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PHOTOEXTRUSION REACTIONS: A COMPARATIVE MECHANISTIC STUDY OF SO_2 PHOTOEXTRUSION

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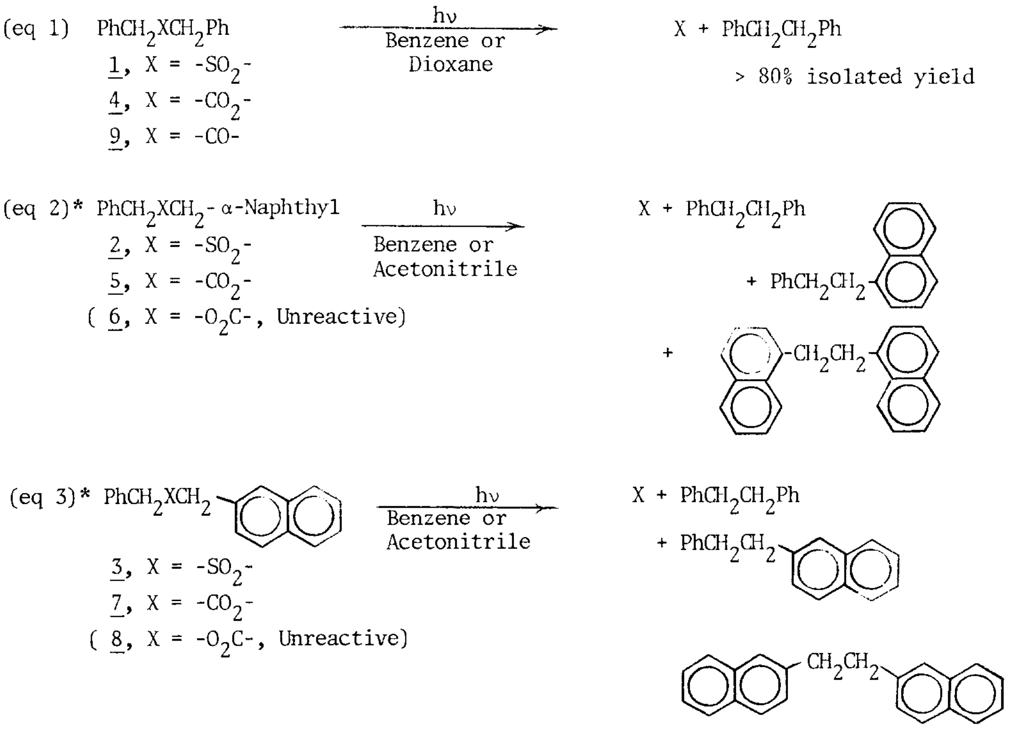
The photoextrusion of a small molecule such as SO_2, CO_2, and CO etc. often forming a new carbon-carbon bond in the parent molecule is an area of wide interest.[1-4] Several applications of this class of photoreactions to synthetic methodology have appeared.[1c,2,3a,4] We wish to report an interesting comparison of the quantum yield and multiplicity requirements for the photoextrusion of SO_2, CO_2, and CO in a series of benzyl sulfones, esters, and dibenzyl ketone and suggest that within these series the extrusion of SO_2 from sulfones is a very efficient means to form carbon bonds.

Sulfones 1, 2, and 3 were selected in order to allow us to make direct comparison with the photoextrusions of CO_2 from esters 4-8 [1e,4-6] and of CO from dibenzyl ketone(9).[3b,c] The photoreactions of all nine reactants are summarized by equations 1-3 and the Table. Although the product yields and distributions were similar for the direct irradiations of these series of reactants, important differences in the excited state efficiencies and multiplicities were noted. For example, the efficiency of SO_2 extrusion from dibenzyl sulfone (1) was found to be much higher than CO_2 extrusion from benzyl phenylacetate (4) (Table). For the case of dibenzyl sulfone, the efficiency approaches that of dibenzyl ketone (9). More striking is the complete reversal in the photoreactivity between the 1- and 2- naphthylmethyl derivatives of esters and sulfones. For the esters, 2-naphthylmethyl phenylacetate (5) reacts ten times more efficiently than the 1-naphthylmethyl derivative (7) while it is the 1-naphthylmethyl derivative (3) which reacts more efficiently in the sulfone series.

Sensitization experiments further revealed that the multiplicity of the reactive excited state for these two functional groups differed. As shown in the Table, the reactive excited state was found to be the triplet state for the naphthylmethyl sulfone 2 whereas a mixture of less than one-third triplet to two-thirds singlet was found for benzyl sulfones 1 and 3. Thus this series of functional groups represents the full spectrum in multiplicity requirements from essentially singlet (esters) to a mixture of singlet and triplet (sulfones) to essentially triplet (ketone).

The ratios of the three hydrocarbon products from the naphthylmethyl esters and sulfones on direct irradiation was 1:~8:1 indicating a solvent cage effect [1e,6] in excess of 55% for cage combination of the initially generated arylmethyl radicals. In sharp contrast to this, the benzophenone sensitized reaction produced the three products in a ratio of 1:2.6:1, ie, less than 15% cage combination. The radicals generated on triplet sensitization appear almost entirely to escape the cage.

SCHEME



* Product ratios were the same within experimental error for the direct irradiations of 2, 3, 5, and 7. For the benzophenone-sensitized reactions, see text.

TABLE: Comparison of Quantum Efficiencies for Direct and Sensitized Irradiations of Sulfones, Esters, and Dibenzyl Ketone.

	$PhCH_2XCH_2Ar$			Quantum Efficiencies for Product Appearance			
				a	b	c	
	X	Ar	Conditions[a]	ϕ_D	ϕ_T	ϕ_S	Reference
4	$-CO_2-$	Ph	A	0.033	0	0.033	5
1	$-SO_2-$	Ph	A	0.59	0.18	>0.41	this work
9	-CO-	Ph	A	0.70	0.70	0	3b
5	$-CO_2-$	1-Naph	B	0.0008	0	0.0008	6
2	$-SO_2-$	1-Naph	B	0.03	0.09	0.0[d]	this work
7	$-CO_2-$	2-Naph	B	0.015	0	0.015	6
3	$-SO_2-$	2-Naph	B	0.003	0.001	0.003	this work

a) Conditions for direct irradiation quantum efficiencies (ϕ_D=direct) were: A. 254 nm, dioxane B. 300 nm, benzene. In several cases, the direct irradiation of the sulfones was carried out under both conditions and also using acetonitrile as a solvent with 254 nm irradiation. Little variation in the measured efficiency for product appearance was noted.

b) Conditions for the sensitized irradiation quantum efficiences (ϕ_T=triplet) were 254 nm, acetone solvent and sensitizer or 350 nm, benzophenone sensitizer (naphthyl analogs), benzene solvent. Energy transfer was 100% efficient.

c) Calculated by $\phi_S=\phi_D-\phi_{ISC}\cdot\phi_T$ (ϕ_S=singlet, ϕ_{ISC}-intersystem crossing and is assumed to be ca 0.4).

d) Assuming an intersystem crossing efficiency of ca 0.4 (naphthalene), the reaction would be entirely from the triplet on direct irradiation.

Little recombination or benzyl migration from S to O occurs, even on direct irradiation for no evidence of sulfinate ester formation [7a,b] was found. Although stereochemical tests of the type employed for the esters[1e] have not been completed with the sulfones, other studies[2b, 8] indicate that recombination of the initially formed radicals does not compete with loss of the SO_2 fragment. Further work is in progress that should extend and delineate the mechanism for the photoextrusion of SO_2.

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