dissolved in acetone, the acetone solution was dried with magnesium sulfate and was evaporated to dryness; the resulting oil was dried for several days at 25°/1.0 mm., and was then analyzed.

Anal. Found: C, 39.49, 39.72; H, 4.58, 4.46; Fe, 3.49; Cl, 3.19, 2.99.

This indicates a mixture of 11% *p*-chlorophenol and 47% of the iron complex.

The experiment was repeated under the same reaction conditions but using 0.03 mole of *p*-chlorophenol. Only a solid hetero polymer formed, after drying at 25°/1.0 mm.

Anal. Found: C, 55.62, 55.26; H, 4.13, 4.17; Fe, 3.77; Cl, 12.64, 12.36; S, 4.55.

This indicates a mixture of 52% of iron complex and 45% of *p*-chlorophenol.

Acknowledgment.—The author wishes to thank Dr. G. R. Coraor for many helpful discussions and suggestions.

Preparation of Halogenated Nitronaphthalenes, Halogenated Naphthylamines, and Their Sulfonic Acids

JOSEPH G. E. FENYES

Hyman Laboratories, Inc., Berkeley 10, California

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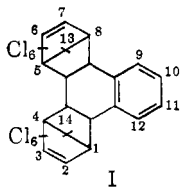
The compounds 3-bromo-2-nitronaphthalene and 3,4-dichloro-2-nitronaphthalene are prepared readily by the basic method of Danish, Silverman, and Tajima[1] for synthesis of β-substituted naphthalenes. From these compounds and their reduced analogs, sulfonic acids are derived having the unusual 3(and/or 4)-halo-2-nitronaphthalene and 3(and/or 4)-halo-2-naphthylamine relationships. Placement of the sulfonic acid functions homonuclear with or heteronuclear to the other substituents may be controlled by variations in the order and techniques of the reduction and sulfonation reactions. The reaction sequences provide an interesting new set of dyestuff intermediates for evaluation.

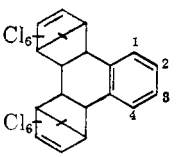
The presence of halogen atoms in dye molecules is known to lend fastness, especially chlorine fastness to the dyes. Thus, halogenated indanthrones are faster to chlorine, halogenated indigos are faster to chlorine and have better fiber affinity than their parent dyes, and chlorinated azo dyes are sometimes brighter and show improved fastness to light, bleaching, and acids.[2]

The aminosulfonic acids described here are of particular interest as dye intermediates, since they bear amino and halogeno functions in the unusual 2,3- and 2,4-relationships on naphthalene. Such configurations can be obtained only with difficulty through the standard aromatic substitution and interconversion reactions, but result directly when the method of Danish, Silverman, and Tajima[1] is applied to the preparation of the halonitronaphthalene precursors. Direct halogenation of 2-nitronaphthalene results only in compounds in which the halogens have entered positions heteronuclear to the nitro group.[3,4] Halogenation of 2-acetylaminonaphthalene[5-8] leads to other isomeric configurations, especially 1-halo-2-acetyl-aminonaphthalene.

Hyman and Danish[9] as well as Danish, Silverman, and Tajima[1] have described the preparation of 1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene (I), from the Diels-Alder adduction of one molecule of naphthalene and two molecules of hexachlorocyclopentadiene, and have outlined the preparation of β-substituted naphthalenes by substitution (nitration, sulfonation) of this molecule and subsequent deadduction. For simplicity this diadduct is also referred to here as DHA (Di-Hexachlorocyclopentadiene-Adduct of naphthalene and numbered as in II).



I



II

During the course of this work it was determined that the DHA may be both halogenated and nitrated in good yields on the aromatic ring and that the resulting compounds may be cracked pyrolytically to the corresponding halogenated nitronaphthalenes. These compounds may then be sulfonated and subsequently reduced, or first reduced and then sulfonated to give a variety of halogenated 2-naphthylamine sulfonic acids.

(1) A. A. Danish, M. Silverman, and Y. A. Tajima, *J. Am. Chem. Soc.*, **76**, 6144 (1954).

(2) K. Venkataraman, "The Chemistry of Synthetic Dyes," Vol. I, p. 458; Vol. II, pp. 939 and 1018–1020, Academic Press, Inc., New York, N. Y., 1952.

