Oxidative Decarboxylation of Phenylacetic Acid[1]

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The cuprous ion catalyzed oxidative decarboxylation of benzoic acid to phenol is not only useful but also an interesting reaction which recently has been shown to proceed through a cyclic 6-membered transition state by use of ^{14}C and ^{18}O tracer techniques.[2,3] Meanwhile this procedure has been used to prepare various aromatic phenolic compounds from the corresponding carboxylic acids; such as substituted benzoic, naphthoic, and heteroaromatic carboxylic acids.[4] Recently Bigot and his co-workers[5] have shown the oxidative decarboxylation reaction of cyclohexanecarboxylic acid. Phenylacetic acid has been known to undergo a facile decarboxylation to give toluene[6] and hence an interesting compound to study the nature of this intriguing oxidative decarboxylation. We have carried out the oxidative decarboxylation of phenylacetic acid catalyzed by cuprous oxide, expecting to obtain either *o*-cresol, benzyl alcohol or diphenylethane. However we found that the reaction is more complicated and gives a variety of products. This paper will describe the detailed accounts of our investigation.

Results and Discussion

The apparatus used for the decarboxylation reaction was the same as the one described previously.[3] The reaction was found to begin at around 180°C. The products isolated were characterized by comparing the IR and NMR spectra with those of the authentic samples. The products initially came out from the reaction vessel were benzaldehyde and carbon dioxide, both of which were trapped as the bisulfite adduct and barium carbonate, respectively. From the residue were isolated the following three neutral products I, II, III, the structures of which were characterized by IR and NMR spectra. The compounds I and II were actually synthesized by the procedures as was found to be identical,[7,8] while the structure of the compound III was suggested based on the NMR spectrum and other evidences. However neither cresol nor other hydroxy compound could be isolated among the products. The products and yields are tabulated in Table 1.

The reaction is undoubtedly catalyzed by copper metal since most phenylacetic acid were recovered without copper catalyst. (Run 9). The presence of oxygen is also important because no products isolated when the reaction was carried out under nitrogen stream. (Run 7). Although benzaldehyde was isolated, diphenylethane and toluene were not found among the products, apparently suggesting that benzyl radical is not the intermediate in this reaction and that the reaction proceeds through ionic mechanism. Recently, Cohen *et al.*,[9] have isolated I and II by the treatment of phenylacetic acid with pyridine-*N*-oxide

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[1] Phenols and Phenolic Esters. XIII.

[2] W. Shoo, V. J. Veenland, J. A. Bigot and F. L. J. Sixma, *Rec. Trav. Chim.*, **80**, 134 (1961).

[3] S. Oae, T. Watanabe and N. Furukawa, This Bulletin, **39**, 1329 (1966).

[4] W. W. Kaeding, *J. Org. Chem.*, **26**, 3144 (1961); W. W. Kaeding, R. O. Lindblom and R. G. Temple, *Ind. Eng. Chem.*, **53**, 805 (1961).

[5] J. A. Bigot and P. L. Kerkhoffs, *Rec. Trav. Chim.*, **82**, 677 (1964).

[6] V. N. Ipatief, J. E. Germain and H. Pines, *Bull. Soc. Chim. France*, **1951**, 259.

[7] R. B. Davis and J. A. Ward, Jr., "Organic Syntheses," Coll. Vol. IV, p. 392 (1963).

[8] S. Gabriel and G. Cohn, *Ber.*, **24**, 3229 (1891).

[9] T. Cohen and L. H. Fragger, *J. Am. Chem. Soc.*, **87**, 5701 (1965).

TABLE 1. PRODUCTS FROM THE OXIDATIVE DECARBOXYLATION OF PHENYLACETIC ACID CATALYZED BY Cu_2O

Run	Reaction time hr	Weight of reactant g	Recovered $C_6H_5CH_2CO_2H$	C_6H_5CHO	Neutral[a] product	I	II	III	$BaCO_3$ g
1	5	2.24	0.65	0.21	0.50	—	0.05	0.05	—
2	4	2.47	—	0.20	0.54	0.03	—	0.05	1.43
3	6.5	8.98	3.54	0.12	1.67	0.03	0.15	0.78	3.37
4	7.3	8.98	—	0.26	1.51	—	—	0.94	3.12
5	7	2.24	4.64	—	—	0.06	—	1.00	2.90
6	6.5	2.24	0.67	0.02	0.80	—	0.02	0.26	—
7[b]	6.5	2.24	1.18	trace	0.11	0	0	0.02	trace
8[c]	6.4	2.24	0.43	0.13	0.78	0.10	—	0	1.76
9[d]	6.5	2.24	1.77	trace	0.14	trace	0	0	0.47

a) Containing I, II, III.
b) Under nitrogen stream.
c) Catalyst, Cu_2O alone without MgO.
d) Catalyst, MgO alone without Cu_2O.

