Photochemical Addition of Tertiary Amines to Electrophilic Cyclopropanes *via* Single Electron Transfer

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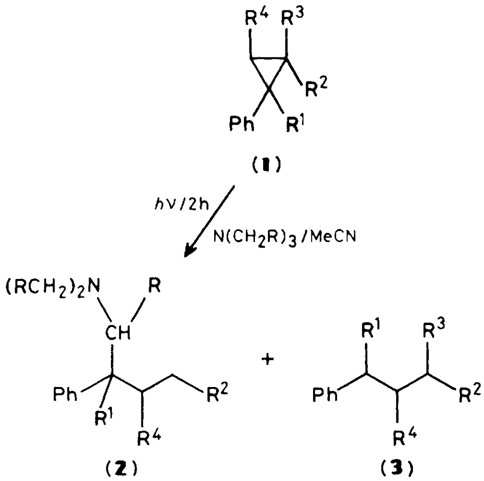
Irradiation of arylcyclopropanes bearing at least one electron-withdrawing group with a tertiary amine in acetonitrile resulted in the formation of the regioselective addition product of the amine along with the reduction product.

Photochemistry of cyclopropanes has received much attention from the mechanistic and synthetic points of view.[1] Direct irradiation generally results in the formation of complex product mixtures, since ring cleavage generates 1,3-biradicals which either undergo *cis–trans*-isomerization, 1,2- and/or 1,3-H migration, and carbene elimination, or give rise to polar adducts. However, Hixson *et al.* showed[2] that the selectivities of the photoreactions are greatly improved by use of electron acceptors which accept a single electron from the cyclopropane to give a cyclopropane cation radical. Since then many useful electron-transfer-mediated photoreactions of cyclopropanes have been reported,[3] but in most of these reactions, cyclopropanes are used as electron donors. We now report that some arylcyclopropanes can act as electron acceptors as well, to give anion radicals which give rise to formation of new C–C bonds as a result of cross combination.

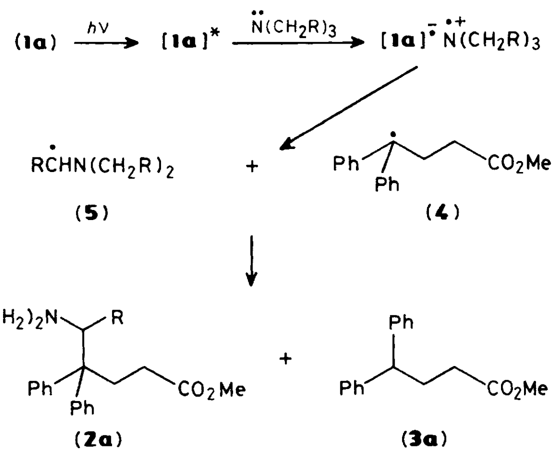
When 1,1-diphenyl-2-methoxycarbonylcyclopropane (**1a**) was irradiated in acetonitrile with a 300 W Hg lamp through quartz, more than 95% of the starting material was recovered unchanged even after 10 h irradiation. In marked contrast, similar irradiation of (**1a**) in the presence of a five-molar excess of trimethylamine led to rapid disappearance of the starting material and concurrent formation of an amine-adduct (**2a**,† R = H) (46.1%) as the major product along with the reductively cleaved product (**3a**)† (15.1%).‡ Careful analysis of the photolytic mixtures showed that no other isomeric amine adducts are formed. Irradiation with triethylamine also resulted in the formation of both products (**2a**)† (R = Me) and (**3a**), but the reduction product (**3a**) predominated over the adduct in this case. Irradiation using secondary (*e.g.*, diethylamine) or primary amines (*e.g.*, propylamine) did not result in the consumption of (**1**) under similar conditions.



Similar irradiation of other arylcyclopropanes (**1b**—**h**) having at least one electron withdrawing group also resulted in smooth reaction to give amine adducts (**2**)† as well as the reduction products (**3**),† as summarized in Table 1. Thus, 1,1-diphenyl-, 1,2-diphenyl-, and even 1-phenyl-1-cyclopropane derivatives underwent relatively efficient photoaminolysis, although the photoreactivities as judged from conversion of the starting cyclopropanes decreased in this order.

The reactions were found to be quite sensitive to the nature of solvent employed. Thus, the reaction proceeded quite smoothly in acetonitrile while (**1a**) was essentially unreactive in other protic (*e.g.*, EtOH) or less polar (*e.g.*, tetrahydrofuran) solvents even in the presence of a large excess of amine. Cyclopropane fluorescence was quenched by the amine. Stern–Volmer plots of fluorescence quenching are linear for amine concentration. Values of $k_q\tau$ obtained from the least-squares slopes of Stern–Volmer plots are given in Table 1. However, no new emission ascribable to exciplex fluorescence is observed in the quenching experiments.

The foregoing findings are strongly reminiscent of the related photochemical reaction[4,5] of stilbene with amines, which has been explained in terms of electron transfer–proton



Scheme 1

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† *Spectroscopic data* for (**2a**; R = H): ^{1}H n.m.r. ($CDCl_3$): δ 1.90 (6H, s, NMe_2), 1.96—2.16 (2H, m, $-CH_2-$), 2.54—2.76 (2H, m, $-CH_2-$), 2.97 (2H, s, $-CH_2N$), 3.54 (3H, s, CO_2Me), 6.96—7.32 (10H, m, aryl); *m/z* 311 (M^+), 58 (base peak). (**3a**); ^{1}H n.m.r. ($CDCl_3$): δ 2.00—2.38 (4H, m, $-CH_2CH_2-$), 3.52 (3H, s, CO_2Me), 3.82 (1H, t, CH), 6.62—7.36 (10H, m, aryl); *m/z* 254 (M^+), 167 (base peak).

