Anal. Calcd. for $C_{13}H_9O_3N$: C, 68.72; H, 3.99. Found: C, 68.86; H, 4.15.

2-(2'-Pyridyl)-10-methoxybenzo[h]quinoline-4-carboxylic Acid (VII).—A solution of 1.4 g. (0.0066 mole) of VI in 60 ml. of 5% aqueous potassium hydroxide solution and 90 ml. of 95% ethanol was brought to reflux when there was added 7.3 g. (6.7 ml., 0.061 mole) of α-pyridyl methyl ketone. Refluxing was continued for 24 hr.; the solvent was removed under vacuum and the residual tar repeatedly extracted with hot 2% aqueous potassium hydroxide solution (chilling each time to solidify the tar so that the aqueous phase could be easily decanted) until the extract no longer gave a precipitate when acidified with acetic acid (care being taken not to add excess acid, otherwise unreacted VI precipitates). The suspension of crude product was heated on a steam-bath, refrigerated and the product collected at the pump. By this procedure there was obtained between 1.13 g. and 1.80 g. of VII (52–83% yield), m.p. 225°. An analytical sample was prepared by successive recrystallization from a large volume of glacial acetic acid by addition of water and by reprecipitation of the acid from a dilute solution of sodium hydroxide by acidification with acetic acid (charcoal), followed by drying at 100° over phosphorus pentoxide at 1 mm., m.p. 236–237°.

Anal. Calcd. for $C_{20}H_{14}O_3N_2$: C, 72.72; H, 4.27; N, 8.48. Found: C, 72.68; H, 3.80; N, 8.67.

The hydrochloride was prepared by allowing the analytical sample to equilibrate with hydrogen chloride gas, whereupon the yellow color of the base turned to the orange of the hydrochloride. The sample was found to revert from orange to yellow on heating to 211–216° and to sinter with decomposition and sublimation at 332–342°.

Anal. Calcd. for $C_{20}H_{15}O_3N_2Cl$: C, 65.49; H, 4.12; N, 7.63; Cl, 9.67. Found: C, 65.4; H, 4.1; N, 7.85; Cl, 7.97.

2-(2'-Pyridyl)-10-hydroxybenzo[h]quinoline-4-carboxylic Acid (VIII).—VII (2.3 g., 0.007 mole) was refluxed for 8 hr. with 20 ml. of 48% aqueous hydrobromic acid containing 1 ml. of hypophosphorous acid. The reaction mixture was diluted with water, chilled and the crude precipitate collected at the pump. The dark colored material was treated with hot dilute potassium hydroxide for 10 minutes and filtered. The precipitate was next suspended in water, made slightly acidic with acetic acid and again collected. After crystallization from boiling pyridine (charcoal) there was obtained, as yellow needles, 1.49 g. (67.5%) of material melting at 350–351°.

Anal. Calcd. for $C_{19}H_{12}O_3N$: C, 77.14; H, 3.87. Found: C, 77.36; H, 4.13.

2'-(2'-Pyridyl)-10-hydroxybenzo[h]quinoline-4-carboanilide (I).—One hundred mg. of VIII (0.00032 mole) was refluxed for 2 hr. with 7 ml. of anhydrous benzene containing 0.45 ml. (0.0023 mole) of thionyl chloride. The reaction mixture was chilled, and 1.4 ml. of aniline (0.052 mole) dissolved in 5 ml. of anhydrous benzene was added. After refluxing for an additional half-hour the mixture was chilled and poured into water. All solvent was evaporated by a stream of air and the amorphous yellow material collected and washed with dilute acetic acid. The product was then extracted with portions of boiling, dilute potassium carbonate solution until the extract remained colorless. The residue was dissolved in boiling dimethylformamide, the solution filtered hot, allowed to cool and once again filtered. The product was recovered by diluting the hot solution with water until just cloudy and then allowing to cool. After collecting and washing with water and dilute acetic acid and drying over calcium chloride, 86 mg. (70%) of a yellow material which melted at 300–301° with decomposition was obtained. For analysis the compound was dried for 5 hr. at 180° over phosphorus pentoxide at 1 mm.

