ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 121 (1999) 111–117

Journal of Photochemistry and Photobiology A:Chemistry

# Photoinduced reaction of polyfunctional nitroaromatics: photoreduction versus photosubstitution reaction of nitrobenzylidene malonic derivatives with triethylamine

F.M. Abd El Latif*, M.A. Barsy, E.A. Rady, M.E. Hassan, M.A. El Maghraby

*Department of Chemistry, Aswan Faculty of Science, Aswan, Egypt*

Received 24 June 1998; received in revised form 29 September 1998; accepted 6 October 1998

**Abstract**

Broad band irradiation of nitrobenzylidene malonic derivatives in benzene solution in the presence of triethylamine leads to two types of photochemical reactions, photoreduction of the nitro group predominantly, and photosubstitution of the cyano group. The formation of the products is suggested to proceed through a radical ion pair via initial electron transfer, followed by proton transfer, and finally through a sequence of ground state reactions leading to different products. © 1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Nitrobenzylidene malonic derivaties; Triethylamine; Photoreduction; Photosubstitution

## 1. Introduction

Interest in the photochemistry of nitro compounds has increased considerably [1,2]. Photoreduction and related reactions which are widely regarded typical for $(n,\pi^*)$ excitation have been extensively investigated in ether or in aliphatic amines [3–5]. It has been reported that various aromatic nitro compounds are photoreduced more efficiency in diethly- and triethylamine than in alcohols or ether, and it has been found that coupling products such as azo and azoxy compounds are predominant as photoreduction products rather than aromatic amines [4–6].

The scope of the present study is to report preliminary results of photochemical reactions of polyfunctional nitroaromatic compounds such as nitrobenzylidene malonic derivatives which have received no attention so far in view of the two competing processes, i.e. the photoreduction of the nitro- and photosubstitution reactions of the cyano group. Therefore, *ortho, para* and *meta* nitrobenzlidene malonic derivatives (**1a**–**f**) were allowed to react photolytically with triethylamine in benzene solution.

