Tetrahedron 65 (2009) 263–269

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Decarboxylative photosubstitution of dicyanobenzenes with aliphatic carboxylate ions

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ARTICLE INFO

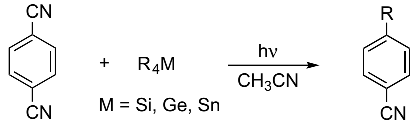
Article history:
Received 1 October 2008
Received in revised form 20 October 2008
Accepted 20 October 2008
Available online 1 November 2008

ABSTRACT

The photoreaction of dicyanobenzenes with aliphatic carboxylate ions afforded alkylcyanobenzenes and alkyldicyanobenzenes via decarboxylative substitution. The redox-photosensitized reaction system was effective in improving the product yield. The efficiency of this photoreaction depended on the structure of the carboxylate ion, and the product distribution varied with the dicyanobenzenes employed. This photoreaction was proved to be a clean process for the preparation of alkylcyanobenzenes.

1. Introduction

Alkylcyanobenzenes are used as liquid crystal components[1] and as important synthetic intermediates in the preparation of functionalized aromatic, heterocyclic, and polymeric materials.[2] Although several methods, which use metals such as Pd,[3] Cu,[4] and pyridine transition metal complexes,[5] have been developed for the synthesis of alkylcyanobenzenes, photosubstitution of aromatic nitriles is one of the most efficient and environmentally friendly method since light is a clean and powerful reagent that can be used to transform organic molecules.[6–9] One such photosubstitution reaction is the photo-NOCAS (nucleophile–olefin combination, aromatic substitution) reaction of 1,4-dicyanobenzene with alkenes that yields 4-alkyl-1-cyanobenzenes.[6] Furthermore, the substitution of dicyanobenzenes with organosilanes, -germanes, and -stannanes via a photoinduced electron transfer (PET) affords a variety of alkylcyanobenzenes (Scheme 1).[7,8]



Scheme 1. Photosubstitution of 1,4-dicyanobenzene with organosilanes, -germanes, and -stannanes via a PET.

However, a less toxic process is still desired from an environmental point of view. In the course of our studies involving the decarboxylative reduction of carboxylic acids by a photogenerated cation radical of phenanthrene in a redox-photosensitized reaction system,[10] the substituted product of 1,4-dicyanobenzene was obtained in a low yield.[11] Although photosubstitution of 1,2,4,5-tetracyanobenzene with aliphatic carboxylic acids has been reported,[12] the decarboxylative photosubstitution of dicyanobenzenes has not yet been investigated. Thus, in this study, we endeavored to investigate the decarboxylative photosubstitution of dicyanobenzenes with a variety of aliphatic carboxylate ions for the synthesis of alkylcyanobenzenes. The use of phenanthrene as the photosensitizer resulted in an efficient photosubstitution in the redox-photosensitized reaction system. This photoreaction technique can serve as a safe, economical, and environmentally friendly method for the preparation of alkylcyanobenzenes.

2. Results and discussion

2.1. Decarboxylative photosubstitution of dicyanobenzenes with aliphatic carboxylate ions via PET

An aqueous acetonitrile solution (CH_3CN/H_2O=9:1)[13] containing 1,4-dicyanobenzene **1** (10 mM) and sodium hexanoate **2a** (30 mM) was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter (λ >300 nm) in an argon atmosphere for 6 h at room temperature. The process yielded 4-pentyl-1-cyanobenzene **3a** (49%) and **1** (27%) was recovered in isolated yields (Table 1, entry 1). The use of the free acid (hexanoic acid) instead of **2a** resulted in the lower yield of **3a** (28%); however, the addition of 1 equiv of NaOH to this solution produced **3a** in a yield similar to that obtained with **2a**. Thus, decarboxylation of the carboxylate ion was more efficient than that of the corresponding free carboxylic acid.

Next, the photoreaction using various carboxylate ions was examined. Aliphatic, allylic, and benzylic carboxylate ions readily underwent photosubstitution (entries 2–5), and the yield of **3** slightly

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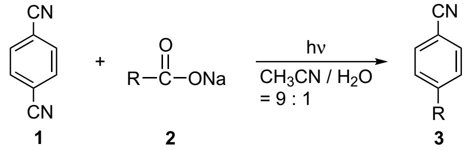
doi:10.1016/j.tet.2008.10.054

Table 1
Decarboxylative photosubstitution of 1,4-dicyanobenzene **1** with carboxylate ions **2**[a]



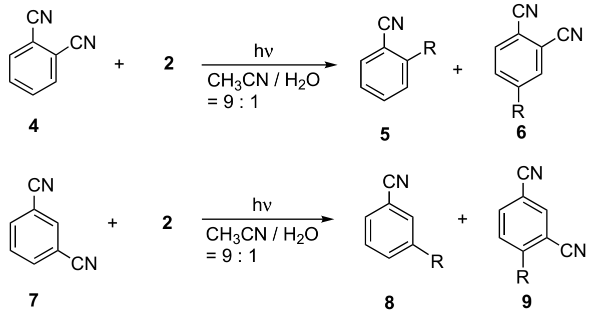
Entry	Carboxylate ion **2**	Yield[b] of **3** (%)	Recovery[b] of **1** (%)
1	**a**; R=pentyl	49	27
2	**b**; R=*c*-hexyl	55	31
3	**c**; R=*t*-butyl	61	10
4	**d**; R=$CH_2CH{=}CH_2$	38	10
5	**e**; R=CH_2Ph	37	20
6	**f**; R=CH_3	0	95
7	**g**; R=$CH{=}CH_2$	0	82
8	**h**; R=Ph	0	95
9[c]	**b**	80	0

