BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3718—3719 (1972)

Decarboxylation of Sodium β-Phenylglycidate under Conditions of Kolbe Electrolysis

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(Received May 16, 1972)

The anodic decarboxylation of glycidic acids has recently been reported by Waters and Witkop.[1] They found that the anodic oxidation of aromatic glycidate such as piperonal glycidate gave a low yield of neutral material consisting of numerous compounds which were not further investigated. As an extension of our previous work on the anodic reaction of aldehyde,[2],[3] ketone,[3] cinnamic acid,[4] 5-alkyl-2-furoic acids,[5] and cyclopropanecarboxylic acids,[6] we studied the anodic decarboxylation of aromatic glycidic acids in protic media and obtained some information on the primary and secondary products in the reaction.

The anodic reaction of sodium β-phenylglycidate (**1**) in a mixed solvent of acetic acid–methanol–water using smooth platinum electrodes gave a neutral mixture in 51—63% yields based on **1**. When the neutral mixture was extracted with an aqueous Girard P reagent, it was separated into active carbonyl component (26% in weight) and non-active carbonyl component (74%), which were further analyzed by glpc. The ratios of peak areas (%) of the constitutents in the active carbonyl and non-active carbonyl components are summaried in Table I. Compounds such as benzaldehyde (**2**), acetophenone (**3**), methyl benzoate (**4**), benzyl acetate (**5**), and 1-phenethyl alcohol (**6**) were detected as principal products by glpc.

The electrochemical reaction of benzaldehyde in an aqueous acetic acid–potassium hydroxide solution has been shown[2] to afford compounds **3**, **4**, and benzyl alcohol (**7**) as principal products and 1-phenethyl alcohol (**8**), *p*-tolualdehyde (**8**), *p*-methylacetophenone (**9**), propiophenone (**10**), and methyl toluates as minor components. A similar electrochemical reaction of acetophenone gave a small amount of neutral mixture which contained **10** as a major constituent (see Experimental). Although the pathway in which these prin-

Table 1. Composition of the active and non-active carbonyl components obtained in the electrolysis of sodium β-phenylglycidate (**1**)

Carbonyl component	Constituent	Relative ratio of peak area[a] (%)
Active toward Girard's reagent (100%)	Benzaldehyde	59.7
	Acetophenone	21.3
	p-Tolualdehyde	2.5
	o-Methylacetophenone	0.6
	Propiophenone	0.6
	p-Methylacetophenone	1.7
	Phenacyl acetate	1.0
	Others	12.5
Non-active toward Girard's reagent (100%)	Methyl benzyl ether	0.5
	Phenyl acetate	0.9
	——	0.6
	——	1.6
	Methyl benzoate	14.2
	Benzyl alcohol	2.8
	Benzyl acetate	30.8
	Methyl phenylacetate	4.4
	Methyl *o*-toluate	2.2
	1-Phenethyl alcohol	8.4
	2-Phenethyl alcohol	1.7
	——	3.1
	Methyl *p*-toluate	3.4
	2-Phenethyl acetate	0.8
	p-Methylbenzyl acetate	trace
	Others (fifteen minor peaks)	24.6

[a] Gas chromatography with a 45 m, 10% SE-30 coated Hitachi Golay column (Z-45) operating at 100°C; carrier gas N_2 (0.5 kg/cm^2).

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[1] J. A. Waters and B. Witkop, *J. Org. Chem.*, **36**, 3233 (1971).

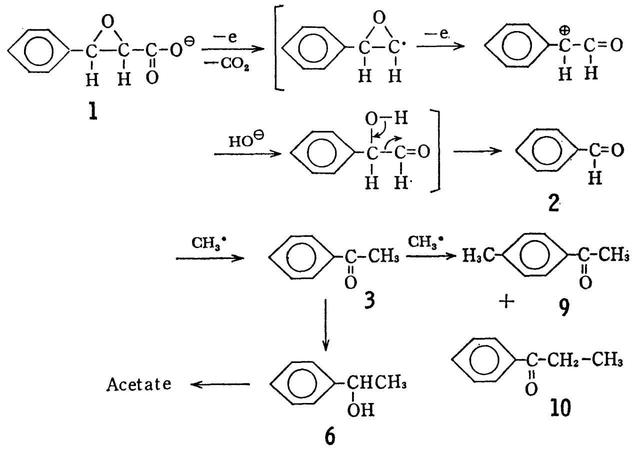
[2] A. Takeda, S. Torii, and H. Oka, *Tetrahedron Lett.*, **1968**, 1781.

