Bull. Chem. Soc. Jpn., **63**, *3233—3237 (1990)*

Photocarboxylation of Naphthalene in the Presence of Carbon Dioxide and an Electron Donor[1)]

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(Received June 11, 1990)

Naphthalene was carboxylated to naphthoic acids by the irradiation of naphthalene and a donor in the presence of carbon dioxide. The UV irradiation through Pyrex caused reactions of naphthalene, itself, giving a naphthalene dimer etc. Such undesirable reactions were partly depressed by using a $CuSO_4$ filter solution; the selectivities of naphthoic acids and dihydronaphthalenecarboxylic acid increased from 2.2—9.8 to 12.2—23.0%. To avoid any direct irradiation to naphthalene and naphthoic acids was critical. Their high selectivities, up to 67%, were obtained upon visible light irradiation by using phenazine as a sensitizer. More than 90% of the naphthoic acids was 1-naphthoic acid, which was confirmed by GC and ms.

Carbon dioxide is a considerable natural source of carbon.[2)] In plant chloroplasts carbon dioxide and water are converted into carbohydrates and oxygen. However, there are only four industrial process in which carbon dioxide is used for organic synthesis.[3)] One way to use carbon dioxide is to activate inert carbon dioxide, itself, using a catalyst, such as a transition metal.[4)] The other way is to react carbon dioxide with highly reactive substances. Examples of reactive electron-rich substances include anion radicals of aromatic compounds and some olefins. Anion radicals are produced by electrical reduction,[5)] reduction with metallic sodium[6)] or photoinduced electron transfer. Tazuke and Ozawa have described the carboxylation of an anion radical - cation radical pairs photochemically formed in a solution. Phenanthrene was carboxylated photochemically to give 9,10-dihydro-9-phenanthrenecarboxylic acid.[7)] The photocarboxylation of anthracene has also been reported in detail.[8)] Though the possibility of the photocarboxylation of naphthalene has been described, there has been no detailed report about it. That might be because the reactivity of naphthalene is small compared to that of phenanthrene and anthracene. This study is related to the photocarboxylation of naphthalene with a UV lamp using various donors (Table 1) and the visible-light carboxylation of naphthalene using a sensitizer.

Table 1. Half-Wave Oxidation Potential of Donor Used in This Study ($E_{1/2}$: Q/Q^+)[a)]

Donor	Oxidation potential V vs. SCE
N,*N*-Dimethyl-*p*-toluidine	0.65
N,*N*-Diethylaniline	0.76
N,*N*-Dimethylaniline	0.78
Diphenylamine	0.83
Tributylamine	0.92
Triethylamine	0.96
N,*N*-Dimethylbenzylamine	1.01
N-Methylaniline	1.03
Dicyclohexylamine	1.12
Dibutylamine	1.17
Dipropylamine	1.22
Indene	1.22
1,3-Dimethoxybenzene	1.45
Naphthalene	1.54

a) R. Ballardini, G. Varani, M. T. Indelli, F. Scandola, and V. Balzani, *J. Am. Chem. Soc.*, **100**, 7219 (1978).

Results and Discussions

Photocarboxylation on a UV Irradiation through Pyrex. Naphthalene was converted as shown in Table 2 when naphthalene was irradiated with a 100-W high-pressure mercury lamp through Pyrex. The reaction times were from 14.5 to 40 h with an excess of donors in *N*,*N*-dimethylformamide. The conversion of naphthalene depended on the kind of donors. Naphthoic acids were confirmed to be the products by both MS and GC. The production of dihydronaphthalenecarboxylic acid was also confirmed by MS and a dehydrogenation reaction of the products. This dehydrogenation reaction was carried out for 4 h at 210 °C in the presence of Pd/C. One GC peak just before the peaks of naphthoic acids disappeared and the relative peak area of 1-naphthoic acid increased through the reaction. This indicated that dihydronaphthalenecarboxylic acid has a carboxylic moiety at the 1-position. Though we did not observe the peaks of any other kind of dihydronaphthalenecarboxylic acid, we did not identify the position of the double bond. The selectivity of naphthoic acids and dihydronaphthalenecarboxylic acid was calculated based on the conversion of naphthalene (Table 2). Their mole ratio is also shown in Table 2. In many cases, more than 90% of them was 1-naphthoic acid. The yields of acids were determined by a gravimetric method. They were, however, fairly larger than the selectivities of naphthoic acids and dihydronaphthalenecarboxylic acid and sometimes were over 100%. In the case of phenanthrene carboxylation, the gravimetric yield agreed with the GC yield.[7)] We