## 2. Mode of photoreactions

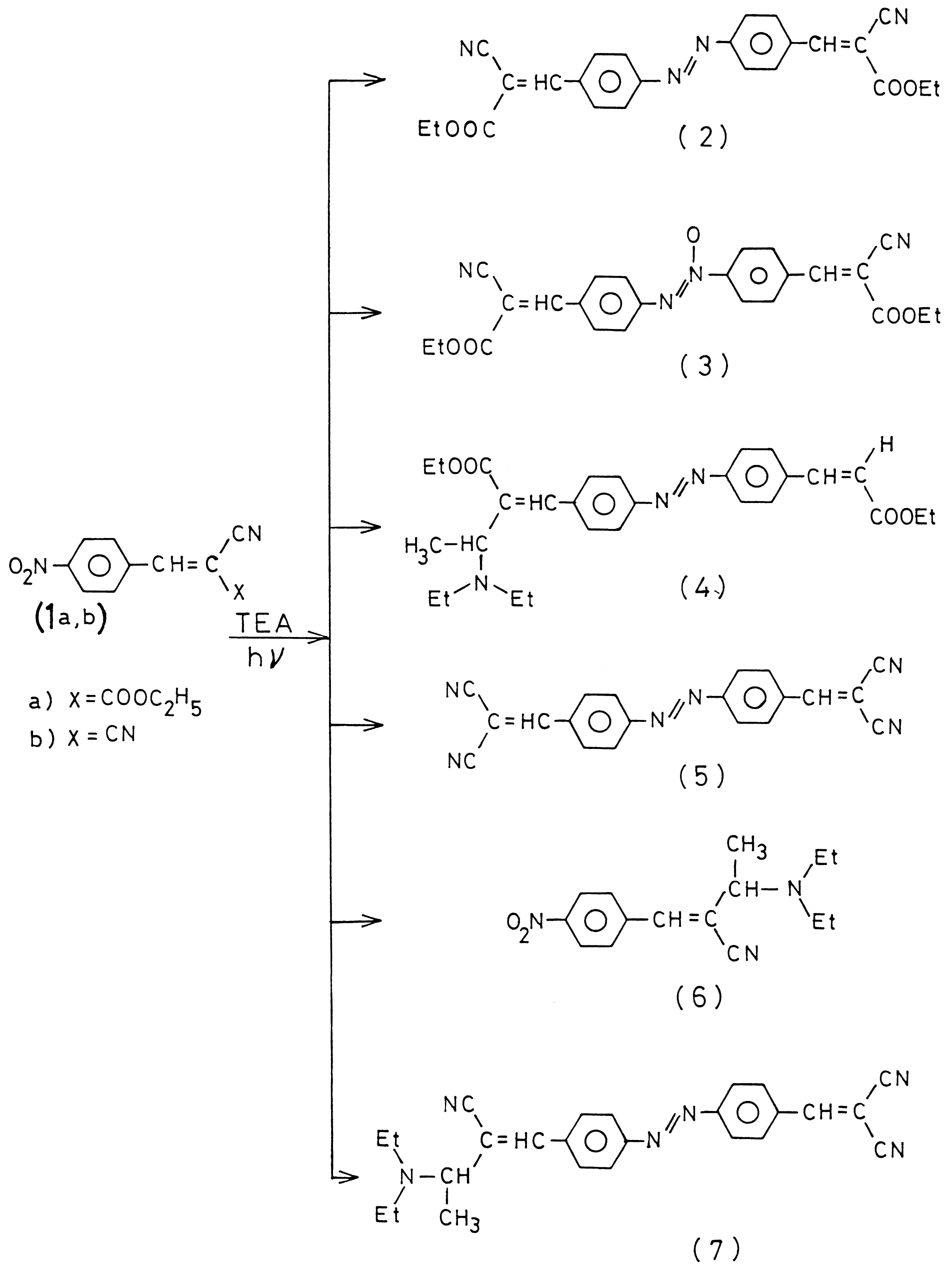
Irradiation of benzene solution containing 1 mmol of *p*-nitrobenzylidene cyanoacetic ester (**1a**) using a 150 W high pressure mercury lamp under a nitrogen atmosphere in the presence of 5 mmol of triethylamine afforded a yellow product in 60% yield. The IR spectrum (KBr) showed absorption bands at 2223 (CN), 1718 (CO), and 1515 cm$^{-1}$ (–N=N–). The analysis with mass spectrum showed *m/z* at 429 for $M+1$, corresponding to a molecular formula $C_{24}H_{20}N_4O_4$ (428.45). Based on these data as well as $^1$H NMR and elemental analysis, structure **2** as azo compound is suggested for the product. However, the azo compound (**2**) was accompanied by two more compounds **3** and **4** in 10% and 5% yields. The IR spectrum of the second compound 3 revealed characteristic bands at 2222, 2182 (CN), 1720 cm$^{-1}$ (CO), and the mass spectrum showed *m/z* at 444 corresponding to a molecular formula $C_{24}H_{20}N_4O_5$ (444.45). Structure **3** is proposed for the product according to its spectral data and elemental analysis. The IR spectrum of the third compound **4** showed only an absorption band due to ester carbonyl with no indication of cyano absorption. Moreover, $^1$H NMR revealed additional signals assigned to alkyl protons. Mass spectrum of the product showed *m/z* at 493 ($M^+$).

The photoinduced reaction of *p*-nitrobenzylidene malononitrile (**1b**) with TEA, afforded also three photoproducts **5**–**7**. Thus, the mass spectrum of **5** showed *m/z* at 334 ($M^+$). The IR spectrum revealed a characteristic absorption for (CN), and its $^1$H NMR spectrum revealed low-field absorption signals only. Based on these data structure **5** is suggested for the product. Also, $^1$H NMR spectrum of product **6** showed characteristic signals for methyl and ethyl protons,

---

*Corresponding author.

1010-6030/99/$ – see front matter © 1999 Elsevier Science S.A. All rights reserved.
PII: S1010-6030(98)00413-4

