(0.01 mole) of the acid I and the mixture was heated at reflux for 24 hours. After removal of the methanol by distillation, the residue was heated under reflux for 1.5 hours with 70 cc. of a 10% aqueous solution of potassium hydroxide. On cooling, the insoluble oil solidified, was removed by filtration, washed and dried. There was obtained 1.5 g. of crude **1,1-di-(*p*-chlorophenyl)-ethylene** (II), m.p. 80–85°, which on recrystallization from pentane gave colorless prisms, m.p. 84–86°.[6] A mixture of it with an authentic specimen of 1,1-di-(*p*-chlorophenyl)-ethylene[7] melted at 84–86°.

Anal. Calcd. for $C_{14}H_{10}Cl_2$: C, 67.49; H, 4.05. Found: C, 67.75; H, 4.27.

The alkaline filtrate was acidified with hydrochloric acid, cooled and the precipitated **di-(*p*-chlorophenyl)-acetic acid** (III) (1.0 g., m.p. 163–167°) was removed by filtration, washed and dried. Recrystallization from 95% ethanol gave the pure acid, m.p. 165–166°.

Anal. Calcd. for $C_{14}H_{10}Cl_2O_2$: C, 59.81; H, 3.59. Found: C, 59.74; H, 3.45.

When mixed with an authentic specimen of III[8] it produced no depression of melting point.

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[6] O. Grummitt, A. C. Buck and E. I. Becker, THIS JOURNAL, **67**, 2265 (1945), report m.p. 84–86°.

[7] Kindly supplied by Prof. Grummitt.

[8] O. Grummitt, A. C. Buck and R. Egan, *Org. Syntheses*, **26**, 21 (1946).

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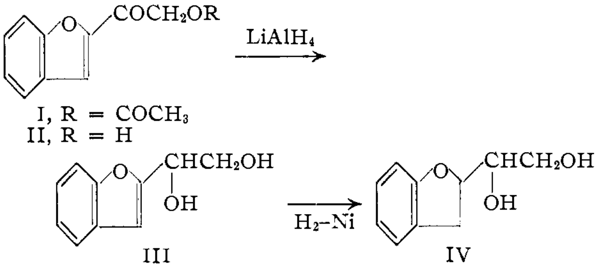
The Preparation of 2-(α,β-Dihydroxyethyl)-benzofuran and 2-(α,β-Dihydroxyethyl)-coumaran

BY HAROLD E. ZAUGG

RECEIVED JULY 6, 1954

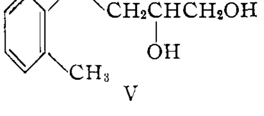
Shriner and Anderson[1] prepared ω-acetoxy-2-acetobenzofuran (I), but found that reduction of it either with sodium amalgam or with hydrogen in the presence of Adams catalyst resulted in cleavage to acetic acid and 2-acetobenzofuran. The present note reports the successful reduction of I with lithium aluminum hydride to 2-(α,β-dihydroxyethyl)-benzofuran (III), and further saturation of it by catalytic hydrogenation to 2-(α,β-dihydroxyethyl)-coumaran (IV), isolated as a mixture of diastereoisomers.



I, R = $COCH_3$
II, R = H

III IV

Compounds III and IV can be viewed as cyclized forms of the skeletal muscle relaxant, Mephenesin (V), formed by abstraction of hydrogen atoms from the *o*-methyl and α-methylene groups.



V

Both III and IV possess paralytic properties in mice; the activity of IV is comparable to that of V. In rabbits, however, IV is considerably less effective than Mephenesin.

As an incidental outcome of this work a by-product formed during the preparation of I was shown to be ω-hydroxy-2-acetobenzofuran (II) by its identity with an authentic sample prepared by treatment of ω-bromo-2-benzofuran with potassium formate.

Acknowledgment.—The author is indebted to Mr. Morris Freifelder for carrying out the catalytic hydrogenation, to Mr. E. F. Shelberg for the microanalyses, and to Dr. G. M. Everett for the pharmacological tests.

Experimental

2-(α,β-Dihydroxyethyl)-benzofuran (III).—To 2.7 g. (0.071 mole) of lithium aluminum hydride in 100 cc. of dry ether was added dropwise with stirring, a solution of 15.5 g. (0.071 mole) of ω-acetoxy-2-acetobenzofuran (I)[1] in 50 cc. of dry ether. The temperature was maintained below 10° until addition was complete, but the suspension was then stirred at room temperature for four hours. The mixture was decomposed by pouring carefully into ice containing an excess of hydrochloric acid. The ether was separated, washed with dilute sodium bicarbonate solution and dried over anhydrous magnesium sulfate. Filtration and removal of the ether by distillation gave 10.2 g. (82.5%) of product, m.p. 80–85°. Two recrystallizations from benzene gave 9.4 g. of III in the form of colorless leaflets, m.p. 87–88°.

