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THE PHOTOLYSIS OF BENZYL AMINOACETATES

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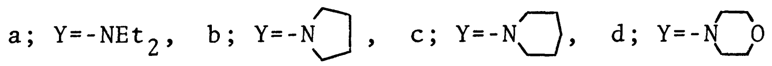
The photolysis of benzyl aminoacetates (1a—1d) in benzene gave β-aminoethylbenzenes (2a—2d) and N,N-disubstituted glycines (3a—3d). Benzyl acetate (4) was also obtained in low yield. Solvent and quenching effect suggest the singlet pathway for this photoreaction.

The photochemistry of α-aminoesters has not been investigated in full, although that of ordinary esters and α-aminoketones has been well studied by many workers.[2] In the present communication, we wish to report the results concerning the photolysis of benzyl aminoacetates.

Irradiation of benzene solution of benzyl N,N-diethylaminoacetate (1a)(0.1 M) in a quartz tube by means of 300 W high pressure Hg lamp under nitrogen at room temperature for 48 hr gave β-(N,N-diethylamino)ethylbenzene (2a), N,N-diethylaminoacetic acid (3a), and benzyl acetate (4) in 25, 5, and 3 % yields, respectively. Toluene, 1,2-diphenylethane, and benzyl alcohol were also formed as by-products. These compounds were separated by glc [3] and identified by comparison with authentic samples. The photolysis of these benzyl aminoacetates (1a—1d) resulted in the photodecarboxylation as the major reaction path in *non*-polar solvent. However, 3 was obtained in considerable yield in polar solvents. It is noteworthy that the formally photo-induced hydrolysis of the esters takes place in these cases.

$$\underset{\underline{1}}{\mathrm{YCH_2COOCH_2Ph}} \xrightarrow{h\nu} \underset{\underline{2}}{\mathrm{YCH_2CH_2Ph}} + \underset{\underline{3}}{\mathrm{YCH_2COOH}} + \underset{\underline{4}}{\mathrm{CH_3COOCH_2Ph}}$$



Givens and Oettle have shown that photodecarboxylation is a general procedure for benzyl esters (including γ-phenyl-γ-butyrolactones), occuring from the triplet state *via* discrete radical intermediates.[4] Analogy was provided by the work of Zimmerman and Sandel with respect to the photolysis of *p*-methoxybenzyl acetate.[5] In the present investigation, the yields of 2 and 3 were little affected by the addition of piperylene as a triplet quencher. And the photoirradiation of ethyl morpholinoacetate as an analogous type of ester having no phenyl substituent resulted in over 70 % recovering of the starting material. From these facts, it can be reasonably assumed that π,π* singlet state is chiefly involved in these

Table 1 Irradiation of benzyl aminoacetates (1a—1d) for 48 hr

Aminoester	Solvent	Products (%) *) 2	3	4	Conversion (%) *)
1a	benzene	25 (17)	5 (5)	3 (3)	100 (99)
	EtOH	12	11	9	96
	CH_3CN	8	8	3	88
1b	benzene	27 (19)	5 (3)	2 (2)	86 (93)
	EtOH	20	16	3	90
	CH_3CN	11	12	1	79
1c	benzene	33 (22)	9 (5)	1 (1)	97 (96)
	EtOH	18	10	4	91
	CH_3CN	7	18	2	84
1d	benzene	34 (31)	5 (4)	1 (2)	98 (87)
	EtOH	19	14	4	91
	CH_3CN	6	18	1	94

*) Yields and conversions are determined by glc analysis and values in paretheses refer to the ones in the presence of piperylene (0.1 M).

reactions. Furthermore, the yields of 2 and 3 are apparently dependent on solvent polarity. The yields of 2 decrease with increasing solvent polarity, but those of 3 increase with solvent polarity. Therefore, it appears more likely that the reaction of the formations of 2 and 3 is at least initiated from π,π^* singlet state of the starting materials, and proceeds *via* a common intermediate in a dualistic nature such as *intimate* ion pair-radical pair.[6)]

Moreover, it might be difficult to presume Norrish Type II elimination for the formation of benzyl acetate (4) because none of Schiff base (*e.g.* ethylidene-ethylamine from 1a) could be detected.

The details of the present investigation will be reported elsewhere.

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References

1) To whom all correspondence should be addressed.
2) S. G. Cohen, A. Parola, and G. H. Parsons, Jr., *Chem. Rev.*, **73**, 141 (1973), and references cited therein.
3) As for amino acids, solvent was evaporated under vacuum and residue was extracted with water. The crude samples were purified by sublimation.
4) R. S. Givens and W. F. Oettle, *J. Amer. Chem. Soc.*, **93**, 3301 (1971).
5) H. E. Zimmerman and V. R. Sandel, *ibid.*, **85**, 915 (1963).
6) S. Fujita, Y. Ozaki, and H. Nozaki, *Bull. Chem. Soc. Japan*, **45**, 2571 (1972).

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