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Reactions of Metal Benzoylacetonates and Acetylacetonates with Formaldehyde

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Synopsis. The reaction of cobalt benzoylacetonate with formaldehyde in water or methanol gave benzoic acid along with 4-hydroxy-3,3-bis(hydroxymethyl)-2-butanone or 4-methoxy-3,3-bis(hydroxymethyl)-2-butanone, respectively. The result suggests the formation of acetic acid in the reaction of metal acetylacetonate.

"Formose Reaction",[1] by which a complex mixture of sugars and sugar alcohols is formed by the base-catalyzed condensation of formaldehyde, has been attracting much attention in connection with the prebiotic synthesis of carbohydrates,[2] the possibility of the production of edible sugars from a simple materials, and the establishment of a metabolic cycle system of carbon resources in sustained space flight.[3] In general, however, the reaction results in complex products mixture, which hinders the utility of the attractive reaction. Selective formation of specific product is actively explored by using inorganic[4] or organic bases[5] as catalyst, or by photo- and γ-irradiation.[6]

During our attempt for a selective formose reaction using metal complexes, it was found out that a variety of metal acetylacetonates afforded 4-hydroxy-3,3-bis(hydroxymethyl)-2-butanone, **1**, and 4-methoxy-3,3-bis(hydroxymethyl)-2-butanone, **2**, selectively in water and methanol, respectively.[7] It was considered that **1** and **2** were formed from C–C bond cleavage of the ligand and the condensation with formaldehyde and the solvent.[7] But the fate of the other half of the ligand remained unknown. To clarify the feature of this reaction, the reaction of cobalt benzoylacetonate, instead of metal acetylacetonates, with formaldehyde was examined.

Experimental

Measurement. The gas chromatography (GC) was carried out with an OKURA Model 103 or a SHIMADZU Model GC-7AG equipped with a glass capillary column (i.d. 0.28 mm, 10 m) containing OV-1 or SE-30, the temperature of which was programmed from 100 °C to 260 °C at 6 °C min^{-1}. IR analyses were observed by JASCO Infrared Spectrophotometer Model A-3 or by JEOL JIR-40X FT-IR Spectrophotometer. ^{1}H NMR spectra were taken by JEOL JNM-GX 270 FT-NMR Spectrometer. Consumption of formaldehyde was determined by the method of Bricker[8] at 579 nm with HIRATA model 6B.

Formaldehyde Solution. Paraformaldehyde (1.20 g, 0.400 mol) was added into 200 ml of distilled water or anhydrous methanol and dissolved by heating to reflux for 6 h under N_2 atmosphere.

Reaction of Cobalt Benzoylacetonate with Formaldehyde. Into 30 ml of above prepared solution containing 1.80 g (60 mmol) of formaldehyde was added 1.0 mmol (0.3813 g) of cobalt benzoylacetonate,[9] and the mixture was stirred at 60 °C for 20 h under N_2 atmosphere. A 2 ml of aliquot was taken out to measure the formaldehyde consumption.

GC Analysis of the Products. After the removal of solvent and the unreacted formaldehyde, the products were trimethylsilylated[10] and analyzed by GC. Quantitative analysis of the silylated products was performed using tetradecane as an internal standard.

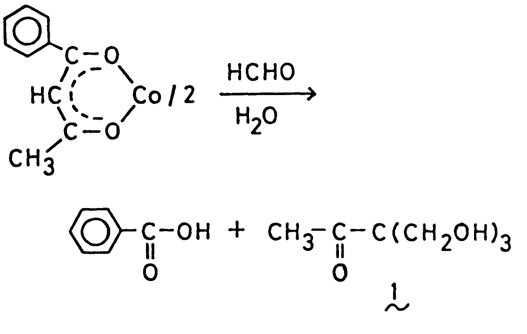
Isolation of the Products. The reaction mixture was treated with cation-exchange resin (Amberlite IR 118), followed by the removal of water and the unreacted formaldehyde, and then purified by column chromatography on silica gel (acetone/chloroform).

From the reaction of cobalt benzoylacetonate (3.813 g, 10 mmol) with formaldehyde (18.0 g, 600 mmol) in 300 ml of water, 0.50 g (4.1 mmol) of benzoic acid was obtained as white or pale-yellow crystal.

Results and Discussion

Reaction of Cobalt Benzoylacetonate with Formaldehyde in Water. Cobalt benzoylacetonate was reacted with formaldehyde in water at 60 °C for 20 h under N_2 atmosphere. The GC pattern of the trimethylsilylated products, as shown in Fig. 1a, was simple and a major peak, **A** in Fig. 1a, appeared, which was not observed in the case of metal acetylacetonates as shown in Fig. 1b.[7] It is to be noticed that a peak **B**, corresponding to **1**, was observed in the GC.

