Available online at www.sciencedirect.com
ScienceDirect
Tetrahedron 63 (2007) 12286–12293
Tetrahedron

Solvent-dependent effect by carbon dioxide on the photoreactions of (9-anthryl)alkylamines

Masahiro Horiguchi and Yoshikatsu Ito*

Department of Synthetic Chemistry and Biological Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Kyoto 615-8510, Japan

Received 5 September 2007; revised 27 September 2007; accepted 27 September 2007
Available online 29 September 2007

Abstract—The effect of CO_2 on a photoreaction was first studied systematically by using (9-anthryl)alkylamines (APA, AEA, and AMA) as the starting compound. From close scrutiny of the results, the CO_2 effect was clearly observed and was well rationalized by the previously reported novel solvent dependence of the amine–CO_2 reversible reactions. For instance, the yield of the dimer (**h–t** from APA or AEA, **h–t+h–h** from AMA) obtained in MeOH or DMSO was higher under CO_2 than under argon and this was ascribed to formation of either ammonium bicarbonate/carbonate in MeOH or carbamic acid in DMSO, which will prevent the nitrogen lone pair from being involved in electron-transfer reactions. In fact, the electron-transfer side reactions producing **1–3** in DMSO were strongly inhibited under CO_2. Also, due to formation of noncovalent linkage between the ammonium cation and the carbamate anion in 2-PrOH, the proportion of **h–h** relative to **h–t** produced from AMA in 2-PrOH was increased by carrying out the reaction under CO_2.

1. Introduction

Many amines react with carbon dioxide to form carbamic acids (Eq. 1).[1] The acids are unstable and easily dissociate back to amines and CO_2, or react with another amine molecule to form ammonium carbamates (Eqs. 1 and 2). In aqueous solution, ammonium bicarbonates/carbonates are also formed (Eq. 3). These reactions are reversible and have recently been utilized for preparation of a variety of reversible supramolecular materials such as switchable solvent systems,[2] switchable surfactants,[3] switchable polymeric hosts,[4] reversible organogels,[5] and reversible organosilicas.[6] They have also been used for controlling the underlying thermal reactions, e.g., enhancement of the reaction rate and the product selectivity.[7]

$$RNH_2 + CO_2 \rightleftarrows RNHCO_2H \quad (1)$$

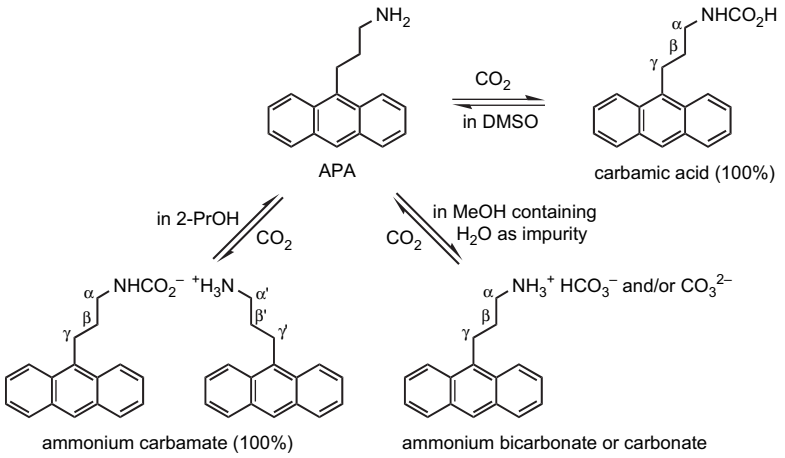
$$RNHCO_2H + RNH_2 \rightleftarrows RNHCO_2^- RNH_3^+ \quad (2)$$

$$RNH_2 + CO_2 + H_2O \rightleftarrows RNH_3^+ HCO_3^- \quad (3)$$

For the past few years we have studied the solvent dependence of the formation of carbamic acid species (i.e., carbamic acid and ammonium carbamate) from particular amines and CO_2: for our previous papers on the amine–CO_2 reaction system, see Ref. 8. In protophilic, dipolar, aprotic solvent such as DMSO, DMF, pyridine, or dioxane (unlike in water), the equilibrium of Eq. 2 lay so far to the left for the amines studied.[8a,b,e] Concurrently, we attempted to apply this solvent dependence to manage photochemical reactions. Now, we wish to report the effect of CO_2 on the photoreactions of ω-(9-anthryl)alkylamines. The original aim was to control their photodimerization regioselectivity by using the ammonium carbamate ionic linkage as a noncovalent linker (see the structure A, which is proposed in Scheme 5). Although we could achieve only a limited success for this purpose, the overall CO_2 effects observed here were consistent with the previously reported[8a,b] novel solvent dependence in the amine–CO_2 reversible reactions (Eqs. 1–3). To our knowledge,

Keywords: Carbon dioxide; Anthryl amine; Carbamic acid; Ammonium carbamate; Solvent dependence; Photoreaction; Reaction control.
* Corresponding author. Tel./fax: +81 75 383 2718; e-mail: yito@sbchem.kyoto-u.ac.jp

0040–4020/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2007.09.069



Scheme 1. Solvent dependence of the 3-(9-anthryl)propylamine (APA)–CO_2 reaction.

the photochemistry of the carbamic acid species has not been systematically studied so far.[†]

2. Results and discussion

2.1. Reaction of APA with CO_2

We have already performed detailed investigations about the solvent dependence of the formation of carbamic acid species from ω-(1-naphthyl)alkylamines.[8a,b] The results were obtained mainly on the basis of NMR and IR analyses before and after bubbling of CO_2 through the amine solution. In a DMSO solution, 3-(1-naphthyl)propylamine (NPA) was exclusively converted to the corresponding carbamic acid, whereas in 2-PrOH or in MeOH it was converted to the ammonium carbamate or to the ammonium bicarbonate/carbonate, respectively.[8a]

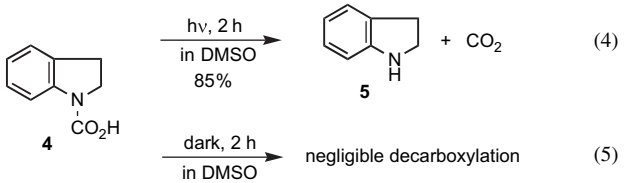
Here the same experiment was repeated for 3-(9-anthryl)propylamine (APA) and exactly the parallel solvent dependence was observed, i.e., formation of carbamic acid in DMSO, ammonium carbamate in 2-PrOH, and ammonium bicarbonate/carbonate in MeOH (Scheme 1). In diethyl ether, the ammonium carbamate precipitated as a pale yellow solid. The main features of the NMR and IR spectra that were obtained after the CO_2 bubbling, are given below ((a)–(c)). These are exactly analogous with those found for NPA.[8a]

