Photocarboxylation in the Presence of Aromatic Amines and Carbon Dioxide

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Phenylethylenes (1), biphenyl, and 1-methyl-2-phenylindole underwent carboxylation upon photolysis in the presence of aromatic amines (2) and carbon dioxide.

Photofixation of carbon dioxide can be accomplished by a variety of methods, *i.e.*, photoreduction with heterogeneous or homogeneous catalysis,[1] photoelectrochemical reduction,[2] photochemical insertion reactions into metal–X bonds (X = H or C),[3] and photofixation through enzyme catalysed reactions.[4] While photochemical incorporation of carbon dioxide into organic compounds is another attractive method for utilization of CO_2, only a few examples have been reported.

The methods reported so far are based on photochemically generated reactive species such as 1,3-dipolar species,[5] carbenes,[6] and radical-ion pairs[7,8] using CO_2. More investigation is definitely required to find efficient ways to utilize this abundant natural carbon resource.

As summarized in Table 1 (runs 1—4, 6, and 7), phenylethylenes (**1a** and **b**) underwent photocarboxylation in the presence of aromatic amines (**2a—c**) and carbon dioxide to

Table 1. Photocarboxylation of phenylethylenes (1) in the presence of aromatic amines (2) and CO_2 in acetonitrile.

Run	Alkene (1) (mol l^{-1})	Amine (2) (mol l^{-1})	Product (Yield/%)[a]
1	(1a) (0.047)	(2a) (0.050)	(3aa) (6.7), (4a) (trace), (5) (1.3)
2	(1a) (0.057)	(2b) (0.034)	(3ab) (22), (4a) (trace), (5) (2.7)
3	(1a) (0.11)	(2b) (0.18)	(3ab) (5.8), (4a) (0.3), (5) (1.2)
4	(1a) (0.085)	(2c) (0.057)	(3ac) (6.5), (4a) (trace), (5) (1.6)
5	(1a) (0.12)	(2d) (0.098)	(4a) (0.1), (5) (1.5), (6) (2.5)
6	(1b) (0.029)	(2a) (0.041)	(3ba) (12), (4b) (0.7)
7	(1b) (0.036)	(2b) (0.034)	(3bb) (15), (4b) (1.1)
8	(1b) (0.014)	(2d) (0.015)	(4b) (17), (6) (8.5)

[a] Isolated yields of coupling products (3) are calculated on the basis of the limiting reagent initially used. Yields of (4) and (5) are based on alkane (1) and that of (6) on amine (2d).
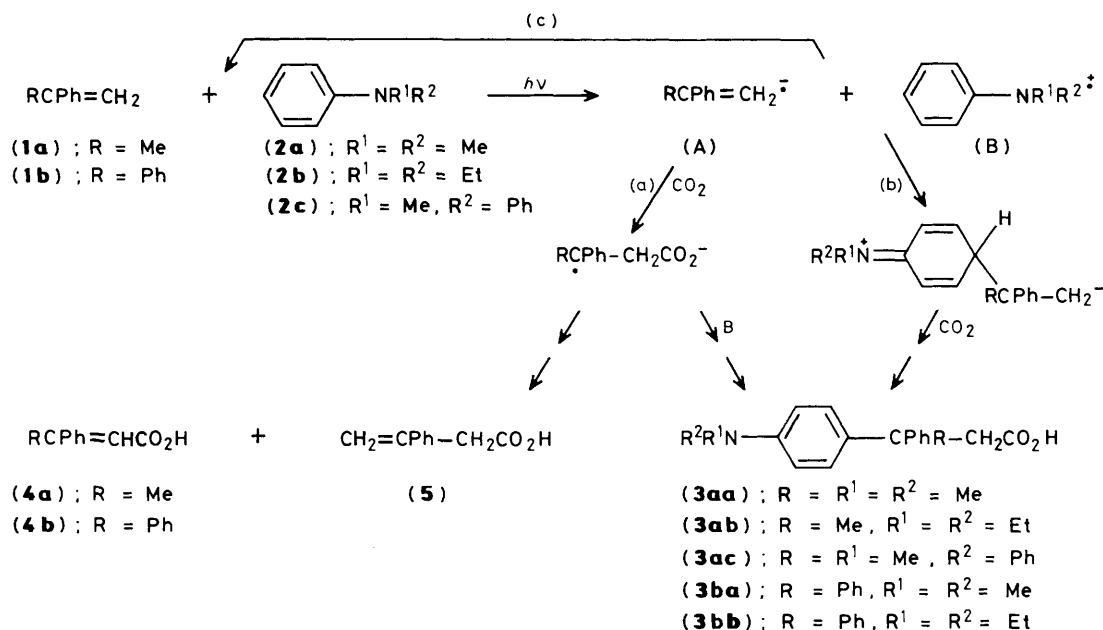
Scheme 1
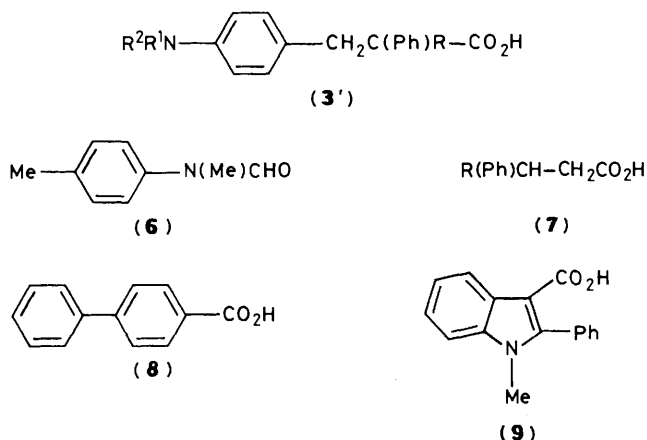
produce carboxylic acids (3)—(5). For example, a mixture of 2-phenylprop-1-ene (1a) (11.4 mmol) and N,N-diethylaniline (2b) (6.7 mmol) in acetonitrile (200 ml) was irradiated with a 400 W high pressure mercury lamp through a Pyrex filter for 8 h under bubbling CO_2 gas. After rotary evaporation of the reaction mixture, the residue was separated by column chromatography (silica gel) to afford (3ab)† (22% yield), (4a) (trace), and (5) (2.7% yield) (run 2).