Anal. Calcd. for $C_{25}H_{17}O_3N_3$: N, 10.71. Found: N, 10.56.

Anilide of 2-(2'-Pyridyl)-cinchoninic Acid (IX).—2-(2'-Pyridyl)-cinchoninic acid[12] was refluxed with excess thionyl chloride until all solid material had dissolved. Excess solvent was removed under vacuum and the residue warmed with an excess of aniline. After washing with dilute acetic acid the product was recrystallized from ethanol, methanol and acetone, m.p. 238°.

Anal. Calcd. for $C_{21}H_{15}ON_3$: N, 12.93. Found: N, 13.20.

The Cu^{II} and Zn^{II} chelates of IX were prepared by mixing dilute solutions of the metal halide and IX in methanol, collecting the precipitate and washing with large volumes of methanol, then drying at 100° over phosphorus pentoxide at 1 mm.

Anal. Calcd. for $C_{21}H_{15}ON_3CuCl_2$: C, 54.85; H, 3.29; Cl, 15.42. Found: C, 54.64; H, 3.52; Cl, 14.90.

Anal. Calcd. for $C_{21}H_{15}ON_3ZnCl_2$: C, 54.63; H, 3.28; Cl, 15.36. Found: C, 54.63; H, 3.57; Cl, 15.4.

Continuous Variation Studies.—Stock solutions of the metallic chlorides or nitrates (analytical grade) and the chelating agent were prepared and aliquots mixed in the proper ratios. Absorption measurements were made at selected wave lengths. Absorbance values were obtained by subtracting the absorbance for zero complexation from the observed readings, all measurements being carried out with a Beckman DU spectrophotometer. Formulas were determined from a plot of absorbance against the mole fraction of chelating agent employed (Fig. 2).

(12) S. P. Massie, *Iowa State Coll. J. Sci.*, **21**, 41 (1946).

NEW HAVEN, CONNECTICUT

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

Quinol Imide Acetates. IV. The Reactions of 2,4-Dimethyl-o-naphthoquinol-p-toluenesulfonimide Acetate

BY ROGER ADAMS AND EDWIN L. DEYOUNG[1]

RECEIVED SEPTEMBER 19, 1956

2,4-Dimethyl-o-naphthoquinol-p-toluenesulfonimide acetate is formed by oxidation with lead tetraacetate of 2,4-dimethyl-1-p-toluenesulfonamidonaphthalene. The quinol imide adds hydrogen chloride, hydrogen bromide and acetic acid with formation of 3-substituted 2,4-dimethyl-1-p-toluenesulfonamidonaphthalenes. On the other hand, hydrogen cyanide gives 2-acetoxy-1-cyano-2,4-dimethyl-1-p-toluenesulfonamido-1,2-dihydronaphthalene, which with alkali is converted to 2,4-dimethyl-1-p-toluenesulfonamidonaphthalene and by acid to 1,1'-dicyano-4,4'-dimethyl-2,2'-dinaphthobenzyl ether. Lead tetraacetate converts 4-methyl-1-p-toluenesulfonamidonaphthalene to 4-methyl-p-naphthoquinol-p-toluenesulfonimide acetate.

Benzoquinol imide acetates[2] and o-benzoquinol imide diacetates[3] have been shown to undergo many of the addition reactions typical of the quinone mono- and di-imides. Similar studies on

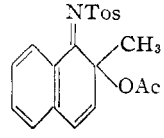
(1) An abstract of part of a thesis submitted by Edwin L. DeYoung to the Graduate College of the University of Illinois, 1956, in partial fulfilment of the requirements for the Degree of Doctor of Philosophy. Minnesota Mining and Manufacturing Co. Fellow, 1953–1956.

(2) R. Adams and K. R. Brower, THIS JOURNAL, **78**, 4770 (1956).

