The Decarboxylation of Some α-Ethoxycarbonyloxybenzyl Cyanides.

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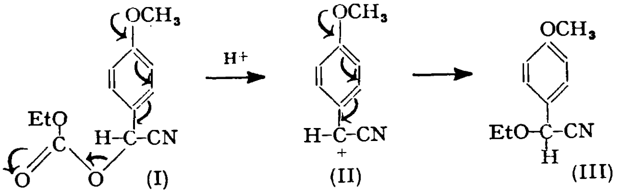
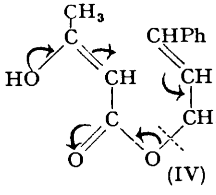
[Reprint Order No. 6109.]

α-Ethoxycarbonyloxybenzyl cyanides with an electron-releasing group in the *ortho-* or *para*-position lose carbon dioxide on being heated with a catalytic quantity of sulphuric acid; if the electron-releasing group is very active, the α-ethoxybenzyl cyanide is formed.

α-Ethoxycarbonyloxy-*p*-methoxybenzyl cyanide (I) was readily decarboxylated in the presence of a trace of sulphuric acid at 80° to the ether (III), and the *o*-methoxy-isomer reacted similarly but more slowly; the ester derived from furfuraldehyde cyanohydrin was sufficiently activated by the heterocyclic oxygen atom to be decarboxylated but the resulting ion was too unstable to survive. The electron-releasing capacity of a methyl group or chlorine atom is less than that of a methoxyl group, and this is reflected in the higher temperature necessary to effect decarboxylation of the esters with these *para*-substituents, and in the instability of the resulting ions. The esters derived from the cyanohydrins of *p*-tolualdehyde and *p*-chlorobenzaldehyde were decarboxylated, but gave only polymeric material. Esters having no *ortho* or *para* electron-releasing substituents did not lose carbon dioxide, and could, in some cases, be recovered to some extent.



(I) (II) (III)



(IV)

The reaction falls into the class of alkyl–oxygen ester fission (see Kenyon *et al.*, *J.*, 1942, 556, 605; 1946, 797, 803, 807; 1951, 376, 380, 382, 385, 386; 1952, 4964; 1953, 3619; 1954, 779, 3474) and requires the same electronic displacements. Related reactions are the acid-catalysed decomposition of the acetoacetates of tertiary ethynylmethanols and *tert.*-butanol, and the pyrolysis of the β-keto-esters of allyl alcohols (see Lacey, *J.*, 1954, 827).

The decomposition of cinnamyl acetoacetate to 1-methyl-2-phenylbut-3-en-1-one (Kimel and Cope, *J. Amer. Chem. Soc.*, 1943, **65**, 1992) is interesting, as the enolate, (IV), *i.e.*, the reacting species, is in some measure a bisvinylogue of the systems described in this paper (*e.g.*, I). The low temperature needed for the reaction recalls the acid-catalysed pyrolysis of β-keto-esters of *tert.*-butanol, the inductive effect of the three methyl groups being replaced by the tautomeric effect of, for example, a methoxyl group. However, the initially formed benzyl cation cannot lose a proton to give an olefin, but must either recombine with a negative ion to give, in this case, an ether, or decompose. Thus the ester, after addition of a proton to its carbonyl group, breaks down to give ethyl hydrogen carbonate, and the ion (II); the former loses carbon dioxide regenerating the proton, and forming an ethoxide ion which recombines with the benzyl cation, if the resonance stabilisation of the latter (II) has been adequate to allow it to survive. The reaction will not occur unless the ester moiety that separates can decompose to give a strong base; the benzoyl and *p*-methoxybenzoyl derivatives of *p*-methoxymandelonitrile (Francis and Davies, *J.*, **1904**, 1404) were refluxed in benzene with a trace of sulphuric acid. Extensive decomposition occurred in both cases, but no carbon dioxide was evolved; in the latter case a small quantity of anisic acid was isolated as the sole crystalline product.

