

39. The Aldehyde Ketone Rearrangement. Rearrangement of Bis(4-methoxyphenyl)-acetaldehyde into 4,4'-Dimethoxydeoxybenzoin

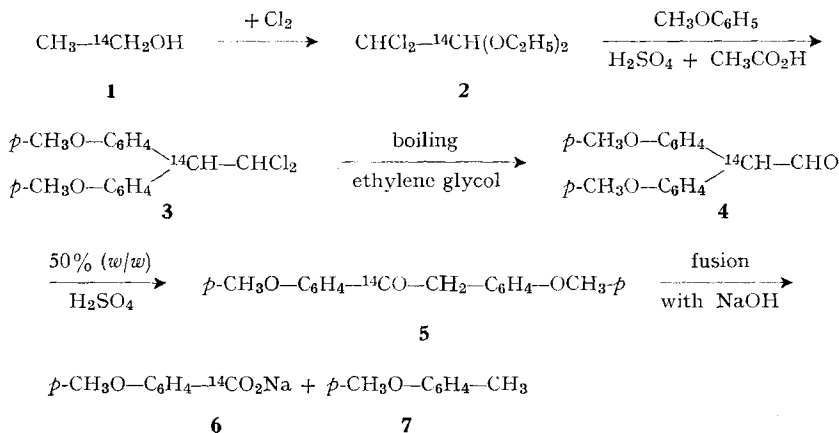
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Summary. The formyl carbonyl group in bis(4-methoxyphenyl)-acetaldehyde does not contribute to the formation of the carbonyl group in 4,4'-dimethoxydeoxybenzoin when the former rearranges to the latter by treatment with 50% (*w/w*) sulfuric acid.

Rearrangement of bis(4-methoxyphenyl)acetaldehyde with 50% (*w/w*) sulfuric acid leads to the formation of 4,4'-dimethoxydeoxybenzoin [1]. The present work shows that the carbonyl group in the deoxybenzoin is not derived from the formyl group. The reactions describing this finding are shown in the following scheme:



This scheme would exclude 3 possible mechanisms: (i) An aldehyde ketone rearrangement of the type postulated [2] [3] for the conversion of diphenyl- and ditolyl-acetaldehydes into the corresponding deoxybenzoin. This mechanism would require the inclusion of ¹⁴C in the methylene group, and not in the carbonyl group as indicated above; (ii) A rearrangement mediated by the formation of an acetylene [4]; (iii) A reversible pinacol-pinacolone rearrangement comparable with that obtained when the aldehyde is treated with acetic anhydride [1], followed by vinylation and then tautomerization to the deoxybenzoin. In the last 2 cases the insertion of ¹⁴C should

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be shared between the carbonyl and the methylene group [4] which was not the case. The mechanism of the reaction will be reported by one of us (*W.T.*) later.

Experimental Part

1-[¹⁴C]-Ethanol (**1**) was purchased from the *Radiochemical Centre*, Amersham, England.

1,1-Diethoxy-1-[¹⁴C]-2,2-dichloroethane (**2**) was prepared by chlorination of ethanol containing **1** according to the method of *Fritsch* [5].

2,2-Dichloro-1,1-bis(4-methoxyphenyl)-1-[¹⁴C]-ethan (**3**) was prepared from **2** and anisole according to the method of *Wiechell* [6]. It had m.p. 114°.

Bis(4-methoxyphenyl)-2-[¹⁴C]-acetaldehyde (**4**) was prepared by heating a solution of the dichloroethane in ethylene glycol [7].

Rearrangement of 4. A mixture of **4** (1.1 g) and 50% sulfuric acid (*w/w*, 20 ml) was heated to boiling for 3 h, and the product was worked out as previously described [1].

Degradation of 4-methoxybenzyl-4'-methoxyphenyl-[¹⁴C]-ketone (5). To fused sodium hydroxide (0.04 g), powdered 4,4'-dimethoxy-deoxybenzoin (0.15 g) was added and heating the fused mixture was maintained for 45 seconds. The partly demethylated product was diluted with water and remethylated with dimethyl sulfate. The solution which should be alkaline was then heated on the steam-bath for 15 min, cooled and extracted with ether. Removal of ether gave *p*-cresyl methyl ether. The alkaline solution was concentrated on the steam-bath, acidified with a few drops of conc. hydrochloric acid, cooled and treated with acetone. The acetone solution was filtered, and the solvent was then removed. Crystallization of the residue from little water gave anisic acid, m.p. and mixed m.p. 180°.

Assay of the radioactivity in *p*-cresyl methyl ether and anisic acid showed that ¹⁴C was mainly (94% of the radioactivity) inserted in the anisic acid fraction.

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