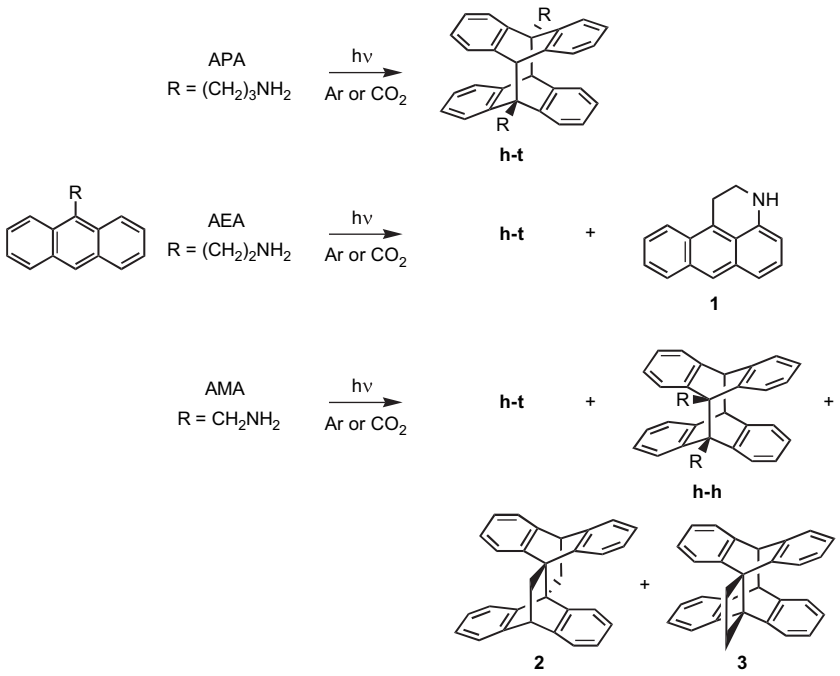
(a) *In DMSO*. The presence of only three signals corresponding to the three methylene groups could be seen from the ^{1}H and ^{13}C NMR spectra (i.e., the carbamic acid yield is 100%). The α-methylene proton was considerably shifted to a lower field upon bubbling of CO_2 ($\Delta\delta$ 0.43 ppm) and resonanced as a quasi-quartet at δ 3.18. The NH proton appeared as a broad triplet at δ 6.97. The carboxy carbon of the carbamic acid appeared at δ 157.0 ppm. An HMBC cross peak was observed between the α-methylene proton and the carboxy carbon. The stretching frequency $\nu_{C=O}$ of NCOOH was 1700 cm^{-1}.

(b) *In 2-PrOH*. There were six methylene-proton signals and six methylene-carbon signals in the ^{1}H and ^{13}C NMR spectra. This corresponds to the formation of the carbamate anion and the ammonium cation. The α-methylene proton appeared at δ 3.33 and the α′-methylene proton appeared at δ 3.00. ^{1}H NMR can neither distinguish between the carbamate anion and the coexistent carbamic acid, nor between the ammonium cation and the coexistent free amine.[8a] However, the observed six methylene-proton signals were almost equal in intensity. Hence, the yield of the ammonium carbamate may be nearly 100%. A broad signal of the carboxy carbon of the carbamate anion resonanced at δ 160.5 ppm. There was an HMBC cross peak between the α-methylene proton and the carboxy carbon.

(c) *In MeOH*. Like in DMSO, three methylene signals were observed by the ^{1}H and ^{13}C NMR measurements. The downfield shift of the α-methylene proton was relatively small ($\Delta\delta$ 0.29 ppm) and it resonanced at δ 3.12. The formation of bicarbonate or carbonate was indicated by the ^{13}C NMR peak at δ 161.3 ppm and by the strong IR bands at 1636 and 1310 cm^{-1}. However, the amount of the residual free amine cannot be estimated, because it is indistinguishable from the ammonium species by ^{1}H NMR.[8a]

[†] The decarboxylation of several *N*-aralkyl- and *N*-arylcarbamic acids, which are formed in situ from the corresponding amines in CO_2-saturated DMSO-d_6,[8a,b] was investigated by us.[8c] It was promoted by irradiation (through Pyrex at room temperature) and an especially large acceleration was observed for certain *N*-arylcarbamic acids. For example, the indoline-derived carbamic acid **4** was decarboxylated in 85% yield into indoline (**5**) after 2 h of irradiation (Eq. 4). In the dark, the decarboxylation was negligible (Eq. 5). The slow decarboxylation in the dark is plausible, because it is an endergonic reaction (ΔG=9 kcal/mol) as mentioned below. Unlike *N*-aralkylamines such as APA (Scheme 1) and 3-(1-naphthyl)propylamine (NPA), *N*-arylamines can be converted only partly to the carbamic acid in CO_2-saturated DMSO-d_6, e.g., **4** vs **5**=22:78.[8a,b] The content of **4**, however, increased at lower temperatures and reached nearly 100% at −52 °C in CO_2-saturated DMF-d_7 (see ^{1}H and ^{13}C NMR in Figs. 1 and 2). The temperature dependence of [**5**]/[**4**] (Fig. 1) was thermodynamically analyzed (Fig. 3) and the free energy change ΔG for the reaction **4** ⇄ **5**+CO_2 was estimated as +9 kcal/mol. The theoretical evaluation of ΔG for $NH_2COOH \rightleftarrows NH_3+CO_2$ afforded +10.5 kcal/mol.[9,1]





Scheme 2. Photoreactions of (9-anthryl)alkylamines under argon or CO_2.

2.2. Photoreactions of (9-anthryl)alkylamines

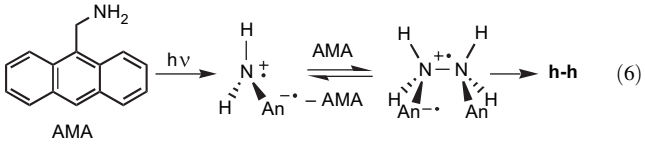
The anthryl chromophore generally undergoes rapid photodimerization.[10,11] With this in mind, the effect of CO_2 on the photodimerization reactivity of APA, 2-(9-anthryl)ethylamine (AEA), and (9-anthryl)methylamine (AMA) was examined. The solvent employed is MeOH, DMSO, or 2-PrOH. The irradiation was carried out with a 400-W high pressure mercury lamp (Pyrex) under argon or CO_2.