The reaction mixture treated with cation-exchange resin and purified by column chromatography to give the major product, corresponding to **A**, as a colorless or yellow crystal, which was identified to be benzoic acid by ^{1}H NMR, IR, and GC. The formation of **1** was also confirmed. Accordingly, equation shown below will be given for this reaction.



(1)

Quantitative analysis of the silylated products by GC using tetradecane as an internal standard gave 53 mg (0.43 mmol) of benzoic acid and 7 mg (0.05 mmol) of **1** from 1.0 mmol of cobalt benzoylacetonate. The conversion of formaldehyde was 8.0%, which means that 4.8 mmol of formaldehyde was consumed.

In the case of benzoylacetone complex, two mode of cleavage of ligand is possible as shown in Scheme 1. Route X leads to the formation of benzoic acid and **1**, and route Y to acetic acid and another polyol. Route X was confirmed here. The possible formation of other products by route Y can not be neglected, but selective formation of benzoic acid and **1**, as shown in Fig. 1a, suggest that Route X is favored in this reaction.

Reaction of Cobalt Benzoylacetonate with Formaldehyde in Methanol. The same procedure was followed using methanol as solvent. The gas chromatogram of the trimethylsilylated products, as shown in Fig. 2a, suggests the formation of benzoic acid in the peak **A**. A peak **C**, corresponding to **2**, also appeared on the gas chromatogram. Benzoic acid was confirmed by isolating it following the above mentioned procedure, giving equation 2, shown below, for this reaction.

The quantitative analysis of the product by GC using tetradecane gave 33 mg (0.27 mmol) of benzoic acid and 2 mg (0.01 mmol) of **2** from 1.0 mmol of cobalt benzoylacetonate. The conversion of form-

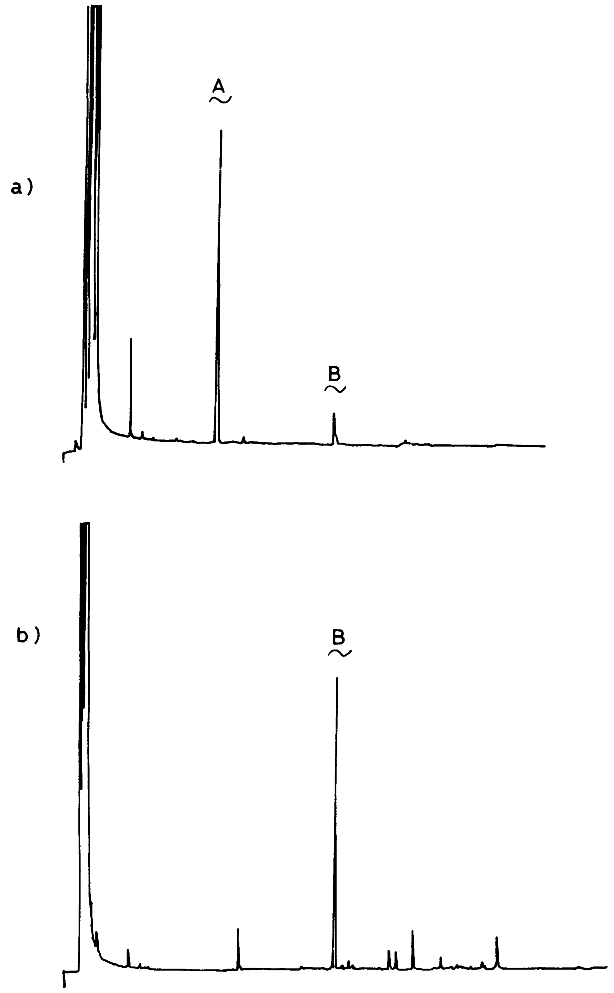


Fig. 1. The gas chromatogram of the TMS derivatives of the products. Column temperature was programmed from 100 to 260 °C at 6 °C min^{-1}. a) TMS-products obtained from cobalt benzoylacetonate/formaldehyde/H_2O at 60 °C for 20 h. b) TMS-products obtained from cobalt acetylacetonate/formaldehyde/H_2O at 60 °C for 20 h.

