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Solar and ultraviolet *N*-dealkylation of *N*,*N*-dimethylaminobenzylidene malonic acid derivatives via photoexcited polycyclic nitroaromatic compounds

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Abstract

Broadband irradiation of *N*,*N*-dimethylaminobenzylidene malonic acid derivatives in benzene solution with polycyclic nitroaromatic compounds, namely 1-nitronaphthalene, 9-nitroanthracene and 1-nitropyrene leads to mono-alkylated products predominant, accompanied by the corresponding photoreduction products of the nitroaromatics. Lower conversion was observed in acetonitrile concomitant with 2–4% of the mono-alkylated products, however, no conversion was observed in methanol as solvent. The structures of the products were assigned based on IR, ^{1}H-, ^{13}C NMR and mass spectra, elemental analyses and comparison with authentic samples. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: *N*,*N*-Dimethylaminobenzylidene malonic acid; Polycyclic nitroaromatic compounds; Dealkylation

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1. Introduction

N,*N*-Dialkylanilines have been dealkylated to *N*-methylanilines, formanilide and primary amines by several photoexcited reagents such as benzophenone, [1,2,27] rose bengal, [1,27] or methylene blue [1,27]. However, photoexcited nitroaromatic compounds were shown to be one of the most effective dealkylating agents [3–8]. In continuation of our recent interest in the photochemical reaction of benzylidene malonic acid derivatives [9], we report herein on the photochemical *N*-demethylations of *N*,*N*-dimethylaminobenzylidene malonic acid derivatives **1a,b** which have received no attention before. 1-Nitronaphthalene **2a**, 9-nitroanthracene **2b** and 1-nitropyrene **2c** were used as highly condensed nitroaromatic compounds compared with nitrobenzenes, but have so far received no attention as photo-oxidants for tertiary amines.

2. Results and discussion

2.1. Dealkylation products

N,*N*-Dimethylaminobenzylidene malonic acid derivatives **1a,b** did not show any conversion when irradiated with Duran-unfiltered light of a 150 W high pressure lamp or when exposed to sunlight in benzene, acetonitrile or methanol solutions for 24 h. Upon irradiation in the presence of nitroaromatic compounds **2a–c** under otherwise identical conditions, however, the mono-*N*-dealkylated products **3a**, **4a** were formed in about 90% yields, accompanied by minor amounts (5–6%) of *N*-methyl-*N*-formyl derivatives **3b**, **4b**. In a standard experiment using 1:2 mol in 200 ml dry benzene, irradiation for 45 min give 50% conversion, and 60–70% conversion was achieved within a period of 3 h irradiation (Scheme 1). In acetonitrile as solvent, 2–4% conversion could be achieved within 10 h, whereas no conversion was observed after 20 h irradiation in methanol. Benzene is used as solvent, in spite of its toxicity and harmful effects because it is not ion solvating, but assists electron transfer. The radical ion pair formed between triplet excited nitro compounds and tertiary amine is more tight in benzene than in other solvents, which enable the pair to internally transfer a proton from the aminium cation to the nitroaryl anion before they can separated off [8]. It is worth noting that, the conversion of **1a** (X = $CO_2C_2H_5$) is faster than the conversion of **1b** (X = CN), since the time of irradiation was shorter and the chemical yields of **3a** and **4a** were rather higher.

2.2. Photoproducts of nitroaromatics

Nitrobenzenes and nitronaphthalenes have been extensively employed as photooxidants for tertiary amines,