^{1}H N.m.r., i.r., and mass spectra of (3) do not unequivocally eliminate the structure (3'). However, the carboxylic carbon signal in the completely proton-coupled ^{13}C n.m.r. spectrum appeared as a triplet [(3ab), δ 176.6, J_{CH} 6.72 Hz;

(3bb), δ 175.3, J_{CH} 6.72 Hz]. This triplet splitting is due to spin–spin coupling with the α-methylene protons,[9] shown by decoupling experiments, since irradiation of the methylene protons at δ 3.03 for (3ab) [or at δ 3.65 for (3bb)] changed the triplet signal of the carboxylic carbon into a singlet. From these results, the structure of the coupling-type carboxylic acid was determined to be (3) rather than (3').

Other runs were carried out in a similar manner. Products other than those listed in Table 1 could not be isolated. In all runs, most of (1) and (2) initially employed were recovered unchanged. Conversions were low even after prolonged irradiations. The low conversion is probably due to destruction of radical ion intermediates (A and B in Scheme 1) by the proton of the carboxylic acids produced as the reaction proceeds. In fact, addition of water (15 vol. % acetonitrile) to the above systems quenched all photoreactions. It was confirmed that in the absence of CO_2 essentially no photoproducts are formed from (1a) and (2a).

A probable mechanism is illustrated in Scheme 1. The quenching of (2a) fluorescence by styrene through exciplex formation has been reported previously.[10] Since no products are formed in the absence of CO_2, pathway (b) is less likely.

When N,N-dimethyl-p-toluidine (2d) was used as the amine component, in which the *para*-position is blocked by methyl substitution, N-methyl-N-(p-tolyl)formamide (6) was produced along with the carboxylic acids (4) and (5) (Table 1, runs 5 and 8). No coupling product like (3) was formed. Residual oxygen in the CO_2 tank could account for the formation of (6).[11] No significant reaction occurred upon photolysis of a mixture of (1) and triphenylamine (2e).

Tazuke[7] and Toki and Takamuku[8] have succeeded in carrying out the *reductive* photocarboxylation of aromatic hydrocarbons and phenylethylenes under similar conditions to those employed here. Our results indicate that the photocarboxylation reaction depends on subtle differences in reaction conditions. Thus, a reductive photocarboxylation product such as (7), a product expected from the previous studies,[7,8] was not obtained in our case. It has been reported that both

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† *Selected data* for (3ab): m.p. 42 °C; ^{1}H n.m.r. (CDCl₃) δ 1.06 (6 H, t, J 7 Hz), 1.82 (3 H, s), 3.03 (2 H, s), 3.23 (4 H, q, J 7 Hz), 6.50 and 6.92 (4 H, AB q, J 9 Hz), 7.17 (5 H, s), 9.05 (1 H, s).

For (3bb): m.p. 55—60 °C; ^{1}H n.m.r. (CDCl₃) δ 1.05 (6 H, t, J 7 Hz), 3.22 (4 H, q, J 7 Hz), 3.65 (2 H, s), 6.50 and 6.98 (4 H, AB q, J 9 Hz), 7.15 (10 H, s), 10.08 (1 H, s).

anthracene and biphenyl are reductively photocarboxylated in the presence of (2a) and CO_2 in dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO).[7] However, we have found that biphenyl underwent (non-reductive) photocarboxylation in the presence of (2a) and CO_2 in acetonitrile, leading to production of (8) [yield 3.5% based on biphenyl (88% consumed)], and anthracene did not react under the same conditions. 1-Methyl-2-phenylindole was also photocarboxylated in the presence of (2a) and CO_2 in acetonitrile, producing 1-methyl-2-phenylindole-3-carboxylic acid (9) [yield 2.5% based on indole (50% consumed)] and a trace of another carboxylic acid isomeric to (9).

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