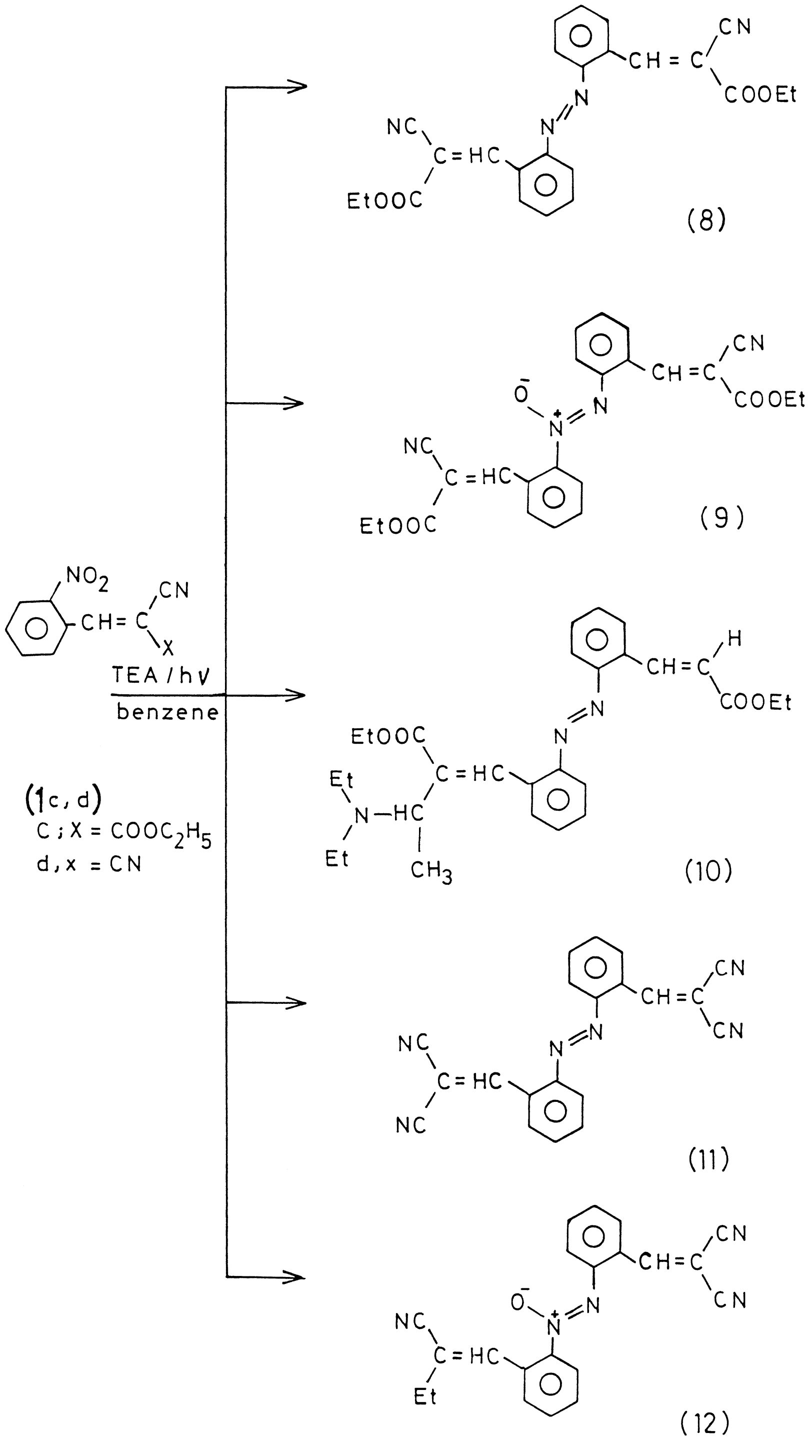


Scheme 1.

whereas its mass spectrum showed *m*/*z* at 273 as $M^+$, corresponding to structure **6**. The third photoproduct **7** was assigned to a substituted azo compound based on elemental analysis and spectral data, (c.f. Scheme 1).

Products of the same modes of photoreduction–photosubstitution were obtained upon photoreactions of *o*-nitrobenzylidene malonic derivatives (**1c**, **d**) with TEA. Three photoproducts were obtained in 25%, 6% and 5% yields, and could be identified as azo and azoxy compounds (**8–10**), respectively, from the reaction with **1c**. The structure of these products were elucidated based on spectral data and elemental analysis. Two products could be isolated from the photoreaction of *o*-nitrobenzlidene malononitrile (**1d**) and were assigned as compounds (**11**,**12**). The IR spectra revealed absorption bands at 2220, 2222 cm$^{-1}$ (CN). However, $^1$H NMR of product (**11**) showed signals assigned to aromatic and methine protons only, whereas $^1$H NMR of compound **12** revealed alkyl signals besides the aromatic and methine protons, (c.f. Scheme 2).

It is remarkable that the *meta* isomers (**1e**) and (**1f**) have a very low reactivity in comparison with that of the *ortho* and/ or *para* isomers under similar reaction conditions, even upon prolonged irradiation in either benzene or acetonitrile solutions. However, minor spots appeared on thin layer chromatography (TLC) which were too minute to warrant isolation or identification. This low reactivity may be

