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ORGANIC SYNTHESIS BY MEANS OF METAL COMPLEXES. XIV.[1]
OXIDATIVE CLEAVAGE OF CATECHOL WITH LABELED OXYGEN ACTIVATED BY CUPROUS CHLORIDE

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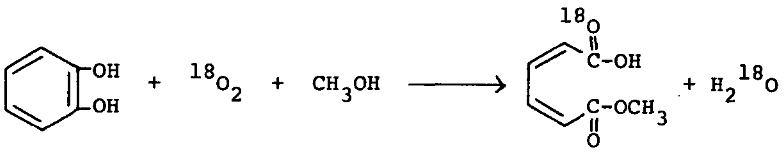
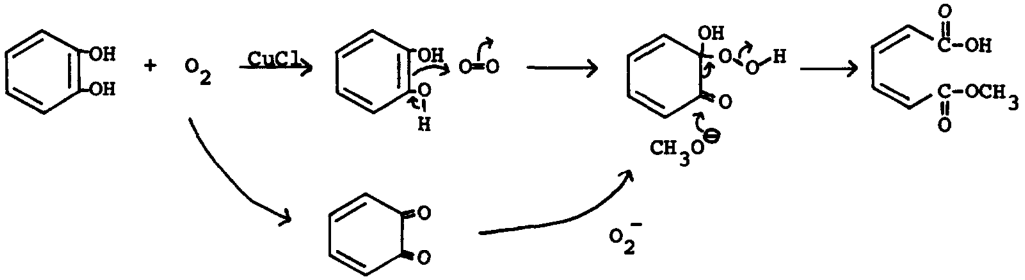
In a previous paper, we have reported the nonenzymatic model reaction of pyrocatechase.[1] The oxidative cleavage reaction of catechol with molecular oxygen activated by cuprous chloride proceeds in a mixture of pyridine and methanol to give monomethyl muconate. The unique feature of this oxidative cleavage is the exclusive formation of the monomethyl ester; no free muconic acid nor dimethyl ester was obtained by the reacitons carried out with various concentrations of methanol. In order to elucidate the mechanism of this interesting reaction, we carried out the oxidation with oxygen labeled with $^{18}O_2$ and confirmed by mass spectrometric studies of the product that one atom of the labeled oxygen was introduced into the free acid group, not to the ester group.



The following experimental observation supports this conclusion. The oxidation reaciton was carried out in the following way. The reaction system containing cuprous chloride in a mixture of pyridine and methanol was filled with nitrogen, and then labeled oxygen (content 10%) was introduced until absorption of the oxygen stopped. A catechol solution was added slowly to the solution under the labeled oxygen atmosphere. Crystalline monomethyl muconate was isolated in 81% yield and subjected to high resolution mass spectrometry.

A peak at m/e 158 (M+2) was observed and its intensity was found to be 11% of that of the parent peak at 156(M^+). This observation indicates efficient incorporation of one atom of the labeled oxygen into the product. No peak appeared at m/e 160. The elemental composition of a peak at m/e 125 was confirmed by high resolution mass spectrometry to be $C_6H_5O_3$(M-OCH_3) and a peak at m/e 127 (intensity ratio 127/125=11%) was observed. A high peak at m/e 97 is assignable to $C_5H_5O_2$(M-$COOCH_3$). Again a peak at m/e 99 was observed with an intensity ratio (99/97) of 11%. Appearance of these two peaks (127 and 99) indicates that ^{18}O was introduced to the COOH group, but not to the $COOCH_3$ group. A high peak at m/e 111 can be assignable to [M-(CO_2+ H)]. A peak at m/e 113 was observed with an intensity ratio (113/111) of 3%. Appearance of the peak at 113 with the low intensity ratio may be explained by a partial contribution of the CO_2 from the ester group. From these spectral data, it can be concluded that the labeled oxygen was introduced to the COOH group and not to the $COOCH_3$ group.

Based on the above result, we wish to propose the following mechanism for this reaction. However, at present there is no evidence which explain the nature of the activated form of oxygen and the role of the copper in this reaction, and the first two steps in this mechanism are tentative nature.



Reference

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‡. Basic Reserch Lab., Toray Industries, Inc.