as pure samples by preparative VPC (4-bromo-2,6-dimethyl-, 5-bromo-2,3-dimethyl-, 4-acetoxy-2,6-dimethyl-, 5-acetoxy-2,3-dimethyl-, and 4-methoxy-2,6-dimethylbenzyl acetate) or by column chromatography (4-carbomethoxy-2,6-dimethyl- and 5-carbomethoxy-2,3-dimethylbenzyl acetate) of the crude products deriving from $Co(OAc)_3$ oxidation and/or NBS bromination (followed by acetoxylation) of the substituted hemimellitene. Structures were assigned on the basis of NMR spectra.

4-Bromo-2,6-dimethylbenzyl acetate: ^1H NMR ($CDCl_3$) δ 7.15 (s, 2 H), 5.10 (s, 2 H), 2.30 (s, 6 H), 2.05 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 258 (2), 256 (2), 198 (100), 196 (95), 117 (63), 91 (44).

5-Bromo-2,3-dimethylbenzyl acetate: ^1H NMR ($CDCl_3$) δ 7.20 (s, 2 H), 5.05 (s, 2 H), 2.25 (s, 3 H), 2.10 (s, 3 H), 2.05 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 198 (100), 196 (95), 117 (20).

4-Acetoxy-2,6-dimethylbenzyl acetate: ^1H NMR (CCl_4) δ 6.60 (m, 2 H), 5.00 (s, 2 H) 2.40 (s, 6 H), 2.20 (s, 3 H), 2.00 (s, 3 H); MS (35 eV), *m/z* (relative intensity) 236 (10), 194 (32), 176 (16), 136 (20), 135 (41), 134 (100).

5-Acetoxy-2,3-dimethylbenzyl acetate: ^1H NMR (CCl_4) δ 6.75 (m, 2 H) 4.95 (s, 2 H), 2.30 (s, 3 H), 2.25 (s, 3 H), 2.20 (s, 3 H), 2.00 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 194 (5), 176 (13), 134 (100).

4-Methoxy-2,6-dimethylbenzyl acetate: ^1H NMR ($CDCl_3$) δ 6.56 (s, 2 H), 5.15 (s, 2 H), 3.70 (s, 3 H), 2.32 (s, 6 H), 1.00 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 208 (10), 149 (100), 135 (13), 117 (10), 105 (15), 91 (33).

4-Carbomethoxy-2,6-dimethylbenzyl acetate: ^1H NMR ($CDCl_3$) δ 7.68 (s, 2 H), 5.20 (s, 2 H) 3.90 (s, 3 H), 2.43 (s, 6 H), 2.07 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 205 (10), 176 (100), 145 (28), 91 (16), 43 (92).

5-Carbomethoxy-2,3-dimethylbenzyl acetate: ^1H NMR ($CDCl_3$) δ 7.78 (s, 2 H), 5.13 (s, 2 H), 3.90 (s, 3 H), 2.35 (s, 3 H), 2.28 (s, 3 H), 2.12 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 205 (8), 176 (100), 145 (25), 91 (16), 43 (85).

5-Methoxy-2,3-dimethylbenzyl Acetate. 5-Methoxyhemimellitene (5.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (6.4 mmol), and di-*tert*-butyl peroxide (20 mmol) were refluxed for 60 h in AcOH (21 mL) containing Ac_2O (9 mL). The reaction mixture was worked up as usual and the desired compound was separated from the unreacted substrate and methylated products[26] by preparative VPC on NPGS at 190 °C: ^1H NMR ($CDCl_3$) δ 6.73 (dd, AB system, J = 2.9 Hz, 2 H), 5.10 (s, 2 H), 3.77 (s, 3 H), 2.28 (s, 3 H), 2.15 (s, 3 H), 2.09 (s, 3 H); MS (70 eV), *m/z* (relative intensity) 208 (5), 148 (100), 117 (20), 105 (30), 91 (50).

Acknowledgment. We gratefully acknowledge the financial support of the Italian National Council of Research and Ministero della Pubblica Istruzione (E.B., A.D., L.M., and C.R.) and the Swedish Natural Science Research Council (L.E.). We also thank Professor D.R. Arnold for communicating a manuscript in advance of publication.