[3] A. Takeda, S. Wada, S. Torii, and Y. Matsui, This Bulletin, **42**, 1047 (1969).

[4] A. Takeda, S. Torii, and H. Oka, *Mem. Sch. Eng.*, *Okayama Univ.*, **3**, 107 (1968).

[5] S. Torii, H. Tanaka, H. Ogo, and S. Yamasita, This Bulletin, **44**, 1079 (1971); S. Torii, H. Tanaka, and T. Okamoto, *ibid.*, **45**, 2783 (1972).

[6] A. Takeda, S. Wada, and Y. Murakami, *ibid.*, **44**, 2730 (1971).



cipal products of the anodic reaction of **1** were formed is not certain at present, it seems that the mechanism proposed by Waters[1] for the electrochemical decarboxylation of α-methyl-α,β-epoxycyclohexylideneacetate and the related compounds can be applied to the formation of **2**. It can be suggested that benzaldehyde produced primarily underwent secondary reactions such as anodic methylation[2,3] to give **3**, and electrochemical reduction to give **7**. Compounds **8** and **9** may be interpreted as the products of ring methylation.[7] The anodic decarboxylation of sodium β-methyl-β-phenylglycidate (**11**) in an aqueous media afforded **3** as a predominant product when the reaction was carried out for a shorter period.

Experimental

All the boiling points are uncorrected. The products were analyzed by vapor-phase chromatography using a Hitachi F6-D instrument, Golay column (Z-45) coated with silicone oil (10%, SE-30). Electrolyses were carried out in the apparatus described previously.[2-4] The cell was immersed in a water-bath cooled with circulating cold water. The electrodes were two platinum foils (1.5×2.0 cm^2) about 2 mm apart and the current direction was changed every 30 sec by means of a commutator.

Analytical grade acetic acid, methanol, acetophenone, and potassium hydroxide were used. Sodium β-phenylglycidate and sodium β-methyl-β-phenylglycidate were prepared by saponification of the corresponding ethyl esters[8] with sodium ethoxide. The following reference compounds were of commercial grade: benzaldehyde, benzyl alcohol, 1- and 2-phenethyl alcohols, benzoic acid, methyl benzyl ether, propiophenone, phenyl acetate, methyl *o*-toluate, methyl benzoate, *p*-tolualdehyde, *m*- and *p*-methylacetophenones, and methyl phenylacetate. The following acetates were prepared from the appropriate hydroxy compounds: benzyl acetate, bp 93°C/10 mmHg,[9] 2-phenethyl acetate, bp 118°C/13 mmHg,[10] *p*-methylbenzyl acetate, bp 95°C/13 mmHg,[11] phenacyl acetate, bp 150—164°C/2 mmHg,[12] *p*-acetoxyacetophenone, bp 165—170°C/19 mmHg.[13] Methyl *p*-toluate was prepared by treating *p*-toluic acid with diazomethane, bp 102—105°C/10 mmHg.[14] *o*-Methylacetophenone was also prepared: bp 110°C/14 mmHg.[15]