The results are summarized in Scheme 2 and Table 1. It is known that irradiation of a 9-substituted anthracene gives predominantly a head-to-tail dimer (**h–t**) with minor formation of a sterically more hindered head-to-head dimer (**h–h**).[10,11] APA and AEA yielded only **h–t** (R=$(CH_2)_3NH_2$ and $(CH_2)_2NH_2$, respectively) without any detectable formation of **h–h** (Table 1). In contrast, AMA produced both **h–h** (R=CH_2NH_2) and **h–t** (R=CH_2NH_2).[‡] As an isolated additional product, AEA gave an intramolecular photoamination product **1** in DMSO under argon atmosphere. Although the mechanism of this interesting cyclization reaction is not elucidated, a similar reaction occurred for some ω-arylalkylamines by photosensitization with some electron acceptors such as 1,4-dicyanonaphthalene or 1,3-dicyanobenzene.[12] In the case of AMA, small amounts of lepidopterene (**2**) and biplanene (**3**) were obtained. These byproducts **2** and **3** may be formed through the competitive C–N bond homolysis followed by the coupling of two 9-anthrylmethyl radicals.[11a,13,14]

2.3. Close scrutiny of the results (Table 1)

Probably, a simple glance into Table 1 will not disclose the important effect of CO_2, which may thus be overlooked. From the closer inspection, however, it can be seen that irrespective of the starting anthrylamines, the total yield of the dimers (**h–t** and **h–h**) obtained in MeOH or DMSO is higher under CO_2 than under argon (see runs 1–4, 7–10, and 13–16), whereas this is not the case for the total dimer yield obtained in 2-PrOH (see runs 5, 6, 11, 12, 17, and 18). The former outcome may be ascribed to the formation of either ammonium bicarbonate/carbonate ($-NH_3^+HCO_3^-/CO_3^{2-}$) or carbamic acid (–NHCOOH) in MeOH or DMSO, respectively, in the presence of CO_2 (Scheme 1). When the amino group is protonated or carboxylated, a single electron transfer from the lone pair of the nitrogen atom will become hard to happen.[8a] Hence, potential side reactions that are caused by the resultant ion radicals will decrease, leading to higher yields for the photodimerization (Scheme 3). On the other hand, the carbamate anion ($-NHCOO^-$) formed in 2-PrOH will not be able to restrain the electron transfer from the amine moiety so effectively, because the electron withdrawing property of the dissociated carboxyl group (COO^-) should be much smaller as compared with the undissociated

[‡] Under argon, **h–h** was produced presumably via an amine dimer cation radical, which may be generated through sequential formation of an intramolecular exciplex (or a radical ion pair) and a three-electron σ bond (Eq. 6): see Lewis, F. D.; Li, L.-S.; Kurth, T. L.; Kalgutkar, R. S. *J. Am. Chem. Soc.* **2000**, *122*, 8573–8574, and the references therein. Much more experiments will be required to prove the participation of this triplex-like intermediate. The intramolecular electron transfer seems less efficient in the case of APA and AEA because of their longer methylene-chain length.

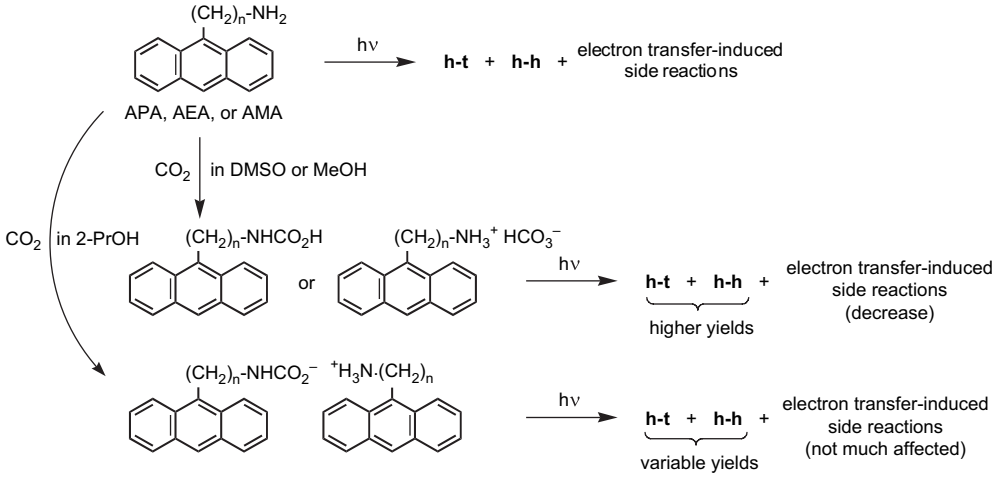


(6)

Table 1. Photoreactions of (9-anthryl)alkylamines under argon or CO_2 in three different solvents

Run	Amine	Solvent	Atmosphere	Irradiation		Conversion (%)	Product yield[a] (%)			**h–t/h–h**
				h	°C		**h–t**	**h–h**	Others	
1	APA	MeOH	Ar	2	3	59	71	0	—	100:0
2			CO_2	2	3	62	86	0	—	100:0
3		DMSO	Ar	2.3	21	~100	78	0	—	100:0
4			CO_2	2.3	21	87	93	0	—	100:0
5		2-PrOH	Ar	2	15	~100	65	0	—	100:0
6			CO_2	2	15	66	78	0	—	100:0
7	AEA	MeOH	Ar	2	3	66	~100	0	—	100:0
8			CO_2	2	3	59	~100	0	—	100:0
9		DMSO	Ar	2	21	61	78	0	**1** (18%)	100:0
10			CO_2	2	21	86	~100	0	—	100:0
11		2-PrOH	Ar	2	15	94	59	0	—	100:0
12			CO_2	2	15	80	50	0	—	100:0
13	AMA	MeOH	Ar	2	3	93	32	24	**2** (trace), **3** (trace)	57:43
14			CO_2	2	3	96	37	23	**2** (trace), **3** (trace)	62:38
15		DMSO	Ar	2	21	65	34	28	**2** (10%), **3** (11%)	55:45
16			CO_2	2	21	93	57	37	**2** (trace), **3** (trace)	61:39
17		2-PrOH	Ar	2	15	~100	46	38	**2** (7%), **3** (6%)	55:45
18			CO_2	2	15	~100	29	40	**2** (10%), **3** (7%)	42:58

[a] Yields are based on the consumed reactant.