Registry No. CAN, 16774-21-3; NBS, 128-08-5; $Co(OAc)_3$, 917-69-1; 5-bromo-1,2,3-trimethylbenzene, 32591-43-8; 3,4,5-trimethylaniline, 1639-31-2; 5-methoxy-1,2,3-trimethylbenzene, 21573-41-1; 3,4,5-trimethylphenol, 527-54-8; 3,4,5-trimethylphenyldiazonium, 77134-16-8; 5-carbomethoxy-1,2,3-trimethylbenzene, 13544-66-6; 3,4,5-trimethylbenzoic acid, 1076-88-6; 5-acetoxy-1,2,3-trimethylbenzene, 6719-74-0; 4-bromo-5-methoxyhemimellitene, 103324-43-2; 4-bromo-2,6-dimethylbenzyl acetate, 104532-00-5; 5-bromo-2,3-dimethylbenzyl acetate, 104532-01-6; 2,6-dimethylbenzyl acetate, 62346-87-6; 5-acetoxy-2,3-dimethylbenzyl acetate, 104532-02-7; 4-methoxy-2,6-dimethylbenzyl acetate, 92516-23-9; 4-carbomethoxy-2,6-dimethylbenzyl acetate, 104532-03-8; 5-carbomethoxy-2,3-dimethylbenzyl acetate, 104532-04-9; 5-methoxy-2,3-dimethylbenzyl acetate, 104532-05-0; 1,2,3-trimethylbenzene, 526-73-8; 5-*tert*-butyl-1,2,3-trimethylbenzene, 98-23-7; 1,2,3,5-tetramethylbenzene, 527-53-7.

Reductive Photocarboxylation of Aromatic Hydrocarbons

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Received May 6, 1986

Photoirradiation of aromatic hydrocarbons such as phenanthrene, anthracene, or pyrene in the presence of an amine and carbon dioxide in dipolar aprotic solvents resulted in reductive carboxylation of the hydrocarbon. The reaction was considered to proceed via the anion radical of the hydrocarbon that reacts with CO_2 and then abstracts hydrogen, possibly from the solvent, to yield the corresponding dihydro carboxylic acid of the hydrocarbon. The highest yield was obtained for phenanthrene with *N,N*-dimethyl-*p*-toluidine as reducing agent in dimethyl sulfoxide. A quantum yield of 0.17 for the formation of 9,10-dihydrophenanthrene-9-carboxylic acid with selectivity of 86% based on consumed phenanthrene was achieved. Addition of a hydrogen donor such as cumene, decalin, or others was shown to be effective in increasing the yield.

Carbon dioxide is among the most stable of all carbon compounds. Direct use of carbon dioxide as a reagent for C–C coupling reactions therefore requires a strongly endoergic reaction process unless the reaction partner is highly activated. Since the classical example of salicylic acid synthesis from phenol and CO_2, several methods of activating CO_2 have been reported, specifically aimed at CO_2 fixation.[1] Of particular interest is the use of CO_2 as a comonomer for ring-opening polymerization of cyclic ethers. Activation by organometallic compounds is also a fashionable subject.

Carbon dioxide is a linear molecule having a large and negative quadrupole moment. Thus, reaction of CO_2 with a carbon-centered nucleophile should provide C–C coupling products, as demonstrated by trapping of carbanions by CO_2 to give the corresponding carboxylic acids.

Recent advances in electron-transfer photochemistry gave birth to many examples of photoreactions via ion-radical intermediates or exciplexes.[2] Depending upon solvent polarity, photoinduced electron transfer between donor and acceptor leads to either exciplex formation or ionic dissociation. The detailed mechanism of electron

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Table I. Photoreaction of Aromatic Hydrocarbons in the Presence of DMA and CO_2 in DMF[a]

ArH	reactn time, h	consumed ArH, %	isolated products[b] (yield %)
phenanthrene	5	90	I (60), II (tr)
anthracene	2	100	III (14), IV (22), V (4)
pyrene	50	<50	V (tr)

[a] Reaction conditions: [ArH] = 2.5×10^{-2} M, [DMA] = 0.5 M. CO_2 bubbling > 150 mL/min. [b] Based on consumed ArH.

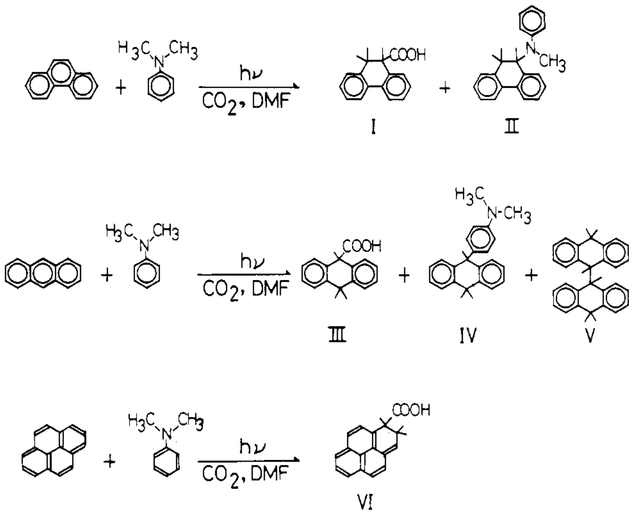
transfer and the factors determining the efficiency of ion-radical formation are still controversial. Although complete quenching of the excited singlet state of D or A by A or D, respectively, via electron transfer is easy, a 100% efficiency of dissociation to the free-ion radicals is difficult to achieve. A geminate ion-radical pair resulting from electron transfer may be subject to electron back-transfer to regenerate the locally excited states of D or A or to relax to the ground state. While a picosecond flash photolysis study revealed a nearly quantitative yield of ion-radical formation, the yield of charge separation depends on time after excitation.[3] Thus, the chemical yield of electron-transfer photoreaction even under conditions of complete fluorescence quenching is usually poor. The factors determining the choice of reaction paths such as ionic dissociation and electron back-transfer were discussed elsewhere, and the importance of Coulombic effect was emphasized.[4]

