[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Quinol Imide Acetates. III. Addition Reactions of 2-Methyl-*o*-naphthoquinol-*p*-toluenesulfonimide Acetate

BY ROGER ADAMS AND JOSEPH E. DUNBAR[1]

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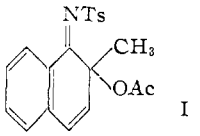
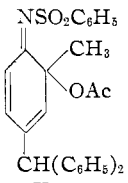
2-Methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate, prepared by lead tetraacetate oxidation of 2-methyl-1-*p*-toluenesulfonamidonaphthalene, adds hydrogen chloride, hydrogen bromide or acetic acid with simultaneous loss of acetic acid to give, respectively, 3-chloro-, 3-bromo-, 3-acetoxy-2-methyl-1-*p*-toluenesulfonamidonaphthalene. Hydrogen cyanide gives 2-acetoxy-1-cyano-2-methyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene which is converted by alkali to 2-methyl-1-*p*-toluenesulfonamidonaphthalene and by sulfuric acid to 4-amino-1-cyano-2-methylnaphthalene. Methylmagnesium iodide reacts to give 1,2,4-trimethylnaphthalene. The mechanisms by which these products are formed are discussed.

The reactions of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate (I) have been the subject of this investigation for the purpose of establishing the character of the adducts and a possible route from the product to a variety of 2,3-disubstituted naphthalenes.



I

Recent studies in this Laboratory[2] have shown that quinol imide acetates add a variety of reagents with subsequent loss of acetic acid and formation of a substituted benzene. To illustrate, hydrogen chloride adds to 3-acetoxy-4-benzenesulfonimido-3-methyl-3,4-dihydrotriphenylmethane (IV) to yield 4-benzenesulfonamido-2-chloro-5-methyltriphenylmethane (V)[2a]; to 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate (VI) to give VII; to 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate (VIII) to give IX.[2b]



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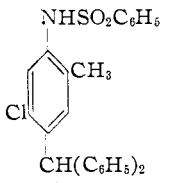

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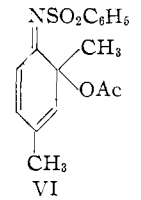

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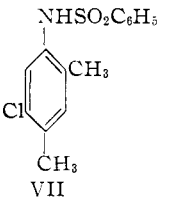

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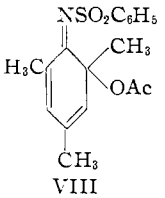
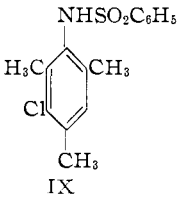


VIII



IX

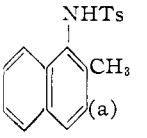
(1) An abstract of a thesis submitted in partial fulfillment of the degree of doctor of philosophy, 1956; Standard Oil of California Fellow, 1954–1955.

(2) (a) R. Adams, E. J. Agnello and R. S. Colgrove, THIS JOURNAL, **77**, 5617 (1955); (b) R. Adams and K. R. Brower, *ibid.*, **78**, 4770 (1956).

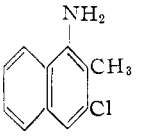
The evidence supports initial 1,4-addition in all these cases.

The naphthalene derivative I was prepared by lead tetraacetate oxidation of 2-methyl-1-*p*-toluenesulfonamidonaphthalene in chloroform solution. The structure assigned to it is based primarily on the infrared spectrum which shows the acetoxyl bands at 1749 and 1248 cm.$^{-1}$ and C=N bands at 1590 and 1620 cm.$^{-1}$. These bands have been found characteristic of *o*-quinol imide acetates.[2b]

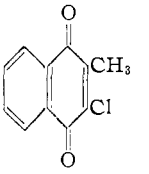
Compound I differs from the other previously described *o*-quinol imide acetates in that 1,4-addition cannot occur without disrupting the aromatic character of the nucleus. As a consequence, 1,6-addition of reagents would be expected with formation, after elimination of acetic acid, of a 3-substituted naphthalene. Thus I should and did yield compound X (a = Cl) by the action of hydrogen chloride.



X



XI

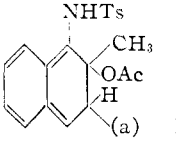


XII

To establish the constitution, compound X (a = Cl) was hydrolyzed with acid to the corresponding amine XI which was oxidized by hydrogen peroxide to the known 3-chloro-2-methyl-1,4-naphthoquinone (XII). Deamination of XI by diazotization and reduction gave 3-chloro-2-methylnaphthalene, an acceptable route to this new product though in a moderate yield (38%).