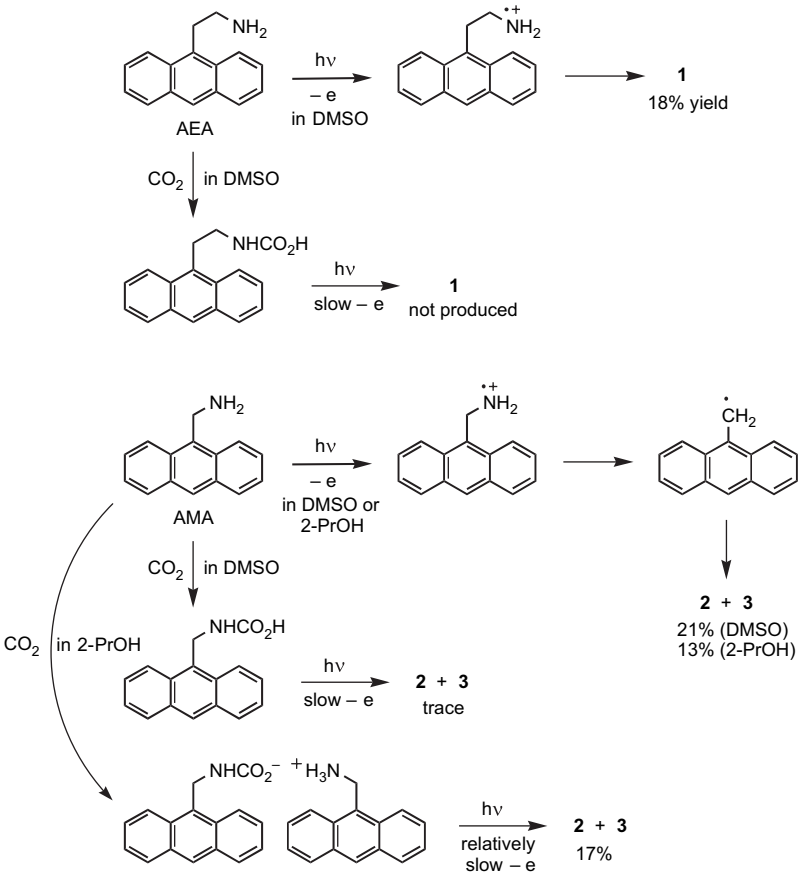


Scheme 3. Effect of electron transfer-initiated side reactions on the photodimerization.

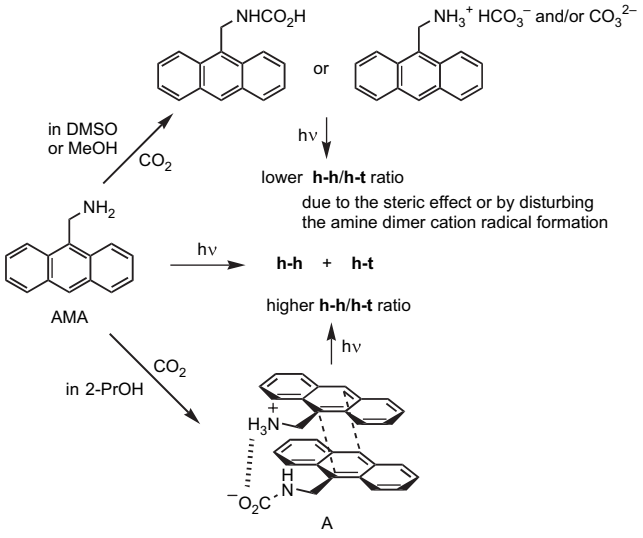
carboxyl group (COOH).[8a] Therefore, the observed CO_2 effect is variable in this solvent.

Furthermore, byproducts such as **1**–**3** are thought to be formed through electron transfer from the amino group or through exciplex involving the amino group.[12,15a,16] Actually, the production of **1** (from AEA) or **2**+**3** (from AMA) in DMSO was inhibited under CO_2 (runs 10 and 16). On the other hand, the production of **2**+**3** in 2-PrOH was not quenched by CO_2 (run 18). Consideration to the CO_2 effect on the byproducts **1**–**3** is illustrated in Scheme 4. The same line of discussion was performed to explain the changes in fluorescence intensities of ω-(1-naphthyl)alkylamines,[8a] where the fluorescence was quenched via intramolecular electron transfer from the amine moiety to the naphthalene moiety at various degrees depending on the solvent (see Scheme 3 in Ref. 8a). Therefore, CO_2 saturation of an amine solution in suitable solvent (DMSO, DMF, pyridine or MeOH) may be utilized to restrain its amine function from causing competing electron-transfer side reactions.

With regard to the ratio of **h**–**t** vs **h**–**h** in the photoreaction of AMA in MeOH (runs 13 and 14) or DMSO (runs 15 and 16), the proportion of **h**–**h** decreased when the irradiation was carried out under CO_2 instead of argon. This is probably because the formation of the bicarbonate/carbonate or the carbamic acid not only makes the 9-substituent more bulky, but also suppresses the formation of the amine dimer cation radical depicted in Eq. 6. On the other hand, in the 2-PrOH solution (runs 17 and 18) the proportion of **h**–**h** increased in the presence of CO_2. This opposite effect by CO_2 may originate in the formation of ammonium carbamate in 2-PrOH. Ionic noncovalent linkage between the ammonium cation and the carbamate anion may enforce two anthracene rings to arrange in a head-to-head fashion (Scheme 5, structure A), thereby favoring the route to the head-to-head dimer.



Scheme 4. Consideration to the CO_2 effect on the byproducts **1**–**3**, which are formed through electron transfer-initiated side reactions.



Scheme 5. Control of the (9-anthryl)methylamine (AMA) photodimerization by using CO_2.

3. Conclusion

A systematic attempt to control photochemistry by using CO_2 was studied for the first time. Although not necessarily big, the overall effect of CO_2 on the photoreactions of (9-anthryl)alkylamines (APA, AEA, AMA) was clearly observed on the basis of close analysis of the results. Thus, the yield for the dimers (**h–t** from APA or AEA, **h–t+h–h** from AMA) obtained in MeOH or DMSO was higher under CO_2 than under argon and this was ascribed to formation of either ammonium bicarbonate/carbonate in MeOH or carbamic acid in DMSO. It is considered that the formation of these species suppresses side reactions, which are initiated by the electron transfer from the amino group. In fact,

production of the electron-transfer-induced byproducts **1**–**3** in DMSO was strongly inhibited under CO_2. Also, due to the formation of ammonium carbamate in 2-PrOH, the proportion of **h**–**h** relative to **h**–**t** produced from AMA in 2-PrOH was increased by carrying out the reaction under CO_2. In this case, the ionic linkage between the ammonium cation and the carbamate anion is probably operating as a noncovalent linker, leading to the head-to-head photodimerization. It is noticeable that this paper not only substantiates the previous[8a,b] spectroscopic finding about the solvent dependence of the amine–CO_2 reactions, but also presents the first example showing that such solvent dependence can be successfully applied to the reaction control.