If charge-separated species D^+ and A^- couple with each other or are scavenged by a nucleophile or an electrophile, respectively, interesting preparative photochemistry can occur. The concept is not new, and various photoredox reactions such as the Birch photoreduction,[5] photocyanation,[6] photocycloaddition,[7] and others[8] fall in this category. In most cases, the research interest has been directed to product selectivity and the reaction mechanism. Little effort has been devoted to improve reaction efficiency. As early as 1975, we briefly reported the first example of reductive photocarboxylation.[9] An objective of the present paper is to develop an understanding of the factors determining the quantum efficiency and to improve the product yield of reductive photocarboxylation.

Results and Discussion

Reaction Products. Conditions of the photoreactions of anthracene, phenanthrene, and pyrene with CO_2 in the presence of *N*,*N*-dimethylaniline (DMA) in dimethylformamide (DMF) are summarized in Table I. The consumption of hydrocarbon is the fastest in the case of anthracene partly because of the high absorbance of anthracene at 366 nm and partly because of the occurrence of various side reactions. Reductive carboxylation was not the main reaction, but instead the major product was identified as the coupling product (see Scheme I). Photoreaction of anthracene with DMA has been studied by Pac et al. in various solvents.[10] In acetonitrile, they observed V as the main product (70%) together with IV (20%) and 9,10-dihydroanthracene (7%). Under the present conditions, it was not possible to quench all the precursors of V by CO_2. 9,10-Dihydroanthracene could not be detected. This compound may be consumed during photoirradiation as a hydrogen donor by analogy with the case of phenanthrene photocarboxylation (see following discussion).

Scheme I



Since phenanthrene has only a weak absorption at 366 nm, its photoreaction is much slower but the selectivity of carboxylation is very high. The only other product identified was II, formed in modest yield.

Pyrene is the least reactive. Even after a 50-h irradiation, only a trace amount of VI was isolated.

In the following sections we chose phenanthrene as the cleanest reaction system for detailed study.

Reaction Conditions Determining Reductive Photocarboxylation of Aromatic Hydrocarbons. Major factors deciding the reaction pathway are considered to be the choice of amine, solvent, and CO_2 pressure. The results in Table II indicate that high solvent polarity is a necessary condition. Protic solvents such as methanol are inappropriate because they react with phenanthrene anion radical. Poor results are obtained in acetonitrile; this may be due in part to the high acceptor number[11] of this solvent and in part to its poor hydrogen-donating property as will be discussed later. We do not understand why reductive carboxylation does not proceed and the consumption of phenanthrene is very slow in HMPA. Suitable solvents (DMF and Me_2SO) are dipolar aprotic solvents having high donor number and comparatively low acceptor number,[11] rendering high activity of anion radicals. Other factors relevant to the solvent effects are quenching rate constant of the excited singlet state of phenanthrene by DMA (k_q)

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Table II. Solvent Effects on Photocarboxylation of Phenanthrene in the Presence of *N,N*-Dimethylaniline[a]

		Y, %				solvent properties[e]		
no.	solvent	total[b]	RCOOH	RCOOH,[c] %	k_q,[d] $\times 10^9$ M^{-1} s^{-1}	ϵ	AN	DN
1	DMF	38	24	64	11.6	36.4	16.0	30.9
2	Me_2SO	40	31	80	4.3	46.7	19.3	29.8
3	sulfolane	27	7.7	29	2.9	43.3		14.8
4	HMPA	2.6	0	0		30.0	10.6	38.8
5	CH_3CN	31	0	0	8.6	37.5	18.9	14.1
6	MeOH	23	0	0	8.4	32.7	41.3	19.0

[a] Reaction conditions: [ArH] = 2.5 × 10^{-2} M, [DMA] = 0.5 M at room temperature, irradiation 300 min. [b] Consumed phenanthrene. [c] [RCOOH]/[consumed ArH], %. [d] Fluorescence quenching rate. [e] ϵ = dielectric constant, AN = acceptor number, DN = donor number.

Table III. Effects of Amines in Photocarboxylation of Phenanthrene in Me_2SO[a]

amine	concn, M	reactn time, min	Φ_{RCOOH}	Φ_{-ArH}	Φ_{RCOOH}/Φ_{-ArH}	Q %
N,N-dimethylaniline	0.5	90	0.087	0.11	0.82	25.4
N-methylaniline	0.5	60	0.042	0.14	0.29	25.9
aniline	0.5	60	0	0.16	0	18.7
N,N-dimethyl-*p*-toluidine	0.5	60	0.17	0.20	0.86	44.8

[a] [ArH] = 2.5 × 10^{-2} M at room temperature.