Hydrogen bromide is oxidized by the previously described *o*-quinol imide acetates, but the *o*-quinol imide acetate I is apparently less powerful an oxidizing agent, and hydrogen bromide adds to give 3-bromo-2-methyl-1-*p*-toluenesulfonamidonaphthalene (X, a = Br).

The probable intermediate in these conversions is shown in XIII; a 1,6-addition followed by elimination of acetic acid is assumed.

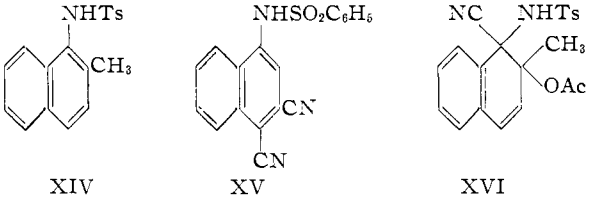


XIII

Hydrogen cyanide adds to I in the presence of triethylamine as catalyst without elimination of

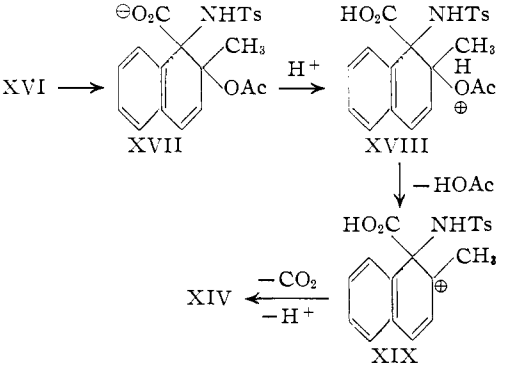
acetic acid. The product is obviously not XIII (a = CN) since treatment with 10% aqueous sodium hydroxide did not induce elimination of acetic acid with formation of 3-cyano-2-methyl-1-*p*-toluenesulfonamidonaphthalene. The adduct was instead converted by alkali to 2-methyl-1-*p*-toluenesulfonamidonaphthalene (XIV).

The reaction of hydrogen cyanide with 1,4-naphthoquinonedibenzenesulfonimide resulted in an initial 1,2-addition of hydrogen cyanide followed by a 1,4-addition and formation of 3,4-dicyano-1-benzenesulfonamidonaphthalene (XV)[3]



XIV XV XVI

Assuming a 1,2-addition of hydrogen cyanide to I, the product would be XVI. The conversion of XVI to XIV by alkali is explicable on the assumption that the cyano group is first hydrolyzed with formation of the sodium salt of XVII. Acidification results in decarboxylation, elimination of acetic acid and aromatization of the nucleus to form XIV. The mechanism may be through the formation of a carbonium ion intermediate XIX followed by loss of a proton and decarboxylation, XVII–XIV.



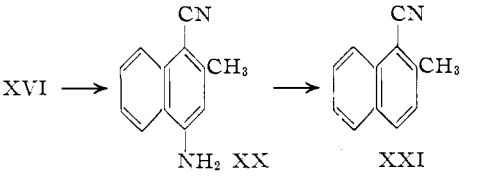
The structure of the adduct as XVI is supported by the fact that it is colorless whereas XIII (a = CN) might be expected to be colored. Moreover, the ultraviolet spectrum of the hydrogen cyanide adduct XVI indicates a benzenoid structure (Table I).

TABLE I

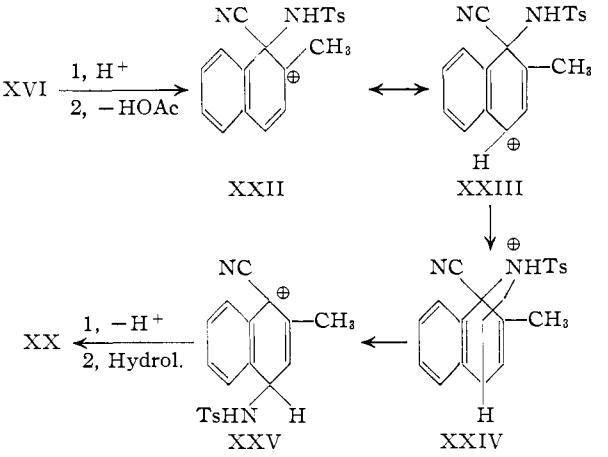
ULTRAVIOLET SPECTRUM OF COMPOUND XVI

Maxima		Minima	
λ, mμ	ε × 10⁻³	λ, mμ	ε × 10⁻³
206	22.7	208	22.1
217	24.4	250	4.5
269	6.7		

