$\lambda_{\text{max.}}$ 250.0 mμ, log E_M 4.146 and $\lambda_{\text{max.}}$ 347.5 mμ, log E_M 4.014.

Acknowledgment.—I am indebted to Mr. G. Gever, of these Laboratories, for the supply of 3-furoic acid used in this synthesis, and to Mr. C. Piepoli for permission to use the data on the antibacterial activity, determined in the Bacteriology Division of Eaton Laboratories.

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Sodium Borohydride–Disodium Diborane

BY JOHN S. KASPER, LEWIS V. MCCARTY AND ARTHUR E. NEWKIRK

We have repeated the preparation of disodium diborane as described by Stock and Laudenklos,[1] and find that the resulting product yields an X-ray powder diffraction pattern identical to that given by them, and also identical with that for sodium borohydride as described by Soldate.[2] The other data reported for these two compounds are similar, and it seems probable that the compounds are the same and of the composition $NaBH_4$.

The disodium diborane was prepared by shaking a sodium amalgam in the presence of diborane gas and the course of the reaction was followed by observing the pressure decrease on a manometer attached to the system. As reported by Stock and Laudenklos, the reaction required several days to go to completion, and more diborane was absorbed than that required by the assumption of the simple reaction to form disodium diborane. At the end of ninety-six hours, however, the amalgam was still absorbing diborane. On plotting the logarithm of the pressure against the time a straight line was obtained for the first twenty-four hours. Mercury was distilled from the product of the reaction under vacuum, and the contents transferred in a dry box filled with nitrogen to a sublimer in which the remainder of the mercury was removed. The resulting residue was loaded into fine capillaries for the X-ray diffraction examination.

Using CuK_α radiation, the samples gave excellent patterns which checked completely the data for $NaBH_4$ reported by Soldate. It was evident that the same pattern (sodium chloride-type structure) was present in the photographs of Stock and Laudenklos for "$Na_2B_2H_6$", but, since no data were given by them for the X-ray work, it was necessary for us to measure these photographs. For "$Na_2B_2H_6$" the measured $\sin\theta$ values for all of 16 lines were in agreement, within experimental error, with our values obtained with CuK_α.

Assuming that all photographs given by Stock and Laudenklos are for CuK_α, the following tentative conclusions can be drawn:

(1) The corresponding potassium salts are isomorphous with the sodium compounds. For example, the compound reported as "$K_2(B_2H_6)$" appears then to be KBH_4, with an a_0 about 10% larger than that for $NaBH_4$.

(2) In addition to the BH_4^- salts, there appears to be another substance present among all the various products. The pattern for this material appears especially prominent in the diffraction patterns of "$K_2(B_4H_8)$" and "$K_2(B_5H_8)$."

(3) The sublimates of the various borane salts reported by Stock consist principally of $NaBH_4$ or KBH_4 with some of the unidentified substance as a separate phase.

In view of these findings, it seems to us that a reinvestigation of the reactions of alkali metals with boron hydrides and of the resulting products is called for.

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GENERAL ELECTRIC COMPANY
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[1] A. Stock and H. Laudenklos, *Z. anorg. allgem. Chem.*, **228**, 178 (1936).

[2] A. M. Soldate, THIS JOURNAL, **69**, 987 (1947).

Preparation of Ethyl β-(Bromomethyl)-cinnamate[1a]

BY ALLEN C. MOORE[1b]

The Wohl–Ziegler bromination,[2] which has been applied successfully to several β-alkyl substituted crotonic esters,[2,3,4] appeared to afford a method for the synthesis of β-(bromomethyl)-cinnamic esters. Since the methyl group in β-methylcinnamic ester is attached to a C–C double bond conjugated on either side with an unsaturated group, its bromination by N-bromosuccinimide would not be predicted[3] to occur with ease. Such was shown to be the case. Under the usual reaction conditions,[3] ethyl β-methylcinnamate did not react. Extension of the reaction period to forty-eight hours gave a 39% yield of crude brominated ester. However, addition of catalytic amounts of benzoyl peroxide[5] caused the reaction to occur smoothly, giving a 50% yield of ethyl β-(bromomethyl)-cinnamate in less than eight hours.