Table IV. Effects of CO_2 Pressure[a]

CO_2, atm	[RCOOH], $\times 10^3$ M	$-$[ArH], $\times 10^3$ M	selectivity, %
1	3.41	4.87	70.0
5	6.56	7.29	90.0

[a] Conditions: [phen] = 2.5 × 10^{-2} M, [DMA] = 0.5 M in Me_2SO, photoirradiation for 120 min.

and solubility of CO_2. The values of k_q obtained by Stern–Volmer plots are on the order of 10^9–10^{10} M^{-1} s^{-1}. The sequence of k_q does not agree either with carboxylation yield or with total consumption of phenanthrene, indicating that the reactions subsequent to the primary electron-transfer quenching are more important.

Solubility of CO_2 in each solvent was estimated by weight increase after bubbling CO_2 into the solvent. In favorable solvents, DMF and Me_2SO, the CO_2 concentration was 0.17 and 0.24 M, respectively, after 40 min bubbling at room temperature. Acetonitrile shows the same order of CO_2 solubility. Therefore, the solubility of CO_2 does not seem to be of great importance.

We chose Me_2SO as the best solvent and examined the effect of amine as shown in Table III. The carboxylation yield is in the order tertiary amine > secondary amine > primary amine = 0. Since the fraction of quenched excited state (Q %) does not differ very much for aniline and its mono- and dimethyl derivatives, the drastic change of carboxylation yield must be attributed to the secondary processes following primary electron transfer. By laser flash photolysis of pyrene–amine systems Mataga and his co-workers were able to detect pyrene radical but not pyrene anion radical when aniline was the quencher, indicating fast proton transfer from the amine to the pyrene anion radical produced by the primary electron transfer.[12] The best results in the sense of both reactivity and selectivity were obtained with *N,N*-dimethyl-*p*-toluidine. It has been demonstrated that photoreaction products of an aromatic hydrocarbon with DMA result from addition of DMA at the para position of the aromatic hydrocarbon.[10] It is reasonable that this side reaction is suppressed, and consequently carboxylation yield increases when the para position is blocked. The same is true for anthracene.

Since the carboxylation reaction is competitive with other reactions, high CO_2 concentration is a favorable condition as shown in Table IV.

Under the standard conditions of [ArH] = 1 × 10^{-2} M and [amine] = 0.5 M, the excited aromatic hydrocarbon is not quenched completely and the quantum yield of carboxylation increases with increasing (DMA) as shown in Figure 1.

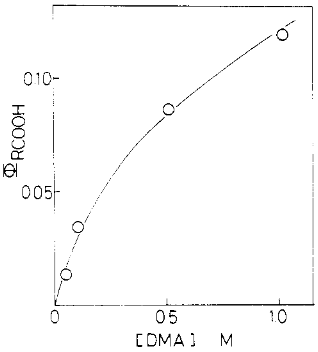

Figure 1. Dependence of photocarboxylation on DMA concentration. [phenanthrene] = 1.0 × 10^{-2} M in Me_2SO.

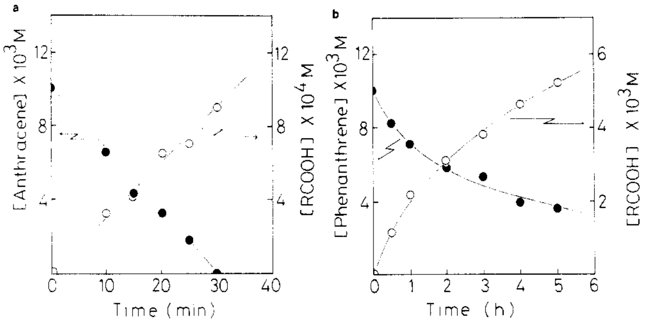

Figure 2. Time–conversion profile of photocarboxylation in Me_2SO. [DMA] = 0.5 M. Key: (a) anthracene; (b) phenanthrene.

Examples of time–conversion profiles are shown in Figure 2. Different shapes of the curves for phenanthrene and anthracene are ascribable to the higher molar absorbance of anthracene at the irradiation wavelength (ϵ 2 × 10^3 at 366 nm)[13] while that for phenanthrene is very low (ϵ 1 at 366 nm).[13] The reaction system of anthracene behaves as a completely absorbing system throughout the photoirradiation, while photoenergy absorbed by the phenanthrene system is reduced gradually during reaction. The selectivity of carboxylation (Φ_{COOH}/Φ_{-ArH}) is constant at a low level for anthracene and increases only slightly with conversion for phenanthrene as shown in Figure 3. We can therefore compare the selectivity determined at