EXPERIMENTAL.

Unless stated otherwise, the light petroleum had b. p. 40—60°.

α-Ethoxycarbonyloxybenzyl Cyanides.—These were prepared by Kindler's method (*Arch. Pharm.*, 1950, **283**, 190) and distilled *in vacuo*. All except those marked * decomposed to some extent on distillation.

Subst.	B. p./mm.	n_D^{21}	Formula	Found (%)				Required (%)			
				C	H	N	Cl	C	H	N	Cl
*None [1]	110°/0·5	1·4972	$C_{11}H_{11}O_3N$	64·7	5·2	6·8	—	64·4	5·4	6·8	—
**p*-Cl	124/0·4	1·5131	$C_{11}H_{10}O_3NCl$	55·2	4·4	6·0	14·9	55·1	4·2	5·9	14·8
m-NO_2 [2]	160/0·4	(1·5272/17)	$C_{11}H_{10}O_5N_2$	53·1	4·2	11·2	—	52·8	4·0	11·2	—
p-NO_2	158/0·4	1·5265	$C_{11}H_{10}O_5N_2$	53·0	4·0	11·0	—	52·8	4·0	11·2	—
p-Me	121/0·6	1·4990	$C_{12}H_{13}O_3N$	66·0	6·1	6·7	—	65·8	5·9	6·4	—
o-MeO.........	136/0·6	1·5061	$C_{12}H_{13}O_4N$	61·8	5·4	6·2	—	61·3	5·5	6·0	—
**m*-MeO ...	132/0·4	1·5048	$C_{12}H_{13}O_4N$	61·3	5·4	5·8	—	61·3	5·5	6·0	—
p-MeO [3]	128/0·25	1·5100	—	—	—	—	—	—	—	—	—
3 : 4-$(MeO)_2$	Decomp.	—	—	—	—	—	—	—	—	—	—
3 : 4-(CH_2O_2)	156/0·4	1·5208	$C_{12}H_{11}O_5N$	57·9	4·6	5·9	—	57·8	4·4	5·6	—

[1] Francis and Davies (*loc. cit.*) gave a poor analysis. [2] Subsequently solidified, plates from MeOH, m. p. 60—61°. [3] Buck (*J. Amer. Chem. Soc.*, 1933, **55**, 2593).

α-Ethoxycarbonyloxyfurfuryl Cyanide.—This nitrile was also prepared by Kindler's method; it had b. p. 94°/0·5 mm., n_D^{21} 1·5208 (cf. Lukes, Kastner, and Herben, *Coll. Czech. Chem. Comm.*, 1947, **12**, 647).

Acetophenone gave no nitrile by this method and was recovered.

α-Ethoxybenzyl Cyanides.—The ethoxycarbonyloxy-cyanide was refluxed with 5 times its volume of solvent (benzene, b. p. 80°; toluene, b. p. 110°; xylene, b. p. 140°; or tetralin, b. p. 206°) containing 2 drops of concentrated sulphuric acid, till evolution of carbon dioxide ceased. If after 10 min. there had been no gas evolved, reaction was assumed not to occur. Much ether was added and the mixture was washed well with water, dried, and distilled. The results are tabulated, the lowest temperature of reaction being given.

Substituent	None	*p*-Cl	*m*-NO_2	*p*-NO_2	*p*-Me	*o*-MeO	*m*-MeO	*p*-MeO	3 : 4-$(MeO)_2$	3 : 4-(CH_2O_2)
Decarboxylation temp.	n.r.*	110	>206	>206	140	80	>206	80	80	80
Volatile product	S	S †	None	None	None	E	S	E	E	E

* n.r.—no reaction, even in tetralin. † If reaction interrupted.
S = Starting material, E = ethoxy-cyanide.

When α-ethoxycarbonyloxyfurfuryl cyanide was treated in the same way at 80° no volatile product was obtained.