Anal. Calcd. for $C_{10}H_{10}O_3$: C, 67.40; H, 5.66. Found: C, 67.48; H, 5.63.

2-(α,β-Dihydroxyethyl)-coumaran (IV).—A solution of 7 g. of III in 50 cc. of absolute ethanol was hydrogenated at 20 pounds initial pressure in the presence of 2.5 g. of Raney nickel. After filtration, and removal of the solvent by distillation, the residual oil was distilled *in vacuo* to give 4.6 g. (65%) of IV, b.p. 155–162° (1.5 mm.), $n^{25}D$ 1.5653. The product set to a semi-solid material which, after pressing between porous plates for several weeks, melted in the range 55–70°.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.72. Found: C, 66.65; H, 6.54.

The wide boiling and melting ranges of this material indicate that it is probably a mixture of diastereoisomers of IV.

ω-Hydroxy-2-acetobenzofuran (II).—A solution of 19.1 g. of ω-bromo-2-acetobenzofuran[1] in 400 cc. of 50% aqueous ethanol was refluxed for two hours with 26 g. of potassium formate and 2 cc. of concentrated hydrochloric acid. Pouring into ice, filtering and drying the resulting precipitate gave 12.6 g. of crude yellow product. A recrystallization from one liter of water followed by another from 50 cc. of 95% ethanol gave 5.9 g. of shiny colorless leaflets, m.p. 129–130°.

Anal. Calcd. for $C_{10}H_8O_3$: C, 68.18; H, 4.58. Found: C, 68.08; H, 4.53.

This product proved, by mixed melting point determination, to be identical with the by-product obtained in only 2% yield during the preparation of I by the method of Shriner and Anderson.[1]

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[1] R. L. Shriner and J. Anderson, THIS JOURNAL, **61**, 2705 (1939).

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The Bromination of Some N-Substituted Phthalimides with N-Bromosuccinimide

BY HAROLD E. ZAUGG

RECEIVED JULY 6, 1954

In 1898 Sachs[1] obtained N-bromomethylphthalimide in good yield by the high temperature (190°) bromination of N-methylphthalimide. However, N-ethylphthalimide, under the same conditions,

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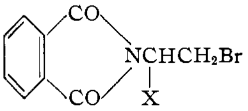
[1] F. Sachs, *Ber.*, **31**, 1225 (1898).

gave as sole product an N-tribromoethylphthalimide of undetermined structure.

The present note reports the peroxide-catalyzed reaction of N-(2-bromoethyl)-phthalimide (I) with N-bromosuccinimide in refluxing carbon tetrachloride to give the product of monobromination II in an 89% yield. The structure of II was established by analysis, by agreement of melting point with the known product prepared by addition of bromine to N-vinylphthalimide,[2] and by the fact that the product contains an active bromine atom which, conforming to expectation, reacts readily with ethanol at room temperature to give the corresponding ether III.



I, X = H
II, X = Br
III, X = OC_2H_5

Attempts to extend this bromination reaction to N-*n*-hexyl- and N-laurylphthalimides failed. Although consumption of the N-bromosuccinimide was complete under all conditions tried, mixtures of oils and low melting solids always resulted. That a non-specific substitution probably occurred throughout the length of the aliphatic chain was indicated by the fact that when N-ethylphthalimide was treated with N-bromosuccinimide, a low yield of the dibrominated product II could be isolated.

Acknowledgment.—The author is grateful to Mr. E. F. Shelberg for the microanalyses.

Experimental

Bromination of N-(2-Bromoethyl)-phthalimide (I). Preparation of N-(1,2-Dibromoethyl)-phthalimide (II).—To a solution of 12.7 g. (0.05 mole) of N-(2-bromoethyl)-phthalimide (I), m.p. 82–84°, in 50 cc. of dry carbon tetrachloride was added 8.9 g. (0.05 mole) of colorless N-bromosuccinimide and 0.5 g. of benzoyl peroxide. After stirring and heating under reflux for 15 minutes, another portion (0.5 g.) of benzoyl peroxide was added and the reaction was continued for an additional 2.5 hours. At the end of this time, the color of the mixture had changed from deep orange to light yellow and a positive test for active bromine (starch–potassium iodide paper) was no longer present. After cooling in ice for one hour, the crystallized product was removed by filtration, dried, suspended in water, collected once more at the filter, washed with more water and dried again. There was obtained 11.0 g. of N-(1,2-dibromoethyl)-phthalimide (II), m.p. 122–123°. Two recrystallizations of a sample from carbon tetrachloride gave colorless prisms, m.p. 123–124°.