4. Experimental

4.1. General

^{1}H and ^{13}C NMR spectra were measured on JEOL or Varian FT NMR spectrometers. Mass and IR spectra were recorded on JEOL JMS-HX110A and SHIMADZU FTIR-8400 spectrometers, respectively. The in situ measurements of ^{1}H and ^{13}C NMR, HMBC, and IR spectra in MeOH, DMSO, and 2-PrOH before and after bubbling CO_2 through the solution of APA were carried out as described previously.[8a]

4.2. Materials

4.2.1. 3-(9-Anthryl)propylamine (APA). It was prepared according to the literature methods from 3-(9-anthryl)propionitrile, which had been prepared from 9-anthraldehyde via 3-(9-anthryl)acrylonitrile.[17–19] APA·HCl: 4.34 g (53% yield) was obtained by $LiAlH_4$ reduction of 3-(9-anthryl)-propionitrile (6.95 g) as pale yellow prisms after recrystallization with MeOH/AcOEt; mp >236 °C dec (lit.[19] mp 242–244 °C dec); ^{1}H NMR (400.4 MHz, DMSO-d_6) δ 1.99 (tt, J=8.0, 8.0 Hz, 2H), 3.04 (br s, 2H), 3.68 (t, J=8.0 Hz, 2H), 7.55 (ddd, J=8.8, 6.4, 1.6 Hz, 2H), 7.50 (ddd, J=8.0, 6.4, 1.2 Hz, 2H), 8.07 (dd, J=8.0, 1.2 Hz, 2H), 8.14 (br s, NH), 8.38 (dd, J=8.0, 0.8 Hz, 2H), 8.48 (s, 1H) ppm; ^{13}C NMR (100.7 MHz, DMSO-d_6) δ 24.29, 28.86, 38.83, 124.19, 124.91, 125.55, 125.68, 128.84, 128.88, 130.90, 133.30 ppm; IR (KBr) 631.6, 731.9, 788.8, 839.9, 878.5, 953.7, 1147.6, 1323.1, 1339.7, 1387.7, 1444.6, 1491.8, 1598.9, 1620.5, 2800–3200 (br), 3423.8 (br) cm^{-1}; MS (FAB) m/z (%) 236 (M^+, 100), 191 (15); HRMS (FAB) calcd for $C_{17}H_{18}N$ 236.1439, found 236.1437.

An aqueous solution of APA·HCl was made alkaline by addition of aqueous NaOH and then extracted with ether. The ether solution was dried with $MgSO_4$ and the solvent was removed by evaporation to afford the free amine APA: ^{1}H NMR (400.4 MHz, DMSO-d_6) δ 1.76 (tt, J=8.4, 6.4 Hz, 2H), 2.75 (t, J=6.4 Hz, 2H), 3.61 (t, J=8.0 Hz, 2H), 7.48 (ddd, J=8.0, 6.8, 1.6 Hz, 2H), 7.53 (ddd, J=8.8, 6.8, 1.6 Hz, 2H), 8.05 (dd, J=8.0, 1.6 Hz, 2H), 8.34 (d, J=8.8 Hz, 2H), 8.43 (s, 1H) ppm; ^{13}C NMR (100.7 MHz, DMSO-d_6) δ 24.82, 35.30, 41.83, 124.27, 124.80, 124.96, 125.39, 128.74, 128.83, 130.92, 134.96 ppm.

4.2.2. 2-(9-Anthryl)ethylamine (AEA). It was prepared from 9-(chloromethyl)anthracene by modifying the reaction conditions of the literature method.[20] Thus, a solution of 9-(chloromethyl)anthracene (20.75 g, 92 mmol) in 300 mL of DMF was added dropwise to a solution of NaCN (9.01 g, 182 mmol) in 400 mL of DMF at 140 °C and was kept at this temperature for 4 h with stirring. After the reaction mixture was cooled to room temperature, ice-water was added and the resulting yellow precipitate was collected by filtration. This was recrystallized from ethanol to afford 12.26 g (56 mmol, 62% yield) of 9-anthrylacetonitrile (**6**) as yellow crystals. Compound **6**: mp 158–159 °C (lit.[20] mp 158–159 °C); ^{1}H NMR (400.4 MHz, $CDCl_3$) δ 4.59 (s, 1H), 7.52 (ddd, J=8.8, 6.4, 1.2 Hz, 2H), 7.63 (ddd, J=8.8, 6.4, 1.2 Hz, 2H), 8.05 (dd, J=8.4, 0.4 Hz, 2H), 8.16 (dd, J=8.8, 0.8 Hz, 2H), 8.50 (s, 1H) ppm; ^{13}C NMR (100.7 MHz, $CDCl_3$) δ 16.34, 117.56, 120.61, 122.81, 125.18, 127.12, 128.70, 129.36, 129.64, 131.28 ppm; IR (KBr) 735.8, 790.8, 885.3, 901.7, 1154.3, 1346.3, 1448.4, 1623.8, 2243.1, 3026.1, 3053.5 cm^{-1}.

The nitrile **6** obtained above was dissolved in 200 mL of dry THF and this was added dropwise to a suspension of $LiAlH_4$ (5.80 g, 153 mmol) in 400 mL of dry THF with stirring. The mixture was refluxed for additional 2 h. After the reaction mixture was cooled to room temperature, 50 mL of MeOH/water was added and the resultant solid was removed by filtration. The filtrate was then evaporated and the residue was dissolved in a small amount of benzene. Then, concentrated hydrochloric acid was added and the precipitated AEA·HCl was collected by filtration. This was recrystallization from MeOH/AcOEt to afford pale yellow crystals: 3.45 g (26% yield), mp 262–264 °C; ^{1}H NMR (300.1 MHz, DMSO-d_6) δ 3.06 (br s, 2H), 3.97 (t, J=9.0 Hz, 2H), 7.53 (ddd, J=8.1, 6.3, 0.9 Hz, 2H), 7.61 (ddd, J=8.4, 6.3, 1.5 Hz, 2H), 8.10 (d, J=7.8 Hz, 2H), 8.36 (br s, NH), 8.44 (d, J=8.7 Hz, 2H), 8.56 (s, 1H) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6) δ 25.39, 39.29, 123.95, 125.21, 126.33, 126.62, 129.10, 129.23, 129.49, 131.05 ppm; IR (KBr) 736.2, 785.9, 839.0, 878.5, 934.4, 954.4, 1007.7, 1015.9, 1143.7, 1590.6, 2918.9, 3005.9 cm^{-1}; MS (EI) m/z (%) 221 ([M−HCl]$^+$, 15), 192 (100), 191 (38); HRMS (EI) calcd for $C_{16}H_{15}N$ 221.1204, found 221.1208.