(3) O. V. Braun, E. Hahn, and J. Seemann, *Ber.*, **55**, 1687, 1695 (1922).

(4) V. Vesely and M. Jakes, *Bull. soc. chim.* [4], **33**, 952 (1923).

(5) P. T. Cleve, *Ber.*, **20**, 1989 (1887).

(6) H. Franzen and G. Stäuble, *J. prakt. Chem.* [2], **103**, 352, 380, 387 (1922).

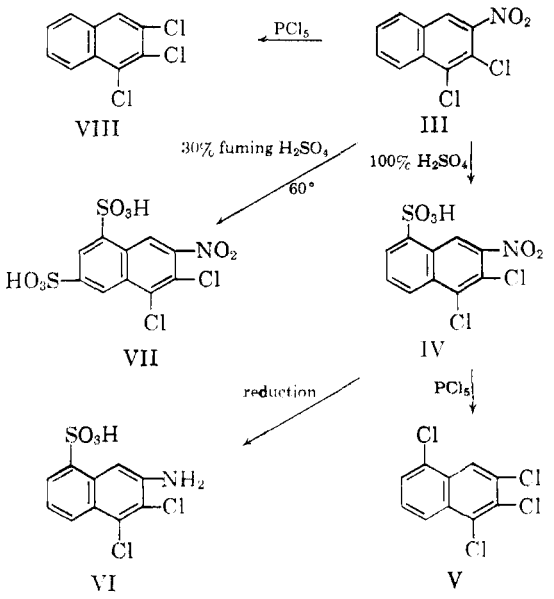
(7) C. Cosiner, *Ber.*, **14**, 58 (1881).

(8) A. Claus and O. Philipson, *J. prakt. Chem.* [2], **43**, 47, 59 (1891).

(9) J. Hyman and A. A. Danish, U.S. Patent 2,658,926, November 10, 1953 and J. Hyman and A. A. Danish, British Patent 730,430, April 17, 1953.

Sulfonation of the halonitronaphthalenes takes place heteronuclearly with one or two sulfonic acid groups entering the second ring. It is reported in the literature that sulfonation of 1,2,3,4-tetrachloronaphthalene with 5% oleum at 150° results in β-sulfonation, the 5- and 8-positions being hindered by the neighboring chlorine atoms.[10,11] When 4-chloro-2-nitronaphthalene and 3,4-dichloro-2-nitronaphthalene are monosulfonated at room temperature with 100% sulfuric acid, the sulfonic acid group enters that α-position which is farthest from the α-chlorine atom of the other ring. Thus, the sulfonation of 3,4-dichloro-2-nitronaphthalene (III) results in 3,4-dichloro-2-nitronaphthalene-8-sulfonic acid (IV).

The position of the substituents was confirmed when on treatment with phosphorus pentachloride both the nitro and sulfonic acid groups were replaced by chlorine, giving the known 1,2,3,5-tetrachloronaphthalene (V).



Two sulfonic acid groups may be introduced into the second ring by treatment with 30% oleum at 60°. The product is 3,4-dichloro-2-nitronaphthalene-6,8-disulfonic acid (VII).

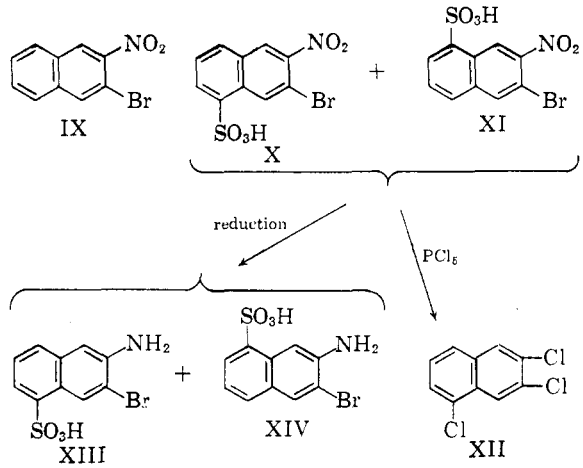
Sulfonation of 3-bromo-2-nitronaphthalene (IX) results in a mixture of 3-bromo-2-nitronaphthalene-5-(and 8)-sulfonic acids (X and XI, respectively), which on treatment with phosphorus pentachloride give the known 2,3,5-trichloronaphthalene (XII).

