm^{-1} (Figure 1A) and 1620 cm^{-1} (Figure 1B), that are related to N-H bending vibrations, is consistent with the same conclusion.

The protonated resin was further characterized using elemental analysis. Thus, the acid-treated resin was heated with barium acetate at 80°C for 12 h. The precipitate formed was shown to be barium acetate, in agreement with the presence of sulfate anions as counter ions for the protonated resin.

The synthesis of products **2** (Equation 1) was conducted by the reaction of dimedone with a benzaldehyde (**1**) in the presence of thiourea, ammonium acetate, or an aniline as the source of nitrogen. A variety of reaction parameters were screened for this reaction. First, we examined thiourea as the nitrogen source. Initially, our investigation was focused on the effect of solvent on the model reaction with unsubstituted benzaldehyde. It was found that water was the most suitable medium for the model reaction carried out in the presence of MRFH. The product **2a** was obtained in 85% yield. Product **2a** was obtained in 30% yield for the reaction conducted in ethanol, and no formation of **2a** was observed for the attempted reaction in tetrahydrofuran, acetonitrile, and toluene. In addition, product **2a** was not formed in the absence of MRFH. Product **2a** was not formed either for the reaction conducted in the absence of water, under solvent-free conditions. To the best of our knowledge, there are no similar methods described in the literature for synthesis of 1,8-dioxo-decahydroacridines with thiourea as the source of nitrogen. As an alternative to thiourea, ammonium acetate was used in this work as a nitrogen source under otherwise similar conditions. The reaction of ammonium acetate with dimedone and benzaldehyde (**1a**) in water was performed but the results were not satisfactory. Solvent-less conditions were the best. Under optimized conditions the heating of the substrates including ammonium acetate in the absence of solvent gave product **2a** in 85% yield. With ethanol, acetonitrile, and toluene as the solvent the reaction in the presence of ammonium acetate furnished product **2a** in the respective yield of 70%, 60%, and 30%. No product **2a** was observed for an attempted reaction conducted in tetrahydrofuran. No product was observed when an attempted reaction was carried out at room temperature under otherwise similar conditions.

Aniline and substituted anilines were also examined as a potential source of nitrogen. When using dimedone, benzaldehyde (**1a**), and aniline with the molar ratio of



1a-q **2a-aa** (1)

1a, **2a**: Ar = Ph; R = H
1b, **2b**: Ar = 4-Me-C_6H_4; R = H
1c, **2c**: Ar = 4-OH-C_6H_4; R = H
1d, **2d:** Ar = 4-N(Me)$_2$-C_6H_4; R = H
1e, **2e**: Ar = 4-Cl-C_6H_4; R = H
1f, **2f**: Ar = 4-NO_2-C_6H_4; R = H
1g, **2g**: Ar = 3,4-Cl_2-C_6H_3; R = H
1h, **2h**: Ar = 3-OMe-C_6H_4; R = H
1i, **2i:** Ar = 3-NO_2-C_6H_4; R = H
1j, **2b**: Ar = 4-OMe-C_6H_4; R = H
1k, **2b**: Ar = 2-Naphthyl; R = H
1l, **2b**: Ar = 2-OMe-C_6H_4; R = H
1m, **2b**: Ar = 2-NO_2-C_6H_4; R = H
1n, **2b**: Ar = 4-CN-C_6H_4; R = H
1o, **2b**: Ar = 2-Cl-C_6H_4; R = H
1p, **2b**: Ar = 4-Cl, 3-NO_2-C_6H_3; R = H
1q, **2b**: Ar = 2-HO-C_6H_4; R = H
2r: Ar = Ph; R = 4-Cl-C_6H_4
2s: Ar = 3-NO_2-C_6H_4; R = 4-Cl-C_6H_4
2t: Ar = 2-Naphthyl; R = 4-Cl-C_6H_4
2u: Ar = 4-OMe-C_6H_4; R = 3-NO_2-C_6H_4
2v: Ar = 4-OMe-C_6H_4; R = Ph
2w: Ar = Ph; R = Ph
2x: Ar = 4-Cl-C_6H_4; R = Ph
2y: Ar = 3-NO_2-C_6H_4; R = Ph
2z: Ar = Ph; R = 4-Br-C_6H_4
2aa: Ar = Ph; R = 4-NO_2-C_6H_4

2:1:1.2 and performing the reaction under reflux conditions in water, product **2a** was obtained in 70% yield after 2 h. The use of ethanol also resulted in the formation of **2a** in 70% yield, whereas the yields were much lower for the reactions conducted in other organic solvents. Further assessment of aniline reaction conditions showed that the formation of product **2a** was more favorable under solvent-less conditions. Product **2a** was obtained in 90% yield after heating to 120°C for 40 min.

