UDC 547.581-126.4-212.07:546.26〔539.16〕

Michiyasu Sugii, Risaburo Nakai, and Chiaki Tanaka : The Use of Radioactive Element. IV.[*1] Decarboxylation of Carboxylic-Carbonic Anhydride.

(*Institute for Chemical Research,*[*2] *University of Kyoto, and Osaka College of Pharmacy*[*3])

It is well known that ethyl benzoate is prepared by heating a mixture of ethyl chlorocarbonate and benzoic acid in the presence of pyridine, according to the following equation :

$$C_6H_5COOH + ClCOOC_2H_5 + C_5H_5N \longrightarrow C_6H_5CO\text{-}O\text{-}CO\text{-}OC_2H_5 + C_5H_5N\cdot HCl$$

$$\downarrow$$

$$C_6H_5COOC_2H_5 + CO_2$$

It is also known that the intermediate product, carboxylic-carbonic anhydride can be separated at a low temperature from the reaction mixture.1) It is relatively unstable and evolves carbon dioxide. According to the work of Tarbell and Price,2) the carbon dioxide would be derived from the ethoxycarbonyl group of the carboxylic-carbonic anhydride. To examine the decarboxylation reaction, ^{14}C-carboxyl-labeled benzoic acid and phenylacetic acid were prepared and used.

The reaction was carried out in a slow stream of air and the carbon dioxide liberated was precipitated as barium carbonate. The ester produced was converted to hydrazide. The radioactivity of barium carbonate and hydrazide was determined. Method of isotopic assay was the same as that described in the previous paper. The results are shown in Table I.

Table I. Radioactivity of Barium Carbonate and Hydrazide

Reactant	Product	Specific activity (μc/mM)
$C_6H_5\text{-}^{14}COOH$		14.6 ± 0.18
	$BaCO_3$	inactive
	$C_6H_5\text{-}^{14}CONHNH_2$	14.3 ± 0.15
$C_6H_5CH_2\text{-}^{14}COOH$		6.6 ± 0.11
	$BaCO_3$	inactive
	$C_6H_5CH_2\text{-}^{14}CONHNH_2$	6.4 ± 0.10

The results indicate that the specific activity of hydrazide is equal to that of the starting acid and that barium carbonate is inactive. These facts clearly show that the carbon dioxide originates from the ethoxycarbonyl group of the carboxylic-carbonic anhydride.

Experimental

Reaction of Ethyl Chlorocarbonate and Pyridine with Benzoic Acid[*carboxyl*-^{14}C]—A mixture of benzoic acid[*carboxyl*-^{14}C] (1 g., 14.6 ± 0.18 μc/mM) and pyridine (5 cc.) was placed in a three-necked flask, the flask was cooled to below 0°, and ClCOOEt (1.2 cc.) was added with shaking. The mixture was allowed to come to room temperature and then refluxed for 20 min. During this treatment a slow stream of dry air, free from CO_2, was passed through the reaction mixture and CO_2 was precipitated as $BaCO_3$ with $0.2N$ $Ba(OH)_2$. Yield of $BaCO_3$ was 1.6 g. and it had no observable radioactivity. The reaction mixture was poured into water and extracted with Et_2O. Et_2O solution was washed with dil. HCl, water, and $NaHCO_3$ solution, dried, and the solvent was removed. The

---

[*1] Part III : This Bulletin, **7**, 645(1959).

[*2] Takatsuki, Osaka-fu (杉井通泰, 中井利三郎).

[*3] Matsubara, Osaka-fu (田中千秋).

1) A. Einhorn : Ber., **42**, 2772(1909); Frdl., **6**, 146, D.R.P. 117,267.

2) D.S. Tarbell, J.A. Price : J. Org. Chem., **22**, 245(1957).

residue was distilled to yield 0.74 g. of ethyl benzoate (b.p. 205~210°). It was converted to benzohydrazide in the usual manner. Yield of benzohydrazide (m.p. 110~112°) was 0.54 g. and its specific activity was 14.3±0.15 μc/mM.

Reaction of Ethyl Chlorocarbonate and Pyridine with Phenylacetic Acid[*carboxyl*-^{14}C]—A mixture of phenylacetic acid[*carboxyl*-^{14}C] (1.2 g., 6.6±0.11 μc/mM), pyridine (5 cc.), and ClCOOEt (1.2 cc.) was treated in the same way as above, and 1.8 g. of $BaCO_3$ and 1.1 g. of ethyl phenylacetate (b.p. 210~215°) were obtained. The former had no observable radioactivity and the latter was converted to phenylacetohydrazide (0.8 g., m.p. 115~116°), specific activity of which was 6.4±0.10 μc/mM.

Summary

Decarboxylation reaction of carboxylic-carbonic anhydride was studied by using ^{14}C-carboxyl-labeled benzoic acid and phenylacetic acid. It was found that the carbon dioxide was liberated from the ethoxycarbonyl group of the carboxylic-carbonic anhydride.

(Received April 23, 1959)