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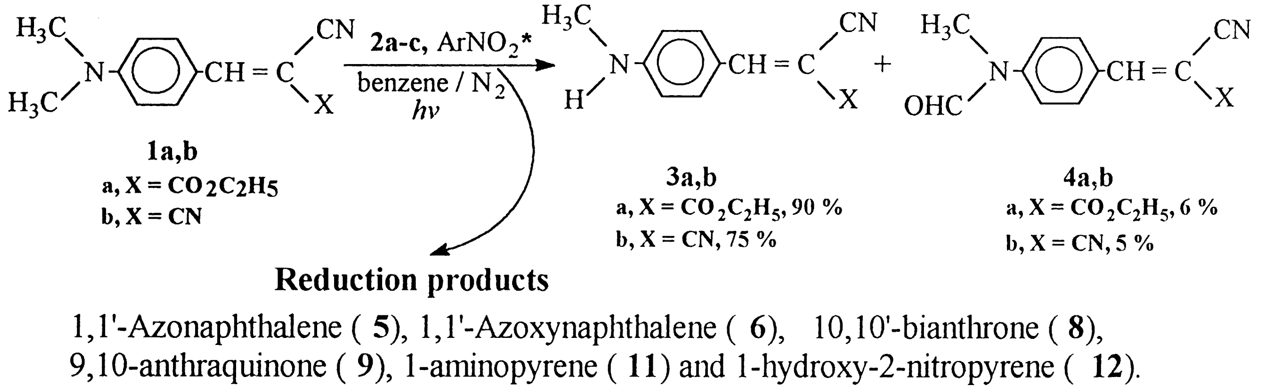


Scheme 1.

and their photoreduction products were reported in detail [10–13]. 1,1′-Azo-, and 1,1′-azoxynaphthalene were isolated as photoreduction products of 1-nitronaphthalene **2a**. However, any photoreduction products of 9-nitroanthracene **2c**, such as 9-aminoanthracene **10** was not isolated under different irradiation conditions. 10,10′-Bianthrone **8** and 9,10-anthraquinone **9** were isolated in remarkable amounts concomitant with the dealkylated products **3** and **4**. Irradiation of **1a,b** in the presence of 9,10-anthraquinone under different conditions gives only the dealkylated products **3** and **4**, however, any of anthracene-9,10-diol as reduction product of 9,10-anthraquinone was not isolated. Finally, the photolysis products of 1-nitropyrene **2c** in the presence of **1a,b** were 1-aminopyrene **11** as the major photo product accompanied by a minor yield of 1-hydroxy-2-nitropyrene **12**.

2.3. Mechanism of dealkylation

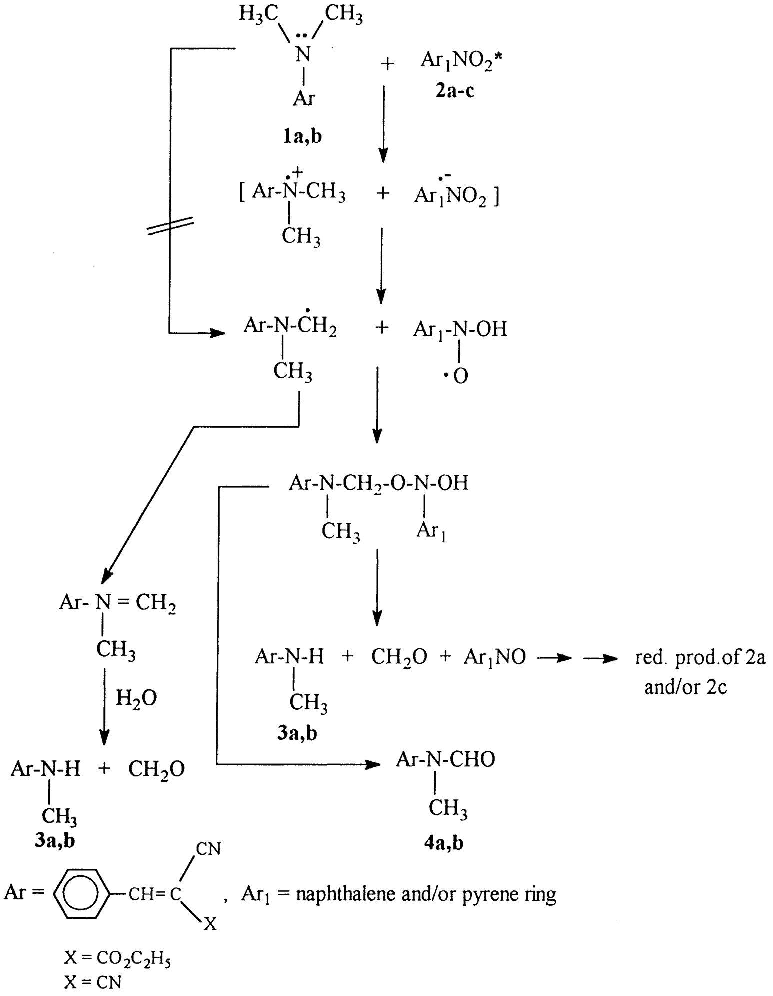
An initial hydrogen atom abstraction (concerted mechanism) from the *N*-methyl group of the tertiary amine effected by the photoexcited nitroaromatic as the first step in a sequence of reactions ultimately leading to demethylation has been reported [3]. The alternative is electron transfer followed by proton transfer (stepwise mechanism) [4,14–18]. Döpp et al., reinvestigated the reaction to distinguish between the two mechanisms using deuterium labeling [10]. 1-Nitronaphthalene **2a** was photoreduced under different basic conditions to give low yields of 1-naphthylamine and the corresponding azo- and azoxy compounds [12]. The generally acceptable mechanism [5,6,10] for α-oxidation of **1a,b** by photoexcited 1-nitronaphthalene **2a** represented by Scheme 2.