The properties of *α-ethoxybenzyl cyanides* are tabulated below.

Substituent	B. p./mm.	n_D^{21}	Formula	Found (%)			Reqd. (%)			Yield †
				C	H	N	C	H	N	
o-MeO	110°/0·8	1·5100	$C_{11}H_{13}O_2N$	69·0	6·6	7·5	69·1	6·8	7·3	16% ‡
p-MeO *	110/0·5	—	$C_{11}H_{13}O_2N$	69·3	7·2	7·5	69·1	6·8	7·3	41 §
3 : 4-$(MeO)_2$ ...	136/0·6	1·5233	$C_{12}H_{15}O_3N$	65·3	6·9	6·2	65·2	6·8	6·3	60 §
3 : 4-(CH_2O_2) ...	142/0·6	1·5213	$C_{11}H_{11}O_3N$	64·5	5·3	7·1	64·4	5·4	6·8	61 §

* n_D^{51} 1·5118; subsequently solidified, forming needles, m. p. 27°, from light petroleum.
† On initial aldehyde. ‡ 66% on ester. § Without isolation of intermediate ester.

These were colourless liquids, except for the 3 : 4-dimethoxy-compound; in this decarboxylation a yellow material was produced (needles from dioxan, m. p. 300°) which sublimed readily (180°/0·4 mm.), and coloured the distillate slightly. Solutions of this solid had an intense blue fluorescence (Found : C, 68·4; H, 5·5; N, 8·1. $C_{20}H_{20}O_4N_2$ requires C, 68·2; H, 5·7; N, 7·9%).

Hydrolysis of the α-Ethoxybenzyl cyanides.—The nitriles were boiled with 10% aqueous-ethanolic potassium hydroxide till evolution of ammonia ceased. The ethanol was evaporated off, and the liquid washed with ether. The aqueous layer was acidified with hydrochloric acid and extracted with ether. This extract was shaken with sodium carbonate solution, and the aqueous layer was reacidified and extracted with ether. Evaporation of the dried extract left a brownish oil which was extracted with light petroleum to yield the corresponding *acids*; the 3 : 4-methylenedioxy-acid was dimorphic. Their properties, together with those of the corresponding *amides* (obtained *via* the acid chlorides) are tabulated below.

				Found (%)			Reqd. (%)		
Substituent	Description	M. p.	Formula	C	H	N	C	H	N
		Acids							
o-MeO	Tablets from benzene–petrol	48°	$C_{11}H_{14}O_4$	63·0	6·6	—	62·8	6·7	—
p-MeO	Oil, decomposing on attempted distillation	—	—	—	—	—	—	—	—
3 : 4-(MeO)$_2$	Prisms from CCl_4–petrol	86	$C_{12}H_{16}O_5$	59·9	6·5	—	60·0	6·7	—
3 : 4-(CH_2O_2)	(*a*) Tablets from CCl_4–petrol	68	$C_{11}H_{12}O_5$	58·9	5·2	—	58·9	5·4	—
	(*b*) Needles from CCl_4–petrol	76	$C_{11}H_{12}O_5$	59·0	5·4	—	58·9	5·4	—
		Amides							
o-MeO	Rhombs and plates from benzene	110—111°	$C_{11}H_{15}O_3N$	63·2	6·9	7·0	63·1	7·2	6·7
p-MeO	Needles from benzene	120	$C_{11}H_{15}O_3N$	63·3	7·0	6·5	63·1	7·2	6·7
3 : 4-(MeO)$_2$	Needles from benzene	107	$C_{12}H_{17}O_4N$	60·1	7·1	6·0	60·3	7·1	5·9
3 : 4-(CH_2O_2)	Plates from petrol (b. p. 60—80°)	102	$C_{11}H_{13}O_4N$	59·4	5·5	6·2	59·2	5·8	6·0

The author is grateful to Mr. J. M. L. Cameron and his assistants for the microanalyses.

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[*Received, February 8th,* 1955.]