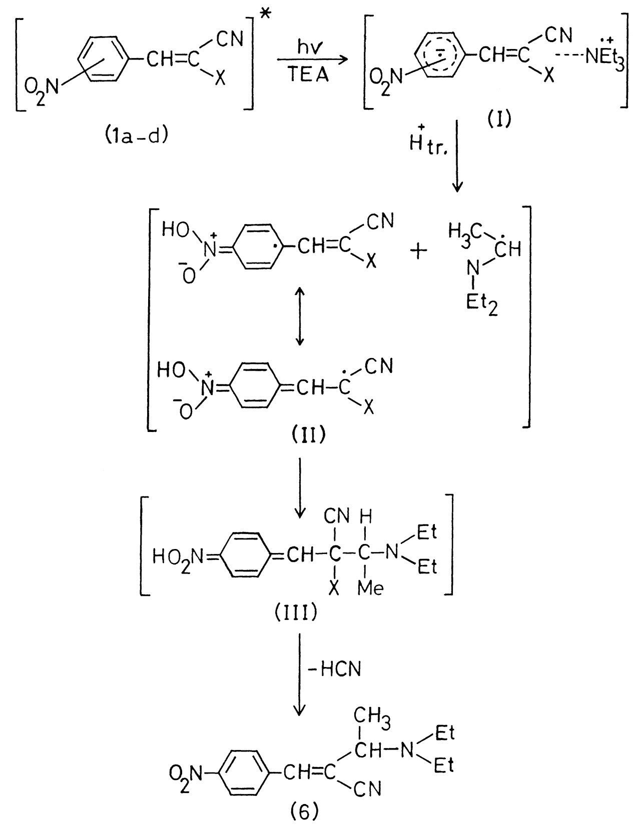


Scheme 2.

accounted for by assuming that the resultant nitroaryl radical (**II**) is less stable in the case of *meta* isomer than in the case of *ortho* and/or *para* isomers which are more stable by conjugation. However, since the triplet lifetimes of the compounds studied in this work are not available to us, one can assume that the triplet lifetime of the less polarized radical ion pair of *meta* isomer is very short, which then rapidly decays to its ground state ($S_0$). However, it has been reported that many *meta* nitrobenzene derivatives have been found to be less reactive than *ortho* and/or *para* nitrobenzenes [7–9] (c.f. Scheme 3).

### 2.1. *Effect of oxygen*

It was found that the photochemical reactions carried out in aerated solutions resulted in a complicated mixture con-



Scheme 3.

taining unidentifiable resinous materials which could be attributed to the effect of oxygen on the product determining dark reaction. However, irradiation of deaerated solution under nitrogen atmosphere minimized the photolysis time to only about 40 min.

### 2.2. *Effect of solvent*

Benzene had been chosen as the main photolysis solvent because it is not ion solvating, and the radical ion pair formed between triplet excited nitro compound and triethylamine is more tight in benzene [5] 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. Also, it assists electron transfer, and it has been successfully used by Matsuura [10], and Döpp [11,12] before. However, nitrobenzylidene malonic derivatives (**1a**–**e**) disappeared faster when irradiated in a polar solvent such as acetonitrile but no remarkable effect was observed on the nature of the photoproducts. However, it is worth noting that the reactants are recovered unchanged from benzene solution after one week in the dark. UV spectra of compounds **1a**–**f** were recorded in benzene, acetonitrile, and/or methanol. Their spectra in methanol and/or acetonitrile consist mainly of two bands and shoulders, whereas the absorption spectra in benzene are much simpler and showed one band only with a maximum absorption around 280–320 nm. However, it is noticed that the absorption spectra of the *p*-isomers have slight red shift than that for *o*-isomers. However, the *m*-isomers showed hypsochromic characters. The UV absorption spectra of compounds **1a**–**f** in the presence of triethylamine were recorded in benzene solution. The spectra showed no complexation between the two reactants and no remarkable bathochromic shift could be seen. These observations could be attributed to the weak ground state interaction between the donor and the acceptor, and the photochemical reaction considered originating from electron transfer. The representative UV spectra are shown in Fig. 1, and their absorption characteristics are collected in Table 1.