Preliminary experiments have indicated that the brominated ester does not react to any significant extent in Reformatsky-type condensations.[6]

Experimental

Ethyl β-methylcinnamate was prepared according to the method of Lindenbaum.[7]

[1a] This investigation was carried out under the sponsorship of the Office of Rubber Reserve, Reconstruction Finance Corporation, in connection with the Government Synthetic Rubber Program.

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[2] Djerassi, *Chem. Rev.*, **43**, 271 (1948).

[3] Ziegler, Späth, Schaaf, Schumann and Winkelmann, *Ann.*, **551**, 80 (1942).

[4] Campbell and Hunt, *J. Chem. Soc.*, 1176 (1947).

[5] Schmid and Karrer, *Helv. Chim. Acta*, **29**, 573 (1946).

[6] Ziegler, Schumann and Winkelmann, *Ann.*, **551**, 120 (1942).

[7] Lindenbaum, *Ber.*, **50**, 1270 (1917).

Ethyl β-(Bromomethyl)-cinnamate (A).—A solution of 36 g. (0.19 mole) of ethyl β-methylcinnamate, 36 g. (0.20 mole) of N-bromosuccinimide, and 10 cc. of carbon tetrachloride was heated on an oil-bath at 95-105° for forty-eight hours. At the conclusion of the heating period, the reaction mixture was diluted with carbon tetrachloride, chilled, and filtered to remove succinimide. The filtrate was shaken with water, dried over anhydrous magnesium sulfate, then fractionated through an 8-in. Vigreux column. There was thus obtained a 23-g. fraction boiling at 120-145° (1-5 mm.). Refractionation of this material gave 20 g. of an oil, boiling at 131-141° (1 mm.). A second refractionation gave an analytical sample boiling at 134-136° (1 mm.); $n^{20}\text{D}$ 1.5773.

Anal. Calcd. for $C_{12}H_{13}BrO_2$: C, 53.54; H, 4.87; Br, 29.70. Found: C, 53.17; H, 4.63; Br, 29.86.

(B).—A solution of 146 g. (0.77 mole) of ethyl β-methylcinnamate, 68.5 g. (0.39 mole) of N-bromosuccinimide, and 9.2 g. (0.04 mole) of benzoyl peroxide in 115 cc. of carbon tetrachloride was heated under reflux in an oil-bath for seven and three-fourths hours. The reaction mixture was chilled and the succinimide crystals removed on a filter, then washed once with hot carbon tetrachloride. The washings were chilled, filtered, and combined with the initial filtrate. This solution was washed thoroughly with saturated, aqueous sodium carbonate, separated, and dried over anhydrous magnesium sulfate. Fractionation under reduced pressure through a 6-in. Vigreux column gave 51 g. of an oil boiling at 142-154° (4-5 mm.), a yield of 50% of theoretical. Refractionation of this material gave 48 g. of a pale yellow oil boiling at 123-127° (0.4 mm.), indicating that the initial cut was essentially homogeneous. The refractive index at 20° of refractionated material boiling at 134-136° (1 mm.), was 1.5770.

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THE NOYES CHEMICAL LABORATORY
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Hydrodiethylstilbestrol Compounds. V. Reinvestigation of the Racemic Octahydro Compounds

BY HERBERT E. UNGNADE AND PAUL W. TUCKER[1,2,3]

A mixture of racemic octahydrodiethylstilbestrol compounds has been prepared by partial hydrogenation of diethylstilbestrol with Raney nickel catalyst.[4] The mixture consisted mainly of two crystalline substances (I) and (II) melting at 147-148° and 47-50°. There is some question about the identity of these substances since a third octahydro compound (III), m. p. 144-145°[4,5] has also been isolated in traces from the same reaction mixture. While this compound is not identical with the two known *meso* compounds,[6,7] it has not been possible to assign it definitely to either series since the hydrogenation of diethylstilbestrol yields traces of *meso* compounds along with the racemic isomers.[4] For this reason the racemic octahydro compounds have now been prepared from authentic *dl*-hexestrol monomethyl ether (IV) according to the method of Wilds and McCormack.[7,8]