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Table V. Additive Effects on Photocarboxylation of Phenanthrene[a]

no.	additive	solvent	reactn time, min	[RCOOH], $\times 10^3$ M	$-$[ArH], $\times 10^3$ M	selectivity, %
1	none	Me_2SO	90	3.41	4.16	82
2	9,10-dihydroanthracene	Me_2SO	90	3.71	5.48	86
3	decaline	Me_2SO	90	5.89	7.10	83
4	cumene	Me_2SO	90	5.89	7.18	82
5	tetralin	Me_2SO	90	4.80	6.40	75
6	9,10-dihydrophenanthrene	CH_3CN	120	4.77	[b]	
7	2,5-dimethyl-2,4-hexadiene	Me_2SO[c]	120	0.65	0.84	79
8	none	Me_2SO[c]	120	0.54	0.67	78

[a] $[ArH]_0$ = 0.21 M, [DMA] = 0.5 M, [additive] = 0.5 M. [b] The concentration of phenanthrene increased owing to dehydrogenation of the additive. [c] Photoreaction in a sealed tube, the initial pressure 1 atm.

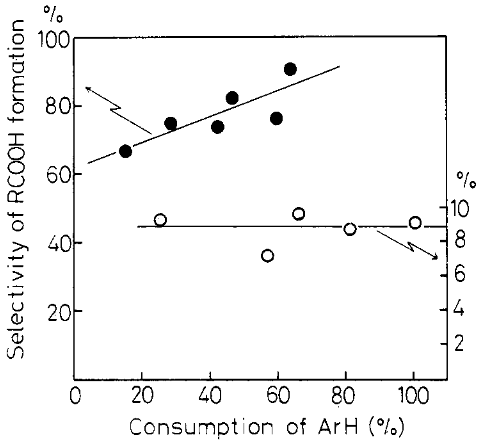

Figure 3. Selectivity of photocarboxylation as a function of consumed aromatic hydrocarbon. $[ArH]_0 = 1.0 \times 10^{-3}$ M, [DMA] = 0.05 M, solvent Me_2SO. Key: ●, phenanthrene; ○, anthracene.

different conversion provided the [amine] and [CO_2] are kept constant. The slight increase in the selectivity shown in Figure 3 may be related to the formation of dihydrophenanthrene during the initial stage of photereaction that facilitates the carboxylation.

Additive Effects. A Mechanistic Investigation. The general reaction pathway requires formation of an anion radical and subsequent addition of CO_2; however, the following two points are still unclear. These are the role and nature of the hydrogen donor for reductive carboxylation and the factors that control the overall consumption of aromatic hydrocarbon. The selectivity of carboxylation approaches 90% for phenanthrene while the total quantum yield is 0.087 (Table I). Taking Q % into account, the efficiency of hydrocarbon consumption corresponding to complete fluorescence quenching (Φ_{-ArH}/Q %) is 0.43–0.45 for DMA or *N,N*-dimethyl-*p*-toluidine. The fate of the other half of the excited phenanthrene is not known.

In the course of HPLC analysis of residual phenanthrene, we made the interesting observation that a trace amount (~0.8%) of 9,10-dihydrophenanthrene, a phenanthrene contaminant, disappeared as photocarboxylation proceeded. We put forward the hypothesis that dihydro aromatic compouns could act as hydrogen donors to complete the reductive photocarboxylation. The effects of hydrogen donors are shown in Table V. Decalin and cumene are most effective, bringing about any increase in Φ_{-ArH} of more than 1.7 times. The selectivity is kept nearly constant, indicating that the hydrogen donor facilitates the forward reaction and suppresses electron back-transfer. The role of the hydrogen donor was more unequivocally shown when the photocarboxylation was carried out in acetonitrile. As shown in Table II, no photocarboxylation occurs in this solvent, but addition of 9,10-dihydrophenanthrene results in the formation of the carboxylic acid (Table V). The yield of 4.8×10^{-3} M is even higher than the value in Figure 2 after a 2-h photoirradiation. The role of the solvent is therefore not only to provide a reaction medium but also to act as a hydrogen donor.

By the use of a hydrogen donor, the efficiency of phenanthrene consumption (Φ_{-ArH}/Q %) can be as high as 0.75. This figure is astonishingly high and much higher than the fluorescence quantum yield of phenanthrene in the absence of quenchers (Φ_f = 0.11–0.125).[13] This result may suggest either a faster quenching rate than intersystem crossing or the participation of the triplet state of phenanthrene. To examine the role of triplet excited state, we added a triplet quencher (2,5-dimethyl-2,4-hexadiene) but found no effect.

