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Photofixation of Carbon Dioxide: Formation of 9,10-Dihydrophenanthrene-9-carboxylic Acid from Phenanthrene–Amine–Carbon Dioxide Systems

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Summary Irradiation of phenanthrene in the presence of various amines and carbon dioxide in dimethyl sulphoxide or dimethylformamide solution yields 9,10-dihydrophenanthrene-9-carboxylic acid with conversions up to 55%.

KNOWN carbon–carbon bond formations using CO_2 indicate that the presence of a highly basic carbon atom in the reaction partner is essential for the addition of CO_2. Change in nucleophilicity under photoirradiation is now well accepted. Flash photolysis studies of weak electron-donor–weak electron-acceptor systems together with results of continuous irradiation experiments,[1–3] have provided evidence for the photochemical formation of anion radical–cation radical pairs in solution, but these active species have been little used synthetically.

Photoirradiation of Me_2SO or $HCONMe_2$ solutions of phenanthrene in the presence of an amine and CO_2 yielded 9,10-dihydrophenanthrene-9-carboxylic acid (Table), identified by its m.p. and n.m.r., i.r., and u.v. spectra.[4] A typical procedure is as follows. The Pyrex vessel containing a solution of phenanthrene and $PhNMe_2$ in Me_2SO was filled with CO_2 (4 kg cm^{-2} pressure), and then irradiated by a 300 W high-pressure mercury lamp at a distance of 7 cm for 14 h at room temperature. Bubbling CO_2 through the solution at atmospheric pressure gave similar results. The gravimetric yield of carboxylic acid agreed with the gas chromatographic yield determined after esterification of the reaction mixture.

We have found the following. (i) Both aromatic and aliphatic amines are effective. (ii) The polarity of solvent is an important factor. Carboxylation proceeds in Me_2SO or $HCONMe_2$ but not in tetrahydrofuran, dioxan, or n-hexane. (iii) Addition of a small amount of water has little influence on the yield of carboxylic acid. (iv) Dark reactions were not detected. (v) Photoreactions without CO_2 or amine give no carboxylic acid.

TABLE. Photocarboxylation of phenanthrene. [Phenanthrene] = 2·8 × 10^{-2} mol dm^{-3} in Me_2SO; $p(CO_2)$ = 4 kg cm^{-2}; irradiation for 14 h.

Amine (mol dm^{-3})	Reaction (%)[a]	Yield of carboxylic acid (%)	Conversion into carboxylic acid (%)[b]
$PhNMe_2$ (0·40)	93[c]	41[c]	45[c]
$PhNMe_2$ (0·40	96	46	48
$PhNEt_2$ (0·44)	47	26	55
PhNHMe (0·40)	57	30	53
Et_3N (0·39)	86	26	33
$PhNH_2$ (0·55	63	0	0
Pyridine (0·40)	0	0	0

[a] Based on phenanthrene consumed. [b] % Yield of carboxylic acid/% reaction. [c] In $HCONMe_2$.

We consider that the reaction proceeds *via* an ion-radical intermediate. Fluorescence spectroscopy of $PhNMe_2$–anthracene–tetrahydrofuran or –dioxan systems indicated that the intensity of exciplex emission was identical for systems saturated with N_2 and with CO_2. Although the fluorescence of amines is quenched by CO_2,[5] the exciplex state is inert to CO_2. The fluorescence spectroscopy results and finding (ii) above favour a mechanism in which CO_2 reacts after ionic dissociation of the exciplex.† The formation of dihydro-aromatic carboxylic acids is comparable to the reaction of anthracenyl sodium with CO_2.[6] The conversion into carboxylic acid in the present systems could not, however, be 100% since photoreactions of the

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† Formation of ion-radicals by direct electron transfer without prior formation of an exciplex is also possible in polar media.

amines with the aromatic hydrocarbons[7] would compete with the carboxylation.

Qualitative tests on the general applicability of the photocarboxylation showed that anthracene, pyrene, naphthalene, and, biphenyl underwent reductive carboxylation upon irradiation of Me_2SO solutions in the presence of $PhNMe_2$ and CO_2. The products were soluble in alkali and shown to be carboxylic acids by their i.r. spectra ($>C=O$ 1700 cm^{-1}). The positions of carboxylation have not yet been determined.

We believe that this is the first example of photofixation of CO_2 in a non-biological system.

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