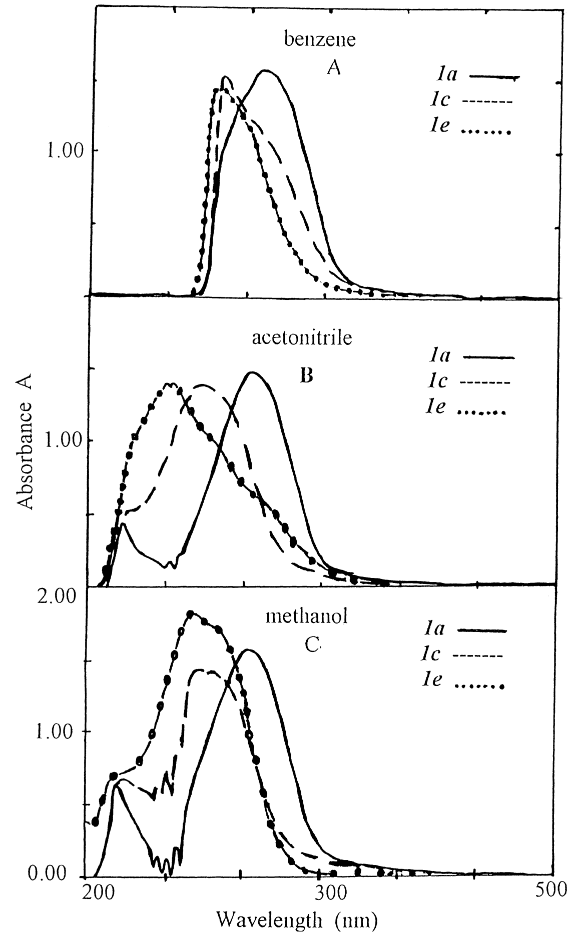


Fig. 1. UV absorption spectra of **1a**, **1c**, **1e** in benzene (A), acetonitrile (B), and methanol (C).

## 3. Discussion

It has been established that nitrobenzenes are photoreduced in alkaline or buffered alcoholic solutions to give aniline and/or coupling photoproducts. The formation of azo and/or azoxy compounds could be accounted for by initial excitation of nitrobenzylidene malonic (NBM) derivatives (**1a**–**d**) by light to the first singlet excited state $^{1}$NBM$^{*}$,

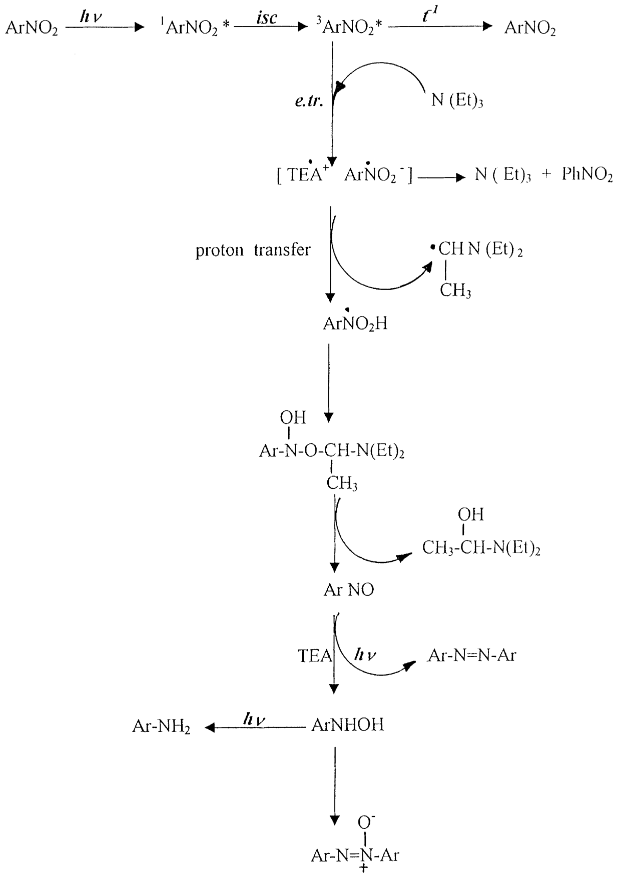
Table 1
$\lambda_{max}$ and log $\varepsilon$ for the UV absorption spectra of compounds **1a–f**

| NBM | Benzene | | Acetonitrile | | Methanol | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | Log $\varepsilon$ | $\lambda_{max}$ | Log $\varepsilon$ | $\lambda_{max}$ | Log $\varepsilon$ |
| **1a** | 280 (sh) | 4.64 | 220 | 4.27 | 220 | 4.78 |
| | 320 | 4.88 | 315 | 4.88 | 310 | 4.90 |
| **1b** | 310 | 4.88 | 220 | 4.18 | 220 (sh), 250 | 4.44, 4.92 |
| | | | 310 | 4.83 | 305 | 4.60 |
| **1c** | 280 | 4.82 | 220 (sh) | 4.40 | 220, 280 | 4.50, 4.86 |
| | 320 (sh) | 4.66 | 280 | 4.83 | 300 (sh) | 4.81 |
| **1d** | 280 | 4.76 | 220 (sh), 250, | 4.80, 4.96 | 220, 280 | 4.96, 4.74 |
| | 320 (sh) | 4.56 | 260, 280 (sh) | 4.92, 4.82 | 305 (sh) | 4.60 |
| | | | 310 (sh) | 4.60 | | |
| **1e** | 280 | 4.79 | 220 (sh), 250, | 4.60, 4.85, | 220 (sh), 280 | 4.54, 4.94 |
| | 305 (sh) | 4.80 | 260, 280 (sh) | 4.85, 4.69 | 300 (sh) | 4.75 |
| | | | 310 (sh) | 4.39 | | |
| **1f** | 290 | 4.88 | 220 (sh), 275 (sh) | 4.40, 4.86 | 220, 280 (sh) | 4.75, 4.81 |
| | | | 295 (sh) | 4.88 | 300 (sh) | 470 |

$^1(n,\pi^*)$, then to its triplet excited state $^3(n,\pi^*)$ through intersystem crossing ISC. The triplet excited state either decayed to its ground state ($S_0$) or picks one electron from TEA resulting in a radical ion pair (RIP), followed by proton transfer to afford the hydroxy-arylaminyl oxide, which is considered the primary key to the nitrosoaryl derivative, then a sequence of ground state reactions leading finally to the coupling products. The suggested pathways [1–5] are shown in Scheme 4.