Reduction of the nitro compounds, before or after sulfonation, may be carried out either catalytically, using palladium on carbon or by means of stannous chloride in a hydrochloric acid solution.

When reduction with stannous chloride precedes sulfonation, the halonitronaphthalene is dissolved in an organic solvent, such as isopropyl alcohol,

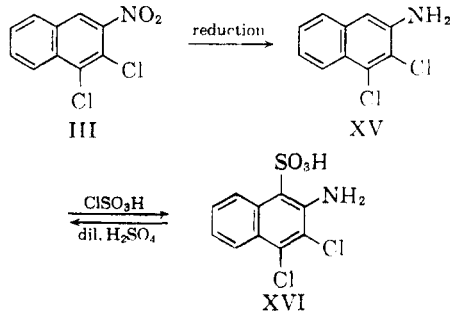
(10) E. G. Turner and W. P. Wynne, *J. Chem. Soc.*, 243 (1941).

(11) Elsevier's Encyclopedia of Organic Chemistry, Series III, "Carbocyclic Condensed Compounds," Vol. 12B, p. 333.



concentrated hydrochloric acid added to the solution, and the mixture heated to boiling. The required amount of stannous chloride is added at the boiling temperature and the reduction allowed to proceed.

After reduction of the nitro group, the halonaphthylamines (XV) may be sulfonated homonuclearly. This is carried out with chlorosulfonic acid in an organic solvent, such as tetrachloroethane, at an elevated temperature.[12] These acids, which are halogenated-Tobias acids (XVI), are easily desulfonated by treatment with hot dilute sulfuric acid.



When reduction is carried out after sulfonation, the use of an organic solvent is unnecessary, and 1:1 aqueous hydrochloric acid with a slight excess of stannous chloride may be employed. In this case the acids formed are the halo derivatives of either Badische (XIII) or Dahl (VI and XIV) acids. These acids cannot be desulfonated under conditions which desulfonate the Tobias acids.

Experimental

Melting points were taken on a Fisher-Johns block and are uncorrected. Molecular weights were determined in toluene solutions with a Mechrolab osmometer, Model 301.

a. 4-Chloro-2-naphthylamine.—A solution of 10.0 g. (0.048 mole) of 4-chloro-2-nitronaphthalene, prepared according to Danish, Silverman, and Tajima,[1] and 40.0 g. (0.177 mole) of technical stannous chloride in 100 ml. of isopropyl alcohol and 50 ml. of concentrated hydrochloric acid was boiled for 1 hr. The initially bright yellow solution

(12) J. Braddiley, J. B. Payman, and H. Wignall, British Patent 175,019, February 3, 1922.

paled considerably within the first few minutes. Evaporation of the reaction mixture to one third its original volume produced an abundant precipitate, which was filtered off and washed free of tin salts with 1:1 cold aqueous hydrochloric acid (50 ml.). On boiling with a saturated sodium carbonate solution the amine hydrochloride was converted to free 4-chloro-2-naphthylamine, which was washed with water and dried. The product weighed 7.6 g., (89%). Melting point was 64.5–65° after one recrystallization from petroleum ether (lit.,[13] 68°).

b. 4-Chloro-2-aminonaphthalene-1-sulfonic Acid (4-Chloro Tobias Acid).—To a solution of 1.4 g. (0.00788 mole) of 4-chloro-2-naphthylamine in 20 ml. of dry tetrachloroethane, a solution of 1.3 g. (0.011 mole) of chlorosulfonic acid in 5 ml. of dry tetrachloroethane was added slowly, with constant stirring. This solution was refluxed for 3 hr., during which time the product precipitated from the reaction mixture. The solid product, filtered from the cooled reaction mixture, was dissolved in 50 ml. of 5% aqueous sodium hydroxide, the resulting solution filtered free of any unsulfonated material and the filtrate acidified with dilute hydrochloric acid to precipitate the 4-chloro-2-aminonaphthalene-1-sulfonic acid. The dry product, a tan crystalline powder, weighed 1.5 g. (77%).