The corresponding free amine was obtained by neutralization of AEA·HCl with aqueous NaOH, as described above. AEA: ^{1}H NMR (400.4 MHz, DMSO-d_6) δ 2.86 (t, J=8.0 Hz, 2H), 3.68 (t, J=8.0 Hz, 2H), 7.48 (ddd, J=8.4, 6.4, 0.8 Hz, 2H), 7.53 (ddd, J=8.8, 6.4, 1.6 Hz, 2H), 8.05 (dd, J=8.0, 1.2 Hz, 2H), 8.38 (d, J=8.8 Hz, 2H), 8.44 (s, 1H) ppm.

4.2.3. (9-Anthryl)methylamine (AMA). It was prepared either (a) from the reaction of 9-(chloromethyl)anthracene with hexamethylenetetramine by using the previous procedure[21] or (b) through reduction of 9-anthraldehyde oxime. Since the method (a) gave the compound in a poor yield, the procedures for the method (b) are described below.

A solution of 9-anthraldehyde (20.69 g, 100 mmol) in 500 mL of pyridine was added to a solution of hydroxylamine hydrochloride (30.58 g, 443 mmol) in 200 mL of pyridine and the mixture was refluxed for 3 h. Then, the mixture was evaporated and the residue was dissolved in $CHCl_3$. After removal of an insoluble material by filtration, the filtrate was washed successively with 0.5 N HCl and a saturated

$NaHCO_3$ solution, and dried over Mg_2SO_4. Evaporation of the solvent afforded 9-anthraldehyde oxime as yellow needles: 14.17 g (64% yield); ^{1}H NMR (269.6 MHz, $CDCl_3$) δ 7.41 (ddd, J=7.7, 6.6, 1.1 Hz, 2H), 7.46 (ddd, J=8.5, 6.6, 1.6 Hz, 2H), 7.91 (d, J=7.4 Hz, 2H), 8.28 (d, J=8.7 Hz, 2H), 8.35 (s, 1H), 9.09 (s, 1H) ppm; IR (KBr) 787.9, 803.5, 844.8, 877.6, 885.3, 918.1, 952.8, 970.1, 1023.2, 1069.4, 1096.4, 1157.2, 1181.3, 1261.4, 1294.1, 1441.7, 1623.9, 2962.4, 3031.6, 3052.1, 3261.1 cm^{-1}; MS (FAB) m/z (%) 222 (78), 221 (M^+, 100), 204 (47). This was used for the next step without further purification.

The oxime (10.18 g, 46 mmol), which was obtained above was dissolved in 150 mL of dry THF and was added dropwise to a suspension of $LiAlH_4$ (5.00 g, 132 mmol) in 200 mL of dry THF. The mixture was heated under reflux for 1 h, and then 50 mL of MeOH/water was carefully added. After removal of an insoluble material by filtration and then evaporation of the solvent, the residue was dissolved in 250 mL of $CHCl_3$ and subsequently 200 mL of 1 N HCl was added. The resulted precipitate was collected by filtration and recrystallized from MeOH/AcOEt to afford AMA·HCl as yellow crystals (3.12 g, 28% yield): mp >221 °C dec (lit.[19] mp 218–220 °C dec); ^{1}H NMR (400.4 MHz, DMSO-d_6) δ 5.04 (s, 2H), 7.58 (ddd, J=8.4, 6.4, 0.8 Hz, 2H), 7.67 (ddd, J=10.0, 6.4, 1.6 Hz, 2H), 8.16 (d, J=8.4 Hz, 2H), 8.44 (dd, J=8.8, 0.8 Hz, 2H), 8.62 (br s, NH), 8.74 (s, 1H) ppm; ^{13}C NMR (100.7 MHz, DMSO-d_6) δ 34.17, 123.94, 124.95, 125.28, 126.73, 128.86, 128.95, 129.92, 130.68 ppm; IR (KBr) 668.4, 731.9, 788.8, 893.0, 930.6, 1110.9, 1162.0, 1187.6, 1264.2, 1340.2, 1448.4, 1489.9, 1554.8, 1597.9, 1624.5, 2921.5, 3002.0, 3046.4, 3417.4 (br) cm^{-1}; MS (FAB) m/z (%) 207 ([M−HCl]$^+$, 32), 191 (100).

The corresponding free amine[22] was obtained by neutralization of AMA·HCl with aqueous NaOH, as described above. AMA: ^{1}H NMR (400.4 MHz, DMSO-d_6) δ 4.66 (s, 2H), 7.49 (ddd, J=8.4, 6.4, 1.2 Hz, 2H), 7.54 (ddd, J=8.8, 6.4, 1.6 Hz, 2H), 8.06 (d, J=8.0 Hz, 2H), 8.40 (d, J=8.8 Hz, 2H), 8.49 (s, 1H) ppm; ^{13}C NMR (100.7 MHz, DMSO-d_6) δ 37.63, 124.38, 124.84, 125.55, 125.86, 128.62, 128.87, 130.97, 135.34 ppm.

4.3. Photolysis

The photolysis was carried out as follows and the results are listed in Table 1.

A solution containing (9-anthryl)alkylamine (APA, AEA, or AMA: ca. 0.05 M) in MeOH, DMSO-d_6, or 2-PrOH was divided into two parts. These were placed either in two Pyrex tubes (in the case of the MeOH or 2-PrOH solution) or in two NMR tubes (in the case of the DMSO-d_6 solution) and were irradiated with a 400-W high pressure mercury lamp (Pyrex filter, >290 nm) for 2–2.3 h under argon and CO_2, respectively. During the irradiation, the solutions were maintained at specified temperatures with thermostated circulating water. After the irradiation, the samples in DMSO-d_6 were directly analyzed by ^{1}H NMR. The samples in MeOH or 2-PrOH were rotary-evaporated below 30 °C, and the residues were immediately analyzed by ^{1}H NMR in DMSO-d_6. The head-to-head dimer **h**–**h** (R=CH_2NH_2) was unstable and returned quantitatively to AMA: the conversion in DMSO-d_6 at room temperature was 74% in 21 h. The photolysis was repeated under similar conditions and the effects by CO_2 were confirmed.

For the purpose of characterizing the photodimers, the respective hydrochlorides of APA, AEA, and AMA were irradiated in MeOH under argon. The dihydrochlorides of the dimers precipitated. They were separated by filtration and their spectral data were measured.

The characterization data for lepidopterene (**2**) and biplanene (**3**) were reported in our previous work.[11a] In order to isolate compound **1**, a solution of AEA (199.8 mg) in DMSO (40 mL) was irradiated for 8 h under argon. Then, the solvent was removed by rotary-evaporation and the residue was separated by preparative TLC (silica gel, $CHCl_3$), followed by HPLC (JAIGEL GS-320, MeOH), to afford 30 mg (14%) of **1**.