When compound XVI is treated with cold concentrated sulfuric acid, hydrolysis to 4-amino-1-cyano-2-methylnaphthalene (XX) occurs. Deamination of XX gives the known 2-methyl-1-naphthonitrile (XXI).[4] This confirms the fact that hydrogen cyanide adds 1,2 to I to give compound XVI. The 4-position for the amino group in compound XX was not positively established, but it is much more likely to be in the 4- than in the 3-position. A mechanism by which compound XX may be formed from XVI is shown in the following

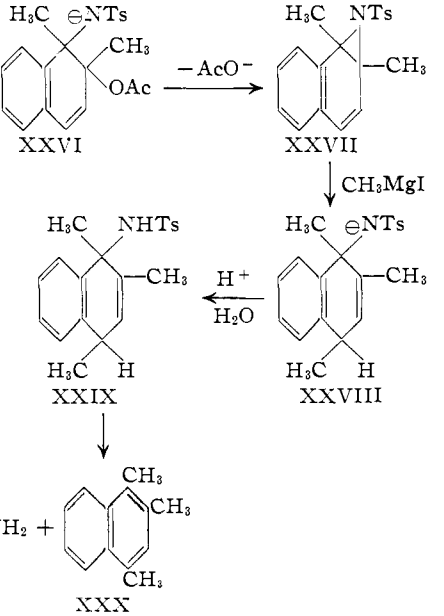


series of reactions XXII–XXV. The protonated acetoxyl group in compound XVI may lose acetic



acid to give the carbonium ion XXII. A resonance form XXIII would permit the migration of the sulfonamido group *via* the bridged ion XXIV to the 4-position XXV. Loss of a proton and hydrolysis of the sulfonamido group would result in formation of XX.

The action of methylmagnesium iodide on compound I followed an unexpected course. Two moles of Grignard reagent react, accompanied by the elimination of both acetic acid and *p*-toluenesulfonamide. The main product in 53% yield is 1,2,4-



(3) R. Adams and W. Moje, THIS JOURNAL, **74**, 5562 (1952).

(4) R. C. Fuson, C. H. McKeever and L. C. Behr, *ibid.*, **63**, 2648 (1941).

trimethylnaphthalene (XXX). A possible mechanism by which it may be formed is shown in XXVI–XXX.

The 1,2-addition of reagent is assumed to be the initial reaction (XXVI). Displacement of the acetate ion could then occur by participation of the sulfonamido group XXVII. A second mole of Grignard reagent might then react 1,4 with formation of the salt XXVIII. By treatment with aqueous ammonium chloride, conjugate elimination of *p*-toluenesulfonamide would give 1,2,4-trimethylnaphthalene (XXX).

Compound I does not add the variety of reagents that the other *o*-quinol imide acetates add. Both thiophenol and mercaptoethanol with triethylamine as catalyst merely caused reduction and elimination of acetic acid with formation of 2-methyl-1-*p*-toluenesulfonamidonaphthalene. No reaction occurred with phenol under the same conditions. Similarly, an active methylene compound, exemplified by acetylacetone, was unreactive. Morpholine did not react.

Acetic acid, however, adds to I and introduces an acetoxyl group into the 3-position in a manner similar to the chlorine of hydrogen chloride. This addition was observed when an attempt was made to add benzenesulfinic acid in glacial acetic acid in presence of sulfuric acid. Only 3-acetoxy-2-methyl-1-*p*-toluenesulfonamidonaphthalene (X, a = OAc) resulted. The infrared spectrum showed the vinyl type ester carbonyl band at 1765 cm.$^{-1}$ and a C–O band at 1211 cm.$^{-1}$.

The reaction of hydrogen fluoride in glacial acetic acid with I gave 3-hydroxy-2-methyl-1-*p*-toluenesulfonamidonaphthalene (X, a = OH). Apparently the hydrogen fluoride catalyzed first the addition of acetic acid and then the hydrolysis of the acetate formed. The infrared spectrum showed the hydroxyl stretching band at 3400 cm.$^{-1}$ and the C–O deformation band at 1244 cm.$^{-1}$.

