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BASE PROMOTED OXIDATIVE DECARBOXYLATION OF ETHYL PHENYLGLYCINATE VIA OXAZIRIDINE

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Abstract: Base catalyzed decompositions of 2-(α-ethoxycarbonyl-benzyl)-3-phenyl-oxaziridines carried out in benzene in an atmosphere of oxygen yielded N-benzoyl benzamides along with ethyl phenylglyoxylate imine and benzaldehydes.

The decomposition of oxaziridines to yield imines and carbonyl compounds under basic conditions can be regarded formally as oxidative deamination of primary amines or amino acids via oxaziridines.[1] The chemical process has become of interest in connection with the biological processes catalyzed by monoamine oxidases and amino acid oxidases, but the study seems to be limited, to date, to the reaction of simple primary amines.[2] We therefore wanted to obtain further information for the chemical process by using oxaziridines derived from α-amino acids. This communication describes the results on adapting phenylglycine.

Schiff bases of type 1 were prepared by condensation of ethyl-(d,l)-α-phenylglycinate with benzaldehydes and then converted to oxaziridines with m-chloroperbenzoic acid in CH_2Cl_2.[3] The oxaziridines were mixtures of E- and Z-isomers, which were separated preparatively with silica-gel/benzene. Elemental analyses and spectral data of the oxaziridines were in good agreement with theory for the structures of type 2.[4] Assignment as the E- or Z-form could be made by nmr on the basis of the diamagnetic shielding effects of the phenyl groups of the oxaziridines.

When 2a was treated with an excess of Et_3N or 1,8-diazabicyclo-[5,4,0]-undecene-7, (DBU), in benzene under nitrogen, a dark blue solution immediately resulted. The solution was treated with dry HCl just after development of the color and then neutralized with aq. $NaHCO_3$. From the organic layer, amide 8a was obtained (50%) along with 4' (27%) and 5a (24%). The amides 8, however, gave an yellow color in benzene under such basic conditions regardless of the substituent, X, on the phenyl ring, and neutralization of the benzene solution with dry HCl gave quantitative recovery of the starting materials unchanged. Therefore, the mechanism of the amide formation is different from that proposed by Rubottom.[5] The structure of the blue-colored intermediate is suggested to be dianion 7, because 2a and 8a gave the same color, ($\lambda_{max.}$ = ~660 nm.), under a more basic condition: EtO^- in hexamethyl phosphoramide.

Since the dark blue color is labile and fades rapidly in the presence of oxygen, we next investigated the reaction of 2 with DBU at an oxygen pressure of 5 kg/cm^2. in benzene. After 30 min. of the reaction the benzene solution was neutralized with aq. HCl and then washed with water. From the organic layer, 3, 4' and 5 were isolated by silica-gel column chromatography eluting with benzene/n-hexane (2:1) (Table 2). The reaction condition is not necessary optimal for preparation of 3. However, the formation of 3, is worthy of remark because the result is formally analogous to oxidative decarboxylation of amino acids catalyzed by amino-acid oxygenases,[6] though the precise mechanism of the biological process is unknown.

The reactions mentioned above are summarized in the scheme. Further work is in progress to fully examine the scope of this synthetic route and the reaction mechanism.

Table 1. Yields, physical constants and nmr data of oxaziridines 2.[a]

					nmr., δ, in $CDCl_3$		
	X	yield[b]	ratio[b, c] (E/Z)	m.p. (E) / (Z)	for (E) CH-CO, ring H		for (Z) CH-CO, ring H
2a	NO_2	72 %	59/41	104-105°/105-106°	3.95, 4.72	/	3.73, 5.36
2b	Cl	68	65/35	89 /67-68	3.92, 4.58	/	3.81, 5.27
2c	H	76	56.5/43.5	113 /110	3.93, 4.61	/	3.90, 5.28
2d	CH_3	46	55/45	72 /68	3.88, 4.52	/	3.85, 5.19
2e	OCH_3	53	63/37	63 /59-60	3.87, 4.53	/	3.90, 5.21

a. The products were recrystallized from ethanol.
b. calculated on the products isolated.
c. determined by nmr

Scheme.

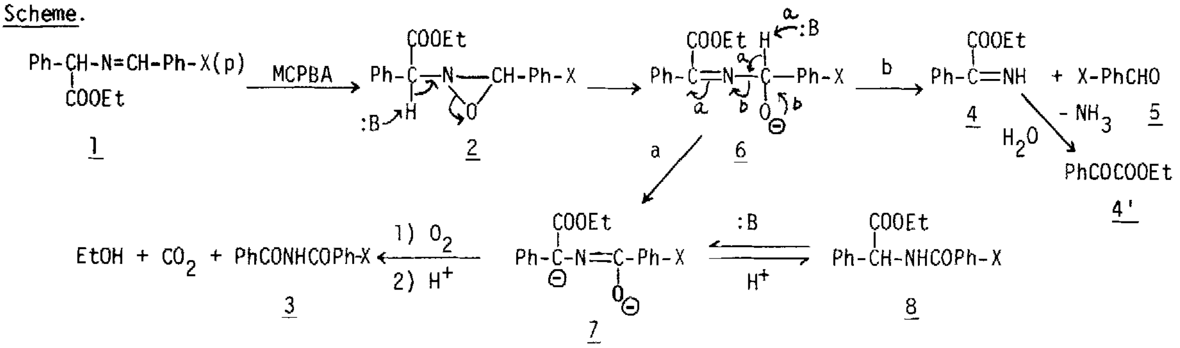

Table 2. Products from DBU-catalyzed decomposition of 2 at an oxygen pressure of 5 kg/cm^2 in benzene: [DBU]/[oxaziridine] = 10^{-1}M/10^{-2}M.

products	2a		2b		2c		2d	2e	
	E	Z	E	Z	E	Z	E	E	Z
3 [a]	75%	27%	68%	32%	73%	39%	52%	55%	25%
4'[b]	20	55	24	60	22	53	34	43	70
5 [b]	24	66	15	48	13	40	30	43	63

a. determined by HPLC.
b. determined by GLC.

References and Notes.

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   b. S.E.Dinizo and D.S.Watt, J.Amer.Chem.Soc., 97, 6900 (1975).
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4. Anal., calcd. for $C_{17}H_{16}N_2O_5$, C,62.19%; H,4.91%; N,8.53%; Found for 2a-E, C,61.98; H,4.81; N,8.59; Found for 2a-Z, C,62.04; H,4.86; N,8.56. M^+(for both the isomers) = 328.
5. G.M.Rubottom, Tetrahedron Letters, 1969, 3887.
6. for example, C.Walsh in "Enzymztic Reaction Mechanisms", W.H.Freemann and Company, San Francisco, 1979, pp 408.

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