[a] The photoreaction was carried out with 1.2 mmol (10 mM) of **1** and 3.6 mmol (30 mM) of **2** using a 500-W high-pressure mercury lamp under an argon atmosphere for 6 h.
[b] Isolated yield based on **1**.
[c] The photoreaction was carried out with 1.2 mmol (10 mM) of **1** and 7.2 mmol (60 mM) of **2b** using a 500-W high-pressure mercury lamp under an argon atmosphere for 12 h.

increased in the following order: primary alkyl (49%)$<$secondary alkyl (55%)$<$tertiary alkyl carboxylate ions (61%). A similar trend was also observed at the shorter irradiation time (2 h): primary alkyl (27%)$<$secondary alkyl (41%)$<$tertiary alkyl carboxylate ions (46%). The use of allylic and benzylic carboxylate ions **2d**,**e** resulted in relatively lower yields of **3** (entries 4 and 5). The photoproduct **3d** could subsequently photoreact with **1** to lower the yield of **3d**. In fact, **3d** was recovered in only 2% yield after the aqueous acetonitrile solution containing **3d** (5 mM) and **1** (5 mM) was irradiated for 6 h. On the other hand, photoreactions of methyl, vinyl, and aromatic carboxylate ions **2f**–**h** did not produce the corresponding cyanobenzenes **3**, and **1** was recovered in 95%, 82%, and 95% yields, respectively (entries 6–8). Higher concentration of **2b** (60 mM) and longer irradiation time (12 h) increased the yield of **3b** (entry 9).

The use of 1,2-dicyanobenzene **4** in place of **1** in the photoreaction predominantly afforded 2-alkyl-1-cyanobenzene **5** in a low yield, and the accompanied formation of 4-alkyl-1,2-dicyanobenzene **6a**,**b**,**e** was observed in the cases of **2a**,**b**,**e** (Table 2, entries 1–5). To the best of our knowledge, this type of alkylation products **6** has never been isolated previously in similar photoreactions when **4** was used as the electron acceptor.[6–9] When 1,3-dicyanobenzene **7** was subjected to this photoreaction, 3-alkyl-1-cyanobenzene **8** and 4-alkyl-1,3-dicyanobenzene **9** were obtained in poor yields, except in the cases when **2d**,**e** were used (entries 7–11). The formation of **9** has been observed only in the photoreaction of **7** with organoborates.[14] In these photoreactions, higher concentration of **2b** (120 mM) and longer irradiation time (24 h) also increased the yield of substituted products (entries 6 and 12).

Table 2
Decarboxylative photosubstitution of 1,2-dicyanobenzene **4** or 1,3-dicyanobenzene **7** with **2**[a]



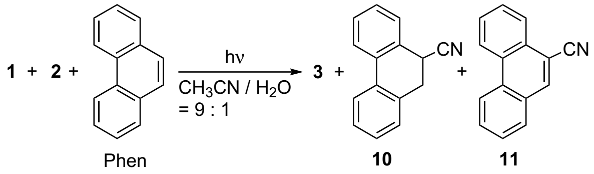
Entry	Dicyanobenzene	2	Product yields[b] (%)				Recovery[b] of **4** or **7** (%)
			5	**6**	**8**	**9**	
1	**4**	**a**	34	6	—	—	45
2	**4**	**b**	39	7	—	—	46
3	**4**	**c**	47	0	—	—	30
4	**4**	**d**	11	0	—	—	35
5	**4**	**e**	18	4	—	—	68
6[c]	**4**	**b**	58	5	—	—	0
7	**7**	**a**	—	—	7	10	73
8	**7**	**b**	—	—	10	6	70
9	**7**	**c**	—	—	18	0	71
10	**7**	**d**	—	—	0	0	65
11	**7**	**e**	—	—	0	0	91
12[c]	**7**	**b**	—	—	17	20	36

[a] The photoreaction was carried out with 1.2 mmol (10 mM) of **4** or **7** and 3.6 mmol (30 mM) of **2** using a 500-W high-pressure mercury lamp under an argon atmosphere for 6 h.
[b] Isolated yield based on **4** or **7**.
[c] The photoreaction was carried out with 1.2 mmol (10 mM) of **4** or **7** and 14.4 mmol (120 mM) of **2b** using a 500-W high-pressure mercury lamp under an argon atmosphere for 24 h.

2.2. Decarboxylative photosubstitution of dicyanobenzenes with aliphatic carboxylate ions in redox-photosensitized reaction system

Addition of phenanthrene (Phen) to the abovementioned system accelerated the decarboxylative photosubstitution, and a low-power light was adequate for this photoreaction. The photoreaction of **1** (10 mM) with **2a** (30 mM) in the presence of Phen (15 mM) using a 100-W high-pressure mercury lamp through a Pyrex filter (λ >300 nm) in an argon atmosphere for 6 h afforded three kinds of products, **3a** (31%), 9,10-dihydro-9-cyanophenanthrene **10** (7%), and 9-cyanophenanthrene **11** (1%); further, **1** (40%) and Phen (76%) were recovered from this reaction (Table 3, entry1). The photoreaction between Phen and the carboxylate ion did not proceed in the absence of **1**.

