called[6] that DDT and its analogs react with Grignard compounds to give substances of the formulas: $(RC_6H_4)_2CHCHCl_2$, $(RC_6H_4)_2CHCCl{=}CClCH(C_6H_4R)_2$ and $(RC_6H_4)_2CHCH{=}CHCH(C_6H_4R)_2$. Although we have not succeeded in elucidating the fate of the trichloroacetate molecule, the following conclusions can be drawn from the experimental material. In the reaction of I with phenylmagnesium bromide, all of the chloride ion and of the biphenyl must derive from an interaction of the Grignard compound with $(ROOCCCl_2)^-MgBr^+$. In the other two cases, both this type of reaction can occur, but equally a direct interaction of the Grignard compound with I, *e.g.*, according to the equation

$$ROOCCCl_3 + 2ArMgBr \longrightarrow ArAr + (ROOCCCl_2)^-MgBr^+ + MgBrCl$$

In all three instances, for each mole of biaryl isolated, approximately three equivalents of chloride ion are found.

The reductive dehalogenation of trichloroacetic acid has been observed in other reactions.[7,8]

It is interesting that according to Pepper and Kulka[9] *p*,ω,ω,ω-tetrachloroacetophenone and *p*-chlorophenylmagnesium bromide give *p*,ω,ω-trichloroacetophenone. It could be shown that also in the reaction between ω-trichloroacetophenone and phenylmagnesium bromide (4 moles per mole), 43% of the chlorine reappears in the form of chloride ions; apart from biphenyl (1.7 moles per mole ketone), no defined organic material could, however, be isolated in this case.

In contradistinction to I, ethyl trifluoroacetate reacts normally with Grignard compounds. This reaction will be described in a forthcoming communication.

Experimental

Ethyl trichloroacetate (I) had b.p. 167°, $n^{20}D$ 1.4505. **ω-Trichloroacetophenone**, b.p. 254–255°, was prepared from trichloroacetyl chloride and benzene[10] and ***p*-chlorobromobenzene**, m.p. 67°, according to Mouneyrat and Pouret.[11]

General Procedure.—A quantity of 0.1 mole of ethyl trichloroacetate (or trichloroacetophenone) and 0.4 mole of the Grignard compound in ether was employed. The second component was added at 0° to the Grignard solution and the reaction completed by refluxing for 90 minutes. (In one experiment, the mixture was kept at 0° for 12 hours, but the result was the same.) The product was decomposed with ice-cold distilled water and dilute sulfuric acid. In the aqueous layer, chloride ion was determined in the usual manner. The ethereal layer was washed with 5% sodium carbonate solution, dried and concentrated and the residue subjected to fractional distillation.

Reaction of I with Phenylmagnesium Bromide.—In two experiments, 11.3 and 10.0 g. of chlorobenzene was isolated (0.1 and 0.09 mole, respectively); b.p. 132°, d^{28}_4 1.104, $n^{20}D$ 0.5252. The quantities of biphenyl were 5.7 g. (0.037 mole) and 8.0 g. (0.050 mole), respectively. Thirty-five and thirty-seven per cent. of the total chlorine of I were found in the aqueous layer.

Reaction of I with *p*-Tolylmagnesium Bromide.—*p*-Chlorotoluene (7.5 g., 0.06 mole) was identified by permanganate oxidation to *p*-chlorobenzoic acid, m.p. 238°; **4,4′-dimethylbiphenyl** (11.0 g., 0.076 mole) by melting point (120°) and mixed m.p. Eighty per cent. of the total chlorine of I was recovered in the aqueous layer.

Reaction of I with *p*-Chlorophenylmagnesium Bromide.—Both ***p*-dichlorobenzene** (2.5 g., 0.017 mole) and **4,4′-dichlorobiphenyl** (9.0 g., 0.04 mole) were identified by m.p. (52–53°, 146–147°) and comparison with authentic specimens. Seventy-five per cent. of the total chlorine had been converted into ionic form.

Reaction of I with Phenyllithium.—The reaction between I (0.05 mole) and phenyllithium (0.2 mole, 31.5 g. of bromobenzene and 2.8 g. of lithium) was carried out as described above, but in an atmosphere of nitrogen. The products obtained were: chlorobenzene (6.3 g., 0.06 mole); biphenyl (2.5 g., 0.016 mole) and chloride ion (31% of the total chlorine in the quantity of the ester employed).

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[6] W. Awe and J. Reinecke, *Experientia*, **6**, 185 (1950).

[7] H. W. Doughty and D. A. Lacoss, THIS JOURNAL, **51**, 853 (1929).

[8] Rathke, *Ann.*, **161**, 166 (1872).

[9] J. M. Pepper and M. Kulka, THIS JOURNAL, **72**, 1417 (1950).