c. Preparation of 3,4-Dichloro-2-nitro-DHA (11-Nitro-1,2,3,4,5,6,7,8,9,10,13,13,14,14-tetradecachloro-1,4,4a,4b,-5,8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene) and 3,4-Dichloro-2-nitronaphthalene (III). Method A.—The dichlorination of 2-nitro-DHA[1] was carried out in a three-necked, round-bottomed flask equipped with a reflux condenser, a thermometer, and a sintered glass gas inlet tube inserted through the neck of the flask. The inlet tube, extending close to the bottom of the flask, was connected to a cylinder of chlorine through a wash bottle which contained about 150 ml. of concentrated sulfuric acid. The hydrogen chloride gas, which formed, escaped through the condenser, the outlet of which was protected against atmospheric moisture by a tube of anhydrous calcium chloride. A mixture of 40 g. of 2-nitro-DHA, 1 g. each of anhydrous ferric chloride, iron powder, and iodine, and 300 ml. of dry *sym*-tetrachloroethane was placed in the flask. This mixture was stirred and heated to reflux temperature at which time all the 2-nitro-DHA dissolved. While maintaining a temperature of 140–146° in the solution a stream of chlorine gas was passed through it for 11 hr.

After chlorination was stopped, the flask contents were filtered and the filtrate washed with dilute hydrochloric acid followed by water and then dried over anhydrous sodium sulfate. The solvent was removed under pump vacuum. The residue was thermally cracked at 300–320° under less than 1.0 mm. pressure. The distillate consisted essentially of a slurry of 3,4-dichloro-2-nitronaphthalene in hexachlorocyclopentadiene. The solids were filtered off, washed three times with 30 ml. of cold hexane, and again filtered. The filter cake was pure 3,4-dichloro-2-nitronaphthalene, weighing 6.0 g. (52%), m.p. 125–125.5°.

Anal. Calcd. for $C_{10}H_5O_2Cl_2N$: Cl, 29.3; mol. wt., 242.06. Found: Cl, 28.9; mol. wt., 243 ± 5.

The infrared spectrum was determined in a potassium bromide disk; maxima (μ) were: 9.82 (m), 10.43(w), 10.81(m), 11.30(m-s), 11.63(m), 11.75(m), 11.97(m-s), 13.10(s), 13.30(s), 13.57(m), 13.89(s), and 14.77(w).

Method B.—A suspension of 200 g. of DHA in 600 ml. of dry methylene chloride was placed in a 2000-ml., three-necked, round-bottom flask equipped with a stirrer and reflux condenser. The flask and its contents were chilled in an ice–salt bath and chlorine gas was bubbled in until 46 g. of chlorine was absorbed. The cooling bath was removed, 4 g. of anhydrous ferric chloride added, stirring started, and the suspension allowed to reach room temperature. The reaction was completed within 3 hr. Eighty milliliters of methylene chloride was distilled from the suspension in order to expell the unchanged chlorine and the hydrogen chloride gas formed during the reaction. To the remaining suspension 376 ml. of white fuming nitric acid (98–100%) was added, and the resulting mixture was stirred at room temperature for 1 hr. The reaction mixture was then filtered, and the small amount of solids collected on the sintered glass filter funnel washed with 100 ml. of 1:1 solution of white fuming nitric acid (98–100%) in methylene chloride. The strongly acidic filtrate was cautiously poured into 2000 ml. of water and agitated briefly. The aqueous upper layer was decanted and the organic layer repeatedly washed with water. Finally the methylene chloride was distilled and the resulting precipitate filtered and washed with 400 ml. of boiling methanol. A yellow crystalline product, consisting mainly of 1,2-dichloro-3-nitro-DHA and a small amount of 2,3-dichloro-DHA, and weighing 157 g. was obtained. The compound was purified by treating with charcoal a solution of the mixture in hot toluene, filtering, and diluting the filtrate with an equal volume of methanol. The pale yellow precipitate obtained melted at 219–221°. Mixed melting point with an authentic sample of 1-chloro-3-nitro-DHA was greatly depressed.

A slurry of 100 g. of the product was made with an equal weight of hexachlorocyclopentadiene and the product cracked pyrolytically in a wiped film molecular type still maintained at an external temperature of 390–400°. Pressure was reduced to less than 0.5 atm. The cracked product was isolated as described in method A above.