From the previous discussion, the charge separation efficiency is quite high. We tried to improve further the charge separation yield by means of salt effect. Recently we have demonstrated neutral salt effect obtained even for electron-transfer process between charged and neutral species[14] and interpreted the results as due to the salt effects on electron back-transfer process. Thus, when oxidized and reduced species in a pair are subjected to attractive Coulombic forces, the salt effect is to promote charge separation. We also found that the exciplex formed between neutral donor and neutral acceptor was quenched by neutral salt, which was explained by assuming enhanced charge separation.[15]

$$\left.\begin{array}{l} A^* + D \\ A + D^* \end{array}\right\} \longrightarrow (A \cdots D)^* \longrightarrow (A^{\bullet -} \cdots D^{\bullet +}) \xrightarrow[\text{salt effect}]{\text{pos neutral}} A^{\bullet -} + D^{\bullet +}$$

However, a neutral salt effect was not observed on either Φ_{-ArH} or Φ_{RCOOH} when tetraethylammonium chloride or cetyltrimethylammonium chloride was added. Probably the charge separation efficiency is so high without neutral salt that further improvement cannot be expected.

Now we can draw a mechanistic picture of the photocarboxylation as shown in Figure 4. The sequence of CO_2 addition and hydrogen abstraction cannot be decided explicitly. By analogy with the electrochemical carboxylation of stilbene,[16] which may be considered as a homologue of phenanthrene, addition of CO_2 to the anion radical should proceed prior to hydrogen transfer. While CO_2 addition will be a diffusion-controlled reaction, hydrogen abstraction needs an activation energy.

We have not confirmed the equilibrium between the phenanthrene anion radical and the CO_2 adduct. However, the experimental results indicating the enhanced yield of photocarboxylation in the presence of added hydrogen donor while the selectivity is nearly kept constant are

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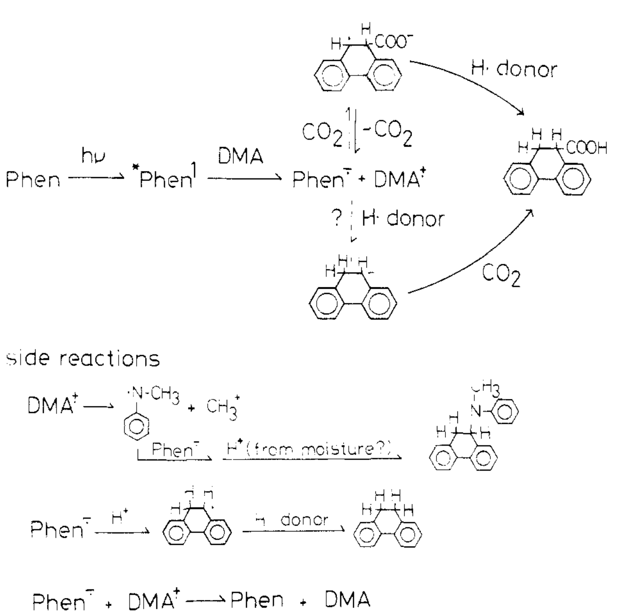

Figure 4. Proposed reaction paths for photocarboxylation of phenanthrene.

better understood by assuming the equilibrium.

The source of hydrogen is in general the solvent in the absence of a more powerful hydrogen donor. Previously we studied reductive photocarboxylation using *N*,*N*-hexadeuteriodimethylaniline in Me_2SO and found no deuteriation on the position to the carboxylate group, indicating that the amine was not the source of hydrogen.[16]

Conclusion

Reasonably efficient and selective photocarboxylation of phenanthrene was achieved. The present procedure will be applicable to the photocarboxylation of many other electron acceptors. In particular, the quantum yield enhancement by the addition of hydrogen donors will be a useful general procedure for photochemical coupling reactions that occur via an electron-transfer process, since most reactions of this kind require hydrogen transfer to convert the reactive intermediate to the final product.

Experimental Section

Materials. All reagents used in photoreaction were of guaranteed reagent grade. Aromatic hydrocarbons (anthracene, phenanthrene, pyrene) were recrystallized twice from ethanol. *N*,*N*-Dimethylaniline (DMA), *N*,*N*-dimethyl-*p*-toluidine, *N*-methylaniline, aniline, and triethylamine were dried over KOH and distilled under reduced pressure. All solvents were purified by accepted procedures.

Photoreaction. Large-Scale Reaction. For the purpose of product separation and identification, an internal irradiation apparatus was used. A 300-W high-pressure mercury lamp equipped with filter solution ($CuSO_4·5H_2O$, 250 g/L) layer was immersed in the solution for photoreaction, through which CO_2 was bubbled before photoirradiation. The bubbling of CO_2 was continued during photoirradiation. The standard sample composition was [aromatic hydrocarbon] = 2.5×10^{-2} M and [amine] = 0.5 M.