Anal. Calcd. for $C_{10}H_7Br_2NO_2$: C, 36.07; H, 2.12; Br, 48.00. Found: C, 36.24; H, 2.15; Br, 47.98.

From the filtrate of the reaction mixture an additional 2.9 g. of II could be obtained, bringing the total yield to 13.9 g. (89.5%).

N-(2-Bromo-1-ethoxyethyl)-phthalimide (III).—A suspension of 1.60 g. of the dibromo compound II in 50 cc. of absolute ethanol was stirred at room temperature overnight. The resulting solution was allowed to stand for another 24 hours and then was treated with 2 g. of solid sodium bicarbonate. After stirring for an hour, the mixture was filtered through a layer of charcoal and the colorless filtrate was concentrated to dryness *in vacuo*. Recrystallization of the residue from 10 cc. of hexane gave 0.90 g. (63%) of III, m.p. 78–81°. Two more recrystallizations gave analytically pure product, m.p. 81.5–82.5°.

Anal. Calcd. for $C_{12}H_{12}BrNO_3$: C, 48.34; H, 4.06. Found: C, 48.56; H, 3.94.

Bromination of N-Ethylphthalimide.—A solution of 17.5 g. (0.1 mole) of N-ethylphthalimide, m.p. 76.5–78°, in 100 cc. of carbon tetrachloride was refluxed and stirred for four hours with a finely powdered mixture of 17.8 g. (0.1 mole) of N-bromosuccinimide and 2 g. of benzoyl peroxide. After cooling to room temperature, insoluble succinimide was removed by filtration and the filtrate was concentrated to a volume of about 40 cc. Cooling in ice and removing crystallized product by filtration, and isolating more product from the filtrate as described above for the bromination of I, yielded a total of 4.5 g. (27% yield, based on the N-bromosuccinimide) of N-(1,2-dibromoethyl)-phthalimide (II), m.p. 121–124°, identified by mixed melting point with a sample of II, m.p. 123–124°.

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[2] M. Bachstez, *Ber.*, **46**, 3087 (1913).

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

The Visible Adsorption Spectra of the Phase Test Intermediates of Chlorophyll-*a* and -*b*[1]

BY ALBERT WELLER[2]

RECEIVED JUNE 25, 1954

Accurate data on the visible absorption spectra of the phase test intermediates of chlorophyll-*a* and -*b* in pyridine have been obtained using a static system. The chlorophyll-*a* intermediate has a comparatively weak long wave length absorption band at 6830 Å., the major maximum at 5240 Å. and three others of comparable strength at 4860, 4280 and 3750 Å. The major maximum of the compound derived from chlorophyll-*b* is at 5580 Å. with two shoulders; one around 5600 Å. and the other around 5050 Å. Another maximum is at 4440 Å. and a very weak long wave length absorption band at 6300 Å. It is suggested that the intermediate compound is an ionized diradical formed by separation of the two electrons which are left after the acid ionization of the CH– group in position 10 of ring V.

The spectrum of the brownish colored intermediate which appears in the Molisch phase test[3] is of interest because of its relation to the reaction of chlorophyll with strong bases. An attempt to measure this spectrum in ethereal solution was made by Livingston and his co-workers,[4] using a flow system. More accurate results which are obtained with pyridine solutions, using a static system, are reported here.

It has been demonstrated by Conant and his

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[1] This work was made possible by the support of the Office of Naval Research (NR 051,028, Contract N 6ori-212.T.O.I) to whom the author is indebted.

[2] Post-doctoral Fellow 1951–1952 at the University of Minnesota. Present address: Laboratorium für physikalische Chemie, Wiederholdstr. 15, Stuttgart, Germany.

[3] H. Molisch, *Ber., dtsch. bot. Ges.*, **14**, 16 (1896).

[4] B. Dunicz, T. Thomas, M. van Pee and R. Livingston, THIS JOURNAL, **73**, 3388 (1951).