Communications

Modified Benzoin Condensation of Terephthalaldehyde with Benzaldehyde

Summary: The preparation of 1,4-bis(phenylglyoxyloyl)benzene via oxidation of the bisbenzoin obtained from the condensation of terephthalaldehyde bisbisulfite adduct and benzaldehyde is described.

Sir: Bis α diketones of the general structure RC(O)C(O)R′C(O)C(O)R are one of two comonomers needed for the production of polyphenylquinoxalines. These diketones have in the past been accessible only via tedious and low yield routes since their potentially very attractive precursors, the corresponding bisbenzoins, have been unknown. We therefore wish to report the first synthesis of a bisbenzoin via a modified benzoin condensation and the high yield oxidation of this product to the corresponding bis α diketone.

Bis(phenylglyoxyloyl)benzene, p-$C_6H_5C(O)C(O)C_6H_4C(O)C(O)C_6H_5$, has been prepared to date from p-phenylenediacetic acid[1] or interaction of terephthalonitrile with benzylmagnesium chloride followed by oxidation of the resulting 1,4-bis(phenylacetyl)benzene with either selenium dioxide[2] or p-nitrosodiethylaniline.[3] The most direct route to α diketones is the classical benzoin condensation followed by oxidation. Although the benzoin condensation has been used successfully to condense a number of dissimilar aldehydes,[4] no syntheses of bisbenzoins, RCH(OH)C(O)R′C(O)CH(OH)R, are discussed. Our attempts at condensation of benzaldehyde with terephthalaldehyde in the presence of potassium cyanide resulted in the isolation of what appeared to be terephthalaldehyde derived benzoins, some benzoin, $C_6H_5CH(OH)C(O)C_6H_5$, and other unidentified compounds. This is in agreement with the findings of Oppenheimer[5] that benzoin-type condensation of terephthalaldehyde involves only one of the two aldehyde groups.

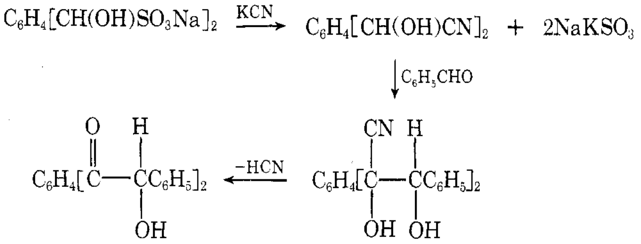
Thus we have concluded that it is necessary to modify the aldehyde functions in terephthalaldehyde to promote condensation with benzaldehyde at both sites. The use of the bisbisulfite adduct wherein hydroxyl moieties "replace" the carbonyl groups seemed to offer a promising approach. The bisbisulfite adduct, $C_6H_4[CH(OH)SO_3Na]_2$, was obtained in quantitative yield by treatment of terephthalaldehyde with aqueous sodium bisulfite.[6] Reaction of this adduct in aqueous solution with potassium cyanide at 0 °C produced readily the biscyanohydrin, $C_6H_4[CH(OH)CN]_2$.

When the cyanohydrin was isolated and subjected to reaction with benzaldehyde in a purely organic medium (in the absence of water and salts) no apparent reaction took place. However, when the in situ generated terephthalaldehyde biscyanohydrin was added to a ten- to threefold excess of benzaldehyde at ~55–85 °C the desired reaction did occur as evidenced by the isolation of 1,4-bis(phenylglyoxyloyl)benzene in 35–73% yields after oxidation of the crude condensation product. The following procedure is representative.

Terephthalaldehyde biscyanohydrin was prepared from 10.0 g (0.0292 mol) of the sodium bisulfite adduct and the stoichiometric quantity of potassium cyanide. This aqueous solution (which contained the inorganic reaction by-products) was then added to stirred benzaldehyde (18.9 g, 0.178 mol) at 68 °C over a period of 10 min. Subsequently the reaction mixture was stirred at 68–70 °C for 2 hr. After cooling the semisolid mass was washed with water and the excess benzaldehyde was removed at reduced pressure at 88–100 °C. The residue (14.8 g) was dissolved in 80% acetic acid (140 ml) and heated with stirring at 101–105 °C together with ammonium nitrate (20 g, 0.2498 mol) and cupric acetate (0.2 g). On cooling yellow crystals (6.39 g, 64% yield), mp 116–119 °C, appeared. Crystallization from ethanol gave 5.74 g, 57% yield, mp 123.5–124.2 °C, of pure 1,4-bis(phenylglyoxyloyl)benzene as shown by mixture melting point (122.5–123.5 °C) with an authentic sample and comparison of the infrared spectra.

The bisbenzoin, $C_6H_5CH(OH)C(O)C_6H_4C(O)CH(OH)C_6H_5$, mp 230–233 °C (Anal. Calcd for $C_{22}H_{18}O_4$: C, 76.29; H, 5.24. Found: C, 75.98; H, 5.29.) was isolated in 46% yield by treatment of the semisolid mass (prior to oxidation) with benzene followed by crystallization from methanol.

The process in view of the presence of the preformed biscyanohydrin is believed to give the bisbenzoin isomer wherein the carbonyl groups are adjacent to the C_6H_4 moiety. The liberation of cyanide ion would be expected to promote self-condensation of the excess benzaldehyde to form benzoin, $C_6H_5CH(OH)COC_6H_5$; however, under the conditions employed this reaction occurred to only a very limited extent.



$$C_6H_4[CH(OH)SO_3Na]_2 \xrightarrow{KCN} C_6H_4[CH(OH)CN]_2 + 2NaKSO_3$$

$$\downarrow C_6H_5CHO$$

$$C_6H_4[\overset{O}{\overset{\|}{C}}-\underset{OH}{\overset{H}{C}}C_6H_5]_2 \xleftarrow{-HCN} C_6H_4[\underset{OH}{\overset{CN}{C}}-\underset{OH}{\overset{H}{C}}C_6H_5]_2$$

We currently are investigating the usefulness of this modified benzoin condensation for the synthesis of the isomeric bis(phenylglyoxyloyl)benzenes and of variously substituted derivatives.

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References and Notes

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