Table 3
Decarboxylative photosubstitution of **1** with **2** in the presence of Phen[a]



Entry	2	Product yields (%)			Recovery[b] of **1** (%)
		3[b]	**10**[c]	**11**[c]	
1	**a**	31	7	1	40
2	**b**	64	12	Trace	28
3	**c**	68	6	0	5
4	**d**	76	10	1	2
5	**e**	53	9	1	6
6	**f**	0 (15)[d]	5 (11)[d]	0(0)[d]	90 (70)[d]
7	**g**	0	1	0	72
8	**h**	0	0	0	92
9[e]	**b**	95	7	Trace	0

[a] The photoreaction was carried out with 1.2 mmol (10 mM) of **1**, 3.6 mmol (30 mM) of **2**, and 1.8 mmol (15 mM) of Phen using a 100-W high-pressure mercury lamp under an argon atmosphere for 6 h.
[b] Isolated yield based on **1**.
[c] Isolated yield based on Phen.
[d] The values in parentheses are for the photoreaction using a 500-W high-pressure mercury lamp for 12 h.
[e] The photoreaction was carried out with 1.2 mmol (10 mM) of **1**, 7.2 mmol (60 mM) of **2**, and 1.8 mmol (15 mM) of Phen using a 100-W high-pressure mercury lamp under an argon atmosphere for 12 h.

Table 4

Decarboxylative photosubstitution of **4** or **7** with **2** in the presence of Phen[a]

$$\mathbf{4} + \mathbf{2} + \text{Phen} \xrightarrow[\substack{CH_3CN\,/\,H_2O\\=9:1}]{h\nu} \mathbf{5} + \mathbf{6} + \mathbf{10} + \mathbf{11}$$

$$\mathbf{7} + \mathbf{2} + \text{Phen} \xrightarrow[\substack{CH_3CN\,/\,H_2O\\=9:1}]{h\nu} \mathbf{8} + \mathbf{9} + \mathbf{10} + \mathbf{11}$$

Entry	Dicyanobenzene	2	Product yields (%)						Recovery[b] of 4 or 7 (%)
			5[b]	6[b]	8[b]	9[b]	10[c]	11[c]	
1	**4**	**a**	32	6	—	—	4	Trace	15
2	**4**	**b**	38	17	—	—	11	Trace	0
3	**4**	**c**	61	0	—	—	14	Trace	Trace
4	**4**	**d**	46	0	—	—	14	4	30
5	**4**	**e**	18	4	—	—	10	Trace	44
6	**7**	**a**	—	—	3	20	1	0	45
7	**7**	**b**	—	—	12	16	1	0	60
8	**7**	**c**	—	—	30	0	5	Trace	48
9	**7**	**d**	—	—	0	0	0	0	95
10	**7**	**e**	—	—	0	0	0	0	95

[a] The photoreaction was carried out with 1.2 mmol (10 mM) of **4** or **7**, 3.6 mmol (30 mM) of **2**, and 1.8 mmol (15 mM) of Phen using a 100-W high-pressure mercury lamp under an argon atmosphere for 6 h.

[b] Isolated yield based on **4** or **7**.

[c] Isolated yield based on Phen.

The photoreaction of the aliphatic, allylic, and benzylic carboxylate ions in the presence of Phen provided the higher yield of **3** as compared to the photoreaction in the absence of Phen (entries 2–5). In particular, the improved yield of **3d** in the redox-photosensitized reaction system could be ascribed to the suppression of the secondary photoreaction of **3d** with **1** (entry 4). Furthermore, a high-power light (a 500-W high-pressure mercury lamp) and a long irradiation time (12 h) led to the formation of **3f** (entry 6, in parenthesis). Therefore, we conclude that the presence of Phen increased the efficiency of the photoreaction. In this reaction, the following similar trend was observed in the yield of **3** from the carboxylate ions: methyl, vinyl, and aromatic (0%)<primary alkyl (31%)<secondary alkyl (64%)<tertiary alkyl carboxylate ions (68%). Similar to the abovementioned system, higher concentration of **2b** (60 mM) and longer irradiation time (12 h) improved the yield of **3b** (entry 9). The results of the photoreaction of **4** or **7** in the presence of Phen, which are listed in Table 4, indicate a slight improvement in the product yields of alkylcyanobenzenes **5** and **8**, and alkyldicyanobenzenes **6** and **9**, and that the distribution of their products is similar.

2.3. Decarboxylative photosubstitution of dicyanobenzenes with long-chain carboxylate ions

In order to verify the effectiveness of the photoreaction, we examined the photoreaction of dicyanobenzenes **1**, **4**, and **7** with long-chain carboxylate ions **2i–j**. The photoreaction of **1** with the long-chain primary alkyl carboxylate ion **2i** in the presence of Phen afforded the corresponding alkylcyanobenzene **3i** in a 25% yield along with a small amount of the decarboxylative reduction product **12i** (Table 5, entry 1). When D_2O was used instead of water in the mixed solvent system, the deuterated product of **12i** was obtained with a high *d*-content (>95%), indicating the intermediary formation of the corresponding anion followed by protonation. In contrast, the photoreaction of **1** with the long-chain secondary alkyl carboxylate ion **2j** afforded **3j** in 50% yield without the formation of **12j** (entry 2). On the other hand, the photoreaction of **4** with **2i** yielded **5i** as a main substituted product, although higher yield of **12i** was obtained as well as in the case of photoreaction of **7** (entries 3 and 4).