The resulting crude 3,4-dichloro-2-nitronaphthalene melted at 119–123°; yield, 13.2 g. (73%). Recrystallization from methanol raised the melting point to 125–125.5°.

d. Conversion of 3,4-Dichloro-2-nitronaphthalene to 1,2,3-Trichloronaphthalene (VIII).—A sample of 150 mg. of 3,4-dichloro-2-nitronaphthalene (0.00062 mole) was ground with (five times its weight) 750 mg. (0.0036 mole) of phosphorus pentachloride and the mixture heated in an oil bath at 162° for 5 hr. The sublimed pentachloride had to be scraped back periodically during the heating. When cold the product was added cautiously to ice. After complete hydrolysis the solids were filtered, washed with water, dried, and once recrystallized from methanol. The infrared spectrum was identical to that of an authentic 1,2,3-trichloronaphthalene.[14]

e. 3,4-Dichloro-2-naphthylamine (XV).—Reduction of 10 g. (0.041 mole) of 3,4-dichloro-2-nitronaphthalene with 34 g. (0.151 mole) of technical stannous chloride dihydrate in a boiling mixture of 100 ml. of isopropyl alcohol and 50 ml. of concentrated hydrochloric acid according to the procedure described in (a) followed by treatment with boiling aqueous sodium carbonate solution, gave 7.8 g. (89.9%) of 3,4-dichloro-2-naphthylamine; m.p. 69–71°. Recrystallization from ether raised the m.p. to 73–74°.

Anal. Calcd. for $C_{10}H_7Cl_2N$: Cl 33.4. Found: Cl, 33.1.

The infrared spectrum was determined in a potassium bromide disk; the maxima (μ) were: 9.53(m), 10.62(s), 11.64(s), 12.03(s), 12.25(m-w), 13.18(m), 13.25(m), 13.61(s).

f. 3,4-Dichloro-2-aminonaphthalene-1-sulphonic Acid (3,4-Dichloro Tobias Acid) (XVI).—Sulfonation of 2 g. (0.0094 mole) of 3,4-dichloro-2-naphthylamine with 1.2 g. (0.01 mole) of chlorosulfonic acid in 30 ml. of dry tetrachloroethane according to the procedure given in (b) gave 2.2 g. (80%) of 3,4-dichloro-2-aminonaphthalene-1-sulfonic acid.

g. Desulfonation of 3,4-Dichloro-2-aminonaphthalene-1-sulfonic Acid.—A suspension of 0.220 g. (0.00075 mole) of 3,4-dichloro-2-aminonaphthalene-1-sulfonic acid in 35 ml. of 75% sulfuric acid was heated at 125–140° for 20–25 min., until most of it dissolved. The hot solution was filtered, the filtrate diluted with water, and the precipitate, unchanged starting material, was filtered. The filtrate was made alkaline with aqueous sodium hydroxide solution and the precipitate formed was filtered and washed with water. The

(13) H. H. Hodgson, *J. Chem. Soc.*, 1850 (1935).

(14) L. Cencelj and D. Hadzi, *Spectrochim. Acta*, **7**, 274 (1955).

product, weighing 0.09 g. (57%), had an infrared spectrum identical to that of an authentic 3,4-dichloro-2-naphthylamine.

h. Preparation of 3-Bromo-2-nitro-DHA (10-Bromo-11-nitro-1,2,3,4,5,6,7,8,13,13,14,14-dodecachloro-1,4,4a,4b,5,-8,8a,12b-octahydro-1,4;5,8-dimethanotriphenylene) and 3-Bromo-2-nitronaphthalene (IX).—The bromination of DHA was accomplished by the method given by Danish, *et al.*[1]

The 3-bromo-DHA was nitrated using sulfuryl chloride solvent and mixed nitric and sulfuric acids. Into a 4000-ml. resin kettle equipped with a stirrer, dropping funnel, and reflux condenser, 2767 g. of freshly distilled sulfuryl chloride, 200 g. of white fuming nitric acid (98–100%) and 1103 g. of 3-bromo-DHA were placed. While the solution was constantly stirred, 530 g. of 30% oleum was added dropwise. The solution was heated slowly to reflux and kept at that temperature for 4.5 hr., after which the condenser was replaced by a distilling head. The sulfuryl chloride solvent was distilled and 1380 g. concentrated sulfuric acid was added slowly to the mixture during distillation. The residue was filtered through a sintered glass funnel and the solids washed once with water and twice with boiling methanol. Pure 3-bromo-2-nitro-DHA weighing 1079 g. (92.5%, based on the weight of the 2-bromo-DHA employed) was obtained, m.p. 279°.