Acknowledgment.—The authors are indebted to Professor R. C. Fuson for a sample of 2-methyl-1-naphthonitrile, to Mr. J. Nemeth, Mrs. M. Benassi and Mr. R. Nesset for the microanalyses and to Mr. J. Brader and Mrs. Louise Griffing for the determination of the infrared spectra.

Experimental

All melting points are corrected.

The infrared spectra were run in Nujol mulls unless otherwise indicated. A Perkin–Elmer Model 21 Double Beam Spectrophotometer was used.

The ultraviolet spectrum was run using a Model 11 Cary Recording Spectrophotometer.

2-Methyl-1-naphthylamine Hydrochloride.—A solution of 50 ml. of 85% hydrazine hydrate in 50 ml. of methanol was added dropwise with stirring to a suspension of 80.4 g. of 2-methyl-1-nitronaphthalene and *ca.* 20 g. of Raney nickel in 500 ml. of methanol. The rate of addition was adjusted so that refluxing was maintained without external heating. The reaction was vigorously exothermic at the beginning but became less vigorous at the end of the addition. Stirring was continued 30 minutes after the addition was complete. The Raney nickel was removed by filtration, and the methanol was evaporated. The amine was taken up in ether, and the ether extract was washed with two portions of water to remove excess hydrazine. The hydrochloride was precipitated from the ether solution by the addition of hydrochloric acid. The product was filtered and dried *in vacuo* over phosphoric anhydride. The yield was 78.5 g. (95%). The crude product was pure chloride or ordinary use.

2-Methyl-1-*p*-toluenesulfonamidonaphthalene.—To a solution of 40.0 g. of 2-methyl-1-naphthylamine hydrochloride in 300 ml. of pyridine was added, with stirring, 42.6 g. of *p*-toluenesulfonyl chloride over a period of about 5 minutes. The reaction mixture became warm, and pyridine hydrochloride precipitated. The mixture was allowed to stand for one hour and was then heated for an additional hour on the steam-bath. The reaction mixture was cooled and poured into a mixture of ice and concentrated hydrochloric acid. The resulting precipitate was filtered, washed with water and recrystallized from glacial acetic acid, giving 52.3 g. (81%) of pure 2-methyl-1-*p*-toluenesulfonamidonaphthalene, m.p. 194–195°.

Anal. Calcd. for $C_{18}H_{17}NO_2S$: C, 69.42; H, 5.50; N, 4.50. Found: C, 69.61; H, 5.85; N, 4.69.

2-Methyl-*o*-naphthoquinol-*p*-toluenesulfonimide Acetate.—A solution of 20.0 g. of 2-methyl-1-*p*-toluenesulfonamidonaphthalene and 28.8 g. of lead tetraacetate in 500 ml. of dry chloroform was refluxed with stirring for two hours. About 5 g. of Filter-Cel was added to the cooled reaction mixture, and the mixture was filtered to remove lead acetate and some lead oxide. The chloroform was evaporated *in vacuo*, and the tarry residue was triturated with about 20 ml. of methanol. The resulting brownish yellow crystals were removed by filtration. The crude product was recrystallized from methanol (Darco) to give 14.81 g. (62%) of large, light yellow, tetragonal crystals, m.p. 159–160°.

Anal. Calcd. for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18; N, 3.79. Found: C, 65.12; H, 5.28; N, 3.75.

The presence of the acetoxyl group was indicated in the infrared spectrum by absorption bands at 1749 and 1248 cm.$^{-1}$. The C=N group was represented by a split band with peaks at 1590 and 1620 cm.$^{-1}$.

A small amount of the product was dissolved in ethanol and treated with an excess of Raney nickel. After the mixture had been warmed on the steam-bath for 10 minutes, the Raney nickel was removed by filtration, and to the warm filtrate was added enough water to cause crystallization upon cooling. This procedure gave white needles, m.p. 193–194°. A mixture of this compound and an authentic sample of 2-methyl-1-*p*-toluenesulfonamidonaphthalene gave no depression of melting point.

3-Chloro-2-methyl-1-*p*-toluenesulfonamidonaphthalene.—A vigorous stream of dry hydrogen chloride was passed through a solution of 4.00 g. of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 30 ml. of dry chloroform for 45 minutes. The solution was then allowed to stand at room temperature for 1.5 hr. after which time the light yellow color had disappeared. The chloroform was evaporated *in vacuo*, and the light tan solid residue was recrystallized from aqueous acetic acid, resulting in the formation of 3.05 g. (82%) of white needles. Two more recrystallizations from aqueous acetic acid gave white, silky needles, m.p. 174–175°.