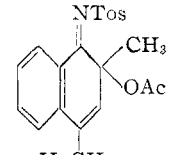
(3) R. Adams, E. J. Agnello and R. S. Colgrove, *ibid.*, **77**, 5617 (1955).

naphthalene analogs also have been reported.[4] 2-Methyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate (I) added in the expected way a variety of reagents of the type HX with concurrent elimination of acetic acid and formation of 3-substituted naphthalene derivatives. On the other hand, hydrogen cyanide and methylmagnesium iodide did not add in the same manner; 1,2-additions occurred, followed by rearrangements which resulted in 4-substituted naphthalene derivatives.

The present investigation describes the addition reactions of 2,4-dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate (II). In this molecule the 4-position is occupied, which prevents any rearrangement leading to substitution in that position. Synthesis of II was achieved in 81% yield by the lead tetraacetate oxidation of 2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene.



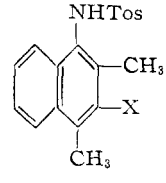
I



II

Hydrogen chloride added to II in chloroform as solvent to give 3-chloro-2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene (III). The position of the chlorine in the 3-position was demonstrated by the following infrared correlations: The single C–H absorption band at 860 cm.$^{-1}$ for a penta-substituted benzene was absent, and the C–Cl absorption band at 704 cm.$^{-1}$ was present. In the known cases of naphthalenes with all positions in one ring substituted, an *o*-disubstituted benzene C–H absorption band at about 750 cm.$^{-1}$ is exhibited.[5] In this molecule the absorption band was present at 752 cm.$^{-1}$. The possibility that the chlorine atom was in the previously unsubstituted ring was thus eliminated.

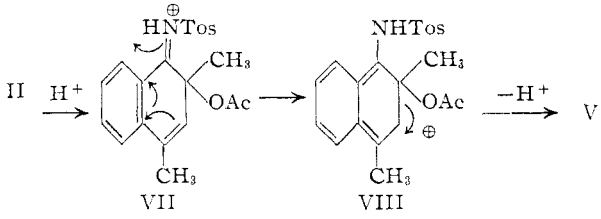
Hydrogen bromide added to II in acetic acid solution to give 3-bromo-2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene (IV) in 47% yield. The position of the entering bromine atom was established in the same way as described for the 3-chloro analog. A band at 704 cm.$^{-1}$ in the infrared spectrum indicated the presence of a C–Br bond.



III, X = Cl
IV, X = Br
V, X = OAc
VI, X = OH

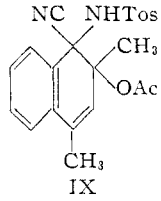
Heating the quinol acetate II in glacial acetic acid, or in ethanol with a catalytic amount of sulfuric acid resulted in migration of the acetoxyl group to the 3-position. Refluxing for 48 hours in ethanol without catalyst did not affect a rearrangement. The structure of the rearranged product V was deduced on the basis of infrared data. The carbonyl infrared absorption band appeared at 1749 cm.$^{-1}$ which is consistent with a naphthol ester, since the carbonyl absorption band of vinyl or phenyl esters is at a higher frequency than that of an alkyl ester. By alkaline hydrolysis the acetoxy group was hydrolyzed and the 3-napththol derivative VI was formed. It gave a positive color test with ammonium phosphomolybdate and its infrared spectrum showed absorption bands for a phenolic hydroxyl group.

This rearrangement can be explained on the basis of protonation of II to give the carbonium ion VII which may exist in a resonance form VIII. Migration of the acetoxyl group followed by loss of a proton would afford V.

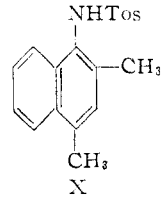


Hydrogen cyanide, when catalyzed with triethylamine, added to II in benzene solution to form a 1,2-addition product of structure IX. The structure IX was deduced from the analytical and infrared data. The infrared spectrum was very similar to that of the hydrogen cyanide adduct described by Adams and Dunbar.[4] The presence of the acetoxyl group was indicated by bands at 1729 and 1275 cm.$^{-1}$; the sulfonamide group was shown by –NH absorption at 3240 cm.$^{-1}$; no bands could be attributed to the nitrile group.

