Photochemical Chlorodecarboxylation *via* an Electron Transfer Mechanism

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A new method of chlorodecarboxylation of carboxylic acids *via* *N*-acyloxyphthalimides is developed; the reaction proceeds upon irradiation of *N*-acyloxyphthalimides in the presence of 1,4-diazabicyclo[2.2.2]octane in Bu^tOH–CCl_4–H_2O (53 : 42 : 5 v/v) in moderate to high yields.

Decarboxylation of carboxylic acids leading to alkanes or haloalkanes (Hunsdiecker reaction) is a useful reaction. Several modifications of this procedure have been published recently, notably an excellent method of iododecarboxylation reported by Suárez *et al.* Barton *et al.* reported an elegant method of chloro- or bromo-decarboxylation which proceeds *via* radical addition to the *O*-ester of thiohydroxamic acid derivatives using halotrichloromethane as a halogen source.[2] More recently, Hasebe and Tsuchiya reported a simple photolytic chlorodecarboxylation method *via* benzophenone oxime esters.[3] We have recently reported a new photochemical method of radical production from carboxylic acids *via* *N*-acyloxyphthalimides which are readily available in high yields from various carboxylic acids and *N*-hydroxyphthalimide, using dicyclohexylcarbodiimide (DCC).[4] We now report a photochemical chlorodecarboxylation method for carboxylic acids using *N*-acyloxyphthalimides.

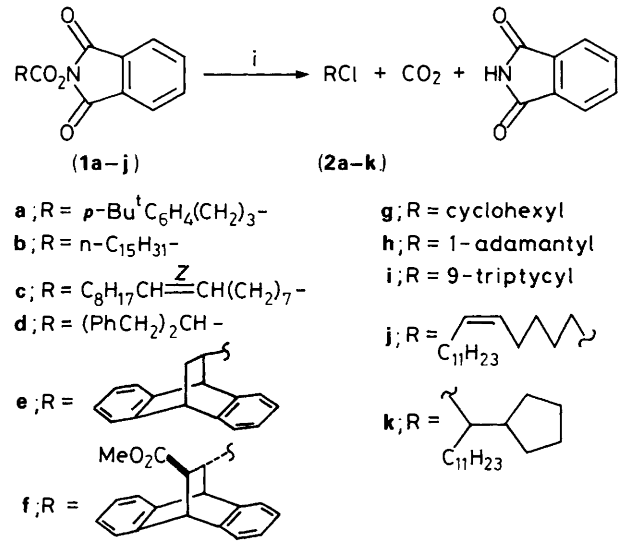
Irradiation of a solution of *N*-acyloxyphthalimide (**1a**) and 1,4-diazabicyclo[2.2.2]octane (DABCO) in a mixed solvent [Bu^tOH–CCl_4–H_2O (53 : 42 : 5 v/v)] through a Pyrex filter with a 100 W high pressure Hg lamp under argon for 3 h gave the corresponding decarboxylated chloride (**2a**) (74%), phthalimide (95%), and hexachloroethane (70%). In control experiments, similar irradiation without DABCO or water gave (**2a**) in poorer yields (runs 2 and 3 in Table 1). The reaction is general and widely applicable to various primary, secondary, and tertiary aliphatic carboxylic acid derivatives (**1a**—**j**) in moderate to high yields (56—98%, Table 1, Scheme 1). The alkenic functional group is stable in this transformation (run 5) and can take part in radical cyclization[5] when appropriately located. Thus, similar irradiation of (**1j**) produced the cyclized chloride (**2k**) (56%) along with the noncyclized chloride (**2j**) (10%). Decrease of carbon tetrachloride content from 42 to 10% increases the selectivity of the cyclization (52 : 4), with slightly poorer yield.