Anal. Calcd. for $C_{18}H_{16}ClNO_2S$: C, 62.51; H, 4.68; N, 4.05. Found: C, 62.42; H, 4.82; N, 3.85.

The infrared spectrum showed a C–Cl absorption band at 707 cm.$^{-1}$.

3-Chloro-2-methyl-1-naphthylamine Sulfate. Method A.—To 70 ml. of concentrated sulfuric acid at 5° was added 6.00 g. of 3-chloro-2-methyl-1-*p*-toluenesulfonamidonaphthalene with stirring. The solution was maintained at 5° for 30 minutes during which time the color changed from brown to dark green. The reaction mixture was then poured on ice, and the resulting pink, crystalline precipitate was collected on a filter and dried *in vacuo* over phosphoric anhydride. The yield of crude product was 3.20 g. (77%). Four successive recrystallizations from acetone–benzene, methanol, glacial acetic acid and methanol resulted in white crystals, m.p. 208° dec.

Anal. Calcd. for $C_{11}H_{10}ClN\cdot{}^1/_2H_2SO_4$: C, 54.89; H, 4.61; N, 5.82. Found: C, 54.98; H, 4.76; N, 5.82.

About 5 mg. of the amine sulfate was suspended in 0.5 ml. of hot water. The solid decomposed to a liquid, having the odor characteristic of a naphthylamine. The aqueous portion, upon being treated with a few drops of barium chloride solution, yielded a dense, white precipitate of barium sulfate.

Method B.—To a solution of 0.95 g. of 3-chloro-2-methyl-1-*p*-toluenesulfonamidonaphthalene in 25 ml. of glacial

acetic acid was added 25 ml. of concentrated hydrochloric acid. The mixture was boiled under reflux for 84 hours, cooled and poured into water. The aqueous solution was made alkaline with aqueous ammonia and extracted with ether. The ether was evaporated, and the residue was treated with 10% sulfuric acid, giving 0.55 g. (83%) of light tan solid. Recrystallization from aqueous methanol gave white needles, m.p. 207–208° dec.

Oxidation of 3-Chloro-2-methyl-1-naphthylamine Sulfate to 3-Chloro-2-methyl-1,4-naphthoquinone.—To a warm solution of 1.00 g. of 3-chloro-2-methyl-1-naphthylamine sulfate in 15 ml. of glacial acetic acid was added 10 ml. of 30% hydrogen peroxide at such a rate as to maintain boiling. At the beginning of the addition the color of the solution became dark blue, changing to wine-red toward the end of the addition. The solution was boiled under reflux for 15 minutes, during which time the color changed to a clear orange. To the solution was added 2 ml. more of 30% hydrogen peroxide, and the mixture was boiled under reflux for an additional 25 minutes. The reaction mixture was cooled and poured into 200 ml. of water. The aqueous solution was cooled in an ice-bath, and the yellow, gummy solid which precipitated was recrystallized from methanol to give 0.05 g. of product. Two more recrystallizations from methanol gave yellow needles, m.p. 151–152°.

A mixture of this compound and an authentic sample of 3-chloro-2-methyl-1,4-naphthoquinone, prepared by the method of Willstaedt,[5] gave no depression of melting point.

The infrared spectrum of this compound and that of the authentic sample of 3-chloro-2-methyl-1,4-naphthoquinone were identical.

3-Chloro-2-methylnaphthalene.—To a well-stirred suspension of 2.40 g. of 3-chloro-2-methyl-1-naphthylamine sulfate in 21 ml. of concentrated hydrochloric acid and 7 ml. of water at −5° was added dropwise 0.73 g. of sodium nitrite in 7 ml. of water over a period of about 40 minutes. After the addition the reaction mixture was stirred at −10 to −5° for 30 minutes. During this time a considerable amount of red solid precipitated. This material was removed by filtration. To the diazonium solution was added 30 ml. of 50% hypophosphorous acid (precooled to −5°). No noticeable evolution of gas occurred until 0.5 g. of cuprous oxide was stirred into the solution. Evolution of gas had completely ceased after the mixture had been allowed to stand in the refrigerator for 4 hours. The mixture possessed the characteristic naphthalene odor. The mixture was extracted with benzene, and the extract was dried over anhydrous magnesium sulfate. The benzene was evaporated, leaving 0.67 g. (38%) of brown oil. To a solution of the oil in 5 ml. of methanol was added 5 ml. of a saturated methanolic solution of picric acid. The mixture was brought to a boil, and upon cooling yielded a light orange crystal mass. Three recrystallizations from methanol gave yellow crystals, m.p. 91–92°.