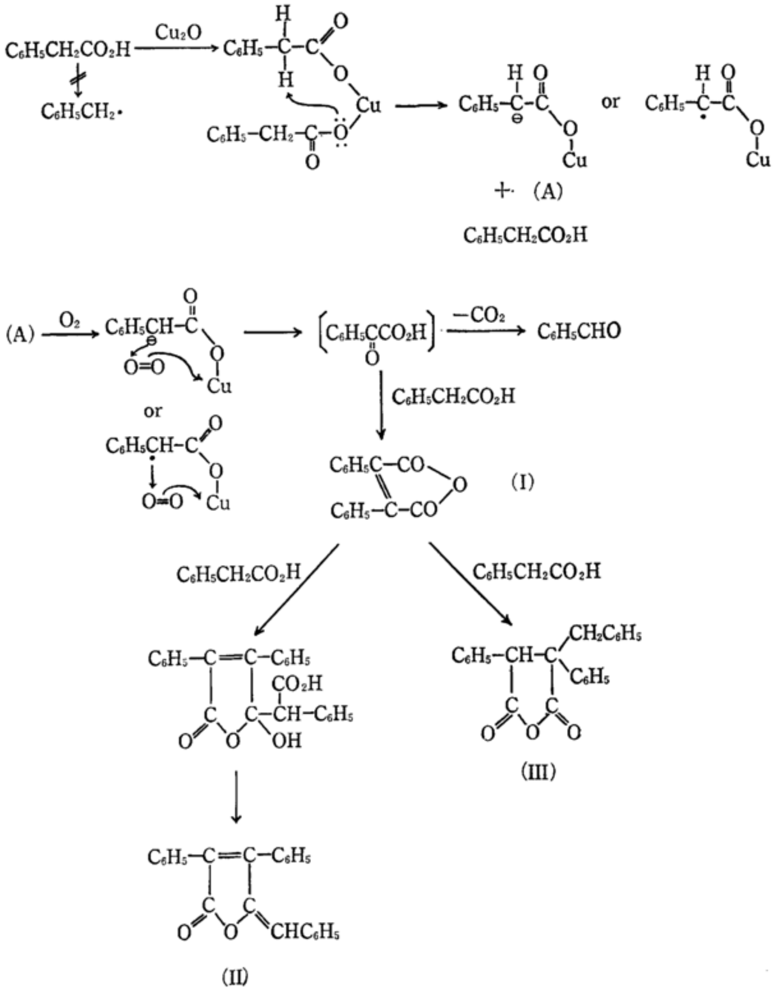

Fig. 1. Mechanism.

in addition to a few other products such as benzoylformic acid and benzaldehyde and suggested that benzoylformic acid might be the key intermediate, while, in this, the copper ion catalyzed decarboxylation, benzoylformic acid might be postulated as the key intermediate, the formation of which is illustrated by either radical or ionic mechanism. The whole reaction may be schematically shown as below. (Fig. 1)

Experimental

The Decarboxylation. A typical example of the reaction is as follows.

Phenylacetic acid (8.98 g) was mixed with 0.16 g of cuprous oxide and 0.37 g of magnesium oxide and then the whole mixture was placed into the reactor and heated with an electric muffle heater with slowly introducing air while keeping the temperature at 195—205°C for 6.5 hr. Benzaldehyde and carbon dioxide eluted were trapped with sodium bisulfite and barium hydroxide, respectively. After the reaction, the residue remaining in the vessel was extracted with ether and washed with water. Ether extract was washed with dilute hydrochloric acid, and then with water and sodium carbonate solution. The ether layer was dried over magnesium sulfate. When ether was removed, red brownish oil (1.67 g) was obtained. Keeping the oil in cold, the crystals appeared. To this crystals ether was added and collected the crystals on a filter paper. Then the ether was removed from the mother liquor and the second crop of the crystals was obtained. Thus, by repeating this operation, three different products were isolated.

The weight and melting point of I, II, III, were, I, 0.03 g, mp 159—160°C (from benzene - *n*-hexane); II, 0.15 g mp 178—179°C (from benzene - *n*-hexane); III, 0.78 g, mp 211.5—212.5°C (from benzene or ethanol). The product I was identified from its mp and IR of that of the authentic 1, 2-diphenylmaleic anhydride which was prepared from benzaldehyde and phenylacetonitrile and sodium cyanide.[7] The product II, having slightly yellow color, IR absorption at 1765 cm^{-1} was identified as 5-oxo-3, 4-diphenyl-2-benzaldihydrofuran II which was prepared authentically from heating a mixture of I and phenylacetic acid with sodium acetate at 230°C for 2 hr.[8]

The product III, IR spectrum 1775, 1813 (doublet; lactone carbonyl) and 1150 cm^{-1} (anhydride); molecular weight determination. Calcd 342, Found, 336—343. Elemental analysis: Found: C, 81.04, H, 4.98%. Calcd: C, 80.68, H; 5.30%. The NMR spectrum of III has methylene quartet centered at 5.70 ppm and complex multiplet centered at 2.75 ppm in which benzene protons and highly deshielded methine proton are involved.

The pyrolysis of II led to 1, 2-diphenylmaleic anhydride which upon the treatment with phenylacetic acid in the presence of the catalyst at 200°C regenerating III. These experimental evidences showed that the products had a five membered lactone ring and three benzene ring involving methylene, thus III was suggested to have the structure of benzylsuccinic anhydride.