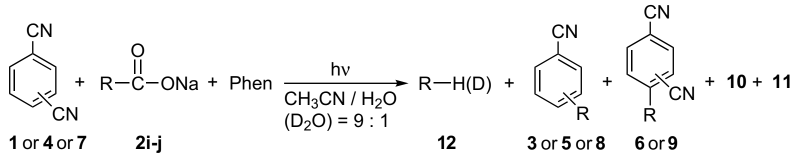
2.4. Mechanism

A plausible mechanism of this photoreaction in the absence and presence of Phen is shown in Scheme 2. A similar mechanism has been reported for the photoreaction between allylic/benzylic silanes and dicyanobenzenes.[7] The fluorescence of **1** in the aqueous acetonitrile solution was efficiently quenched by **2a** ($kq=4.1\times 10^9\ M^{-1}\ s^{-1}$), as shown in Figure 1, indicating that PET from the carboxylate ion **2** to the excited dicyanobenzenes occurred smoothly to form the anion radicals of dicyanobenzenes **13** and the carboxy radical **14** (Eq. 1). It has been confirmed from the Rehm–Weller equation[15] that PET is an exothermic process, as indicated by the negative ΔG values ($-141\ kJ\ mol^{-1}$) that were calculated using the reduction potential (1.64 V vs SCE)[16] and excited singlet energy ($412\ kJ\ mol^{-1}$)[17] of **1** and the oxidation potential of **2a** (1.16 V vs SCE).[18,19] In the presence of Phen, **14** is also formed by the oxidation of **2** by the photogenerated cation radical of Phen, as reported earlier (Eq. 2). The high efficiency of the redox-photosensitized reaction system could be attributed to the higher absorption of Phen at 313 nm as compared to that of dicyanobenzenes.

Since the rate of decarboxylation of **14** to **15** is dependent on the stability of **15**, the decarboxylation is very slow for methyl, alkenyl, and aryl carboxy radicals. Thus, the decarboxylation of **2f–h** does not proceed efficiently, and **3** is not obtained in most cases. When aliphatic carboxylate ions **2a–e** are used, **14** is rapidly decarboxylated to form **15**. The generated alkyl radical **15** is coupled with **13**,

Table 5

Decarboxylative photosubstitution of **1** or **4** or **7** with long-chain carboxylate ions **2i–j** in the presence of Phen[a]



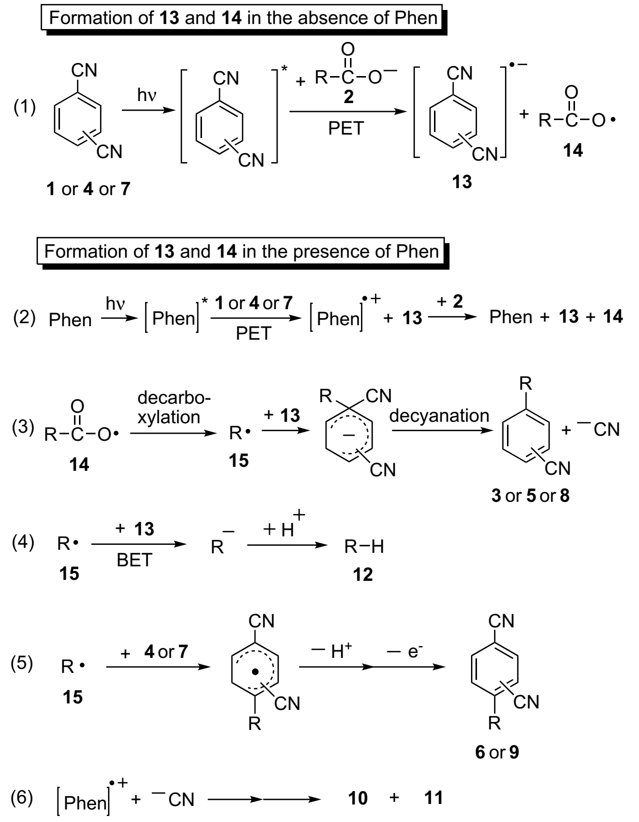
Entry	Dicyanobenzene	2	Product yields (%)							
			12[b]	3[c]	5[c]	6[c]	8[c]	9[c]	10[d]	11[d]
1	**1**	**i**; R=–$(CH_2)_{10}OCH_3$	8	25	—	—	—	—	1	Trace
2	**1**	**j**; R=–$CH[(CH_2)_3CH_3](CH_2)_5CH_3$	0	50	—	—	—	—	2	0
3	**4**	**i**	20	—	24	5	—	—	1	0
4	**7**	**i**	26	—	—	—	4	11	1	0

[a] The photoreaction was carried out with 1.2 mmol (10 mM) of **1** or **4** or **7**, 3.6 mmol (30 mM) of **2**, and 1.8 mmol (15 mM) of Phen using a 100-W high-pressure mercury lamp under an argon atmosphere for 6 h.

[b] Isolated yield based on **2**.

[c] Isolated yield based on **1**.

[d] Isolated yield based on Phen.



Scheme 2. Plausible mechanism of the photoreaction in the absence and presence of Phen.

and then undergoes decyanations to yield **3** or **5** or **8** and CN^- (Eq. 3). The efficiency of this substitution can vary according to the type of dicyanobenzenes used. When 1,4-dicyanobenzene **1** is used, radical **15** efficiently adds to its anion radical, thereby yielding 1-alkyl-4-cyanobenzene **3** selectively; however, this addition is not very effective when either **4** or **7** is used. In addition, a back electron transfer (BET) from **13** to **15** results in the formation of an anion, which is subsequently protonated by water to yield the reduction product **12** (Eq. 4).[20] In the photoreaction of **4** or **7**, the low efficiency of the substitution of **13** by **15** increases the BET, and the yield of the substituted product **5** or **8** was lower. Furthermore, since the efficiency of the anion formation from the primary alkyl or benzyl radicals[21] via BET is higher than that from the secondary alkyl or tertiary alkyl or allylic radicals, the yield of **3** is drastically decreased. This observation is substantiated by the high yield of alkylcyanobenzene obtained in the photoreaction of **1** with **2b**–**d**.