Subsequently, a series of reactions were carried out with dimedone using a variety of aromatic aldehydes, ammonium acetate, thiourea, and aromatic amines (Equation 1). The preparations were successfully conducted on a 30-mmol scale. To explore the recyclability of the catalyst, the MRFH under solvent-less condition was used as catalyst for the same reaction repeatedly and the change in the catalytic activity was studied. It was found that MRFH could be reused for up to five cycles with negligible loss of activity.

Conclusion

A general, simple, and efficient synthetic method for preparation of 1,8-dioxo-decahydroacridine derivatives from dimedone, aromatic aldehydes, and thiourea, ammonium acetate, or aromatic amines using MFRH as catalyst was developed. The mild reaction conditions, excellent yields, large-scale synthesis, easy and quick isolation of products, recyclability of the catalyst, cost-effectiveness, environmentally friendly, and high generality are the main advantages of this procedure.

Experimental section

General

Melting points were recorded on an IA 9000 Series melting point apparatus and IR spectra were obtained on a Bruker Penssor 27 spectrophotometer using KBr disks.

^{1}H NMR (400 MHz) spectra and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker AC 400 MHz Avance spectrometer in $CDCl_3$ or DMSO-d_6 using TMS as internal standard.

Preparation of melamine-formaldehyde resin supported H+ (MFRH)

Melamine-formaldehyde resin (purchased from Fars Chemical Company; http://www.farschemical.com (10 g) was added to 100 mL H_2SO_4 (60%) at 0°C and the mixture was stirred for 72 h, then filtered and washed with acetone (200 mL). The resin was kept at 80°C for 10 h in an oven to furnish MFRH as a free-flowing powder.

General procedure for products 2

Method A A mixture of an aromatic aldehyde (1 mmol), dimedone (2 mmol), ammonium acetate or amine (1.2 mmol), and MFRH (0.1 g, 3.9 mol%) was heated to 100°C for a period of time indicated below. After completion of the reaction, as indicated by TLC, the mixture was washed with warm ethanol (3×10 mL) and the catalyst was filtered off. The recovered catalyst was dried and reused for subsequent runs. The pure product was obtained by crystallization from ethanol.

Method B A mixture of aldehyde (1 mmol), dimedone (2 mmol), thiourea (1.5 mmol), and MFRH (0.3 g, ~12 mol%) in distilled water (15 mL) was stirred at 100°C. After completion of the reaction (TLC), the mixture was cooled to room temperature and the solid precipitate was filtered and treated with ethanol. The solution was filtered and solid MFRH isolated. The organic phase was concentrated and the residue was crystallized from ethanol to furnish pure crystalline product **2**. The recovered catalyst was washed with ethanol, dried, and reused in subsequent runs.

3,3,6,6-Tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2a) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 7 min; yield 85%. This compound was obtained by Method B in the presence of thiourea; reaction time 75 min; yield 85%, mp 279–280°C; reported mp 277–278°C [32].

3,3,6,6-Tetramethyl-9-(4-methylphenyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2b) This compound was obtained by Method B in the presence of thiourea; reaction time 75 min; yield 60%; mp >300°C; reported mp >300°C [33].

9-(4-Hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2c) This compound was obtained by Method B in the presence of thiourea; reaction time 60 min; yield 85%; mp >300°C; reported mp >300°C [33].

9-[4-(Dimethylamino)phenyl]-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2d) This compound was obtained by Method B in the presence of thiourea; reaction time 60 min; yield 85%; mp 263–265°C; reported mp 265–267°C [34].

9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2e) This compound was obtained by Method B in the presence of thiourea; reaction time 80% min; yield 80%; mp 290–292°C; reported mp 294–296°C [32].