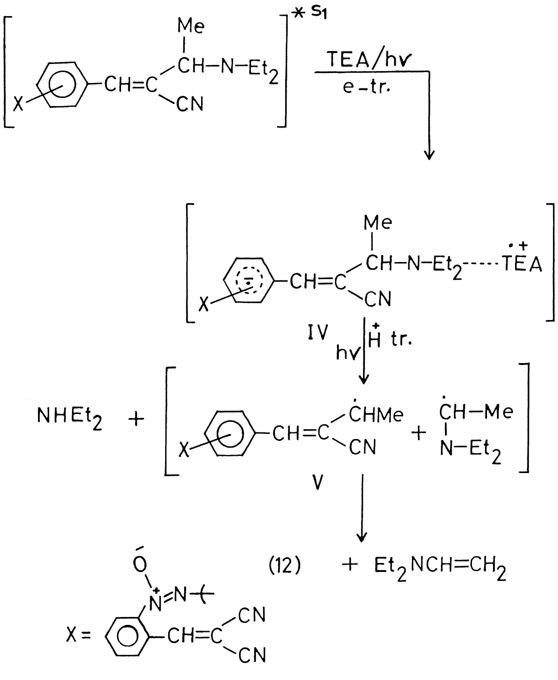
Photochemical reactions of dicyanobenzenes with triethylamine and/or di-isopropylamine have been reported to give substituted products [9]. Similarly, irradiation of 1,2- and 1,4-dicyanobenzenes with allylic silanes, germanes and stannanes in acetonitrile have resulted in replacement one of the cyano groups by allylic [13,14]. Thus, the mechanism of formation of the photosubstituted product **6** is suggested to proceed through a radical ion pair mechanism, as shown in Scheme 3. The key step is assumed to be a photoinduced electron transfer from triethylamine to the photoexcited nitrobenzylidene malonic derivatives (NBM$^*$) resulting in a formation of a radical ion pair (**I**), ($NBM^{\cdot-}\cdots Et_3N^{\cdot+}$). This is followed by proton transfer which occurs predominantly from the $\alpha$-CH position of the aminium ion leading to the formation of nitroaryl radical (II) and the transient (III). Subsequent thermal elimination of CN and $H^+$ afforded the substituted product (*6*).

Among the substituted products the alkylated product **12** is particularly interesting, because only one ethyl group of the TEA has replaced the cyano group of the nitrobenzylidene. A reasonable explanation is that a secondary photochemical reaction between the primary photosubstituted product (e.g. **7**) and the excess of triethylamine resulted in a radical ion pair (**IV**). Electron transfer, followed by proton transfer formed a radical intermediate (**V**) with elimination of one mole of diethylamine. The radical ion pair (**V**) leads finally to the alkylated product **12**, as shown in (Scheme 5).



Scheme 4.

The results presented in this paper indicate that nitrobenzylidene malonic derivatives NBM are effectively photoreduced by triethylamine in benzene solution. Meanwhile, the photoreduction is accompanied by photosubstitution of one cyano group by triethylamine. Hence, the photosubstitution reaction is a potentially useful carbon–carbon bond forming reaction.



Scheme 5.

## 4. Experimental

All melting points are uncorrected. UV absorption spectra were recorded on a Shimadzu Spectrophotometer UV-240. IR spectra were recorded (KBr) on a Shimadzu 408 and a Pye Unicam Spectrometer. $^1$H NMR spectra were recorded on a Varian EM 390 (90 MHz) using $CDCl_3$ as solvent, the chemical shifts are expressed ($\delta$, ppm), TMS was used as internal standard. Mass Spectrometer MS 9 (AET) EI Mode. Elemental analysis were obtained from the Microanalytical Centre at Cairo University, Egypt.

### 4.1. Materials

Nitrobenzylidene malonic derivatives (**1a–f**) were prepared according to the reported method [15], and were crystallized twice from ethanol. Merck triethylamine was dried over $P_2O_5$, and spectrograde benzene was distilled before use and kept over anhydrous $CaCl_2$. Authentic samples were prepared according to standard methods [16–18].

