Assuming that the ratio of the values of the solubility product and instability constants for the cobaltous hydroxide and hydroxy–cobalt complex ion, respectively, remain constant over the range of hydroxyl ion concentration involved, we may plot the logarithm of the absorbancy *versus* the logarithm of the hydroxyl ion activity. Hydroxyl ion activities[8] are used instead of molar concentrations because of the high concentrations used. We should obtain a straight line whose slope is $(n - 2)$, where n is the number of hydroxyl ions complexing the cobaltous ion to form the light-absorbing ion species in strongly alkaline solutions.

The data for the determination of $(n - 2)$ are presented in Fig. 4. The straight lines for the values at the two absorption peaks of 535 and 585 mμ were drawn from the equations determined by the method of least squares for the concentration range of 5 to 5 *M*. The corresponding slopes, which are both equal to 1.24, yield a value of 3.24 for n, the number of hydroxyl ions in the coördination sphere of the hydroxy-cobalt(II) complex ion. Above 5 *M* hydroxyl ion concentration the straight line veers off and forms another straight line which was similarly treated by the method of least squares. The values for their slopes were found to be 0.784 and 0.774, at 535 and 585 mμ, respectively. These values for $(n - 2)$ resulted in n being equal to 2.78 and 2.77, respectively. Again, they are approximately equal to a hydroxyl ion coördination value of three for the complex. Considering the ionic strengths and activities of these strongly alkaline solutions and their consequent departures from ideality, the experimentally determined value is indicative of the existence of the trihydroxy-cobalt(II) complex ion in the alkali hydroxide solutions.

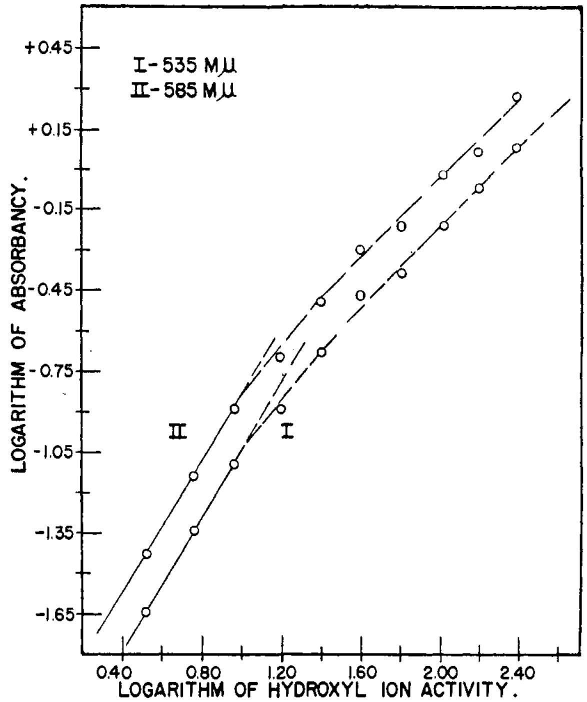

Fig. 4.—Logarithm of absorbancy as a function of hydroxyl ion activity in potassium hydroxide solutions saturated with cobalt(II); 1.00 cm. cells; 0.020 mm., slit width; 25°.

The reaction for the formation of this complex ion may be represented by the equation

$$Co(H_2O)_6^{++} + 3OH^- \rightleftarrows Co(OH)_3(H_2O)_3^- + 3H_2O$$

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[8] R. A. Robinson and R. H. Stokes, *Trans. Faraday Soc.*, **45**, 612 (1949).

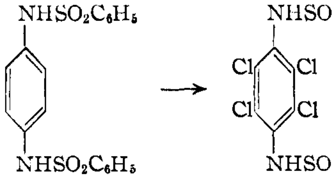
NOTES

Chlorination of Benzenesulfonyl Derivatives of Aromatic Amines

BY ROGER ADAMS AND B. H. BRAUN[1]

RECEIVED JANUARY 14, 1952

Chlorination of *p*-phenylenedibenzenesulfonamide (I) in nitrobenzene by means of chlorine resulted in the formation of a mixture of dichloro derivatives. The tetrachloro derivative (II), which was desired, has been prepared previously by the rather tedious route of successive oxidations and additions of hydrogen chloride to *p*-phenylenedibenzenesulfonamide.[2] By use of the solvent, dimethylformamide, the synthesis of the tetrachloro derivative (II) was readily achieved in a one step chlorination. This solvent is itself chlorinated with an exothermic reaction, but by keeping the reaction mixture below 60° through regulation of the flow of chlorine, the tetrachloro compound resulted in good yield. The amount of chlorine used was a critical factor and was determined empirically. Too large an excess of chlorine failed to give the compound desired.



