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DECARBOXYLATION OF α-KETO CARBOXYLIC ACIDS BY PERSULFOXIDE

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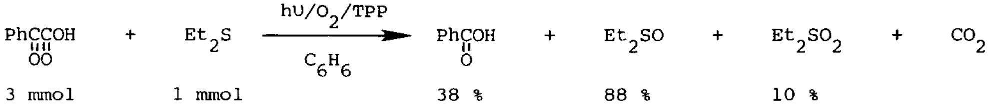
Abstract: Photosensitized oxygenation of diethyl sulfide in the presence of α-keto carboxylic acids caused oxidative decarboxylation of the acids by persulfoxide and gave carboxylic acids, carbon dioxide, diethyl sulfoxide and diethyl sulfone.

Oxygen atom transfer reactions of oxenoid reagents are focused as models of monooxygenase enzymes[1)] and much attention has been devoted to their structures and reactivities. Foote and Peters[2)] suggested that in the photosensitized oxygenation of sulfides, a persulfoxide intermediate (i.e., diethyl persulfoxide, 1) oxidized another sulfide molecule to sulfoxide electrophilically in protic solvent.[2,3)] On the other hand, persulfoxide (1) in aprotic solvent showed a nucleophilic nature in the oxidation of sulfoxide to sulfone.[4)] This ambiphilic property of persulfoxide (1) is similar to the case of carbonyl oxide.[5)] Recently, we reported an oxidative decarboxylation of α-keto carboxylic acids by carbonyl oxides[6)], which provided an useful mechanistic insight into the reactivity of carbonyl oxide. We report here a similar oxidative decarboxylation of α-keto carboxylic acids by persulfoxide intermediate (1).

In a typical reaction, phenylglyoxylic acid (3 mmol), diethyl sulfide (1 mmol) and tetraphenylporphine (TPP, 150 mg as sensitizer) were dissolved in benzene (30 ml) and the resulting solution was irradiated by 500 W Halogen lamp while passing oxygen until disappearance of diethyl sulfide (about 2 hrs). The products were analyzed by glc.



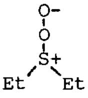
$$\mathrm{Ph}\underset{\mathrm{O}}{\mathrm{C}}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{OH} + \mathrm{Et_2S} \xrightarrow[\mathrm{C_6H_6}]{h\nu/\mathrm{O_2}/\mathrm{TPP}} \mathrm{Ph}\underset{\mathrm{O}}{\mathrm{C}}\mathrm{OH} + \mathrm{Et_2SO} + \mathrm{Et_2SO_2} + \mathrm{CO_2}$$

3 mmol 1 mmol 38 % 88 % 10 %

Benzoic acid[7)], diethyl sulfoxide and diethyl sulfone were obtained in 38, 88 and 10 % yields, respectively, based on diethyl sulfide used. No benzoic acid was obtained in the absence of diethyl sulfide or dye sensitizer, which apparently indicated that the intermediate persulfoxide eventually acts as an oxygen atom transfer agent. The results obtained are summarized in Table.

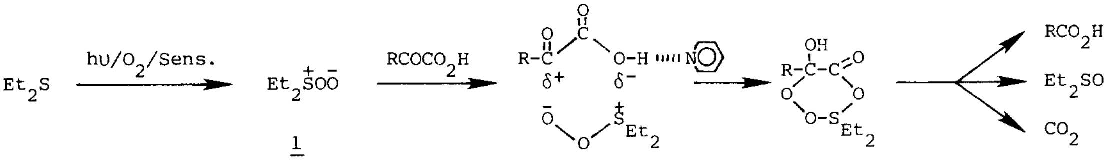
Under neutral conditions, decarboxylations were favored in aprotic solvents (i.e., benzene and acetonitrile); this may be due to the nucleophilic nature of persulfoxide (1). In methanol under both neutral and basic conditions, the nucleophilic nature of persulfoxide

Table. Photosensitized Oxygenation of Diethyl Sulfide in the Presence of α-Keto Carboxylic Acids.

Oxidant	α-Keto acid	Solvent	Additive (3 ml)	Sens.	Products and Yields[a]		
					RCO$_2$H[b]	Et$_2$SO	Et$_2$SO$_2$
 1	PhCOCO$_2$H	C$_6$H$_6$	None	TPP	38 %	88 %	10 %
		MeCN	"	MB[c]	21	67	trace
		MeOH	"	"	13	96	"
		C$_6$H$_6$	Pyridine	TPP	17	77	6
		MeOH	"	MB	24	81	trace
		MeCN	"	"	53	66	15
	MeCOCO$_2$H	"	"	"	64[d]	65	3
	EtCOCO$_2$H	"	"	"	52	100	0
	n-PrCOCO$_2$H	"	"	"	19	92	0

a) Evolution of CO$_2$ was confirmed by precipitation of barium carbonate. b) Determined as trimethylsilyl ester. c) Methylene blue. d) In the absence of diethyl sulfide, acetic acid was obtained only in 13 % yield.[8]

(1) may be altered by hydrogen bonding.[2,4] Since the C-C bond of α-keto carboxylic acids is elongated by hydrogen bonding[9] in the presence of pyridine, the nucleophilic attack of persulfoxide (1) to carbonyl carbon and subsequent cyclization may be easily occurred in acetonitrile which enhances the charge separation in α-keto carboxylic acids.



Since the present data shows that the persulfoxide causes oxidative decarboxylation of α-keto carboxylic acids similarly to the case of carbonyl oxide reported by us[6], we are now challenging to elucidate the reaction mechanism.

References and Notes

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