The 3-bromo-2-nitro-DHA was slurried with three times its weight of hexachlorocyclopentadiene and then cracked pyrolytically according to the procedure described above for the preparation of 3,4-dichloro-2-nitronaphthalene. The substance was converted by the cracking to hexachlorocyclopentadiene and 3-bromo-2-nitronaphthalene; the latter being obtained in a yield of 87% after crystallization from hexane, m.p. 87° (lit., 84°[15]).

Anal. Calcd. for $C_{10}H_6O_2NBr$: Br, 31.7; mol. wt. 252.08. Found: Br, 32.1. mol. wt., 249 ± 5.

i. 3-Bromo-2-naphthylamine.—Reduction of 2 g. (0.0078 mole) of 3-bromo-2-nitronaphthalene with 6.5 g. (0.029 mole) of technical stannous chloride in a boiling mixture of 10 ml. of concentrated hydrochloric acid and 30 ml. of isopropyl alcohol according to the procedure described in (a), followed by hydrolysis in boiling aqueous sodium carbonate solution gave 1.8 g. (theoretical yield) of 3-bromo-2-naphthylamine melting at 152–158°. One recrystallization from methanol raised the m.p. to 174.5° (lit., 169°,[16,17] 173°[18]).

j. 3-Bromo-2-aminonaphthalene-1-sulfonic Acid (3-Bromo Tobias Acid).—To a solution of 1.2 g. (0.0054 mole) of 3-bromo-2-naphthylamine in 50 ml. of dry tetrachloroethane a solution of 0.7 g. (0.006 mole) of chlorosulfonic acid in 5 ml. of dry tetrachloroethane was added slowly with constant stirring at room temperature. The solution was then refluxed for 3 hr., during which time the product precipitated from the reaction mixture. After cooling to room temperature the product was worked up according to the procedure described in (b). The dry product weighed 1.3 g. (82.5%).

k. 4-Chloro-2-nitronaphthalene-8-sulfonic Acid, Sodium Salt.—A solution of 0.5 g. (0.0024 mole) of 4-chloro-2-nitronaphthalene in 20 ml. of 100% sulfuric acid was left at room temperature for 30 min. It was then stirred into an excess of ice, heated to 50–60°, and filtered from the small amount of starting material. On cooling precipitate appeared (free acid), and more was forced out by saturating the solution with sodium chloride. The precipitate was filtered, washed with brine and dried giving 0.65 g. (85%) of 4-chloro-2-nitronaphthalene-8-sulfonic acid, sodium salt, a light yellow crystalline powder.

l. 4-Chloro-2-aminonaphthalene-8-sulfonic Acid.—A solution of 0.5 g. (0.0016 mole) of 4-chloro-2-nitronaphthalene-8-sulfonic acid, sodium salt, and 1.4 g. (0.0062 mole) of technical stannous chloride in 15 ml. of isopropyl alcohol and 15 ml. of concentrated hydrochloric acid was boiled for 45 min., the volume reduced to approximately one third by evaporation. After cooling the mixture, the resulting precipitate was filtered and washed with dilute (1:1) aqueous hydrochloric acid. The yield was 0.38 g. (77%) 4-chloro-2-aminonaphthalene-8-sulfonic acid.

m. 3,4-Dichloro-2-nitronaphthalene-8-sulfonic Acid, Sodium Salt (IV).—Sulfonation of 0.5 g. (0.002 mole) of 3,4-dichloro-2-nitronaphthalene in 20 ml. of 100% sulfuric acid at room temperature required 2 hr. The dark-colored reaction mixture was worked up according to the procedure given in (k) above. The product was salted out of the solution by saturation with sodium chloride, giving 0.6 g. (83%) of 3,4-dichloro-2-nitronaphthalene-8-sulfonic acid, sodium salt, a light yellow crystalline powder.