I II

In a similar manner, several other polychlorinated

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[1] An abstract of a portion of a thesis submitted by Mr. B. H. Braun to the Graduate College of the University of Illinois, 1952, in partial fulfillment of the requirements of the Degree of Doctor of Philosophy.

[2] R. Adams, E. F. Elslager and K. F. Heumann, THIS JOURNAL, **74**, 2608 (1952).

products were synthesized which were not accessible by chlorination in customary solvents; 2-methyl-3,5,6-trichloro-*p*-phenylenedibenzenesulfonamide from 2-methyl-*p*-phenylenedibenzenesulfonamide; 3,4,5,6-tetrachloro-*o*-phenylenedibenzenesulfonamide from *o*-phenylenedibenzenesulfonamide; 4-methyl-3,5,6-trichloro-*o*-phenylenedibenzenesulfonamide from 4-methyl-*o*-phenylenedibenzenesulfonamide. The ortho compounds react less vigorously than the para and a larger excess of chlorine is required.

When the benzenesulfonyl derivative of aniline was chlorinated in nitrobenzene, the product was the benzenesulfonyl derivative of 2,4-dichloroaniline. With dimethylformamide as solvent, however, the 2,4,6-trichloro compound resulted.

The dibenzenesulfonyl derivative of 3,3'-dichlorobenzidine was also chlorinated in dimethylformamide to the 3,3',5,5'-tetrachloro derivative when the use of other solvents failed. This is reported in another[2a] communication.

Experimental

All melting points are corrected.

Chlorination of Benzenesulfonanilide in Nitrobenzene: 1-Benzenesulfonamido-2,4-dichlorobenzene.—Into a solution of 10 g. of benzenesulfonanilide in 50 ml. of nitrobenzene (induced by prolonged agitation) a vigorous stream of chlorine was passed. The solution rapidly became warm and the flow of chlorine was regulated so that the temperature of the reaction mixture did not rise over 60°. After 15 minutes, the temperature dropped and did not rise even on increasing the rate of addition of chlorine. The gain in weight at this point was 5.7 g. The solvent was removed by steam distillation and the resulting heavy brown oil solidified on cooling. After one crystallization from 95% ethanol, 11.1 g. (86%) of pale brown crystals resulted. By recrystallization from the same solvent white needles were formed, m.p. 127–128° (lit. m.p. 128°).[3]

By heating 2.75 g. of the product with 10 ml. of concentrated sulfuric acid to 105–110° for 45 minutes, hydrolysis occurred. After pouring the reaction mixture into 100 ml. of water, the solution was basified with aqueous ammonia. The amine which separated was taken up in two 50-ml. portions of ether, the ether layers were combined, dried over potassium hydroxide, and the solvent distilled. The oily residue was dissolved in petroleum ether (b.p. 80–110°) and after partial evaporation and cooling, crystals formed. The balance of the solvent was removed at room temperature by an air stream. The yield of 2,4-dichloroaniline was 1.40 g. (93%) of product which on recrystallization from petroleum ether melted at 62.5–63° (lit. m.p. 63°).[4]

Chlorination of Benzenesulfonanilide in Dimethylformamide: 1-Benzenesulfonamido-2,4,6-trichlorobenzene.—Into a solution of 10 g. of benzenesulfonanilide in 40 ml. of dimethylformamide, chlorine was passed until the gain in weight was 16.3 g. The temperature of the reaction mixture was maintained below 60°. The mixture was poured into water, filtered, and the precipitate recrystallized from glacial acetic acid. The yield was 11.5 g. of needles and dilution of the mother liquor with water gave an additional 1.0 g. The total yield was 12.5 g. (85%). Three recrystallizations from glacial acetic acid gave a pure product, m.p. 152–154°.