Small-Scale Cell Reaction. The sample solution placed in a 1-cm quartz cell for spectroscopy was irradiated externally with a high-pressure mercury lamp. A combination of filters (D335 + UV35, Toshiba Electric Co.) was used to monochromatize the light at 366 nm. During photoirradiation CO_2 was bubbled through the solution. Analysis of the reaction mixture was performed by HPLC (vide infra). For the determination of quantum yield, the light intensity was determined by means of anthracene photodimerization [$\Phi = 0.0706$ when [anthracene] = 1.0×10^{-2} M in benzene under deaerated condition][18] carried out in the same reaction vessel. The incident intensity was then determined as 6.67×10^{16} quanta/s. While the anthracene actinometer is a completely absorbing system, the actual reaction system containing 1.0×10^{-2} M of phenanthrene is weakly absorbing at 366 nm (absorbance 0.102). Change of optical density during photoirradiation was taken into account to determine the total photon number absorbed, and then the quantum yield was calculated.

A screw-capped pressure bottle was used to study CO_2 pressure effect.

Product Analysis. Phenanthrene–DMA–CO_2–DMF System. After photoreaction, the solvent and the amine were evaporated in vacuo. The residue was made alkaline with aqueous KOH and extracted with ether and then with chloroform. The aqueous layer was acidified to separate the carboxylic acid as a precipitate. The precipitate was redissolved in aqueous KOH and reprecipitated by acidification. This procedure was repeated several times. The final trace amount of amine was eliminated by passing the carboxylic acid through Toyopearl HW-40 resin (Toyo Soda Co.), and the pure carboxylic acid (I) was eluted with ethanol. All analytical data agreed with those of authentic 9,10-dihydrophenanthrene-9-carboxylic acid prepared by reduction of phenanthrene-9-carboxylic acid on sodium amalgam. The identification was reported previously.[9] Besides 60% of 9,10-dihydrophenanthrene-9-carboxylic acid, a trace amount of *N*-methyl-*N*-(9,10-dihydrophenanthren-9-yl)aniline was isolated from the ether–chloroform layer. Anal. Calcd: C, 88.37; H, 6.72; N, 4.91. Found: C, 87.84; H, 7.16; N, 4.55. NMR (acetone-d_6) δ 2.8 (3 H, s), 3.0 (1 H, t), 3.3 (2 H, d), 6.7 (5 H, m), 7.3 (6 H, m), 7.8 (2 H, m).

Anthracene–DMA–CO_2–DMF System. By procedures similar to the phenanthrene system, the following products were identified. 9,10-Dihydroanthracene-9-carboxylic acid (III): Anal. Calcd: C, 80.34; H, 5.39. Found: C, 79.90; H, 5.00. NMR (acetone-d_6) δ 4.0 (2 H, d), 5.0 (1 H, s), 7.3 (8 H, m); IR (KBr disk, cm^{-1}) 3000 (ν_{OH}), 1700 ($\nu_{C=O}$); mp 206–210 °C; yield 14%. An authentic sample of III was prepared[19] and the analytical data agreed with those of photochemically obtained III. 9-[4-(*N*,*N*-Dimethylamino)phenyl]-9,10-dihydroanthracene (IV): Anal. Calcd: C, 88.25; H, 7.07; N, 4.68. Found: C, 88.01; H, 7.01; N, 4.51. NMR (acetone-d_6) δ 2.8 (6 H, s), 3.9 (2 H, d), 5.4 (1 H, t), 6.45–7.05 (4 H, m), 7.06–7.40 (8 H, m); mp 146–150 °C; yield 22%. 9,9′-Bis(9,10,9′,10′-tetrahydroanthryl) (V): Anal. Calcd: C, 93.81; H, 6.19. Found: C, 93.08; H, 6.01. NMR, not measurable; mp 248–250 °C; yield 4%. **Pyrene–DMA–CO_2–DMF System.** The photoreaction was very slow. Irradiation for 50 h produced only a small amount of 1,2-dihydropyrene-1-carboxylic acid (VI): Anal. Calcd: C, 82.24; H, 4.87. Found: C, 82.47; H, 5.66. NMR (acetone-d_6) δ 3.6 (2 H, t), 4.2 (1 H, t), 6.1 (1 H, br), 7.5–7.7 (7 H, m); IR (KBr, cm^{-1}) 3000 (ν_{OH}), 1700 ($\nu_{C=O}$); mp 167–169 °C; yield, not determined.

Analysis by HPLC. Analysis of carboxylic acids in the presence of a large excess of amines is very difficult because of partial salt formation. Carboxylic acids are usually analyzed by HPLC under acidic conditions. However, when the reaction mixture of phenanthrene–DMA–CO_2–DMF was acidified by HCl, the DMA–HCl salt interfered with the analysis of the carboxylic acid. The elution time of the salt was nearly identical with that of the desired product. The HPLC analysis was best performed under alkaline condition as follows.

A 20-μL sample of the reaction mixture was added to five drops of 1 M NaOH solution and then diluted 500 times with methanol. This pretreated sample was analysed by a Hitachi 635A high-pressure liquid chromatograph equipped with a DuPont Zorbax ODS column (15.0 cm × 4.6 mm) and a UV absorption detector. The eluent was aqueous acetonitrile (CH_3CN/H_2O = 9/1, v/v), the flow rate being 0.5 mL/min.