Anal. Calcd. for $C_{17}H_{12}ClN_3O_7$: C, 50.32. H, 2.98; N, 10.35. Found: C, 50.50; H, 2.80; N, 10.06.

3-Bromo-2-methyl-1-*p*-toluenesulfonamidonaphthalene.—To a warm solution of 1.00 g. of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 25 ml. of glacial acetic acid was added 5 ml. of 48% hydrobromic acid. The mixture was warmed on the steam-bath for 2 hours. Enough water was then added to the hot solution to cause slight turbidity, and the solution was allowed to cool in an ice-bath. This resulted in the precipitation of 0.62 g. (58%) of product. Two recrystallizations from ethanol gave white needles, m.p. 197.5–198° dec.

Anal. Calcd. for $C_{18}H_{16}BrNO_2S$: C, 55.39; H, 4.13; N, 3.59. Found: C, 55.33; H, 4.11; N, 3.43.

The infrared spectrum was nearly identical to that of 3-chloro-2-methyl-1-*p*-toluenesulfonamidonaphthalene.

2-Acetoxy-1-cyano-2-methyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene.—To a solution of 4.00 g. of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate and 2 ml. of triethylamine in 75 ml. of reagent benzene was added 4 ml. of liquid hydrogen cyanide (not anhydrous). The reaction mixture was sealed in a 100-ml. heavy wall, screw-cap bottle fitted with a rubber gasket and allowed to stand at room temperature for 17 hours. During this time the color of the solution changed from yellow to a turbid brown. The reaction mixture was treated with Darco and concentrated to 35 ml. Enough petroleum ether (b.p. 30–60°) was added to the hot solution to cause slight turbidity. Upon cooling the solution yielded 3.63 g. (85%) of light tan crystals. Two recrystallizations from ethanol (Darco) gave white crystals, m.p. 210° dec.

Anal. Calcd. for $C_{21}H_{20}N_2O_4S$: C, 63.62; H, 5.09; N, 7.07. Found: C, 63.65; H, 4.83; N, 7.10.

The infrared spectrum indicated the presence of the sulfonamido group and the acetoxyl group, but no absorption bands could be attributed to the nitrile group.

No reaction occurred when a similar experiment was carried out without the addition of the catalyst triethylamine.

A portion of the adduct was dissolved in 10% aqueous sodium hydroxide and allowed to stand at room temperature for 11 hours. When the solution was acidified with dilute (1:1) sulfuric acid, 2-methyl-1-*p*-toluenesulfonamidonaphthalene was recovered.

Action of Concentrated Sulfuric Acid on the Hydrogen Cyanide Adduct: 4-Amino-1-cyano-2-methylnaphthalene.—A solution of 0.5 g. of the hydrogen cyanide adduct in 10 ml. of concentrated sulfuric acid was permitted to stand at room temperature for 15 minutes, then poured onto ice. About 0.1 g. of unidentified solid was removed by filtration and the filtrate was made alkaline by the addition of dilute aqueous sodium hydroxide. A light brown solid precipitated, weighing 0.10 g. (45%). Two recrystallizations from ethanol resulted in white crystals, m.p. 188°.

Anal. Calcd. for $C_{12}H_{10}N_2$: C, 79.09; H, 5.53; N, 15.38. Found: C, 79.24; H, 5.26; N, 15.45.

The infrared spectrum showed a strong band at 2205 cm.$^{-1}$, indicating the presence of a nitrile group; NH stretching bands at 3310 and 3200 cm.$^{-1}$ and an NH_2 deformation band at 1657 cm.$^{-1}$.

Deamination of 4-Amino-1-cyano-2-methylnaphthalene: 2-Methyl-1-naphthonitrile.—A solution of 0.57 g. of sodium nitrite in 10 ml. of water was added during 20 min. to a suspension of 1.38 g. of 4-amino-1-cyano-2-methylnaphthalene in 5 ml. of water and 15 ml. of concd. hydrochloric acid at −5°. The solution was stirred at −5° for an additional 30 min., and 25 ml. of 50% hypophosphorous acid (precooled to −5°) was added slowly. Nitrogen was evolved, and a precipitate of 0.90 g. (71%) of light tan solid was formed upon allowing the solution to warm to room temperature over a period of one hour. Two recrystallizations from aqueous ethanol (Darco) gave white needles, m.p. 86°.