Table 2. Photocarboxylation of Naphthalene on UV Irradiation in *N*,*N*-Dimethylformamide Bubbling with Carbon Dioxide

Donor	Conversion	Selectivity (mol ratio)
	mol%	mol%[a]
None	89.4	0.2 (50.6 : 44.8 : 4.6)
None[b]	90.0	0.0
N,*N*-Dimethyl-*p*-toluidine	96.8	2.2 (48.1 : 49.6 : 2.3)
N,*N*-Diethylaniline	83.2	4.7 (2.3 : 92.3 : 5.4)
N,*N*-Dimethylaniline	71.7	9.8 (34.6 : 57.9 : 7.5)
N,*N*-Dimethylaniline[c]	39.5	7.0 (0.1 : 93.7 : 6.2)
N,*N*-Dimethylaniline[d]	92.8	—
Diphenylamine	50.5	3.2 (73.2 : 26.4 : 0.4)
Triethylamine	94.8	0.0
N,*N*-Dimethylbenzylamine	93.2	0.1 (34.6 : 64.2 : 1.2)
N-Methylaniline	41.4	6.0 (2.1 : 92.2 : 5.7)
N-Methylaniline[c]	30.4	3.7 (4.0 : 93.2 : 2.8)
Dicyclohexylamine	98.3	0.8 (9.1 : 90.6 : 0.3)
Dibutylamine	89.1	1.1 (0.0 : 100 : 0.0)
Dipropylamine	84.5	1.1 (0.0 : 100 : 0.0)
Indene	32.4	0.0
1,3-Dimethoxybenzene	56.0	0.0

a) Selectivity of naphthoic acids and dihydronaphthalenecarboxylic acid (dihydronaphthalenecarboxylic acid: 1-naphthoic acid: 2-naphthoic acid). b) Argon bubbling. c) In acetonitrile. d) Phenanthrene was used as substrate.

should pay attention to the fact that the acids yield calculated by the gravimetric method was sometimes uncertain in the case of naphthalene. Dicarboxylic acid was not obtained.

When naphthalene, itself, without a donor was irradiated, nearly 90% of the naphthalene was converted. However, the selectivity was as low as 0.2%. It is well known that the interaction between excited aromatic hydrocarbons and amines gives complete transfer of an electron from amines to hydrocarbons[9] (Reaction (1) in the Scheme). Carboxylic acids would be produced by the reaction of the naphthalene anion radical with carbon dioxide as Reaction (2) in the Scheme. In the case without a donor, we do not deny the possibility that impurities of *N*,*N*-dimethylformamide donated an electron to naphthalene. No acids were obtained in the absence of carbon dioxide, in which case argon gas was bubbled instead of carbon dioxide.

When aliphatic amines such as triethylamine, dicyclohexylamine, dibutylamine, and dipropylamine were used as a donor, lower yields of acids than other donors were obtained. Aliphatic amines do not have a large absorptivity at over 300 nm, indicating that undesirable reactions of naphthalene, itself, like dimerization, occurred in the case of aliphatic amines since naphthalene mainly absorbed the light through Pyrex. Furthermore, photoreactions of the amines with naphthalene were known.[10] These reactions would compete with carboxylation. In the case of indene and 1,3-dimethoxybenzene, we did not confirm the production of naphthoic acids. Carboxylation of indene was confirmed instead of naphthalene carboxylation. This might be because indene was not only a donor, but was also a reactive compound. The amount of indene used was 0.5 mol, fairly larger than the amount (0.025 mol) of naphthalene.