n. Conversion of 3,4-Dichloro-2-nitronaphthalene-8-sulfonic Acid, Sodium Salt, to 1,2,3,5-Tetrachloronaphthalene (V). Treatment of a sample of 0.35 g. (0.001 mole) of 3,4-dichloro-2-nitronaphthalene-8-sulfonic acid, sodium salt with 1.65 g. (0.0079 mole) of phosphorus pentachloride according to the procedure described in (d) resulted in a crystalline product, the infrared spectrum of which was identical to that of authentic 1,2,3,5-tetrachloronaphthalene.[14]

o. 3,4-Dichloro-2-aminonaphthalene-8-sulfonic Acid (VI).—Reduction of 0.5 g. (0.00145 mole) of 3,4-dichloro-2-nitronaphthalene-8-sulfonic acid, sodium salt, with 1.3 g. (0.0057 mole) of technical stannous chloride in a mixture of 15 ml. of isopropyl alcohol and 15 ml. of concentrated hydrochloric acid according to the procedure outlined in (l) gave 0.36 g. (85%) of 3,4-dichloro-2-aminonaphthalene-8-sulfonic acid, a light gray crystalline powder.

p. 3-Bromo-2-nitronaphthalene-5(and 8)-sulfonic Acid, Sodium Salt (X and XI).—The sulfonation of 50 g. (0.1984 mole) 3-bromo-2-nitronaphthalene with 400 ml. of 100% sulfuric acid at room temperature for 2 hr. produced 62.5 g. (70.2%) of the mixed isomers; 3-bromo-2-nitronaphthalene-5-(and 8)-sulfonic acid, sodium salts. The product was a light tan-colored crystalline powder.

q. Conversion of 3-Bromo-2-nitronaphthalene-5(and 8)-sulfonic Acid, Sodium Salts to 1,6,7-Trichloronaphthalene (XII).—A well powdered mixture of 0.24 g. (0.00067 mole) of 3-bromo-2-nitronaphthalene-5(and 8)-sulfonic acid, sodium salts, and 1.2 g. (0.0057 mole) of phosphorus pentachloride was heated at 165–172° for 3.5 hr. The mixture was worked up according to the procedure given in (d). The infrared spectrum of the resulting crude product was identical to that of an authentic 1,6,7-trinitronaphthalene.[14]

r. 3-Bromo-2-aminonaphthalene-5(and 8)-sulfonic Acids (XIII and XIV).—Reduction of 55 g. (0.155 mole) of 3-bromo-2-nitronaphthalene-5-(and 8)-sulfonic acid, sodium salts, with 140 g. (0.622 mole) of technical stannous chloride in 400 ml. of 1:1 aqueous hydrochloric acid according to the procedure outlined in (l) produced 40 g. (82.5%) of 3-bromo-2-aminonaphthalene-5(and 8)-sulfonic acids. The product was a tan crystalline powder.

s. 3,4-Dichloro-2-nitronaphthalene-6,8-disulfonic Acid, Barium Salt (VII).—A stirred solution of 25 g. (0.103 mole) of 3,4-dichloro-2-nitronaphthalene in 275 ml. of 30% oleum was heated at 65° for 2.5 hr. After cooling to room temperature, the mixture was stirred slowly into an excess of ice. The strongly acidic solution was brought to a boil and then neutralized with barium carbonate. The resulting suspension was filtered and the barium sulfate filter cake twice leached with boiling water. The extracts were combined with the original filtrate and evaporated to dryness. The reddish product, 3,4-dichloro-2-nitronaphthalene-6,8-disulfonic acid, barium salt, weighed 43.8 g. (79%).

t. 3,4-Dichloro-2-aminonaphthalene-6,8-disulfonic Acid. — Reduction of 33 g. (0.061 mole) of 3,4-dichloro-2-nitronaphthalene-6,8-disulfonic acid, barium salt, with 50 g. (0.22 mole) of technical stannous chloride in 400 ml. of 1:1 aqueous hydrochloric acid, according to the procedure de-

(15) N. McLeish and N. Campbell, *J. Chem. Soc.*, 1103 (1937).
(16) W. P. Wynne, *Proc. Chem. Soc.*, **30**, 204 (1914).
(17) R. B. Sandin and T. H. Evans, *J. Am. Chem. Soc.*, **61**, 2916 (1939).
(18) R. Consden and J. Kenyon, *J. Chem. Soc.*, 1591 (1935).

scribed in r, produced 18.5 g. (81.1%) of 3,4-dichloro-2-aminonaphthalene-6,8-disulfonic acid, a gray crystalline powder.

