Photochemical Type II Reaction of Carbonates and *S*-Alkyl Thiocarbonates

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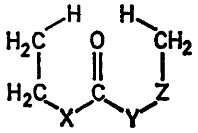
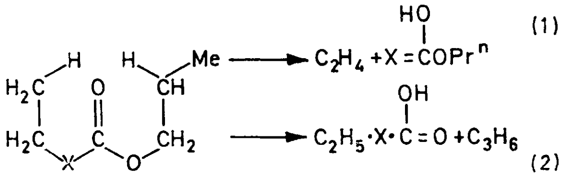
Summary Carbonates and *S*-alkyl thiocarbonates which contain γ-hydrogen atoms on both sides of the carbonyl group undergo photochemical type II reactions at both sites.

RECENT reports[1,2] have extended to five the number of known varieties of photochemical type II elimination reactions.[+] These reactions occur in compounds (I)—(IV), and although the reaction was originally observed in ketones, it still occurs when either the α- or β-methylene groups are replaced by –O–.

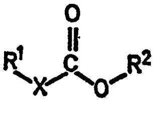


	X	Y	Z	
(I)	C	C	C	(ref. 3)
(II)	C	C	O	(refs. 4 and 5)
(III)‡	C	O	C	(ref. 2)
(IV)	C	O	H	(ref. 1)

We report here that the photochemical type II elimination reaction occurs in carbonates (V) and *S*-alkyl thiocarbonates (VI); the reaction has previously not been observed for such compounds.



Although the reaction in carbonates may be viewed as an extension of the alcohol type II reaction of organic esters,[2] the observation of the type II reaction in thiocarbonates is novel. It is possibly the first example† in which a sulphur atom is part of the cyclic transition state. The longer C–S bond and the possible interaction of the sulphur *d* orbitals with the carbonyl group are a large perturbation of the heretofore strictly first row (C and O) system.[6,7] Since the type II reaction is characteristic of *n*–π* excited states, the present observations indicate that carbonates and thiocarbonates possess low-lying *n*–π* excited states. Compounds (Va,d) and (VIc) exhibit distinct low intensity maxima in the 250—260 nm region which is consistent with *n*–π* excitation.



	(V; X = O)		(VI; X = S)
a;	R^1 = Et, R^2 = Pr^i	a;	R^1 = Et, R^2 = Pr^i
b;	R^1 = Et, R^2 = Pr^n	b;	R^1 = Et, R^2 = Pr^n
c;	R^1 = Me, R^2 = Bu^s	c;	R^1 = Et, R^2 = Bu^i
d;	R^1 = Et, R^2 = Bu^t		

The competitive technique used to study alcohol and acid type II reactions of organic esters was employed.[2] The carbonates and thiocarbonates in the Table were studied; each could undergo two different type II reactions [reactions (1) and (2); X = O or S]. In the absence of products having free-radical precursors, the ratio $C_2H_4 : C_3H_6$ may be equated to the ratio of the quantum yield of reaction (1) relative to that of (2). In the mercury-sensitized photolysis of the carbonates and thiocarbonates in the Table, in the presence of nitric oxide and at conversions of $<5\%$, free-radical products always constituted less than 0·2% of the total yield of the olefins produced in the two possible reactions. This clearly shows the occurrence of the type II elimination in both carbonates and thiocarbonates. The relative quantum yields are given in the Table. The last column, which gives relative quantum yields divided by the number of γ-hydrogen atoms, allows two generalizations to be drawn. Within each class, except for ethyl isopropyl carbonate which appears to be anomalous, the extent of the competition depends upon the γ C–H bond strength. In

† Two reactions in addition to the five cited are thought to be type II reactions. Acetophenone has been observed as a product of the photolysis of *NN*-dibenzylphenacylamine (A. Padwa, W. Eisenhardt, R. Gruber, and D. Pashayan, *J. Amer. Chem. Soc.*, 1969, **91**, 1857) and from the photolysis of α-ethylthioacetophenone (H. Hogeveen and P. J. Smit, *Rec. Trav. chim.*, 1966, **85**, 489). The mechanism of the former is thought to involve electron transfer while that of the latter has not been investigated.

‡ Esters with γ-hydrogen atoms on both sides of the CO group undergo two different type II eliminations.

TABLE

Competitive type II reactions of carbonates (V) and thiocarbonates (VI).

	Ethyl			Alkyl				
Carbonate	No [c]	Type γ-H[d]	Olefin	No	Type γ-H	Olefin	ϕ(Et)/ϕ(Alk)[a]	ϕ(Et)/ϕ(Alk)[b]
(Va)	3	1°	C_2H_4	6	1°	C_3H_6	0 089 ± 0 003	0 178
(Vb)	3	1°	C_2H_4	2	2°	C_3H_6	1 12 ± 0 02	0 748
(Vc)	3	1°	C_4H_8[e]	2	2°	2-C_4H_8	1 07 ± 0 01	0 713
(Vd)	3	1°	C_2H_4	1	3°	iso-C_4H_8	1 3 ± 0 4	0 43
Thiocarbonate								
(VIa)	3	1°	C_2H_4	6	1°	C_3H_6	0 25 ± 0 03	0 50
(VIb)	3	1°	C_2H_4	2	2°	C_3H_6	0 53 ± 0 03	0 35
(VIc)	3	1°	C_2H_4	1	3°	iso-C_4H_8	0 46 ± 0 02	0 15

[a] Minimum of three determinations for each value [b] Per γ-hydrogen atom [c] Number of γ-hydrogen atoms available [d] 1° = primary, 2° = secondary, 3° = tertiary [e] In this case the abstraction of the primary γ-hydrogen atom and the subsequent formation of but-1-ene is taken as the "Ethyl' reaction. The abstraction of the secondary γ-hydrogen and the subsequent formation of *cis*- and *trans*-but-2-ene is considered the "Alkyl" reaction

addition, the type II reaction is more efficient when the atom in the α position is oxygen rather than sulphur Oxygen has also been demonstrated to be more effective than an α-methylene group in promoting the type II reaction in organic esters [2]

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