One of the important characteristics of a donor should be its oxidation potential.[11] We used various donors with oxidation potentials between 0.65 and 1.45 V (vs. SCE),[12] as shown in Table 1. The conversion of naphthalene and the selectivities, however, did not depend on the oxidation potential. The spectroscopic-excited state energy of *N*,*N*-dimethylaniline, for example, is 3.83 eV,[13] which is larger than 3.05 eV of the oxidation potential of *N*,*N*-dimethylaniline minus the reduction potential of naphthalene. Certainly the free-energy change in an electron transfer was favorable in all of the donors used in this study and, thus, the oxidation potential of donors was not an important factor.

The naphthalene anion radical was easily produced by a reaction with metallic sodium. When the naphthalene anion radical was reacted with dry ice, the production of dihydronaphthalenedicarboxylic acids was confirmed. Since in a metallic-sodium reduction of naphthalene, almost all of the naphthalene was reduced before any contact with carbon dioxide, dicarboxylic acids were obtained. In the case of photocarboxylation, since the concentration of the photoproduced anion radical was small, dicarboxylic acid was probably not produced in the case photocarboxylation.

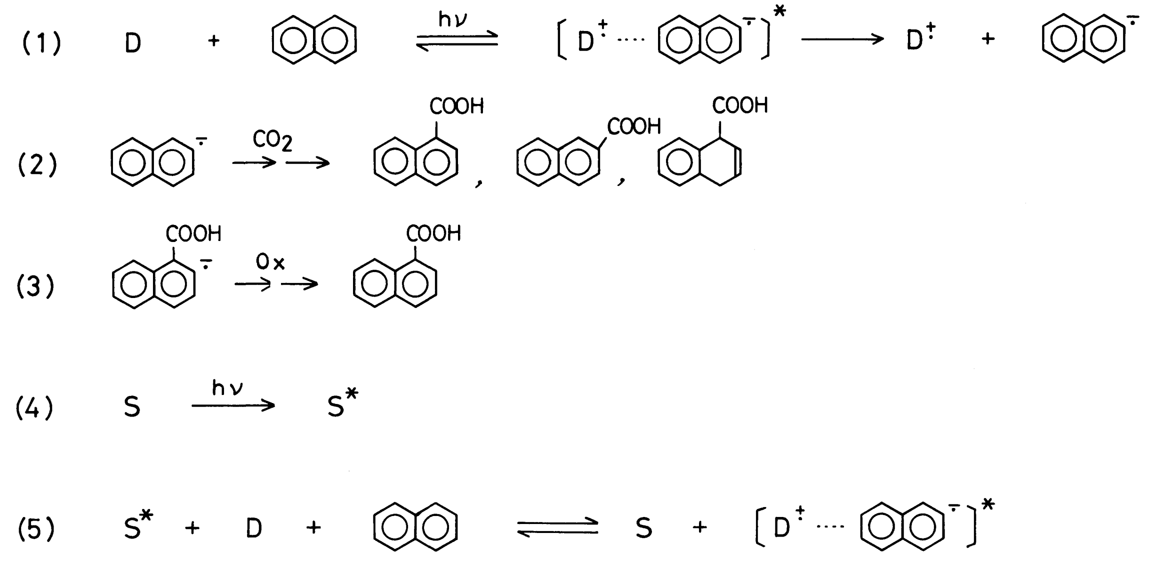
It is reported that in the case of phenanthrene, nearly 50% of the converted phenanthrene was a hydrogenated compound, 9,10-dihydro-9-phenanthrenecarboxylic acid. The result was different from that of naphthalene in which case 1-naphthoic acid was the main product. It was considered that the electron-transfer reaction from the intermediate anion radical to the oxidizing agent (as Reaction (3) in the Scheme) occurred. It is well-known that the 1-position of naphthalene is more reactive than that of the 2-position.[14] The high ratio of 1-naphthoic acid in the products agreed with those reactivities of the positions.