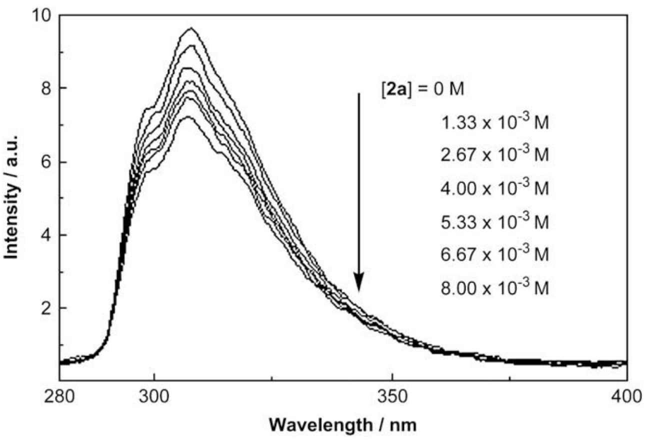


Figure 1. Fluorescence quenching of **1** (1.0×10^{-5} M) by **2a** excited at 270 nm in aqueous acetonitrile solution.

Radical **15** can also add to the dicyanobenzenes to form alkyldicyanobenzenes **6** and **9** (Eq. 5);[22] however, the detailed mechanism of the formation of the alkyldicyanobenzenes **6** and **9** is unclear and it is under investigation in our laboratory. As reported, the cyanation of the cation radical of Phen in the presence of CN^- yields **10** and **11** (Eq. 6).[23]

3. Conclusion

In conclusion, we found that the decarboxylative photosubstitution of dicyanobenzenes by carboxylate ions afforded alkylcyanobenzenes and alkyldicyanobenzenes, irrespective of the absence or presence of Phen. The product distribution depended on the used dicyanobenzene, and the efficiency of this photoreaction was strongly influenced by the structure of the carboxylate ion. Since carboxylic acids are usually inexpensive and commercially available, this photoreaction can prove to be useful in the synthesis of alkylcyanobenzenes. The application of the generated radical to organic synthesis is in progress in our laboratory.

4. Experimental section

4.1. General

Melting points were taken on a hot stage apparatus and are uncorrected. IR spectra were recorded on JASCO FT/IR-620, and GC–MS spectra were obtained using a Shimadzu GCMS-QP5000. ^{1}H and ^{13}C NMR spectra were recorded on JEOL JNM-AL500 (500 and 125 MHz) spectrometer and for solutions in $CDCl_3$ containing tetramethylsilane as an internal standard. High resolution mass spectra (HRMS) were obtained on JEOL JMS-700T. The light source was Riko UV-100HA 100-W and Eiko-sha PIH 500-W high-pressure mercury arc. Dicyanobenzenes **1**, **4**, and **7**, and Phen were recrystallized from hexane and EtOAc.

4.2. Preparation of sodium carboxylate 2

Carboxylic acids (10 mmol) were added to a solution of NaOH (10 mmol) in methanol (50 ml) and the mixture was refluxed for 2 h. After cooling to room temperature, ether (25 ml) was added to the solution and filtered. The filtrate was dried in vacuo to afford sodium carboxylates **2a**–**j** in quantitative yields.

4.3. General procedure for the photoreaction of dicyanobenzenes 1, 4, and 7 with 2

An aqueous acetonitrile solution (CH_3CN/H_2O=9:1, 120 ml) containing dicyanobenzenes **1**, **4**, and **7** (1.2 mmol) and sodium carboxylate **2** (3.6 mmol) was irradiated with a 500-W high-pressure mercury lamp through a Pyrex filter in an argon atmosphere for 6 h at room temperature. The solution was filtered and evaporated. Then, the residue was dissolved in EtOAc, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to afford the substituted products. These products were isolated by silica gel column chromatography using hexane and EtOAc as eluents and then by preparative HPLC using a GPC column.

4.3.1. *4-Pentyl-1-cyanobenzene **3a***

Colorless oil; IR (neat) 2226 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 2.66 (t, J=7.6 Hz, 2H), 1.65–1.59 (m, 2H), 1.35–1.27 (m, 4H), 0.90 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.6, 132.1, 129.2, 119.2, 109.5, 36.1, 31.3, 30.7, 22.5, 14.0; HRMS (FAB) calcd for $(M+H)^+$ $C_{12}H_{16}N$: 174.1283, found: 174.1273.

4.3.2. 4-Cyclohexyl-1-cyanobenzene ***3b***[9b]

Colorless oil; IR (neat) 2224 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (d, J=8.2 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 2.55 (br s, 1H), 1.87–1.63 (m, 5H), 1.44–1.35 (m, 4H), 1.29–1.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 153.2, 132.2, 127.7, 119.2, 109.5, 44.8, 34.0, 26.6, 25.9; HRMS (FAB) calcd for (M+H)$^+$ $C_{13}H_{16}N$: 186.1283, found: 186.1300.

4.3.3. 4-tert-Butyl-1-cyanobenzene ***3c***[24]

Colorless oil; IR (neat) 2227 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, J=8.2 Hz, 2H), 7.48 (d, J=8.2 Hz, 2H), 1.33 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.6, 132.0, 126.1, 119.1, 109.3, 35.2, 30.9; HRMS (FAB) calcd for (M+H)$^+$ $C_{11}H_{14}N$: 160.1127, found: 160.1145.

4.3.4. 4-Allyl-1-cyanobenzene ***3d***[25]

Colorless oil; IR (neat) 2228 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, J=8.2 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 5.96–5.88 (m, 1H), 5.15–5.08 (m, 2H), 3.44 (d, J=6.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.6, 135.6, 132.3, 129.4, 119.0, 117.2, 110.0, 40.1; HRMS (FAB) calcd for (M+H)$^+$ $C_{10}H_{10}N$: 144.0813, found: 144.0814.