[10] H. Biltz, *J. prakt. Chem.*, [2] **142**, 196 (1937).

[11] A. Mouneyrat and Ch. Pouret, *Bull. soc. chim. France*, **19**, 801 (1898).

2,3-Bis-(*p*-aminophenyl)-2,3-butanediol

BY NELSON J. LEONARD, SHERLOCK SWANN, JR., AND GLENN FULLER

RECEIVED JUNE 10, 1953

Because of increasing interest in 2,3-bis-(*p*-aminophenyl)-2,3-butanediol (I)[1] as an immediate precursor of compounds having pronounced physiological activity,[2] we wished to provide a method for the synthesis of I by the electrolytic reduction of *p*-aminoacetophenone which would require only readily available apparatus. The electrolytic reduction has been carried out under the following conditions to give acceptable yields of 2,3-bis-(*p*-aminophenyl)-2,3-butanediol dihydrochloride (55–59%): the cathode used was tin,[3] the anode, platinum,[4] both anolyte and catholyte were 1.6 *N* hydrochloric acid, the temperature was maintained at 24–30°, and the initial cathode current density was in the range 0.01–0.02 amp. per cm.².

Experimental

Electrolytic Reduction of *p*-Aminoacetophenone.—The tin cathode (of 99.9% purity or better), with a surface area of 100 cm.², was cast in a graphite mold initially at a temperature of 70°. It was prepared prior to use by the customary procedure.[5] The anode was of smooth platinum. A porous alundum diaphragm was first cleaned in 20% nitric acid, soaked in 20% aqueous sodium silicate, then in 20% sulfuric acid and finally in 20% hydrochloric acid.[5] The catholyte was prepared by dissolving 13.5 g. (0.1 mole) of *p*-aminoacetophenone (Eastman Kodak Co. material recrystallized) in 100 ml. of 1.6 *N* hydrochloric acid. The anolyte was 1.6 *N* hydrochloric acid. The electrolysis cell was assembled in the usual manner,[5] and stirring was effected by a magnetic stirrer. The line potential was 6 v. The temperature of the cell was maintained at 24–30° while a current of 1 amp. was allowed to flow through the solution (100 ml. of 1 *M* *p*-aminoacetophenone hydrochloride). The initial cathode current density was therefore 0.01 amp. per cm.². During the course of the reduction, the current diminished to 0.84 amp. after 4 hours. Approximately 1.5 l. of hydrogen was evolved, the rate of evolution increasing toward the end of the reaction. After 5.3 hours

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[1] M. J. Allen and A. H. Corwin, THIS JOURNAL, **72**, 114 (1950).

[2] *E.g.*, Amphenone "B": A. E. Heming, D. E. Holtkamp, J. F. Kerwin, L. F. Mansor and J. G. Dacanay, *Proc. Soc. Exptl. Biol. Med.*, **80**, 154 (1952).

[3] S. Swann, Jr., P. E. Ambrose, R. C. Dale, R. C. Rowe, H. M. Ward, H. D. Kerfman and S. Axelrod, *Trans. Electrochem. Soc.*, **85**, 231 (1944).

[4] Past experience indicates that an anode of carbon or graphite would be equally satisfactory.

[5] S. Swann, Jr., "Electrolytic Reductions" in A. Weissberger, editor, "Technique of Organic Reactions," Vol. II, Interscience Publishers, Inc., New York, N. Y., 1948.

(twice the time theoretically required), the electrodes were removed and the catholyte and washings were collected. The isolation of the 2,3-bis-(*p*-aminophenyl)-2,3-butanediol dihydrochloride was accomplished by the method of Allen and Corwin,[1] with the exception that the temperature was kept under 50° (rather than 25°) in the evaporation of the final catholyte solution *in vacuo;* yield 10.2 g. (59%) of yellow-brown solid which decomposed slowly above 230°.

2,3-Bis-(*p*-aminophenyl)-2,3-butanediol.—Saturated aqueous potassium carbonate solution was added to a solution of 51.5 g. of the pinacol dihydrochloride in 300 ml. of water until the mixture was strongly alkaline. The solid precipitate was filtered and treated with hot acetone. The 2,3-bis-(*p*-aminophenyl)-2,3-butanediol separated from acetone as faintly yellow platelets, m.p. 239–242° dec. (reported[1] 248–249°), of analytical purity; yield 16.3 g. (40%).