However, the absence of 9-aminoanthracene, and from the known facts concerning the photochemistry of 9-nitroanthracene [19–24] and non-excited 9-nitroanthracene **2b**, several other potential reactants acting on the *N*,*N*-dimethylaminobenzylidene malonic acid derivatives **1a,b** lead to demethylation: photo-excited 9,10-anthraquinone **9**, anthryloxyl radical **7** and/or nitrogen monoxide (Scheme 3). Since anthracene-9, 10-diol was not isolated as reduction product, photoexcited 9,10-anthraquinone **9** cannot be directly responsible for the dealkylation process. Also, it was suggested that the anthryloxy radical **7** may be the key intermediate for the dealkylation through H-atom abstraction from tertiary amine affording 9-anthrol which undergoes further oxidation to 9,10-anthraquinone **9** [10]. On the other hand, nitrogen monoxide liberating during photolysis of 9-nitroanthracene may play a plausible role as dealkylating agent for **1a,b**, as shown in Scheme 5. In fact, Döpp et al., demonstrated that the amount of liberating nitrogen monoxide in the absence of tertiary amines was remarkably larger than that in the presence of added amine, and this led to suppose that the amine may be either consumes nitrogen monoxide or quenches its formation [10].

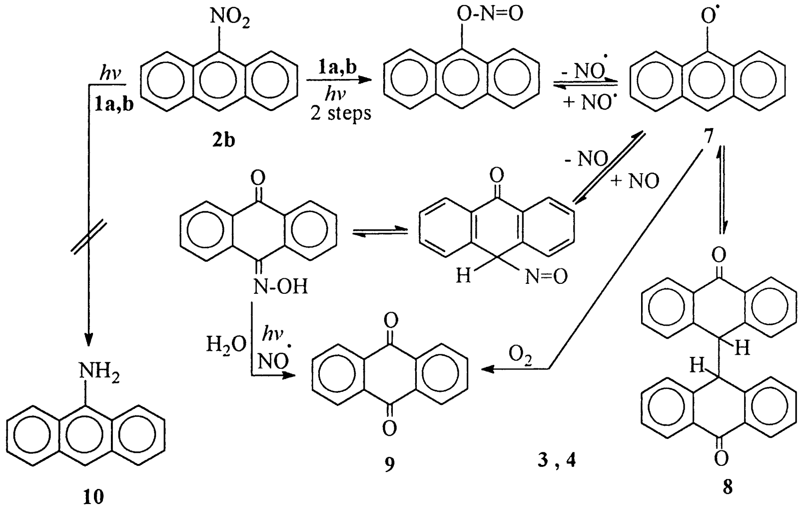
Finally, in the case of 1-nitropyrene **2c** the competitive reactions should be taken into consideration [25] because these reactions may have an effect on the overall rate of the dealkylation process. However, isolation of 1-aminopyrene **11** as the major photoproduct accompanied by a minor amount of 1-hydroxy-2-nitropyrene **12** led to expect that there are probably two mechanisms leading to demethylation (Scheme 4). The course of the α-oxidative dealkylation reaction between 1-nitropyrene **2c** and *N*,*N*-dimethylaminobenzylidene malonic acid derivatives **1a,b** follows the same pathway reported for nitroarenes and tertiary amines, as for 1-nitronaphthalene (Scheme 2). On the other hand, 1-pyrenyloxyl radical **13** could be another candidate which may act on **1a,b** in the same manner as well as the 9-anthryloxyl radical **7**, but formation of 1-hydroxy-2-nitropyrene **12** makes this possibility less favored (Scheme 5).