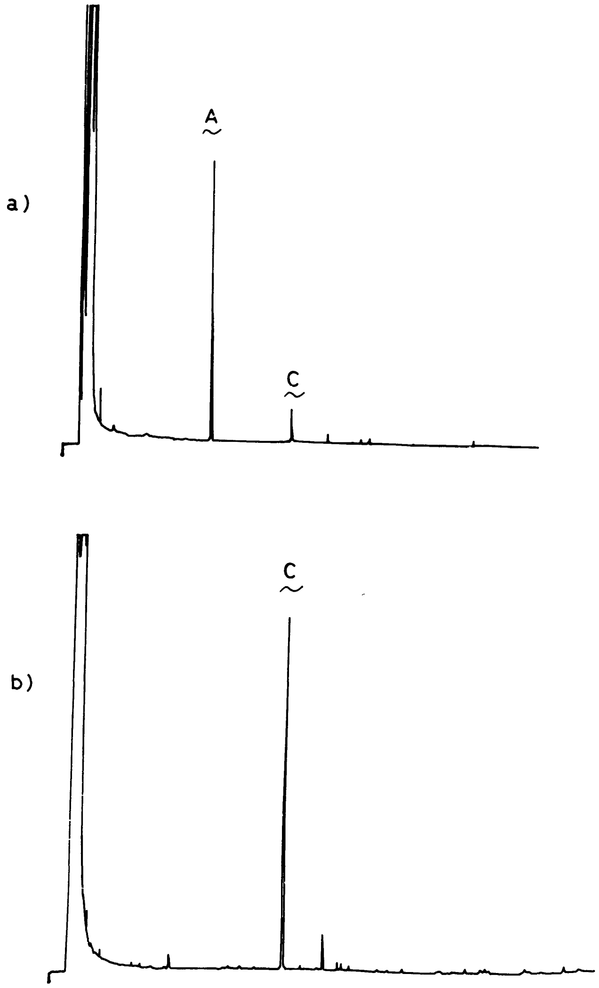
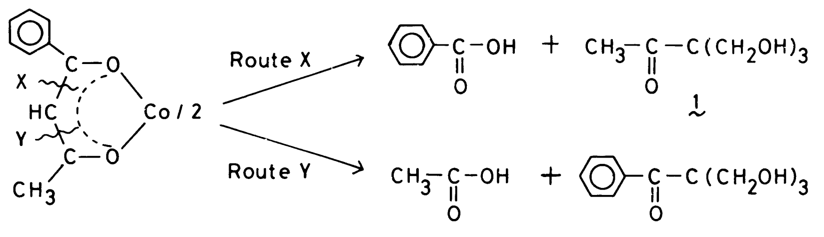
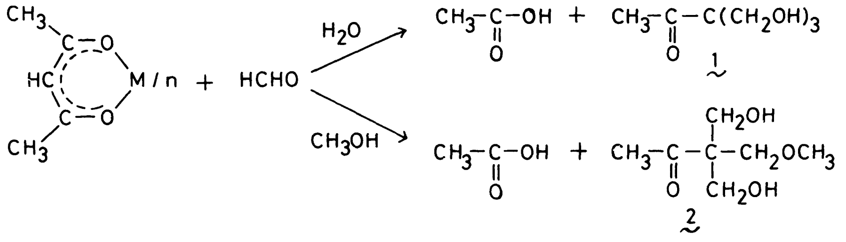


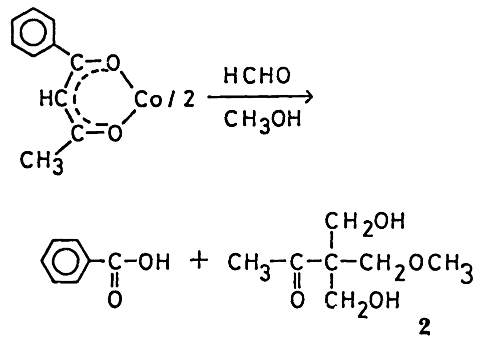
Fig. 2. The gas chromatogram of the TMS derivatives of the products. Column temperature was programmed from 100 to 260 °C at 6 °C min^{-1}. a) TMS-products obtained from cobalt benzoylacetonate/formaldehyde/methanol at 60 °C for 20 h. b) TMS-products obtained from manganese(III) acetylacetonate/formaldehyde/methanol at 60 °C for 20 h.



Scheme 1.



Scheme 2.



(2)

aldehyde was 1.9%, which correspond to 1.1 mmol of formaldehyde consumption.

Reaction of Metal Acetylacetonates. As menthioned before, the reaction of metal acetylacetonate with formaldehyde in water and methanol gave **1** and **2**, respectively, but the fate of the other half of the acetylacetone ligand was unknown. From the similarity of the reactions of acetylacetone and benzoylacetone complexes, the formation of benzoic acid in the reaction of metal benzoylacetone with formaldehyde, in turn, suggests the structure of the other half of the acetylacetone in the reaction of metal acetylacetonates, as acetic acid, which could not be isolated due to the volatility.

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