*Anodic Reaction of Sodium β-Phenylglycidate (**1**).* A mixture of **1** (18.6 g, 0.1 mol) with acetic acid (100 m*l*), methanol (50 m*l*), water (70 m*l*) and potassium hydroxide (4 g, 0.07 mol) was electrolyzed for 54 hr at 31—35°C with terminal voltage 10—13 V and a current of 0.8—0.9 A/cm^2. During the electrolysis a 40 m*l* portion of acetic acid was added every 8 hr. The reaction mixture was diluted with 300 m*l* of water and extracted with ether. The extract was washed with aqueous sodium chloride and sodium hydrogen carbonate, and was concentrated *in vacuo* to afford 9.5 g (51%) of neutral oil. 0.2 g of acidic product was obtained from the aqueous layer. After 5 g of the neutral mixture was treated with an excess (10 g) of Girard P reagent in ethanol at reflux temperature, 2.3 g of an oil consisting of non-active carbonyl components was recovered by extraction with ether. From the residual solution, 0.8 g of active carbonyl component was recovered by acid hydrolysis. The composition of the active carbonyl and the non-active carbonyl components analyzed by glpc is given in Table 1.

*Anodic Decarboxylation of Sodium β-Methyl-β-phenylglycidate (**11**).* A solution of 30 g (0.15 mol) of **11** in 150 m*l* of water was electrolyzed for 8 hr at 30—35°C with terminal voltage 11—12 V and a current of 0.9—1.0 A/cm^2. The reaction mixture was extracted with ether, washed with water and dried (Na_2SO_4). After evaporation of the solvent, 2.8 g of an oil was obtained which was chromatographed on silica gel and eluted with benzene (200 m*l*), ether (500 m*l*), and methanol (250 m*l*). From the fractions eluted by ether and methanol, 2.2 g of an oil was isolated. The IR spectrum of this oil was identical with that of an authentic sample of **3** and gave 2,4-DNP which was identified as that of **3** by mixed mp 235—237°C, IR spectrum, and microanalyses.

*Anodic Methylation of Acetophenone (**3**).* A mixture of **3** (12.1 g, 0.1 mol) with acetic acid (53 m*l*), methanol (67 m*l*), water (110 m*l*) and potassium hydroxide (4.0 g) was electrolyzed for 53 hr at 23—33° with terminal voltage 11—13 V and a current of 0.8—0.9 A/cm^2. During the course of electrolysis 30 m*l* of acetic acid was added every 7 hr. The reaction mixture was washed as usual and dried. After distilling off unreacted **3** with a Widmer column, 2.2 g of neutral oil was obtained from the reaction mixture. The glpc analysis of the mixture is given in Table 2.

TABLE 2. COMPOSITION OF THE PRODUCTS OBTAINED IN THE ANODIC METHYLATION OF ACETOPHENONE

Constituent	Peak Area[a]
Acetophenone	13.6
o-Methylacetophenone	10.6
Propiophenone	31.4
m-Methylacetophenone	7.3
p-Methylacetophenone	12.2
——	6.6
——	2.4
p-Acetoxyacetophenone	3.6
Phenacyl acetate	3.2
Others	9.1

a) Gas chromatographic peak area (%) with a 45 m, 10% SE-30 coated Hitachi Golay colum (Z-45) operating at 140°C; carrier gas N_2(0.5 kg/cm^2).

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7) F. D. Mango and W. A. Bonner, *J. Org. Chem.*, **29**, 1367 (1964).

8) W. S. Johnson, J. S. Belew, L. T. Chinn, and R. H. Hund, *J. Amer. Chem. Soc.*, **75**, 4995 (1953); L. Claisen, *Ber.*, **38**, 693 (1905).

9) M. Gomberg and C. C. Buchler, *J. Amer. Chem. Soc.*, **42**, 2064 (1920).

10) R. Huisgen, *Ann. Chem.*, **573**, 163 (1951).

11) C. K. Ingold and E. Rothstein, *J. Chem. Soc.*, **1928**, 1279.

12) J. B. Rather and E. E. Reid, *J. Amer. Chem. Soc.*, **43**, 630 (1921).

13) P. D. Gardner, *ibid.*, **77**, 4674 (1955).

14) J. Kendal and J. E. Booge, *ibid.*, **38**, 1723 (1916).

15) K. V. Auwers, A. Boennecke, F. Krollpfeiffer, and G. Peters, *Ann. Chem.*, **408**, 212 (1915).