3. Experimental details

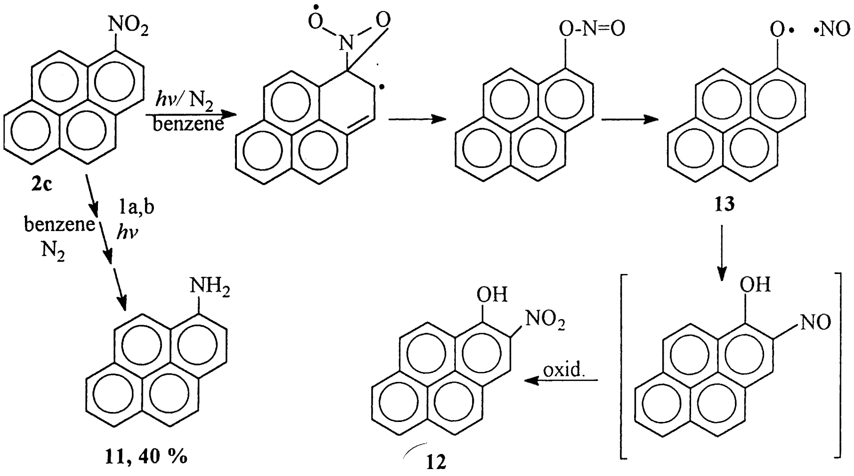
All melting points are uncorrected. IR spectra were recorded (KBr) on a Shimadzu 408. ^{1}H NMR spectra (δ, ppm) were recorded on a Varian EM 390 (90 MHz) using



Scheme 2.



Scheme 3.

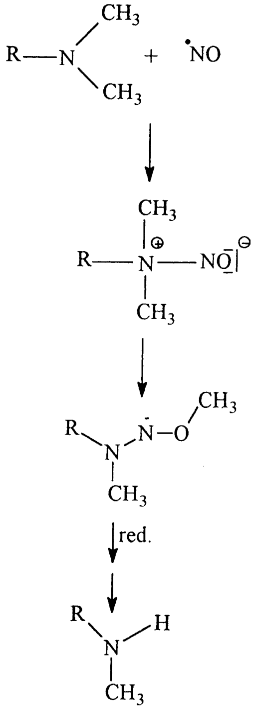


Scheme 4.

$CDCl_3$ as solvent and TMS as internal standard. A mass spectrometer MS 9 (AET) in the EI Mode was used, and the elemental analyses were obtained from the Microanalytical Center at Cairo University, Egypt.

3.1. Materials

N,*N*-Dimethylaminobenzylidene malonic acid derivatives **1a,b** were prepared according to the standard method [26,28,29] and were recrystallized twice from ethanol and were checked for impurities by means of thin-layer chromatography using toluene–ethyl acetate (3:1 by volume). Nitroaromatic compounds **2a–c** were purchased from Aldrich Chemical and were used as received. Spectrograde benzene was distilled before use and kept over anhydrous $CaCl_2$. Authentic samples of the reduction products were prepared according to standard methods [11,12,22,25].



Scheme 5.

3.2. Dealkylation on a preparative scale

Nitrogen-purged benzene solutions (200 ml) containing both of nitroaromatic compound **2a–c** (2 mol) and *N*,*N*-dimethylaminobenzylidene derivatives **1a,b** (1 mol) were irradiated with a 150 W high pressure mercury lamp in connection with a water-cooled immersion well made out of Duran-glass ($\lambda > 280$ nm) and a 250 ml cylindrical vessel. After irradiation, the solutions were evaporated to dryness. The residue was subjected to preparative layer chromatography on 30 cm × 20 cm plates covered with air-dry silica gel (thickness, 1 mm) using toluene–ethyl acetate (3:1 by volume) for all samples. All zones were detected by indicator fluorescence quenching upon exposure to a 254 nm lamp. The materials contained in the zones were recovered by extraction using acetone, recrystallized and identified using spectral and elemental analysis. The photoproducts of the nitro compounds were compared when possible with the authentic samples.