(**2a**; R = Me): ^{1}H n.m.r. ($CDCl_3$) δ 0.6—1.2 (9H, m, CH_3), 2.0—3.9 (9H, m, CH_2, CH), 3.50 (3H, s, CO_2Me), 6.92—7.28 (10H, m, aryl); *m/z* 353 (M^+), 100 (base peak). All other compounds described herein gave satisfactory spectroscopic data consistent with the structures assigned.

‡ A solution of cyclopropane (10 mM) and amine (50 mM) in acetonitrile was irradiated. Product mixtures were analysed by g.c.–m.s. using an ionization voltage of 20 eV, before chromatographic separation. Products were separated by thick-layer chromatography without appreciable decomposition and were characterized spectroscopically.

Table 1. Photoreaction[a] of arylcyclopropanes (**1**) with tertiary amines.

(**1**)	R^1	R^2	R^3	R^4	in Amine	Conv. (%)	Yield (%)[b] (**2**)	Yield (%)[b] (**3**)	k_q (M^{-1})[c]
a	Ph	CO_2Me	H	H	H	76.4	60.4	30.4	—
				Me		77.8	36.8	51.9	29
b	Ph	CO_2Et	CO_2Et	H	H	87.0	66.9	26.4	—
					Me	88.2	28.5	49.9	5.9
c	Ph	CO_2Me	H	CO_2Me	H	86.8	60.7	25.8	—
					Me	83.8	0	61.4	23
d	Ph	CN	H	H	H	75.8	54.6	42.3	—
					Me	87.5	45.5	52.5	158
e	Ph	COMe	H	H	H	49.2	48.8	36.4	—
					Me	87.1	47.4	49.1	12
f	H	Ph	$P(O)(OMe)_2$	H	H	38.1	69.2	26.4	—
					Me	42.9	43.2	50.6	7.5
g	H	Ph	CO_2Me	H	H	34.9	56.0	20.5	—
					Me	31.3	65.3	23.7	21
h	H	H	CO_2Me	H	H	30.9	52.3	26.5	—
					Me	20.9	35.9	23.0	1.5

[a] Irradiations were carried out on 10 mM degassed solution of (**1**) in MeCN in the presence of 5 molar excess of tertiary amine for 2 h through quartz with a 300 W high-pressure Hg lamp. [b] Determined by g.c. [c] Fluorescence quenching constants in MeCN.

transfer, and can be better explained in terms of a similar mechanism involving initial single-electron transfer as outlined in Scheme 1, rather than a simple free-radical mechanism. Thus, (**1a**) is first excited to its singlet excited states, which accept an electron from the ground-state amine to generate a cyclopropane anion radical and an amine cation radical. The cyclopropane anion radical then undergoes ring cleavage initiated by protonation with highly acidic α-C–H protons of the amine cation radical to give a diphenylmethyl (**4**) and α-aminoalkyl (**5**) radical pair. The observed high regioselectivity in adduct formation suggests that the cyclopropane anion radical undergoing protonation has a significantly weakened C-1–C-2 bond where negative charge is delocalized on C-2 due to the presence of an electronegative substituent. Thus the proton attacks C-2 almost exclusively to give the diphenylmethyl radical (**4**) which is much more stable than that formed from C-1 protonation. The radical pair then undergoes either a cross combination leading to adducts (**2**) or a cross disproportionation to give (**3**). The α-amino-radical from trimethylamine cannot yield (**3**) by cross disproportionation with the diphenylmethyl radical. Almost all of compound (**3**) formed in the reaction of (**1**) with trimethylamine must then be formed by abstraction of hydrogen from trimethylamine itself, since the solvent acetonitrile is a notoriously poor donor. Autodisproportionation of the diphenylmethylradical might conceivably also give rise to (**3**), but this is not the case since olefinic products are not detected in the product mixtures. The α-amino-radical from triethylamine, on the other hand, can undergo cross disproportionation and therefore displays a higher (**3**)/(**2**) ratio.

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References

1 A general overview of photochemistry of cyclopropanes in solution phase is given by S. S. Hixson in 'Organic Photochemistry,' ed. A. Padwa, Dekker, New York, 1979, Vol. 4, pp. 191.

2 V. R. Rao and S. S. Hixson, *J. Am. Chem. Soc.*, 1979, **101**, 6458.

3 See for review, S. L. Mattes and S. Farid in 'Organic Photochemistry', ed. A. Padwa, Dekker, New York, 1983, Vol. 6. See also, Y. Otsuji and K. Mizuno, *Rep. Asahi Glass Found. Ind. Technol.*, 1986, **49**, 215; K. Mizuno, *J. Syn. Org. Chem., Jpn.*, 1986, **44**, 1010.

4 See for review, F. D. Lewis, *Acc. Chem. Res.*, 1986, **19**, 401.

5 F. D. Lewis and T.-I. Ho, *J. Am. Chem. Soc.*, 1977, **99**, 7991; F. D. Lewis, T.-I. Ho, and J. T. Simpson, *J. Org. Chem.*, 1981, **46**, 1077; *J. Am. Chem. Soc.*, 1982, **104**, 1924.