Anal. Calcd. for $C_{12}H_8Cl_3NO_2S$: C, 42.81; H, 2.39; N, 4.16. Found: C, 43.08; H, 2.61; N, 4.26.

After heating 1.00 g. with 7 ml. of concentrated sulfuric acid to 110–115° for one hour, the solution was cooled and poured into water. The 2,4,6-trichloroaniline, weighing 0.55 g. (94%), precipitated. It was purified by crystallization from petroleum ether (b.p. 80–110°), m.p. 77.5–78° (lit. m.p. 78.5°).[5]

Chlorination of *p*-Phenylenedibenzenesulfonamide in Various Solvents: Acetic Acid.—No exothermic reaction occurred on passing chlorine into a glacial acetic acid solution of the *p*-phenylenedibenzenesulfonamide at 70°. Only low melting mixtures were isolated which obviously were lower chlorinated products.

Nitrobenzene: 2,5- and 2,3-Dichloro-*p*-phenylenedibenzenesulfonamide.—Into a suspension of 50 g. of *p*-phenylenedibenzenesulfonamide in 200 ml. of nitrobenzene containing a catalytic amount of ferric chloride, chlorine was passed with vigorous stirring at such a rate that the temperature was held between 52–56°. After 80 minutes the temperature dropped and did not rise even on increasing the rate of addition of chlorine. Addition of 200 ml. of carbon tetrachloride caused precipitation of 43.6 g. (74%) of almost white crystals which sintered at 173° and melted with much decomposition above 182°. A small portion was recrystallized from glacial acetic acid and then melted with only slight darkening at 187–229.5°, after sintering at 172°. This sample was submitted for infrared analysis which indicated it to be a mixture of 2,5- and 2,3-dichloro-*p*-phenylenedibenzenesulfonamide by comparison with a similar mixture which had been prepared previously in this Laboratory by another route.[2]

Dimethylformamide: 2,3,5,6-Tetrachloro-*p*-phenylenedibenzenesulfonamide.—Into a solution of 50 g. of *p*-phenylenedibenzenesulfonamide in 200 ml. of dimethylformamide, chlorine was passed at such a rate that the temperature did not rise above 60° until the gain in weight of the reaction mixture was 32.2 g. After pouring into water, the precipitate that separated was filtered by suction, then dissolved in the minimum amount of dimethylformamide at 100° (about 500 ml. was required). The color of the solution became a deep violet with a red fluorescence. Upon addition with stirring of 1 liter of hot acetic acid to the hot solution, white needles started to separate. After cooling, the precipitate weighed 46.5 g. (68%). From the mother liquors by dilution with water an additional 4 g. resulted. The product had an m.p. 278–281° (dec.) (lit. m.p. 273–274°).[2] This melting point with decomposition varies with rate of heating. By four additional recrystallizations from nitrobenzene, the product darkened at 303° and melted at 309–310° (dec.). For oxidation to the diimide, the product, m.p. 278–281°, is entirely satisfactory.

Use of less chlorine usually resulted in a mixture of tri- and tetrachloro derivatives. If saturated with chlorine, no solid products could be obtained from the reaction mixture. The use of a temperature of from 30 to 60° gave the same results, but at 80° a vigorous reaction occurred after which no solid products could be obtained. Ferric chloride was added in several chlorinations, but the yields were unaffected.

Chlorination of 2-Methyl-*p*-phenylenedibenzenesulfonamide: 2-Methyl-3,5,6-trichloro-*p*-phenylenedibenzenesulfonamide.—Into a solution of 10 g. of 2-methyl-*p*-phenylenedibenzenesulfonamide in 40 ml. of dimethylformamide, chlorine was passed at such a rate that the temperature was maintained below 60° until the gain in weight of the reaction mixture was 6.2 g. The product was isolated as previously described and once crystallized from dimethylformamide and glacial acetic acid. The yield was 8.5 g. (68%), m.p. 273–274° (dec.) (lit. m.p. 270–271°).[2] The melting point was unchanged after a second similar crystallization, but after four recrystallizations from nitrobenzene, the product darkened at 284° and melted at 292–293° (dec.). The infrared spectra of the crude sample, m.p. 273–274°, and of that recrystallized from nitrobenzene were identical. However, a sample of material made by another route with m.p. 270–271°,[2] had an extra band at 1027 cm.$^{-1}$. This disappeared after recrystallization from nitrobenzene which raised the melting point to that reported in this investigation.