Naphthoic acids have received much attention recently since they are raw materials of 2,6-naphthalenedicarboxylic acid, which gives a liquid-crystalline polymer and a high-quality polyester resin.[15] In this study, however, the maximum selectivity of naphthoic acids and dihydronaphthalene-carboxylic acid was only 9.8%. The production of carboxylic acid of the naphthalene dimer was confirmed by MS. Two routes to produce acid of the dimer were considered. In one route, the naphthalene dimer was carboxylated to give an acid of the dimer. In the another route, naphthoic acid reacted with naphthalene to give an acid of the dimer. In any case, the direct irradiation of naphthalene and/or naphthoic acid was harmful to the selectivities.

Photocarboxylation on UV Irradiation through a $CuSO_4$ Filter Solution. Naphthalene was irradiated with a 400-W high-pressure mercury lamp through a 1 M $CuSO_4$ solution (1 M=1 mol dm^{-3}) in order to cut the light below 310 nm.[16] Higher selectivities were obtained upon irradiation through a $CuSO_4$ filter solution than those through Pyrex (Table 3). A maximum selectivity of 23% was obtained in the case of *N*-methylaniline. In the case of *N*,*N*-diethylaniline and *N*,*N*-dimethylaniline, the conversions of naphthalene were 86.5 and 71.3%, respectively, which were similar to 83.2 and 71.7% of those through Pyrex, respectively. However, the selectivities of naphthoic acids and dihydronaphthalenecarboxylic acid increased from 4.7 and 9.8% to 12.2 and 16.6%, respectively. Avoiding short-wavelength light was an effective way to increase the selectivity.

Nevertheless, we also confirmed the decomposition of naphthoic acids upon UV irradiation, even through a $CuSO_4$ filter solution. The extinction coefficients of naphthoic acids are more than 1×10^3 mol dm^{-3} cm^{-1} at a wavelength around 310 nm. It was therefore concluded that UV irradiation was not preferable to obtain high selectivities of naphthoic acids.

Photocarboxylation upon Visible-Light Irradiation. Little naphthalene was converted when naphthalene alone was irradiated with a 500-W Xe lamp (Table 4). This was because naphthalene and triethylamine



Scheme. (D: Donor, S: Sensitizer, Ox: Oxidizing agent)

Table 3. Photocarboxylation of Naphthalene on a UV Irradiation through $CuSO_4$ Filter Solution in *N*,*N*-Dimethylformamide Bubbling with Carbon Dioxide

Donor	Conversion mol%	Selectivity (mol ratio) mol%[a]
N,*N*-Dimethyl-*p*-toluidine	65.0	13.3 (1.2 : 96.9 : 1.9)
N,*N*-Diethylaniline	86.5	12.2 (6.4 : 92.5 : 1.2)
N,*N*-Dimethylaniline	71.3	16.6 (1.8 : 94.6 : 3.6)
N-Methylaniline	27.1	23.0 (1.7 : 97.2 : 1.1)

a) Selectivity of naphthoic acids and dihydronaphthalenecarboxylic acid based on naphthalene consumed (dihydronaphthalenecarboxylic acid: 1-naphthoic acid: 2-naphthoic acid).

Table 4. Photocarboxylation of Naphthalene on a Visible Light Irradiation by Using Sensitizer in *N,N*-Dimethylformamide Bubbling with Carbon Dioxide

Donor (reaction time; h)	Conversion mol%	Selectivity (mol ratio) mol%[a]
N,N-Dimethyl-*p*-toluidine (40)	22.1	8.0 (0.5 : 99.0 : 0.5)
N,N-Dimethyl-*p*-toluidine[b] (40)	6.6	5.5 (15.4 : 84.6 : 0.0)
N,N-Dimethylaniline (40)	26.5	46.8 (2.3 : 94.5 : 3.2)
N,N-Dimethylaniline (60)	39.5	55.8 (0.0 : 100 : 0.0)
Tributylamine (20)	28.0	49.7 (2.5 : 95.9 : 1.6)
Tributylamine (40)	36.7	44.2 (0.8 : 94.2 : 5.0)
Tributylamine[b] (40)	6.6	14.1 (44.9 : 45.5 : 9.6)
Tributylamine (60)	42.9	63.7 (3.3 : 92.8 : 3.9)
Triethylamine[c] (50)	0.3	0.0
Triethylamine (20)	22.3	50.1 (9.0 : 91.0 : 0.0)
N,N-Dimethylbenzylamine (40)	11.2	19.0 (1.3 : 97.3 : 1.5)
N,N-Dimethylbenzylamine[b] (40)	1.5	19.7 (2.3 : 92.5 : 5.2)
N-Methylaniline (40)	21.6	67.3 (0.3 : 99.7 : 0.0)
Dibutylamine (40)	41.3	16.4 (0.0 : 100 : 0.0)
Dibutylamine[b] (40)	6.0	9.9 (0.0 : 100 : 0.0)
Dipropylamine (40)	11.5	20.8 (12.5 : 79.8 : 7.7)
None (50)	16.5	27.0 (0.0 : 100 : 0.0)