### 4.2. Photolysis

A 150 W high pressure mercury lamp was used in connection with a water-cooled immersion well made out of Duran glass ($\lambda > 280$ nm), and a 250 ml cylindrical vessel. The solutions were nitrogen purged for 30 min prior to irradiation and throughout the entire photolysis.

### 4.3. General workup procedure

The photolyzed solutions were concentrated to dryness in vacuo, and the residue was subjected to preparative layer chromatography. 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, crystallized and identified by elemental analysis and spectral data.

## 5. Irradiation of nitrobenzylidene malonic derivatives with triethylamine

### 5.1. General procedure

A mixture of 1.0 mmol of nitrobenzylidene malonic derivatives (**1a–f**), and 5.0 mmol of triethylamine in 200 ml of dry benzene solution was photolyzed for various times. The reactions were monitored by TLC, and worked up as described above.

### 5.2. Product 2

Yellow crystals (MeOH). Yield: 60%. M.p.: 200–203°C. IR ($\nu$ = cm$^{-1}$): 2223 (CN), 1718 (CO). $^1$H NMR: 1.2–1.3 (t, 6H, $2CH_3$); 4.3–4.4 (q, 4H, $2CH_2$); 7.1–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 429$. *Anal.* Calc. for $C_{24}H_{20}N_4O_4$ (428.45): C, 67.28; H, 4.71; N, 13.08. Found: C, 67.13; H, 4.53; N, 12.88%.

### 5.3. Product 3

Yellow crystals (EtOH). Yield: 10%. M.p.: 145–148°C. IR: 2222, 2182 (CN), 1720 (CO). $^1$H NMR: 1.2–1.3 (t, 6H, $2CH_3$); 4.3–4.3 (q, 4H, $2CH_2$); 7.1–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 444$; *Anal.* Calc. for $C_{24}H_{20}N_4)_5$ (444.45): C, 64.86; H, 4.54; N, 12.61. Found: C, 64.67; H, 4.34; N, 12.80%.

### 5.4. Product 4

Brown crystals (MeOH). Yield: 8%. M.p.: 160–174°C. IR: 1725 (CO). $^1$H NMR: 1.1–1.2 (m, 12H, $4CH_3$); 1.3 (d, 3H, $CH_3$); 4.1–4.2 (q, 8H, $4CH_2$); 4.5–4.55 (q, 1H, CH); 7.1–7.9 (m, 11H, Ar-H + methine-H). MS: $m/z = 493$; *Anal.* Calc. for $C_{28}H_{35}N_3O_5$ (493.60): C, 68.13; H, 7.15: N, 8.51. Found: C, 68.01; H, 7.32; N, 8.31%.

### 5.5. Product 5

Brown crystals (MeOH). Yield: 45%. M.p.: 290–92°C. IR: 2195, 2120 (CN). $^1$H NMR: 7.1–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 334$; *Anal.* Calc. for $C_{20}H_{10}N_6$ (334.34): C, 71.85; H, 3.01; N, 25.14. Found: C, 71.73; H, 2.86; N, 24.97%.

### 5.6. Product 6

Orange crystals (acetone). Yield: 10%. M.p.: 270–272°C. IR: 2189 (CN). $^1$H NMR: 1.3–1.4 (t, 6H, $2CH_2$); 2.2 (d, 3H,

$CH_3$); 4.2–4.4 (q, 4H, $2CH_2$); 4.7 (q, 1H, CH); 7.1–7.9 (m, 5H, Ar-H + methine-H). MS: $m/z = 273$; *Anal.* Calc. for $C_{15}H_{19}N_3O_2$ (273.34): C, 65.91; H, 7.01; N, 15.37. Found: C, 65.73; H, 6.85; N, 15.22%.

### 5.7. Product 7

Brown crystals (MeOH). Yield: 5%. M.p.: 165–67°C. IR: 2212, 2220 (CN). $^1H$ NMR: 1.3–1.4 (t, 6H, $2CH_3$); 2.2 (d, 3H, $CH_3$); 4.2–4.4 (q, 4H, $2CH_2$); 4.7 (q, 1H, CH); 7.1–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 408$; *Anal.* Calc. for $C_{25}H_{24}N_6$ (408.51): C, 73.50; H, 5.92; N, 20.57. Found: C, 73.38; H, 5.79; N, 20.46%.

### 5.8. Product 8

Yellow crystals (acetone). Yield: 25%. M.p.: 280–283°C. IR: 2220 (CN), 1705, 1695 (CO). $^1H$ NMR: 1.2–1.3 (t,6H,$2CH_3$), 4.3–4.4 (q, 4H, $2CH_2$), 7.2–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 429$. *Anal.* Calc. for $C_{24}H_{20}N_4O_4$ (428.45): C, 67.28; H, 4.71; N, 13.08. Found: C, 67.11; H, 4.56; N, 12.92%.

