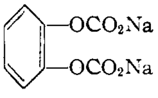
NOTES

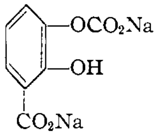
Preparation of 2,3-Dihydroxybenzoic Acid

By James Cason* and Guy Oren Dyke, Jr.

For use in study of bacterial metabolism,[1] a sample of 2,3-dihydroxybenzoic acid was required. A survey of the literature indicated that this is most easily prepared by a Kolbe type of reaction, and the procedure of Schmitt and Hähle[2] appears to give pure material most conveniently. According to these authors, the disodium salt of catechol reacts rapidly with carbon dioxide to give the carbonic acid derivative, I.



I



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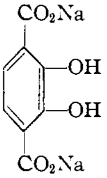

III

By heating the salt I under carbon dioxide pressure at 120–140°, there was obtained mono-rearrangement to II, which on acidification gave 2,3-dihydroxybenzoic acid. Di-rearrangement to III was reported as occurring at an appreciable rate only above 140°, with moderately rapid conversion to III at 210°.

When we carried out this rearrangement at 135°, starting with dry disodium catecholate as specified by Schmitt and Hähle, we recovered most of the starting catechol, no 2,3-dihydroxybenzoic acid, and a very small yield of 2,3-dihydroxyterephthalic acid. It later developed that mono-rearrangement occurred at 135° only when damp disodium catecholate was used; furthermore, di-rearrangement to III does not occur even at 210° if damp salt is used. With rigorously dried salt, no mono-rearranged product was ever isolated, and III was obtained slowly at 135°, more rapidly at 210°. Disodium catecholate is very hygroscopic, and it appears that the results obtained by Schmitt and Hähle were dependent on the dryness of their salt. The results obtained in some of our runs are assembled in Table I.

Although the literature[3] contains numerous references to the importance of dryness in the Kolbe reaction, in view of our results with disodium catecholate, we verified the importance of dryness using sodium phenolate. With carefully dried sodium phenolate, salicylic acid was readily obtained, whereas with damp sodium phenolate no salicylic acid could be isolated. It appears, then, that mono-rearrangement of salt I to give II proceeds by some other mechanism than that of the normal Kolbe reaction, and that water is necessary for this reaction, whereas absence of water is essential for the normal Kolbe reaction.

Table I

Preparation of 2,3-Dihydroxybenzoic Acid

Time heated, hr.	Temp., °C.	Condition[a] of di-sodium catecholate	2,3-Dihydroxybenzoic acid %	2,3-Dihydroxyterephthalic acid %
37	135	Dry	0	2.7
16	135	Dry[b]	0	0
23	135	Damp	36	0
40	135	Damp	56	0
43	145	Damp	58	0
5	210	Slightly damp	43.5	11.5
6	210	Damp	25	0
6	210	Dry	0	28.4

[a] Salt which had been dried at 100° and 20 mm. pressure for 2–3 hours, then ground in a mortar in air was termed "slightly damp." Such ground salt which was then dried at 100° and 20 mm. pressure for 24–48 hours was termed "dry." Such dry salt which had been allowed to absorb 10% of its weight of water, in a closed vessel, was termed "damp." [b] Since damp salt frequently darkened slightly from exposure to air, it was thought possible that the mono-rearrangement might be catalyzed by an oxidation product; so this sample was allowed to darken considerably in air.

Experimental

Data in Table I were obtained by the same general procedure as described below for preparation of 2,3-dihydroxybenzoic acid. The 2,3-dihydroxyterephthalic acid crystallized almost completely from dilute aqueous solution, while the 2,3-dihydroxybenzoic acid was obtained after concentration of the solution. In the first run described in Table I, much of the starting catechol was recovered by continuous ether extraction of the residual aqueous solution.

2,3-Dihydroxybenzoic Acid.—For preparation of disodium catecholate, commercial catechol was treated, in an atmosphere of nitrogen, with two equivalents of 6 *N* aqueous sodium hydroxide. Water was distilled in a vacuum, admitting nitrogen through the capillary, and the residue was heated for two to three hours at 100° at reduced pressure. The nearly colorless salt so obtained was ground briefly in a mortar, then dried at 100° and 20 mm. pressure for twenty-four to forty-eight hours, and finally placed in a closed vessel overnight with water equal to 10% of the weight of the salt. The water was absorbed.

Moist salt (5.1 g. dry weight) prepared as above was placed in a 105-cc. steel bomb and placed under 850 lb. p. s. i. of carbon dioxide pressure. After heating and shaking for forty hours at 135°, the contents of the cooled bomb were dissolved in about 100 cc. of water and acidified with concentrated hydrochloric acid (in runs in which 2,3-dihydroxyterephthalic acid was obtained; this product, melting with decomposition at about 270°, precipitated at this point). The acid solution was heated with charcoal, filtered, and concentrated to about 30 cc. There crystallized 2.85 g. (56%) of 2,3-dihydroxybenzoic acid, m. p. 203–205° (sintering at about 200°), and giving a

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[1] Experiments carried out by Dr. Roger Y. Stanier, Department of Bacteriology, University of California, Berkeley.

[2] Schmitt and Hähle, *J. prakt. Chem.*, [2] **44**, 2 (1891).