A mixture of this material and an authentic sample of 2-methyl-1-naphthonitrile gave no depression of melting point and the infrared spectra of the two were identical.

Action of Methylmagnesium Iodide on 2-Methyl-*o*-naphthoquinol-*p*-toluenesulfonimide Acetate; 1,2,4-Trimethylnaphthalene.—A solution of methylmagnesium iodide was prepared by the action of 10.08 g. of methyl iodide in 100 ml. of absolute ether on 1.60 g. of magnesium turnings covered with 50 ml. of absolute ether.

The Grignard solution was added through a sintered glass filter to a solution of 6.00 g. of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 100 ml. of dry benzene at room temperature. The yellow color disappeared within 5 minutes. The mixture was allowed to stand at room temperature for 4.5 hours and then was shaken with 100 ml. of saturated aqueous ammonium chloride. The organic layer was separated, washed with water and dried over anhydrous magnesium sulfate. The solution was concentrated to about half of its original volume, and 100 ml. of petroleum ether (b.p. 30–60°) was added, resulting in the precipitation of 1.42 g. of white solid which proved to be *p*-toluenesulfonamide.

The filtrate from the *p*-toluenesulfonamide was evaporated to 3.02 g. of viscous gum. This material was heated to 60° at 1 mm. in a sublimation apparatus, and a total of 1.47 g. (53%) of white crystals was collected on the cold finger. Two recrystallizations from methanol gave white platelets, m.p. 53–54° (lit.[6] m.p. 54–55°). The residue, after sublimation, weighed 1.55 g. and could not be purified.

Anal. Calcd. for $C_{13}H_{14}$: C, 91.71; H, 8.29. Found: C, 91.73; H, 8.61.

The infrared spectrum (taken on the melt) exhibited methyl deformation bands at 1473 and 1388 cm.$^{-1}$. It also presented evidence for an *o*-substituted benzene structure,

(5) H. Willstaedt, *Svensk Kem. Tid.*, **56**, 267 (1944).

(6) M. C. Kloetzel, THIS JOURNAL, **62**, 1708 (1940).

751 cm.$^{-1}$, and penta-substituted benzene structure 874 cm.$^{-1}$.

A portion of the product was converted to the picrate in methanol as solvent. Recrystallization from methanol gave orange needles, m.p. 149° (lit.[6] m.p. 148–148.5°).

Anal. Calcd. for $C_{19}H_{17}N_3O_7$: C, 57.14; H, 4.29. Found: C, 57.16; H, 4.14.

Action of Mercaptoethanol, Thiophenol, Acetylacetone, Morpholine and Phenol on 2-Methyl-*o*-naphthoquinol-*p*-toluenesulfonimide Acetate.—Attempts to add mercaptoethanol and thiophenol in presence of triethylamine in chloroform solution to 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate failed and only 2-methyl-1-*p*-toluenesulfonamidonaphthalene resulted. Acetylacetone with sodium methoxide as catalyst in anhydrous dioxane, morpholine in chloroform, phenol with triethylamine catalyst were unreactive and the starting material was recovered unchanged.

3-Acetoxy-2-methyl-1-*p*-toluenesulfonamidonaphthalene.—An attempt to add benzenesulfinic acid to 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate failed, but under the reaction conditions acetic acid reacted with formation of 3-acetoxy-2-methyl-1-*p*-toluenesulfonamidonaphthalene. Omission of the sodium benzenesulfinate in the experiment described would probably not have affected the result.

To a solution of 2.00 g. of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate and 0.92 g. of sodium benzenesulfinite in 80 ml. of glacial acetic acid was added 6 drops of concentrated sulfuric acid. A turbidity was immediately apparent. The mixture was allowed to stand at room temperature for 46 hours and was then concentrated to one half its original volume in a stream of air. The concentrate was poured into water, and a gummy solid was formed. The crude material was recrystallized from ethanol (Darco) to give 1.16 g. (58%) of a slightly-yellow, crystalline solid. Four recrystallizations from glacial acetic acid gave white crystals, m.p. 202–203°.