The quantum yield of the chlorodecarboxylation for (**1a**) is 1.4×10^{-4} at [DABCO] = 9.5×10^{-3} M and [(**1a**)] = 5.1×10^{-3} M.† The reaction was almost completely quenched by dissolved oxygen under aerated conditions or by piperylene ($k_q \tau = 2.6 \times 10^3$ dm^3 mol^{-1}) under argon, indicating that the triplet of (**1**) is the reactive state. A plausible reaction

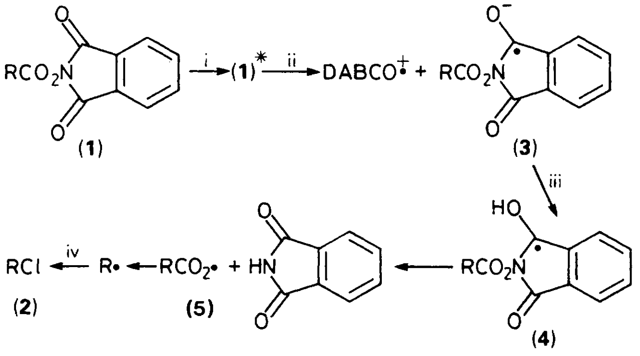
Table 1. Photochemical chlorodecarboxylation of various *N*-acyloxyphthalimides (**1a**—**j**) in Bu^tOH–CCl_4–H_2O (53 : 42 : 5 v/v).[a]

Run	Substrate	Irr. time /h	[DABCO] /$\times 10^{-3}$ M	Decarboxylated chloride/%		Phthalimide /%
1	(**1a**)	3	8.8	(**2a**)	74	95
2	(**1a**)	3	—	(**2a**)	12[b]	—
3[c]	(**1a**)	3	8.7	(**2a**)	43[c,d]	—
4	(**1b**)	2	19.0	(**2b**)	94	93
5	(**1c**)	3	9.3	(**2c**)	68	82
6	(**1d**)	4	19.4	(**2d**)	96	85
7	(**1e**)	4	16.9	(**2e**)	76	81
8	(**1f**)	5	19.4	(**2f**)	51	73
9	(**1g**)	4	8.4	(**2g**)	86	—
10	(**1h**)	10	8.9	(**2h**)	98	—
11	(**1i**)[e]	3	9.7	(**2i**)	59	89
12	(**1j**)	3	8.8	(**2j**)	10	90
				(**2k**)	56	
13	(**1j**)[f]	3	8.9	(**2j**)	4[f]	—
				(**2k**)	52[f]	

[a] Irradiation was performed with a 100 W high pressure Hg lamp through a Pyrex filter under argon at [substrate] = 3.0—3.2×10^{-3} M unless otherwise noted. [b] With 60% recovery of (**1a**). [c] In the absence of water. [d] With 43% recovery of (**1a**). [e] [(**1i**)] = *ca.* 1×10^{-3} M. [f] In Bu^tOH–CCl_4–H_2O (85 : 10 : 5 v/v).



Scheme 1. *Reagents and conditions*: i, *hv*, DABCO, Bu^tOH–CCl_4–H_2O.



Scheme 2. *Reagents and conditions*: i, *hv*; ii, DABCO; iii, H_2O; iv, CCl_4.

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† The quantum yield was determined in Bu^tOH–CCl_4–H_2O (53 : 42 : 5) at 313 nm excitation using a potassium ferrioxalate actinometer.

mechanism is shown in Scheme 2. The electron transfer from DABCO to the triplet excited state of (**1**) produces the anion radical (**3**), which would be protonated by water to give the radical (**4**). The cleavage of the weak N–O bond at the β-position to the radical centre gives the carboxyl radical (**5**), which in turn undergoes decarboxylation and chlorine abstraction from carbon tetrachloride to afford the chloride (**2**). Electron transfer from DABCO to the triplet state of (**1**) is calculated to be an exothermic process (ΔG −15 kcal mol^{-1}).[6‡]

To conclude, we have developed a useful method of chlorodecarboxylation of carboxylic acids through readily available *N*-acyloxyphthalimides. Further clarification of the mechanistic details is currently in progress.

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[‡] Calculated according to ref. 6 using the value of dielectric constant of the present mixed solvent (ε 6.05 at 20 °C). The reduction peak potential of (**1a**) was determined to be −1.39 V *vs.* standard calomel electrode (SCE). The triplet energy of *N*-acyloxyphthalimides was assumed to be *ca.* 70 kcal mol^{-1}, a typical value for *N*-alkylphthalimides: see J. D. Coyle, G. L. Newport, and A. Harriman, *J. Chem. Soc., Perkin Trans. 2*, 1978, 133; 1979, 799.