Chlorination of *o*-Phenylenedibenzenesulfonamide: 3,4-5,6-Tetrachloro-*o*-phenylenedibenzenesulfonamide.—A solution of 5 g. of *o*-phenylenedibenzenesulfonamide in 20 ml. of dimethylformamide was cooled and chlorine passed in, keeping the temperature below 40°. After the gain in weight of the reaction mixture was 6.3 g., it was poured into water. A dark red oil separated which slowly turned pale and crystallized overnight. It was recrystallized by dissolving in a minimum of hot dimethylformamide and addition of twice the volume of hot glacial acetic acid. The yield was 4.8 g. (71%). An additional 1.2 g. (17%) was

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(2a) R. Adams and R. R. Holmes, *ibid.*, **74**, 3033 (1951).

(3) F. D. Chattaway, *J. Chem. Soc.*, **85**, 1181 (1904).

(4) F. Beilstein and A. Kurbatow, *Ann.*, **182**, 94 (1876).

(5) P. J. Montagne, *Rec. trav. chim.*, **21**, 376 (1902).

obtained after dilution of the mother liquor with water. After two recrystallizations from glacial acetic acid the product melted at 231–232° (lit. m.p. 230–231°).[6]

Chlorination of 4-Methyl-*o*-phenylenedibenzenesulfonamide: 4-Methyl-3,5,6-trichloro-*o*-phenylenedibenzenesulfonamide.—Into a solution of 10 g. of 4-methyl-*o*-phenylenedibenzenesulfonamide in 40 ml. of dimethylformamide, chlorine was passed until the reaction mixture had gained 9.5 g. in weight, keeping the temperature below 50°. The mixture was worked up as described for the methyl-free product. The yield was 7.8 g. (62%). A sample was recrystallized for analysis from glacial acetic acid; white microcrystalline powder, m.p. 237–238°.

Anal. Calcd. for $C_{19}H_{15}Cl_3N_2O_4S_2$: C, 45.12; H, 2.95; N, 5.54. Found: C, 45.36; H, 3.20; N, 5.53.

Acknowledgment.—The authors are indebted to Miss Emily Davis, Mrs. Jean Fortney and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas and Miss Elizabeth Petersen for the infrared spectra determinations.

(6) R. Adams and C. N. Winnick, This Journal, **73**, 5687 (1951).

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Preparation and Hydrolysis of Optically Active 2-Butyl Acetal

By Elliot R. Alexander,[1] Hirsh M. Busch[2] and George L. Webster

Received February 11, 1952

O'Gorman and Lucas[3] have recently shown that hydrolysis with 5% aqueous phosphoric acid of D-(+)-2-octyl acetal leads to totally unracemized D-(+)-2-octanol. They concluded that the reaction does not proceed through a secondary octyl carbonium ion.

We have confirmed their conclusions using D-(+)-2-butyl acetal from D-(+)-2-butyl orthoformate.[4] The hydrolysis of this acetal to D-(+)-2-butanol gives alcohol of the same specific rotation as that used initially. It is, therefore, probable that none of the reactions employed in this cycle involves cleavage of the oxygen–butyl bond and that no secondary butyl carbonium intermediate is involved.

Experimental[5]

D-(+)-2-Butanol.—2-Butanol, Eastman Kodak Company White Label, was resolved by the method of Pickard and Kenyon[6] according to the modification of Sprung and Wallis[7] and had an observed rotation of +7.98 ± 0.02° in a one-decimeter tube at 25°.

D-(+)-2-Butyl Orthoformate.—The preparation of D-(+)-2-butyl orthoformate, $[\alpha]^{25}_D$ +27.07 ± 0.02° (*l* 1, no solvent), was carried out as described by Alexander and Busch.[4]

D-(+)-2-Butyl Acetal.—To 24.0 g. (0.103 mole) of D-(+)-2-butyl orthoformate, 2.0 g. (0.025 mole) of granulated ammonium nitrate and 6.0 ml. of D-(+)-2-butanol was added 15.0 g. (0.34 mole) of freshly prepared acetaldehyde. After the mixture was refluxed for 90 minutes, 150 ml. of ether was added to the cooled solution. It was then washed with aqueous ammonium hydroxide (1:1) and distilled water. The ether solution was dried over anhydrous potassium carbonate. The ether was removed and the solution was distilled under vacuum through a five-inch column packed with glass helices. Active *s*-butyl acetal (11.5 g., 64.5%) was obtained as a colorless liquid, b.p. 66–68° (16 mm.); n^{20}_D 1.4050; d^{20}_4 0.8279, $[\alpha]^{25}_D$ +25.40 ± 0.02° (*l* 1, no solvent).