4.3.5. 4-Benzyl-1-cyanobenzene ***3e***[26]

Colorless oil; IR (neat) 2228 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.57 (d, J=8.2 Hz, 2H), 7.32–7.24 (m, 5H), 7.17–7.15 (m, 2H), 4.03 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 146.7, 139.3, 132.3, 129.6, 128.9, 128.7, 126.6, 119.0, 110.0, 42.0; HRMS (FAB) calcd for (M+H)$^+$ $C_{14}H_{12}N$: 194.0970, found: 194.1010.

4.3.6. 2-Pentyl-1-cyanobenzene ***5a***

Colorless oil; IR (neat) 2224 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.59 (d, J=7.6 Hz, 1H), 7.52–7.47 (m, 1H), 7.52–7.47 (m, 2H), 2.83 (t, J=7.7 Hz, 2H), 1.70–1.64 (m, 2H), 1.39–1.30 (m, 4H), 0.90 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 146.9, 132.8, 132.7, 129.5, 126.3, 118.2, 112.3, 34.6, 31.4, 30.6, 22.4, 14.0; HRMS (FAB) calcd for (M+H)$^+$ $C_{12}H_{16}N$: 174.1283, found: 174.1283.

4.3.7. 2-Cyclohexyl-1-cyanobenzene ***5b***

Colorless oil; IR (neat) 2221 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.60 (d, J=7.6 Hz, 1H), 7.54–7.51 (m, 1H), 7.37 (d, J=8.2 Hz, 1H), 7.28–7.25 (m, 1H), 3.00 (br s, 1H), 1.92–1.77 (m, 5H), 1.50–1.46 (m, 4H), 1.31–1.26 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 151.5, 132.9, 132.8, 126.5, 126.3, 118.3, 111.8, 42.7, 33.7, 26.6, 25.9; HRMS (FAB) calcd for (M+H)$^+$ $C_{13}H_{16}N$: 186.1283, found: 186.1288.

4.3.8. 2-tert-Butyl-1-cyanobenzene ***5c***

Colorless oil; IR (neat) 2221 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.67 (d, J=7.6 Hz, 1H), 7.53–7.46 (m, 2H), 7.30–7.23 (m, 1H), 1.52 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 153.8, 135.6, 132.6, 126.3, 126.1, 120.4, 110.7, 35.6, 30.2; HRMS (FAB) calcd for (M+H)$^+$ $C_{11}H_{14}N$: 160.1127, found: 160.1099.

4.3.9. 2-Allyl-1-cyanobenzene ***5d***

Colorless oil; IR (neat) 2224 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.63 (d, J=7.6 Hz, 1H), 7.55–7.52 (m, 1H), 7.35–7.30 (m, 2H), 6.00–5.91 (m, 1H), 5.17–5.11 (m, 2H), 3.62 (d, J=6.7 Hz, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 143.8, 134.9, 132.9, 132.8, 129.7, 126.8, 117.9, 117.4, 112.5, 38.5; HRMS (FAB) calcd for (M+H)$^+$ $C_{10}H_{10}N$: 144.0813, found: 144.0854.

4.3.10. 2-Benzyl-1-cyanobenzene ***5e***

Colorless oil; IR (neat) 2224 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.64 (d, J=7.6 Hz, 1H), 7.51–7.48 (m, 1H), 7.34–7.23 (m, 7H), 4.21 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 145.0, 138.8, 132.9, 132.8, 130.1, 129.0, 128.7, 126.8, 126.7, 118.2, 112.6, 40.2; HRMS (FAB) calcd for (M+H)$^+$ $C_{14}H_{12}N$: 194.0970, found: 194.0949.

4.3.11. 4-Pentyl-1,2-dicyanobenzene ***6a***

Colorless oil; IR (neat) 2234 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.72 (d, J=8.2 Hz, 1H), 7.62 (s, 1H), 7.54 (d, J=8.2 Hz, 1H), 2.72 (t, J=7.8 Hz, 2H), 1.68–1.60 (m, 2H), 1.37–1.30 (m, 4H), 0.92 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.6, 133.5, 133.4, 133.3, 115.8, 115.6, 113.0, 35.7, 31.2, 30.3, 22.3, 13.9; HRMS (FAB) calcd for (M+H)$^+$ $C_{13}H_{15}N_2$: 199.1236, found: 199.1282.

4.3.12. 4-Cyclohexyl-1,2-dicyanobenzene ***6b***

White solid; mp 60–61 °C; IR (KBr) 2233 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.71 (d, J=8.2 Hz, 1H), 7.64 (s, 1H), 7.55 (d, J=8.2 Hz, 1H), 2.62 (br s, 1H), 1.90–1.78 (m, 4H), 1.42–1.25 (m, 6H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.3, 133.5, 132.1, 131.8, 115.9, 115.6, 113.1, 44.4, 33.7, 26.3, 25.6; HRMS (FAB) calcd for (M+H)$^+$ $C_{14}H_{15}N_2$: 211.1236, found: 211.1214.

4.3.13. 4-Benzyl-1,2-dicyanobenzene ***6e***

White solid; mp 104–105 °C; IR (KBr) 2232 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.73 (d, J=8.2 Hz, 1H), 7.59 (s, 1H), 7.55 (d, J=8.2 Hz, 1H), 7.37–7.26 (m, 3H), 7.15 (d, J=7.9 Hz, 2H), 4.08 (s, 2H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 147.8, 137.7, 133.8, 133.6, 133.5, 129.2, 129.0, 127.3, 116.1, 115.4, 113.5, 41.6; HRMS (FAB) calcd for (M+H)$^+$ $C_{15}H_{11}N_2$: 219.0923, found: 219.0924.