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For the analysis of aromatic hydrocarbon, the reaction mixture was injected without pretreatment. The eluent was aqueous methanol (CH_3OH/H_2O = 7/3), and the flow rate was 1.5 mL/min.

Spectroscopy. A Hitachi UV-320 spectrometer and a Hitachi MPF-4 spectrofluorometer were used for absorption and fluorescence spectroscopies, respectively. A JNM-PMX 60-MHz ^1H NMR spectrometer (JEOL) and an IR 260-10 infrared spectrometer (Hitachi) were used for structure identification.

Registry No. I, 2222-30-2; II, 104848-69-3; III, 104834-81-3; IV, 104834-82-4; V, 104834-83-5; VI, 104834-84-6; CO_2, 124-38-9; $PhN(Me)_2$, 121-69-7; phenanthrene, 85-01-8; anthracene, 120-12-7; pyrene, 129-00-0.

Catalytic Electrophilic Reactions of Chrysanthemic Acid Derivatives with Unsaturated Organosilanes. An Application to Synthesis of Modified Types of C_{15} and C_{20} Isoprenoids with Non-Head-to-Tail Linkages

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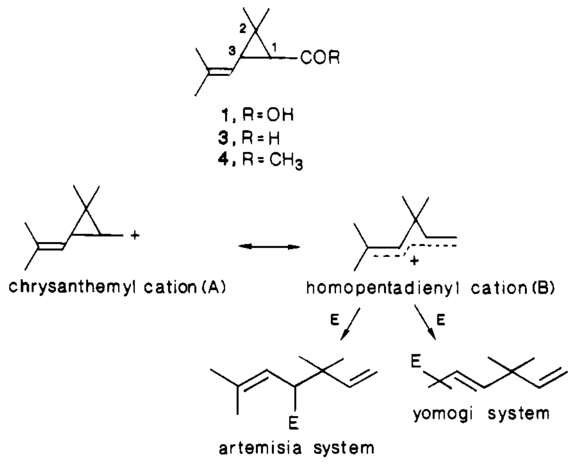
Received July 28, 1986

Chrysanthemyl silyl ether (**2b**) reacted with allylic and enolic silanes in the presence of $TiCl_4$ as a catalyst to give selectively C_1–C_3 ring-opened and ϵ-substituted products (yomogi type product). Chrysanthemaldehyde (**3**) and the corresponding methyl ketone **4** underwent similar electrophilic reactions with these reagents. These results are rationalized by the electrophilic attack of the intermediate homopentadienyl cation formed by the aid of the catalyst on an unsaturated organosilane. As for the reactivity, the trans isomer prevailed over the cis isomer, coinciding with the solvolytic behavior of chrysanthemyl 2,4-dinitrobenzoate (**2c**). The different product pattern from that in the reaction of Ti(IV) enolate with **3** giving a straightforward 1,2 addition product supported that the mechanism for the Mukaiyama reaction involves the initial polarization of a carbonyl group with $TiCl_4$ rather than Ti(IV) enolate formation. This method employing C_5 organosilanes constructed modified C_{15} and C_{20} isoprenoid skeletons with non-head-to-tail linkages by combinations $C_5 + C_{10}$ and $C_5 + C_{10} + C_5$, respectively. Thereby, even the C_{20} compound with all the isoprenoid fusions in middle-to-tail was obtainable. Of particular interest was the reaction of the enone **42** derived from the condensation reaction of the aldehyde **3** and lithium enolate of methyl isopropyl ketone; the reaction occurred at the η-position to the carbonyl center. The unusual elongation of the reactive site may originate from the cyclopropane ring strain relief.

Chrysanthemic acid (1) is a unique terpene possessing a "middle-to-tail" isoprenoid fusion. The cyclopropane ring in 1 and its derivatives is known to be cleaved by catalysis,[1] thermolysis,[2] and photolysis,[3] and thereby, the possible three ways of the ring cleavage give rise to a variety of open-chain and ring-expanded compounds depending on the structure. Specifically, carbonium ion mediated reaction of the chrysanthemyl system results in the formation of the artemisia and/or yomogi systems via a selective C_1–C_3 fission due to the cation-stabilizing ability of the isobutenyl group at C_3[4] (Scheme I).

In this decade unsaturated organosilanes are documented to be reactive with various carbon electrophiles.[5] Among them are resonance-stabilized primary and secondary alkyl cations[6] as well as tertiary alkyl cations,[7] conceptionally S_N1-reactive carbonium ions, as pronounced by Reetz.[8] From our continuous interest in the chemistry of strained organic molecules, it is reasonable to consider a cyclopropylmethyl cation generated in the chrysanthemyl system as an efficient electrophile toward such organosilicon reagents. Thus, we decided to study the Lewis acid

Scheme I[a]



[a] E = electrophile. Allylic and enolic silanes in this work.

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