3.3. Photoproducts

3.3.1. 4-(N-Methylamino)benzylidene cyanoacetate 3a

Colourless crystals (MeOH). Yield: 90%. m.p. 110–112°C. IR: 3230–3175 (NH), 2215 (CN), 1725 (CO). ^1H NMR: 1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2), 4.4 (s, 3H, N–CH_3), 4.5–4.6 (br, 1H, NH), 6.8 (s, 1H, CH=) and 7.1–7.8 (m, 4H, Ar–H). ^{13}C NMR: 163.7 (CO), 134.4–118.6 (Ph), 117.8 (CN), 91.3

(CH=), 67.6 (OCH_2), 61.5 (N–CH_3), 40.5 (C=), and 10.9 (CH_3). MS, $m/z = 230$ (M + 1, 100%), 202 (55), 185 (36), and 158 (38). Anal. calc. for $C_{13}H_{14}N_2O_2$ (230.27): C, 67.81; H, 6.13; N, 12.17; found: C, 67.71; H, 6.01; N, 12.04%.

3.3.2. 4-(N-Formyl-N-methylamino)benzylidene cyanoacetate 3b

Pale yellow crystals (MeOH). Yield: 6%. m.p.: 150–152°C. IR: 2220 (CN), 1665, 1715 cm^{-1} (CO). ^{1}H NMR: 1.2 (t, 3H, CH_3), 4.2 (q, 2H, CH_2), 4.5 (br, 3H, NCH_3), 7.1–7.8 (m, 5H, Ar–H + CH=) and 10.5 (s, 1H, CHO). MS, $m/z = 259$ (M + 1, 95%). Anal. calc. for $C_{14}H_{14}N_2O_3$ (258.28): C, 65.11; H, 5.46; N, 10.85; found: C, 65.01; H, 5.32; N, 10.73%.

3.3.3. 4-(N-Methylamino)benzylidene propanedinitrile 4a

Colourless crystals (MeOH). Yield: 75%. m.p 135–137°C. IR: 3275–3125 (NH), 2220 (CN). ^{1}H NMR: 4.4 (s, 3H, NCH_3), 5.2 (br, 1H, NH), 7.1–7.8 (m, 5H, Ar–H + CH=). MS, $m/z = 183$ (M, 85%). Anal. calc. for $C_{11}H_9N_3$ (183.21): C, 72.11; H, 4.95; N, 22.94; found: C, 72.01; H, 4.81; N, 22.82%.

3.3.4. 4-(N-Formyl-N-methylamino) benzylidene propanedinitrile 4b

Colourless crystals (MeOH). Yield: 5%. m.p 185–187°C. IR: 2220 (CN), 1665 (CO). ^{1}H NMR: 4.4 (s, 3H, NCH_3), 7.1–7.8 (m, 5H, Ar–H + CH=), 10.0 (s, 1H, CHO). MS, $m/z = 211$ (M, 80%). Anal. calc. for $C_{12}H_9N_3O$ (211.22): C, 68.24; H, 4.30; N, 19.89; found: C, 68.10; H, 4.17; N, 19.78%.

3.3.5. 1-Aminopyrene 11

Green plates (EtOH). Yield: 40%. m.p. 116–117°C. IR: 3432–3235 (NH_2). ^{1}H-NMR: 4.5 (br, 2H, NH_2), 7.2–7.8 (m, 9H, Ar–H). MS, $m/z = 217$ (M, 100), 189 (35), 108 (25), 94 (35). Anal. calc. for $C_{16}H_{11}N$ (217.27): C, 88.45; H, 5.10; N, 6.54; found: 88.31; H, 5.00; N, 6.42%.

1,1′-Azo-, azoxynaphthalene [10], bianthrone **8** and 9,10-anthraquinone **9** [22], and 1-hydroxy-2-nitropyrene **12** [25] were identified and compared with authentic samples.

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^{13}C NMR were recorded ($CDCl_3$) at Chemistry Department, Duisburg University, Germany. Deep thanks should presented to Prof. Dr. Dietrich Döpp, Chemistry Department, Duisburg University, Germany, for his valuable help and providing the nitroaromatic compounds.

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