4.3.14. 3-Pentyl-1-cyanobenzene ***8a***

Colorless oil; IR (neat) 2228 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.48–7.35 (m, 4H), 2.63 (t, J=7.6 Hz, 2H), 1.64–1.58 (m, 2H), 1.38–1.31 (m, 4H), 0.90 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 144.2, 133.0, 132.0, 129.5, 129.0, 119.2, 112.2, 35.5, 31.3, 30.8, 22.5, 14.0; HRMS (FAB) calcd for (M+H)$^+$ $C_{12}H_{16}N$: 174.1283, found: 174.1284.

4.3.15. 3-Cyclohexyl-1-cyanobenzene ***8b***

Colorless oil; IR (neat) 2227 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.52–7.35 (m, 4H), 2.53 (br s, 1H), 1.87–1.76 (m, 5H), 1.42–1.38 (m, 4H), 1.27–1.10 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 149.3, 131.6, 130.5, 129.6, 129.0, 119.3, 112.2, 44.2, 34.1, 26.6, 25.9; HRMS (FAB) calcd for (M+H)$^+$ $C_{13}H_{16}N$: 186.1283, found: 186.1291.

4.3.16. 3-tert-Butyl-1-cyanobenzene ***8c***

Colorless oil; IR (neat) 2229 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.66 (s, 1H), 7.63 (d, J=8.2 Hz, 1H), 7.48 (d, J=6.4 Hz, 1H), 7.42 (m, 1H), 1.33 (s, 9H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 152.4, 130.0, 129.2, 129.1, 128.8, 119.4, 112.1, 34.9, 31.1; HRMS (FAB) calcd for (M+H)$^+$ $C_{11}H_{14}N$: 160.1127, found: 160.1135.

4.3.17. 4-Pentyl-1,3-dicyanobenzene ***9a***

White solid; mp 49–50 °C; IR (KBr) 2235 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.78 (d, J=8.2 Hz, 1H), 7.48 (d, J=8.2 Hz, 1H), 2.91 (t, J=7.6 Hz, 2H), 1.71–1.63 (m, 2H), 1.37–1.35 (m, 4H), 0.91 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 154.1, 136.1, 135.6, 130.6, 116.9, 115.9, 111.0, 34.9, 31.2, 30.6, 22.3, 13.8; HRMS (FAB) calcd for (M+H)$^+$ $C_{13}H_{15}N_2$: 199.1236, found: 199.1247.

4.3.18. 4-Cyclohexyl-1,3-dicyanobenzene ***9b***

White solid; mp 89–90 °C; IR (KBr) 2234 cm^{-1}; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (s, 1H), 7.80 (d, J=8.2 Hz, 1H), 7.51 (d, J=8.2 Hz, 1H), 3.06 (m, 1H), 1.92–1.80 (m, 5H), 1.55–1.41 (m, 4H), 1.31–1.24 (m, 1H); ^{13}C NMR (125 MHz, CDCl$_3$) δ 156.5, 136.2, 135.9, 127.8, 116.9, 116.0, 110.1, 43.1, 33.3, 26.3, 25.7; HRMS (FAB) calcd for (M+H)$^+$ $C_{14}H_{15}N_2$: 211.1236, found: 211.1226.

4.4. General procedure for the photoreaction of dicyanobenzenes 1, 4, and 7 with 2 in the presence of Phen

An aqueous acetonitrile solution (CH_3CN/H_2O=9:1, 120 ml) containing dicyanobenzene **1**, **4**, and **7** (1.2 mmol), sodium carboxylate **2** (3.6 mmol), and phenanthrene (1.8 mmol) was irradiated with a 100-W high-pressure mercury lamp through a Pyrex filter in an argon atmosphere for 6 h at room temperature. The solution was filtered and evaporated. Then, the residue was dissolved in EtOAc, washed with water, dried over Na_2SO_4, and concentrated under reduced pressure to afford the substituted products **10** and **11**. These products were isolated by silica gel column chromatography using hexane and EtOAc as eluents and then by preparative HPLC using a GPC column.

4.4.1. 9,10-Dihydro-9-cyanophenanthrene ***10***[27]

White solid; mp 84–85 °C; IR (KBr) 2237 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, J=7.6 Hz, 1H), 7.78 (d, J=7.6 Hz, 1H), 7.57 (d, J=7.6 Hz, 1H), 7.47–7.28 (m, 5H), 4.10 (t, J=7.8 Hz, 1H), 3.22 (d, J=7.8 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 133.6, 133.2, 132.7, 129.8, 129.2, 128.4, 128.3, 128.2, 128.2, 127.0, 124.5, 124.1, 119.9, 32.9, 31.2; MS m/z 205 (M^+).

4.4.2. 9-Cyanophenanthrene ***11***[28]

White solid; mp 108–109 °C; IR (KBr) 2222 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.74–8.70 (m, 2H), 8.32–8.30 (m, 1H), 8.27 (s, 1H), 7.96 (d, J=10.1 Hz, 1H), 7.83–7.71 (m, 3H), 7.71–7.67 (m, 1H); MS m/z 203 (M^+).

4.4.3. 4-Methyl-1-cyanobenzene ***3f***[24]

Colorless oil; IR (neat) 2273 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, J=8.2 Hz, 2H), 7.27 (d, J=8.2 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (500 MHz, $CDCl_3$) δ 143.6, 132.0, 129.8, 119.1, 109.4, 21.8; MS m/z 117 (M^+).