A separation of the octahydro compounds can be effected by extraction of the mixture first with 5% aqueous potassium hydroxide solution and then with Claisen alkali.[7] The material obtained from the aqueous alkali extract can be crystallized and affords (III), m. p. 141-142°. The Claisen alkali extract yields a mixture of isomers, m. p. 47-50°, which cannot be separated by crystallization or sublimation similar to the "mixture I" of Ludutsky.[4,9] Chromatographic adsorption of the mixture, however, permits a direct separation to give (I), m. p. 146-147°, and (II), m. p. 47-50°.

It has thus been shown that (I), (II) and (III) belong to the racemic series. Compounds (I) and (III) are regarded as pure *trans*- and *cis*-isomers, (II) probably represents a mixture of these alcohols.[10]

Experimental[11]

***dl*-Hexestrol Monomethyl Ether (IV).**—*dl*-Hexestrol (41.87 g.) was methylated according to the procedure of Bretschneider.[12] The separation of the methylation products was analogous to the separation of the *meso*-isomers.[7] The monomethyl ether was extracted with benzene. The extract was washed until neutral and dried by distillation. The dry product (16.31 g.) crystallized on standing. It melted at 78-79° (from Skellysolve B).

Anal. Calcd. for $C_{19}H_{24}O_2$: C, 80.24; H, 8.51. Found: C, 80.44; H, 8.72.[13]

***cis* and *trans*-*dl*-*r*-3-(*p*-Hydroxyphenyl)-4-(4-hydroxycyclohexyl)-hexane.**—*dl*-Hexestrol monomethyl ether (16.31 g.), dissolved in 100 cc. of purified dioxane was reduced at 250° and 440 atm. of hydrogen with 4.5 g. of copper-chromium oxide catalyst as described by Wilds and McCormack.[7] The clear glassy product (15.39 g.) was refluxed for eight hours with 100 cc. of sodium methoxide solution containing 5 g. of sodium. Most of the methanol was distilled off. The residue was diluted with water and extracted with benzene. The benzene solution was washed and distilled. The residual product weighed 15.39 g. Part of the product (8.0 g.) was demethylated with methylmagnesium iodide according to Wilds and McCormack.[7] The ether solution obtained after decomposition of the Grignard reaction mixture was washed with four portions of 5% aqueous potassium hydroxide solution. Regeneration of the phenolic material from the washings yielded 1.50 g. of dark glassy material. The main product was extracted from the ether solution with Claisen alkali. It consisted of 3.91 g. of yellow glassy solid which melted

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(1) George Breon Fellow, 1946-1948.

(2) In part from the Ph.D. thesis of P. W. Tucker (1948).

(3) Present address: Research Department, Phillips Petroleum Company, Bartlesville, Okla.

(4) Ungnade and Ludutsky, THIS JOURNAL, **69**, 2629 (1947).

(5) Hoehn and Ungnade, *ibid.*, **67**, 1617 (1945).

(6) Ungnade and Tucker, *ibid.*, **70**, 4132 (1948).

(7) Wilds and McCormack, *ibid.*, **70**, 884, 4127 (1948).

(8) The authors are indebted to Dr. A. L. Wilds for advance information on his procedures.

(9) Mrs. Anna Pringle, present address, Rockefeller Institute, New York, N. Y.

(10) The present evidence does not permit to state with certainty which of the pure isomers is *cis* or *trans*.[7] The low melting mixtures (II) have been characterized previously by analyses, spectra and perhydrogenation.[4] The low melting points of (II) as compared to mixtures of the pure isomers are probably accounted for by polymorphism which has also been observed with other mixtures in this series. The glassy melts are very difficult to resolidify.

(11) All temperatures uncorrected.

(12) Bretschneider, Bretschneider and Ajtai, *Ber.*, **74**, 583 (1941).

(13) Semi-microanalysis by Karl Zilch.