3,3,6,6-Tetramethyl-9-(4-nitrophenyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2f) This compound was obtained by Method B in the presence of thiourea; reaction time 75 min; yield 80%; mp 296–298°C; reported mp 286–288°C [25].

9-(3,4-Dichlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2g) This compound was obtained by Method B in the presence of thiourea; reaction time 75 min; yield 85%; mp >300°C; reported mp >300°C [32].

9-(3-Methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2h) This compound was obtained by Method B in the presence of thiourea; reaction time 60 min; yield 75%; mp 287–289°C; IR (cm^{-1}): 3276, 3050, 2957, 1642, 1604, 1476, 1217; ^1H NMR ($CDCl_3$): δ 1.13 (s, 6H), 1.26 (s, 6H), 2.41 (m, 8H), 3.76 (s, 3H), 5.54 (s, 1H), 6.69–7.23 (m, 4H), 11.98 (s, 1H); Mass: 381(M^++2), 380(M^++1), 379 (M^+, 97.4). Anal. Calcd for $C_{24}H_{29}NO_3$ (379.492): C, 75.96; H, 7.70. Found: C, 80.08; H, 7.58.

9-(3-Nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2i) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 3 min; yield 80%. This compound was obtained by Method B in the presence of thiourea; reaction time 80 min; yield 75%; mp287–289°C; reported mp 287–289°C [22].

9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2j) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 7 min; yield 80%. This compound was obtained by Method B in the presence of thiourea; reaction time 65 min; yield 85%; mp 272–273°C; reported mp 272–273°C [34].

3,3,6,6-Tetramethyl-9-(2-naphthyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2k) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 15 min; yield 85%; mp >300°C; IR (cm^{-1}): 3280, 3054, 2952, 1647, 1603, 1485, 1214; ^1H NMR (DMSO-d_6), δ 0.86 (s, 6H), 1.02 (s, 6H), 2.08 (m, 4H), 2.43 (m, 4H), 4.99 (s, 1H), 7.40–7.80 (m, 7H), 9.39 (s, 1H); ^{13}C NMR (DMSO-d_6): 26.8, 29.6, 31.2, 32.6, 33.8, 50.7, 111.7, 125.5, 126.1, 126.2, 127.3, 127.6, 127.7, 128.0, 132.0, 133.2, 145.0, 149.9, 194.9. Anal. Calcd for $C_{27}H_{29}NO_2$ (399.525): C, 81.17; H, 7.32. Found: C, 81.03; H, 7.43.

9-(2-Methoxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2l) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 6 min; yield 80%; mp 293–295°C; reported mp 293–295°C [35].

3,3,6,6-Tetramethyl-9-(2-nitrophenyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2m) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 10 min; yield 95%; mp 290–292°C; reported mp 293–295°C [36].

4-(3,3,6,6-Tetramethyl-1,8-dioxo-1,2,3,4,5,6,7,8,9,10-decahydro-9-acridinyl)-benzonitrile (2n) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 3 min; yield 95%; mp >300°C; reported mp 324–326°C [25].

9-(2-Chlorophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2o) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 5 min; yield 95%; mp 220–222°C; reported mp 220–222°C [36].

9-(4-Chloro-3-nitrophenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2p) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 15 min; yield 90%; mp >300°C; IR (cm^{-1}): 3280, 3052, 2958, 1643, 1596, 1524, 1487, 1358, 1219; ^1H NMR (DMSO-d_6): δ 0.88 (s, 6H), 1.02 (s, 6H), 2.09 (m, 4H), 2.43 (m, 4H), 4.87 (s, 1H), 7.48–7.73 (m, 3H), 9.50 (s, 1H); ^{13}C NMR (DMSO-d_6): 27.0, 29.4, 32.7, 33.9, 50.4, 110.6, 122.5, 124.8, 131.5, 133.7, 147.4, 148.6, 150.7, 194.9. Anal. Calcd for $C_{23}H_{25}ClNO_4$ (428.908): C, 64.41; H, 5.88. Found: C, 64.29; H, 5.74.

9-(2-Hydroxyphenyl)-3,3,6,6-tetramethyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2q) This compound was obtained by Method A in the presence of ammonium acetate; reaction time 5 min; yield 95%; mp: >300°C; reported mp 310–312°C [35].