4.4.4. 4-(10-Methoxydecyl)-1-cyanobenzene ***3i***

White solid; mp 44–45 °C; IR (KBr) 2227 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J=8.2 Hz, 2H), 7.28 (d, J=8.2 Hz, 2H), 3.36 (t, J=6.6 Hz, 2H), 3.33 (s, 3H), 2.65 (t, J=7.6 Hz, 2H), 1.60–1.52 (m, 4H), 1.29–1.27 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.9, 132.0, 129.1, 119.1, 100.5, 72.9, 58.5, 36.1, 30.9, 29.6, 29.5, 29.4, 29.3, 29.1; HRMS (FAB) calcd for $(M+H)^+$ $C_{18}H_{28}NO$: 274.2172, found: 274.2163.

4.4.5. 4-(2-Butylheptyl)-1-cyanobenzene ***3j***

Colorless oil; IR (neat) 2227 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, J=8.2 Hz, 2H), 7.23 (d, J=8.2 Hz, 2H), 2.56–2.50 (m, 1H), 1.67–1.58 (m, 2H), 1.56–1.47 (m, 2H), 1.29–0.99 (m, 12H), 0.85–0.80 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.3, 132.1, 128.4, 119.2, 109.5, 46.3, 36.6, 36.3, 31.6, 29.7, 29.2, 27.4, 22.6, 22.5, 14.0, 13.9; HRMS (FAB) calcd for $(M+H)^+$ $C_{18}H_{28}N$: 258.2271, found: 258.2246.

4.4.6. 10-Methoxydecane ***12i***

Colorless oil; IR (neat) 2933, 2853 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (t, J=6.7 Hz, 2H), 3.33 (s, 3H), 1.62–1.53 (m, 4H), 1.30–1.20 (m, 14H), 0.88 (t, J=7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.0, 58.5, 31.9, 29.7, 29.6, 29.6, 29.5, 29.3, 26.6, 22.6, 14.1; MS m/z 172 (M^+).

4.4.7. Deuterated 10-methoxydecane

Colorless oil; IR (neat) 2928, 2850, 1110 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.36 (t, J=6.7 Hz, 2H), 3.33 (s, 3H), 1.62–1.53 (m, 4H), 1.30–1.20 (m, 14H), 0.88 (t, J=7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 73.0, 58.5, 31.9,29.7, 29.6, 29.6, 29.5, 29.3, 26.6, 22.6, 14.1; MS m/z 173 (M^+).

4.4.8. 2-(10-Methoxydecyl)-1-cyanobenzene ***5i***

Colorless oil; IR (neat) 2224 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (d, J=7.6 Hz, 1H), 7.53–7.48 (m, 1H), 7.32–7.25 (m, 2H), 3.36 (t, J=6.7 Hz, 2H), 3.33 (s, 3H), 2.82 (t, J=7.6 Hz, 2H), 1.69–1.53 (m, 4H), 1.36–1.28 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.8, 132.7, 132.6, 129.4, 126.2, 118.2, 112.3, 72.9, 58.5, 34.6, 30.9, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 26.1; HRMS (FAB) calcd for $(M+H)^+$ $C_{18}H_{28}NO$: 274.2172, found: 274.2154.

4.4.9. 4-(10-Methoxydecyl)-1,2-dicyanobenzene ***6i***

White solid; mp 47–48 °C; IR (KBr) 2234 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J=8.2 Hz, 1H), 7.61 (s, 1H), 7.53 (d, J=8.2 Hz, 1H), 3.36 (t, J=6.7 Hz, 2H), 3.33 (s, 3H), 2.71 (t, J=7.6 Hz, 2H), 1.62–1.50 (m, 4H), 1.30–1.27 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.5, 133.5, 133.4, 133.2, 115.5, 113.0, 72.9, 58.5, 35.7, 30.6, 29.6, 29.4, 29.5, 29.3, 29.2, 29.0, 26.1; HRMS (FAB) calcd for $(M+H)^+$ $C_{19}H_{27}N_2O$: 299.2125, found: 299.2131.

4.4.10. 3-(10-Methoxydecyl)-1-cyanobenzene ***8i***

Colorless oil; IR (neat) 2227 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49–7.44 (m, 2H), 7.41–7.35 (m, 2H), 3.36 (t, J=6.7 Hz, 2H), 3.33 (s, 3H), 2.64 (t, J=7.6 Hz, 2H), 1.61–1.53 (m, 4H), 1.30–1.27 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 133.0, 131.9, 129.4, 128.9, 119.1, 112.2, 72.9, 58.5, 35.5, 31.0, 29.6, 29.5, 29.4, 29.4, 29.3, 29.0, 26.1; HRMS (FAB) calcd for $(M+H)^+$ $C_{18}H_{28}NO$: 274.2172, found: 274.2171.

4.4.11. 4-(10-Methoxydecyl)-1,3-dicyanobenzene ***9i***

White solid; mp 70–71 °C; IR (KBr) 2235 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.78 (d, J=8.2 Hz, 1H), 7.51 (d, J=8.2 Hz, 1H), 3.36 (t, J=6.7 Hz, 2H), 3.33 (s, 3H), 2.82 (t, J=7.6 Hz, 2H), 1.69–1.53 (m, 4H), 1.36–1.28 (m, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.1, 136.1, 135.6, 130.6, 116.9, 116.0, 111.0, 72.9, 58.5, 34.9, 30.5, 29.7, 29.5, 29.4, 29.3, 29.2, 29.1, 26.1; HRMS (FAB) calcd for $(M+H)^+$ $C_{19}H_{27}N_2O$: 299.2125, found: 299.2100.

Acknowledgements

We thank Kazuyuki Kamiya and Tomoyuki Mizunashi, University of Fukui, Graduate School of Engineering, for their assistance with HRMS measurement.

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