Anal. Calcd. for $C_{10}H_{22}O_2$: C, 68.91; H, 12.73; *MR*, 51.68. Found: C, 68.62; H, 12.95; *MR*, 51.59.

Hydrolysis of Acetal.—A mixture of 11.5 g. (0.066 mole) of D-(+)-2-butyl acetal and 100 ml. of 5% phosphoric acid was refluxed for 1 hour. The cooled solution was saturated with potassium carbonate and extracted with ether. After drying over anhydrous potassium carbonate, the ether solution was distilled. Alcohol, (6.7 g., 71%) b.p. 97–98° with $[\alpha]^{25}_D$ +8.00 ± 0.02° (*l* 1), was obtained.

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[1] Deceased.

[2] University of Illinois, College of Dentistry, Chicago, Illinois.

[3] J. M. O'Gorman and H. J. Lucas, This Journal, **72**, 5489 (1950).

[4] E. R. Alexander and H. M. Busch, *ibid.*, **74**, 554 (1952).

[5] All boiling points are uncorrected.

[6] R. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1937 (1913).

[7] M. Sprung and E. Wallis, This Journal, **56**, 1717 (1934).

The Addition of Fluorene to, and the Fine Structure of, Benzylidenefluorene

By Ernst D. Bergmann and David Lavie

Received October 29, 1951

Like all fulvenes,[1] benzylidenefluorene has a polar semicyclic double bond; the moment of the latter is directed toward the five-membered ring. It is, therefore, correct to regard the addition of fluorene to benzylidenefluorene, which has been observed by Pinck and Hilbert,[2] as a special case of the Michael condensation; the latter occurs only with polar unsaturated systems.[3]

The direction of the dipole moment in benzylidenefluorene demands that in the addition of fluorene the proton derived from the 9-hydrogen atom of fluorene combines with the 9-carbon atom of the benzylidene compound and the fluorenyl anion with the phenylated carbon atom, thus giving di-(9-fluorenyl)-phenylmethane (I), in analogy to the addition of lithium aluminum hydride in which the negative hydrogen ion[4] combines with the phenylated carbon atom, the $(LiAlH_3)^+$ ion with the central carbon atom of benzylidenefluorene.[5]

Pinck and Hilbert[2] have not decided whether their condensation product of m.p. 240° was (I) or the isomeric 9-benzyl-9,9′-difluorenyl (II), which would have resulted from the inverse addition of fluorene to benzylidenefluorene. (II)[6] has, moreover, the same melting point as Pinck and Hilbert's hydrocarbon.

It has now been shown that this hydrocarbon is not identical with (II); a mixture of the two compounds gives a strong melting point depression.[7] It is, therefore, concluded that formula (I) is correct. The Michael condensation of fluorene and benzylidenefluorene (I), is, thus, an additional proof for the direction of the moment in the latter which has been predicted by the theory.

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[1] A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950), and previous publications; G. W. Wheland and D. E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); H. Lumbroso, A. Pacault and B. Pullman, *Bull. soc. chim. France*, 34 (1950); E. D. Bergmann and E. Fischer, *ibid.*, 1084 (1950).

[2] L. A. Pinck and G. E. Hilbert, This Journal, **68**, 2014 (1946).

[3] E. D. Bergmann, D. Ginsburg and R. Pappo, in preparation.

[4] L. W. Trevoy and W. G. Brown, This Journal, **71**, 1675 (1949).

[5] D. Lavie and E. D. Bergmann, *Bull. soc. chim. France*, 250 (1951).

[6] R. C. Fuson and H. D. Porter, This Journal, **70**, 895 (1948).

[7] The referee kindly informed the authors that he has made the same observation with the two original samples obtained by Pinck and Hilbert and by Fuson and Porter, respectively.