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The Preparation of Samarium Metal[1]

BY E. I. ONSTOTT

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In a recent communication to the editor, Daane, Dennison and Spedding[2] described the preparation of samarium metal of at least 98% purity by reaction of samarium oxide with lanthanum metal. They also mentioned that barium had been tried as a reductant with little success. In this Laboratory relatively pure samarium metal has been produced by reaction of barium with anhydrous samarium(III) bromide. The reaction is carried out in a tantalum crucible[3] in an argon atmosphere by heating the mixture to a temperature of 1650–1700° for a period of about 20 minutes. During this heating period the samarium metal is collected in the bottom of the crucible and the excess barium is distilled out. The yield of metal is about 10 g. or 50% for a 50-g. batch of bromide. This technique of heating the charge to a high temperature to facilitate separation of the metal in the massive state has been used previously by Spedding, *et al.*, in the preparation of other rare earth metals.[4]

The purity of samarium metal prepared in this manner is believed to be greater than 99.5%. Spectrographic analysis showed the metal to contain: Li, Na, Mg, Ca, Mn, Fe, Cu, each less than 0.001%; Ba, Si, Sn, each less than 0,01%; Bi, 0.001–0.1%. Europium content was about 0.08%, since the samarium oxide used to make the anhydrous bromide contained this amount of europium oxide, as determined by a combination of gravimetric, colorimetric[5] and tracer analysis. No other rare earths were detected by spectrographic analysis. The samarium oxide as received from the Société de Produits Chimique des Terres Rares contained 1.5% calcium and 1.5% europium oxide. Purification was made by two electrolyses according to the method of McCoy,[6] followed by two oxalate precipitations and ignition to the oxide.

An experiment in this Laboratory confirms the report of Daane, Dennison and Spedding[2] that samarium metal is relatively volatile. When recasting samarium metal at about 1700° in an atmosphere of argon, approximately 1 g. of metal distilled to the lid of the crucible in a period of 5–10 minutes.

The density of three samples of samarium metal was determined by weighing in air, then weighing while suspended in acetylene tetrabromide. Density data are as follows: massive metal as made, 7.499 g./cc.; recast metal, 7.509 g./cc.; distilled metal, 7.495 g./cc. Accuracy of these data, which compare favorably to the value of 7.53 g./cc. obtained by Daane, Dennison and Spedding,[2] is believed to be ±0.005 g./cc.

Acknowledgment.—Some of the analyses were performed by Richard Wilhelm, O. R. Simi and F. H. Ellinger. Valuable suggestions were made by Dr. Henry Taube, Dr. E. R. Jette, Dr. R. D Fowler and Dr. R. P. Hammond.

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[1] This work is a contribution from the Chemical and Metallurgical Research Division of the Los Alamos Scientific Laboratory, Los Alamos, New Mexico, under the auspices of the Atomic Energy Commission.

[2] A. H. Daane, D. H. Dennison and F. H. Spedding, THIS JOURNAL, **75**, 2272 (1953).

[3] A. H. Daane, *Rev. Sci. Instruments*, **23**, 245 (1952).

[4] F. H. Spedding and A. H. Daane, THIS JOURNAL, **74**, 2783 (1952).

[5] T. Moeller and J. C. Brantley, *Anal. Chem.*, **22**, 433 (1950).

[6] H. N. McCoy, THIS JOURNAL, **63**, 3432 (1941).

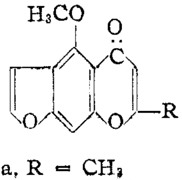
Furochromones and -Coumarins. VIII. Action of Hydrazine Hydrate and Hydroxylamine on Khellin, Khellol and Visnagin

BY ALEXANDER SCHÖNBERG AND MAHMOUD MOHAMED SIDKY

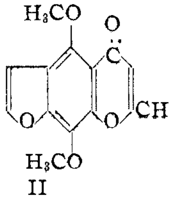
RECEIVED APRIL 10, 1953

The action of hydrazine hydrate on 2-methylchromone has been studied by Koenigs and Freund,[1] and on chromone itself by Baker, Harborne and Ollis.[2] Both groups of researches agree that the reaction products are pyrazole derivatives and not hydrazones of the chromones in question as previously believed. In the case of chromone itself, the product is 5(3)-*o*-hydroxyphenylpyrazole (IIId or IVd).

We have investigated the action of hydrazine hydrate on visnagin (Ia), khellol (Ib) and khellin (II), and believe that the reaction products are the pyrazole derivatives IIIa, IIIb and IIIc or IVa, IVb and IVc, respectively.



Ia, R = CH_3
Ib, R = CH_2OH



II

These substances are soluble in aqueous alkali, and their alcoholic solutions give a blue color with aqueous ferric chloride solution, and with titanium chloride a deep orange color is developed. From IIIa and IIIc—each containing one active hydrogen in the phenolic hydroxy group and one active hydrogen atom attached to a nitrogen atom—dibenzoyl derivatives were obtained when they were treated with benzoyl chloride (Schotten–Baumann).

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[1] E. Koenigs and J. Freund, *Ber.*, **80**, 143 (1947).

[2] W. Baker, J. B. Harborne and W. D. Ollis, *J. Chem. Soc.*, 1303 (1952).