### 5.9. Product 9

Orange crystals (MeOH). Yield: 6%. M.p.: 140–142°C. IR: 2228 (CN), 1722 (CO). $^1H$ NMR: 1.2–1.3 (t, 6H, $2CH_3$); 4.3–4.4 (q, 4H, $2CH_2$); 7.1–8 (m, 10H, Ar-H + methine-H). MS: $m/z = 444$. *Anal.* Calc. for $C_{24}H_{20}N_4O_5$ (444.45): C, 64.86; H, 4.54; N, 12.61. Found: C, 64.72; H, 4.36; N, 12.50%.

### 5.10. Product 10

Yellow crystals (EtOH). Yield: 5%. M.p.: 180–183°C. IR: 1710, 1720 (CN). $^1H$ NMR: 1.1–1.2 (m, 12H, $4CH_3$); 1.3 (d, 3H, $CH_3$); 4.1–4.2 (q, 8H, $4CH_2$); 4.5–4.55 (q, 1H, CH); 7.1–7.9 (m, 11H, Ar-H + methine-H). MS: $m/z = 494$, *Anal.* Calc. for $C_{28}H_{35}N_3O_5$ (493.60): C, 68.13; H, 7.15; N, 8.50. Found: C, 68.03; H, 7.25; N, 8.36%.

### 5.11. Product 11

Pale orange crystals (EtOH). Yield: 40%. M.p.: 192–198°C. IR: 2215, 2222 (CN). $^1H$ NMR: 7.1–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 335$. *Anal.* Calc. for $C_{20}H_{10}H_6$ (334.34): C, 71.85; H, 3.01; N, 25.14. Found: C, 71.95; H, 2.87; N, 25.02%.

### 5.12. Product 12

Brown crystals (acetone). Yield: 6%. M.p.: 150–152°C. IR: 2195, 2220 (CN). $^1H$ NMR: 1.2–1.3 (t, 3H, $CH_3$); 2.1 (q, 2H, $CH_2$); 7.1–7.9 (m, 10H, Ar-H + methine-H). MS: $m/z = 337$. *Anal.* Calc. for $C_{21}H_{15}N_5O$ (357.39): C, 71.37; H, 4.28; N, 19.82. Found: C, 71.50; H, 4.09; N, 19.66%.

## References

[1] J.A. Barltrop, N.J. Bunce, J. Chem. Soc. C (1968) 1467.
[2] R. Hurley, A.C. Testa, J. Am. Chem. Soc. 88 (1966) 4330.
[3] D. Döpp, Top. Current Chem. 55 (1975) 51.
[4] S.G. Cohen, A. Parola, G.H. Parson, Chem. Rev. 73(2) (1973) 141.
[5] D. Döpp, Photochemical reactivity of the nitro group, in: W.M. Horspool (Ed.), Organic Photochemistry and Photobiology, Ch. 81, CRS Press, Boca Raton; Pill-Soon Song 81 (1995) 1019.
[6] A.V. El'tsov, N.A. Kuznetsova, A.N. Frolov, Zh. Org. Khim 7 (1971) 817.
[7] G.G. Wubbles, R.L. Letsinger, J. Am. Chem. Soc. 96(12) (1974) 6698–6706.
[8] P. Wan, K. Yates, Can. J. Chem. 64 (1986) 2076.
[9] M. Ohashi, K. Migake, K. Tsujimote, Bull. Chem. Soc. Japan 53 (1980) 1683.
[10] T. Matsuura, M. Takami, I. Saito, Tetrahedron Lett. 8 (1974) 661.
[11] D. Döpp, J. Heufer, Tetrahedron Lett. 23 (1982) 1553.
[12] D. Döpp, J. Photochem. 32 (1986) 243.
[13] K. Mizuno, T. Nishiyama, K. Terasaka, M. Yasuda, K. Shima, Y. Otsuji, Tetrahedron 88(44) (1992) 9673.
[14] K. Nakanishi, K. Mizuno, Y. Otsuji, Bull. Chem. Soc. Japan 66 (1993) 2371.
[15] F. Freeman, Chem. Rev. 69(5) (1969) 591.
[16] R.J. Corruccinic, E.C. Gilbert, J. Am. Chem. Soc. 61 (1939) 2925.
[17] H.P. Bigelow, A. Palmer, Org. Synth. 16 (1931).
[18] H.B. Nishet, J. Chem. Soc. (1927) 2081.