[3] For a typical procedure, see Fierz-David and Blangey, "Fundamental Processes of Dye Chemistry," Interscience Publishers, Inc., New York, N. Y., 1949, p. 154.

strong blue-black coloration with ferric chloride. Recrystallization from water yielded 2.35 g. of essentially the same m. p. Schmitt and Hähle[2] reported m. p. 204°.

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Reanalysis of the Electron Diffraction Data on $Be(BH_4)_2$ and $Al(BH_4)_3$

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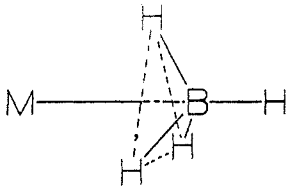
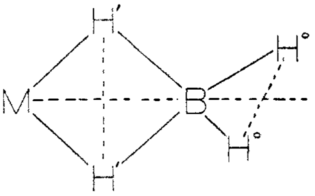
Some time ago electron diffraction data were presented in THIS JOURNAL for the borohydrides of aluminum[1] and beryllium.[2] These were interpreted as favoring structures of the type



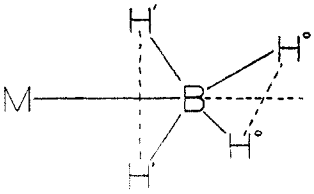
(α)

The symmetrical hydrogen bridge structures



(β)

were definitely eliminated. However, highly unsymmetrical bridges



(γ)

wherein the H' atoms are considerably closer to the boron than to the M atom, had not been considered. Since X-ray diffraction data indicate the presence of essentially tetrahedral BH_4^- ions in $LiBH_4$,[3] $NaBH_4$[4] and $U(BH_4)_4$,[5] we have reanalyzed the published electron diffraction results to check whether type γ structures are admissible. We found that when the ∠MBH' > 50°, and the MH' distances get to be about 0.3 Å. greater than the BH' distances, the computed patterns can no longer be distinguished from those of type α, within our rather large experimental error. The same conclusion, that is, that the bridge structures must be considerably unsymmetric in order to be compatible with the infrared data, has been reached by Dr. W. C. Price.[6]

Beryllium Borohydride.—Intensity curves were computed for the following sequence of type γ models. The interatomic distances common to all are:

Be-B 1.66 Å. ∠BBeB 180° ∠H°BH° 110°

I(α)	∠BeBH' [85°]	B-H' 1.19 Å.	Be-H' 1.87 Å.	B-H° 1.15 Å.
II	80	1.19	1.96	1.15
III	65	1.22	1.59	1.17
IV	50	1.26	1.29	1.20
V	47.5	1.28	1.23	1.22
VI	53	1.30	1.42	1.19

The last model (VI) is the one suggested by Dr. Price, with Be–B 1.73 Å. and ∠H°BH° 120°. Examination of the intensity curves clearly shows that the qualitative agreement between the computed and observed intensities is best for III; IV and V are definitely eliminated while I, II and VI are admissible. The quantitative agreement is best for model I (α), and gets poorer as the molecule is deformed to II, to III and to VI. It is possible that the quantitative agreement for III might have been better were the BeB/BeH' ratio made closer to 0.9, leaving the other distances as given above. Since the distant H–H terms contribute negligibly to the pattern, due to their relatively large temperature factors, one cannot tell from these diffraction data whether the bonds around the beryllium are quasi-square or quasi-tetrahedral; presumably, they are the latter.

We may now conclude that the available electron diffraction data are compatible with unsymmetric bridge models for $Be(BH_4)_2$ wherein: Be–B, 1.74 Å.; Be–H', 1.63; B–H', 1.28 Å.; B–H°, 1.22; ∠BeBH', 65°.

Aluminum Borohydride.—There are two types of unsymmetric bridge models possible for $Al(BH_4)_3$. The first group, designated by $\gamma_\perp$, are those in which the three planes including AlH'-H'B_i (i = 1,2,3) are perpendicular to the plane of $AlB_1B_2B_3$; the second, designated by $\gamma_\angle$, are those wherein these planes are inclined at 45° with respect to each other. In the former case, the H' atoms appear at the corners of a trigonal prism around the Al atom, while in the latter they form an octahedron. In both groups, the planes of H°B_iH° are perpendicular to those of B_iH'H'Al.

Models A · · · E are of the $\gamma_\perp$ type; the common distances are:

Al–B 2.14 Å. B-H' 1.28 Å. Al–H° 2.98 Å.
B–B 3.71 H°–H° 1.97 B–H° 1.20

A	∠AlBH' = 80°	Al–H' = 2.30 Å.	H'–H' = 2.52 Å.
B	65	1.98	2.32
C	50	1.64	1.96
D	45	1.42	1.65
E	53	1.74	2.06

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*Harvard University Postdoctoral Fellow 1949.

[1] J. Y. Beach and S. H. Bauer, THIS JOURNAL, **62**, 3440 (1940).

[2] G. Silbiger and S. H. Bauer, *ibid.*, **68**, 312 (1946).

[3] P. M. Harris and E. P. Meibohm, *ibid.*, **69**, 1231 (1947).

[4] A. M. Soldate, *ibid.*, **69**, 987 (1947).

[5] W. H. Zachariasen, private communication.

[6] W. C. Price, private communication, and W. C. Price, H. C. Longuet-Higgins, B. Rice and T. F. Young, *J. Chem. Phys.*, **17**, 217 (1949).