4.4. Spectral data for photoproducts

4.4.1. 5,12:6,11-Di-*o*-benzenodibenzo[*a*,*e*]cyclooctene-5,11(6*H*,12*H*)-bis(propanamine)dihydrochloride, h-t·2HCl (R=$(CH_2)_3NH_2$). ^{1}H NMR (399.7 MHz, C_5D_5N) δ 1.58 (quin, J=7.3 Hz, 4H), 2.87 (t, J=7.3 Hz, 4H), 2.99 (t, J=6.1 Hz, 4H), 4.03 (s, 2H), 4.77 (br, NH), 6.88–6.96 (multi, 8H), 7.01 (d, J=5.3 Hz, 4H), 7.23 (d, J=5.3 Hz, 4H) ppm; ^{13}C NMR (100.4 MHz, C_5D_5N) δ 29.46, 35.16, 43.28, 56.79, 65.16, 125.51, 125.51, 126.95, 127.91, 143.67, 144.49 ppm; MS (FAB) m/z (%) 471 ([M−2HCl+H]$^+$, 57), 236 (98), 219 (27), 191 (100), 178 (23); HRMS (FAB) calcd for $C_{34}H_{35}N_2$ 471.2800, found 471.2801.

4.4.2. 5,12:6,11-Di-*o*-benzenodibenzo[*a*,*e*]cyclooctene-5,11(6*H*,12*H*)-bis(ethanamine)dihydrochloride, h-t·2HCl (R=$(CH_2)_2NH_2$). ^{1}H NMR (399.7 MHz, DMSO-d_6) δ 2.64 (br s, 4H), 3.03 (br t, J=6.7 Hz, 4H), 3.97 (s, 2H), 6.83 (t, J=6.8 Hz, 4H), 6.86 (td, J=7.4, 1.3 Hz, 4H), 6.93 (d, J=6.8 Hz, 4H), 7.12 (d, J=6.6 Hz, 4H), 8.08 (br s, NH) ppm; ^{13}C NMR (100.4 MHz, DMSO-d_6) δ 33.14, 35.55, 54.31, 62.85, 125.41, 125.41, 125.70, 127.41, 141.52, 142.85 ppm; IR (KBr) 647.4, 690.8, 763.9, 784.4, 818.2, 917.8, 960.3, 1045.6, 1139.4, 1314.7, 1452.5, 1473.6, 1602.1, 2923.6, 3006.9, 3435.0 cm^{-1}; MS (FAB) m/z (%) 443 ([M−2HCl+H]$^+$, 100), 222 (71), 205 (89); HRMS (FAB) calcd for $C_{32}H_{31}N_2$ 443.2487, found 443.2486.

4.4.3. 5,12:6,11-Di-*o*-benzenodibenzo[*a*,*e*]cyclooctene-5,11(6*H*,12*H*)-bis(methanamine)dihydrochloride, h-t·2HCl (R=CH_2NH_2). ^{1}H NMR (399.7 MHz, CD_3OD) δ 4.07 (s, 2H), 5.22 (s, 4H), 6.94 (td, J=7.4, 1.5 Hz, 4H), 6.99 (td, J=7.5, 1.6 Hz, 4H), 7.06 (dd, J=7.7, 1.2 Hz, 4H), 7.10 (dd, J=7.1, 1.6 Hz, 4H) ppm; ^{13}C NMR (100.4 MHz, CD_3OD) δ 42.09, 57.08, 60.91, 125.40, 127.85, 127.93, 129.67, 141.25, 144.05 ppm; IR (KBr) 646.1, 732.9, 756.7, 772.4, 783.2, 897.8, 969.9, 982.7, 1108.1, 1136.9, 1459.5, 1476.2, 1596.6, 2920.8, 2984.6, 3422.0 (br) cm^{-1}; MS (FAB) m/z (%) 415 ([M−2HCl+H]$^+$, 32), 207 (23), 191 (100); HRMS (FAB) calcd for $C_{30}H_{27}N_2$ 415.2174, found 415.2173. The structure was confirmed by NOESY and HMBC.

4.4.4. 5,12:6,11-Di-*o*-benzenodibenzo[*a*,*e*]cyclooctene-5,6(11*H*,12*H*)-bis(methanamine)dihydrochloride, h-h·2HCl (R=CH_2NH_2). ^{1}H NMR (399.7 MHz, DMF-d_7) δ 4.78 (s, 2H), 5.03 (s, 4H), 6.96–7.02 (multi, 8H), 7.09 (dd, J=5.9, 2.7 Hz, 4H), 7.67 (d, J=9.0 Hz, 4H), 8.81 (br s, NH) ppm; ^{13}C NMR (100.4 MHz, DMF-d_7) δ 36.60, 53.70, 59.93, 126.73, 127.10, 127.29, 128.84, 141.38, 144.94 ppm. As expected,[11b,c] the bridgehead proton of **h–h** (δ 4.78) appeared at a lower field than that of **h–t** (δ 4.07).

4.4.5. 2,3-Dihydro-1*H*-naphtho[1,2,3-*de*]quinoline (1). ^{1}H NMR (500.0 MHz, DMSO-d_6) δ 3.51 (d, J=5.1 Hz, 2H), 3.53 (d, J=4.9 Hz, 2H), 6.44 (br s, NH), 6.52 (dd, J=6.0, 2.2 Hz, 1H), 7.21 (dd, J=13.0, 8.4 Hz, 1H), 7.21 (d, J=6.2 Hz, 1H), 7.44 (td, J=6.8, 3.2 Hz, 1H), 7.45 (td, J=6.8, 3.2 Hz, 1H), 7.97 (dt, J=9.7, 3.5 Hz, 1H), 8.15 (dd, J=6.4, 3.7 Hz, 1H), 8.22 (s, 1H) ppm; ^{13}C NMR (100.4 MHz, DMSO-d_6) δ 25.72, 39.97, 103.20, 115.10, 120.41, 123.30, 123.64, 124.46, 125.05, 126.29, 126.40, 128.38, 129.07, 131.06, 131.83, 144.92 ppm; IR (KBr) 668.0, 731.0, 750.7, 761.8, 836.3, 880.4, 1141.1, 1151.4, 1306.7, 1336.3, 1360.7, 1528.4, 1559.9, 1569.9, 1617.8, 2851.1, 2924.4, 2955.7, 3050.2, 3381.5 cm^{-1}; MS (FAB) *m/z* (%) 219 (M^+); HRMS (FAB) calcd for $C_{16}H_{13}N$ 219.1048, found 219.1052. The structure was confirmed by NOEDF, COSY, NOESY, HMQC, and HMBC.

Acknowledgements

We thank Mr. Koji Masuda for his contribution to the initial stage of this investigation.