a) Selectivity of naphthoic acids and dihydronaphthalenecarboxylic acid (dihydronaphthalenecarboxylic acid: 1-naphthoic acid: 2-naphthoic acid). b) Acridine was used as a sensitizer. c) No phenazine was used.

scarcely absorb visible light. However, a 22.3% conversion and 50.1% of the selectivity were obtained by using phenazine as a sensitizer under the same conditions. This fact indicates the occurrence of photosensitized carboxylation (Reactions (4) and (5) in the Scheme). Furthermore, upon irradiation without a donor, 16.5% of the naphthalene converted and a selectivity of 27.0% was obtained. This suggests that a direct electron transfer from phenazine to naphthalene also occurred. In the case of *N,N*-dimethylaniline, tributylamine, triethylamine, and *N*-methylaniline, selectivities of more than 40% were obtained and a maximum selectivity of 67.3% was obtained in the case of *N*-methylaniline. In the case of *N,N*-dimethyl-*p*-toluidine, *N,N*-dimethylbenzylamine, dibutylamine, and dipropylamine, however, the selectivities were 8 to 20.8% and smaller than 27.0% of that without a donor. This fact suggests that such amines quenched the excited state of phenazine[17] and that this quenching reaction did not contribute to an electron transfer to naphthalene.

Though acridine was also an effective sensitizer the selectivities using acridine were still smaller than those obtained using phenazine. In any case, visible-light irradiation with a sensitizer prevented any side reactions of naphthalene and/or donors.

A one-step carboxylation of aromatic compounds like benzene has been attempted using paladium catalysts; the conversions of such one-step carboxylations, however, were very small.[18] The photocarboxylation of naphthalene to give naphthoic acids in which more than 90% of them is 1-naphthoic acid is an attractive one-step carboxylation process, since the reaction occurrs under mild conditions by using photoenergy. We can obtain a high selectivity of 1-naphthoic acid of up to 67%.

Experimental

Materials. Naphthalene and phenanthrene were purified by recrystallization and sublimation. The naphthalene anion radical was prepared by contact of metallic sodium with naphthalene in dry ethylene glycol dimethyl ether. The donors (Table 1) and solvents were of reagent grade and were used after distillation or without further purification.

Photocarboxylation. The photolysis was performed with a 100-W mercury lamp using a Pyrex filter, a 400-W high-pressure mercury lamp using a $CuSO_4$ filter solution or a 500-W Xe lamp using a IRA-25S filter. A solution of naphthalene (0.025 M), a donor (0.5 M) and/or a sensitizer (0.0025 M) in 120 or 10 ml was irradiated in bubbling CO_2 or Ar at room temperature. Gas chromatography was performed on a Hitachi 063 gas chromatograph in order to determine the amount of naphthalene consumed. After the reaction, the solvent was removed under reduced pressure and the residue was made alkaline with 5% sodium hydroxide. An acid was produced by the acidification of the alkaline solution after filtration with concentrated hydrochloric acid. The yield of acids was of gravimetric yield, based on the conversion of naphthalene. The selectivity of naphthoic acids and dihydronaphthalenecarboxylic acid was obtained by a Shimazu GC-9A capillary gas chromatograph after esterification of carboxylic acids. It was based on the conversion of naphthalene.

The present work was partially supported by the Saneyoshi Scholarship Foundation.

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