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Potassium-Catalyzed Reactions of β-Alkylstyrenes and Anethol with Alkylbenzenes[1]

JOSEPH SHABTAI,[2,3] E. M. LEWICKI, AND HERMAN PINES

Ipatieff High Pressure and Catalytic Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois

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β-Methyl-, β-ethyl-, and β-isopropylstyrene react with toluene at 110° in the presence of dispersed potassium to form the corresponding 1,3-diphenyl-2-alkylpropanes in 60–95% yields. Anethol reacts similarly to form 1-*p*-methoxyphenyl-2-methyl-3-phenylpropane in 68% yield. β,β-Dimethylstyrene, however, fails to react with toluene. β-Ethylstyrene undergoes also ring closure with the formation of 1-methylindene.

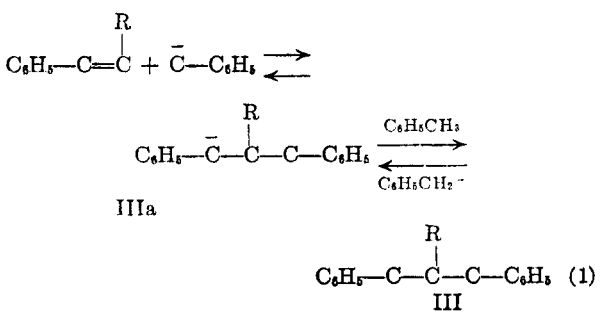
It was reported recently that α-methylstyrene[4] reacts with *n*-alkylbenzenes in the presence of dispersed potassium to form 1,3-diphenylalkanes in high yield and purity. The study indicated that the introduction of a methyl substituent in the vinyl group of the styrene molecule, unlike ring substitution,[5] increases sharply the selectivity of the aralkylation reaction. As an extension of this study we are reporting the reactions of alkylbenzenes with a series of β-alkylstyrenes in the presence of potassium as catalyst. The influence of the type and number of β-substituents upon the relative rate of aralkylation was examined by a comparative study of the addition reactions of toluene to β-methyl-, β-ethyl-, β-isopropyl-, and β,β-dimethylstyrene. The reactions were carried out in the presence of an excess of toluene. The study of the reaction with anethol was undertaken with the purpose of obtaining information on the possible application of the synthesis to alkoxy derivatives.

A comparative study of the aralkylation of β-methylstyrene with toluene, ethyl-, propyl-, and isopropylbenzene was also carried out in order to determine the effect of the substituent in the alkylbenzene reactant upon the addition reaction.

The experimental procedure was similar to that described previously.[4,5] The reaction products were separated and analyzed by a combination of fractional distillation, selective hydrogenation, ozonization, gas chromatography, infrared and ultraviolet spectroscopy.[1,4,5] The 1,3-diphenylalkanes formed in the reactions were also compared with synthetically prepared samples. The results are summarized in Tables I and II.

Discussion

β-Methyl-, β-ethyl-, and β-isopropylstyrene react with toluene to form the corresponding 1,3-diphenyl-2-alkylpropanes (III) in yields of 60 to 95% (Table I):



(1)

The reaction with β-isopropylstyrene, however, is relatively slow, probably as a result of steric hinderance due to the isopropyl group. The steric effect of a β-substituent may be due either to interference with the approach of the benzyl carbanion to the β-position in the addition step of the above reaction and/or to a hindering action preventing the protonation of the adduct carbanion IIIa. The steric effect is sharply increased by introducing a second substituent in the β-position. β,β-Dimethylstyrene, for instance, fails to react with toluene (experiment 6), but instead undergoes

(1) Paper XXIII of the series *Base-catalyzed Reactions*. For paper XXII, see H. Pines and J. Shabtai, *J. Am. Chem. Soc.*, **83**, 2781 (1961).

(2) National Science Foundation Postdoctoral Fellow, 1960–1961.

(3) On leave of absence from the Weizmann Institute of Science, Rehovoth, Israel.

(4) J. Shabtai and H. Pines, *J. Org. Chem.*, **26**, 4225 (1961).

(5) H. Pines and J. Shabtai, *J. Org. Chem.*, **26**, 4220 (1961).