Anal. Calcd. for $C_{20}H_{19}NO_4S$: C, 65.02; H, 5.18; N, 3.79. Found: C, 65.08; H, 5.23; N, 3.52.

The infrared spectrum indicated the presence of the acetoxyl group.

3-Hydroxy-2-methyl-1-*p*-toluenesulfonamidonaphthalene.—An attempt to add hydrogen fluoride to 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in glacial acetic acid as solvent failed. However, the addition of acetic acid apparently was catalyzed and during the separation of the product hydrolysis of the acetoxyl group was effected.

To a solution of 0.50 g. of 2-methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 20 ml. of glacial acetic acid at *ca.* 50° was added one ml. of 49% hydrofluoric acid. The yellow color disappeared in about 5 minutes. After the mixture had been allowed to stand at room temperature for 9 hours, it was poured into water, and the resulting pink solid was removed by filtration. The crude material was dissolved in ethanol and treated twice with Darco. Enough water was added to the hot ethanolic solution to cause slight turbidity; and, upon cooling, the solution yielded 0.18 g. (41%) of white crystals. Two recrystallizations from aqueous acetic acid gave white crystals, m.p. 197° dec.

Anal. Calcd. for $C_{13}H_{17}NO_3S$: C, 66.03; H, 5.24; N, 4.28. Found: C, 65.67; H, 5.03; N, 4.19.

The infrared spectrum indicated the presence of a phenolic hydroxyl group: OH stretching band at 3400 cm.$^{-1}$ and C–O deformation band at 1244 cm.$^{-1}$.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Ortho Esters, Imidic Esters and Amidines. VII. N-Alkylformanilides from Alkyl Orthoformates and Primary Aromatic Amines; Rearrangement of Alkyl N-Arylformimidates[1]

BY ROYSTON M. ROBERTS AND PAUL J. VOGT

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The major product of the reaction of an alkyl orthoformate and a primary aromatic amine in the presence of sulfuric acid catalyst at temperatures above 140° has been shown to be an N-alkylformanilide. Alkyl N-arylformimidates, which are the major products of these same reactants at lower temperatures, undergo molecular rearrangement to N-alkylformanilides at higher temperatures under the influence of sulfuric acid. Good yields of several N-alkylformanilides have been obtained directly from primary aromatic amines and alkyl orthoformates. Since the latter are easily obtained by transesterification of methyl or ethyl orthoformate and since N-alkylformanilides are readily hydrolyzed to N-alkylanilines, this sequence of reactions provides a new convenient synthesis of pure secondary amines of the type Ar-NH-R.

The reaction of ethyl orthoformate with aniline was shown by Wichelhaus[2] in 1869 to produce N,N′-diphenylformamidine. Later, Claisen[3] demonstrated that another product, ethyl N-phenylformimidate, could be obtained in low yield from the same reactants under slightly different conditions. Recently, the mechanism of these reactions has been studied,[4] and it has been shown that excellent yields of ethyl N-phenylformimidate may be obtained by the use of acid catalysts.[5] In the course of these studies, while investigating the use of various acids as catalysts, it was observed that in certain experiments in which sulfuric acid was used low yields of ethyl N-phenylformimidate resulted and significant amounts of a higher-boiling material were produced. This higher-boiling material was easily identified as N-ethylformanilide, which is isomeric with ethyl N-phenylformimidate. After considerable investigation, conditions were established under which good yields of N-ethylformanilide could be obtained. Thus, by varying catalysts and experimental conditions, it is now possible to produce in good yield any one of three different products from the reaction of ethyl orthoformate with aniline!

N,N′-Diphenylformamidine is obtained from the reactants in the absence of an acid catalyst or in the presence of such a catalyst whenever there are present two moles of aniline per mole of ethyl orthoformate, since ethyl N-phenylformimidate,

(1) Presented before the Division of Organic Chemistry at the Minneapolis Meeting of the American Chemical Society, September 16, 1955. Taken from the M.A. thesis of Paul J. Vogt, University of Texas, January, 1955.

(2) H. Wichelhaus, *Ber.*, **2**, 116 (1869).

(3) L. Claisen, *Ann.*, **287**, 363 (1895).

(4) R. M. Roberts and R. H. DeWolfe, THIS JOURNAL, **76**, 2411 (1954).

(5) (a) R. M. Roberts, *ibid.*, **71**, 3848 (1949); (b) R. M. Roberts and P. J. Vogt, *Org. Syntheses*, **35**, 64 (1955).