Supplementary data

The variable temperature ^{1}H and ^{13}C NMR of carbamic acid **4** (Figs. 1 and 2) and the thermodynamic plot of the data in Figure 1 (Fig. 3). Supplementary associated with this article can be found in the online version, at doi:10.1016/j.tet.2007.09.069.

References and notes

1. Dell'Amico, D. B.; Calderazzo, F.; Labella, L.; Marchetti, F.; Pampaloni, G. *Chem. Rev.* **2003**, *103*, 3857–3897.
2. Jessop, P. G.; Heldebrant, D. J.; Li, X.; Eckert, C. A.; Liotta, C. L. *Nature* **2005**, *436*, 1102.
3. Liu, Y.; Jessop, P. G.; Cunningham, M.; Eckert, C. A.; Liotta, C. L. *Science* **2006**, *313*, 958–960.
4. Stastny, V.; Rudkevich, D. M. *J. Am. Chem. Soc.* **2007**, *129*, 1018–1019; Xu, H.; Rudkevich, D. M. *Org. Lett.* **2005**, *7*, 3223–3226.
5. Carretti, E.; Dei, L.; Baglioni, P.; Weiss, R. G. *J. Am. Chem. Soc.* **2003**, *125*, 5121–5129.
6. Alauzun, J.; Mehdi, A.; Reyé, C.; Corriu, J. P. *J. Am. Chem. Soc.* **2005**, *127*, 11204–11205.
7. Vaidyanathan, R.; Kalthod, V. G.; Ngo, D. P.; Manley, J. M.; Lapekas, S. P. *J. Org. Chem.* **2004**, *69*, 2565–2568; Wittmann, K.; Wisniewski, W.; Mynott, R.; Leitner, W.; Kranemann, C. L.; Rische, T.; Eilbracht, P.; Kluwer, S.; Ernsting, J. M.; Elsevier, C. J. *Chem.—Eur. J.* **2001**, *7*, 4584–4589; Fürstner, A.; Ackermann, L.; Beck, K.; Hori, H.; Koch, D.; Langemann, K.; Liebl, M.; Six, C.; Leitner, W. *J. Am. Chem. Soc.* **2001**, *123*, 9000–9006; Minakata, S.; Yoneda, Y.; Oderaotoshi, Y.; Komatsu, M. *Org. Lett.* **2006**, *8*, 967–969.
8. (a) Masuda, K.; Ito, Y.; Horiguchi, M.; Fujita, H. *Tetrahedron* **2005**, *61*, 213–229; (b) Ito, Y.; Ushitora, H. *Tetrahedron* **2006**, *62*, 226–235; (c) Ito, Y. *Tetrahedron* **2007**, *63*, 3108–3114; (d) Ito, Y.; Uozu, Y.; Matsuura, T. *J. Chem. Soc., Chem. Commun.* **1988**, 562–564; (e) Ito, Y. *Photochemistry* **2002**, *33*, 205–212.
9. Kaur, D.; Kaur, R. P.; Kaur, P. *Bull. Chem. Soc. Jpn.* **2006**, *79*, 1869–1875.
10. (a) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P.; Lapouyade, R. *Chem. Soc. Rev.* **2001**, *30*, 248–263; (b) Becker, H. D. *Chem. Rev.* **1993**, *93*, 145–172; (c) Bouas-Laurent, H.; Desvergne, J.-P. *Photochromism: Molecules and Systems*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; Chapter 4, pp 561–630; (d) Bouas-Laurent, H.; Castellan, A.; Desvergne, J.-P. *Pure Appl. Chem.* **1980**, *52*, 2633–2648.
11. (a) Horiguchi, M.; Ito, Y. *J. Org. Chem.* **2006**, *71*, 3608–3611; (b) Ito, Y.; Fujita, H. *J. Org. Chem.* **1996**, *61*, 5677–5680; (c) Ito, Y.; Olovsson, G. *J. Chem. Soc., Perkin Trans. 1* **1997**, 127–133.
12. (a) Lewis, F. D.; Reddy, G. D.; Cohen, B. E. *Tetrahedron Lett.* **1994**, *35*, 535–538; (b) Pandey, G.; Sridhar, M.; Bhalerao, U. T. *Tetrahedron Lett.* **1990**, *31*, 5373–5376.
13. (a) Adam, W.; Schneider, K.; Stapper, M.; Steenken, S. *J. Am. Chem. Soc.* **1997**, *119*, 3280–3287; (b) Vermeersch, G.; Febvay-Garot, N.; Caplain, S.; Couture, A.; Lablache-Combier, A. *Tetrahedron Lett.* **1979**, *20*, 609–612.
14. Lepidopterene (**2**) was reported to be produced from 9-substituted anthracenes by photochemical[13] or thermal[15] reactions.
15. (a) Vadakkan, J. J.; Mallia, R. R.; Prathapan, S.; Rath, N. P.; Unnikrishnan, P. A. *Tetrahedron Lett.* **2005**, *46*, 5919–5922; (b) Fernandez, M.-J.; Gude, L.; Lorente, A. *Tetrahedron Lett.* **2001**, *42*, 891–893; (c) Higuchi, H.; Otsubo, T.; Ogura, F.; Yamaguchi, H.; Sakata, Y.; Misumi, S. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 182–187; (d) Felix, G.; Lapouyade, R.; Bouas-Laurent, H.; Gaultier, J.; Hauw, C. *Tetrahedron Lett.* **1975**, *16*, 409–412.
16. (a) Schneider, S.; Rehaber, H.; Schüßlbauer, W.; Lewis, F. D.; Yoon, B. A. *J. Photochem. Photobiol., A: Chem.* **1996**, *99*, 103–114; (b) Lewis, F. D.; Cohen, B. E. *J. Phys. Chem.* **1994**, *98*, 10591–10597.
17. Hann, R. A. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1379–1380.
18. Rhodes, R. A.; Boykin, D. W. *Synth. Commun.* **1988**, *18*, 681–687.
19. Kumar, C. V.; Punzalan, E. H. A.; Tan, W. B. *Tetrahedron* **2000**, *56*, 7027–7040.
20. Gardner, R. A.; Delcros, J.-G.; Konate, F.; Breitbeil, F., III; Martin, B.; Sigman, M.; Huang, M.; Phanstiel, O., IV. *J. Med. Chem.* **2004**, *47*, 6055–6069.
21. Kumar, C. V.; Asuncion, E. H. *J. Am. Chem. Soc.* **1993**, *115*, 8547–8553.
22. Teodori, E.; Dei, S.; Quidu, P.; Budriesi, R.; Chiarini, A.; Garnier-Suillerot, A.; Gualtieri, F.; Manetti, D.; Romanelli, M. N.; Scapecchi, S. *J. Med. Chem.* **1999**, *42*, 1687–1697.