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2r) This compound was obtained by Method A in the presence of 4-chloroaniline; reaction time 5 min; yield 95%; mp 309–311°C, IR (cm^{-1}): 3050, 2956, 1633, 1574, 1487, 1216, 695; ^1H NMR (DMSO-d_6): δ 0.72 (s, 6H), 0.89 (s, 6H), 1.89 (m, 4H), 2.20 (m, 4H), 5.04 (s, 1H), 7.09–7.70 (m, 9H).

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-(3-nitrophenyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2s) This compound was obtained by Method A in the presence of 4-chloroaniline; reaction time 10 min; yield 80%; mp 297–299°C; IR (cm^{-1}): 2950, 1634, 1575, 1529, 1490, 1348, 1217; ^1H NMR ($CDCl_3$): δ 0.81 (s, 6H), 1.00 (s, 6H), 2.00 (m, 4H), 2.19 (m, 4H), 5.36 (s, 1H), 7.29–8.20 (m, 8 Hz); ^{13}C NMR ($CDCl_3$): 26.7, 29.7, 32.6, 32.8, 41.8, 50.0, 114.2, 121.3, 121.7, 128.9, 130.6, 131.1, 135.4, 135.8, 137.2, 148.1, 148.4, 150.1, 195.7. Anal. Calcd for $C_{29}H_{29}ClN_2O_4$ (505.004): C, 68.97; H, 5.79. Found: C, 69.08; H, 5.87.

10-(4-Chlorophenyl)-3,3,6,6-tetramethyl-9-(2-naphthyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2t) This compound was obtained by Method A in the presence of 4-chloroaniline; reaction time 10 min; yield 80%; mp 270–273°C; IR (cm^{-1}): 3050, 2956, 1632, 1575, 1489, 1217, 732; ^1H NMR ($CDCl_3$): δ 0.83 (s, 6H), 0.99 (s, 6H), 1.99 (m, 4H), 2.20 (m, 4H), 5.48 (s, 1H), 7.25–7.86 (m, 11H); ^{13}C NMR ($CDCl_3$): 26.8, 29.8, 32.5, 32.7, 41.9, 50.2, 114.8, 125.1, 125.5, 126.3, 126.6, 127.4, 127.8, 128.1, 132.3, 133.5, 135.5, 137.6, 143.3, 149.4, 195.8. Anal. Calcd for $C_{33}H_{32}ClNO_2$ (510.065): C, 77.71; H, 6.32. Found: C, 77.86; H, 6.25.

9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-10-(3-nitrophenyl)-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2u) This compound was obtained by Method A in the presence of 3-nitroaniline; reaction time 6 min; yield 90%; mp269–272°C; reported mp 276–278°C [24].

9-(4-Methoxyphenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2v) This compound was obtained by Method A in the presence of aniline; reaction time 20 min; yield 95%; mp 220–222°C; reported mp 220–222°C [24].

3,3,6,6-Tetramethyl-9,10-diphenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2w) This compound was obtained by Method A in the presence of aniline; reaction time 40 min; yield 90%; mp 252–254°C; reported mp 254–256°C [37].

9-(4-Chlorophenyl)-3,3,6,6-tetramethyl-10-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2x) This compound was obtained by Method A in the presence of aniline; reaction time 10 min; yield 80%; mp 244–246°C; reported mp 244–246°C [38].

3,3,6,6-Tetramethyl-9-(3-nitrophenyl)-10-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2y) This compound was obtained by Method A in the presence of aniline; reaction time 10 min; yield 85%; mp 297–299°C; reported mp 297–299°C [37].

10-(4-Bromophenyl)-3,3,6,6-tetramethyl-9-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2z) This compound was obtained by Method A in the presence of 4-bromoaniline; reaction time 20 min; yield 90%; mp 269–272°C; reported mp 269–272°C [37].

3,3,6,6-Tetramethyl-10-(4-nitrophenyl)-9-phenyl-3,4,6,7,9,10-hexahydro-1,8(2*H*,5*H*)-acridinedione (2aa) This compound was obtained by Method A in the presence of 4-nitroaniline; reaction time 10 min; yield 85%; mp 190–192°C; reported mp 194–196°C [39].

Acknowledgment: We are thankful to Firoozabad Branch, Islamic Azad University Research Council for partial support of this work.

Received April 11, 2012; accepted July 22, 2012; previously published online January 23, 2013

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