Further proof of structure IX was afforded by treatment of the product with base and acid. With 10% methanolic potassium hydroxide followed by acidification, both nitrile and acetoxyl groups were lost and the amide X was formed. The mechanism for this conversion is assumed to be similar to that proposed by Adams and Dunbar[4] for the 2-methyl analog.



IX

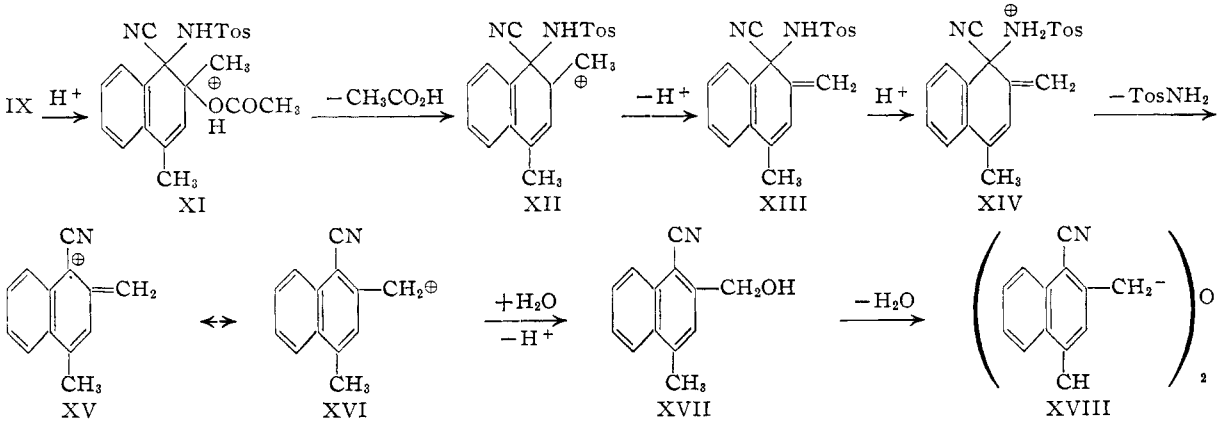


X

Treatment of IX with cold, concentrated sulfuric acid gave two products, *p*-toluenesulfonamide, and a yellow compound for which the structure 1,1′-dicyano-4,4′-dimethyl-2,2′-dinaphthobenzyl ether (XVIII) is proposed. The infrared absorption spectrum of XVIII shows the nitrile band at 2215 cm.$^{-1}$, and an ether band at 1280 cm.$^{-1}$.

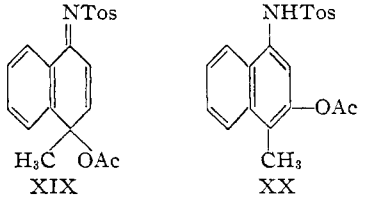
A possible reaction leading to these products could be initiated by protonation of the acetoxyl group to give the carbonium ion XI. Loss of acetic acid would lead to the carbonium ion XII, which could then lose a proton to give the methylene compound XIII. Protonation of the toluenesulfonamido group, as shown in XIV, followed by loss of *p*-toluenesulfonamide, would give the carbonium ion XV. This could aromatize to give the carbonium ion XVI. Hydration of XVI followed

(4) R. Adams and J. E. Dunbar, THIS JOURNAL., **78**, 4774 (1956).
(5) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954, p. 66.



by intramolecular dehydration would result in formation of the dinaphthobenzyl ether XVIII.

4-Methyl-*p*-naphthoquinol-*p*-toluenesulfonimide acetate (XIX) was prepared by the lead tetraacetate oxidation of N-*p*-toluenesulfonyl-1-amino-4-methylnaphthalene.



Structure XIX was deduced from the infrared absorption spectrum and its comparison with the spectra of other similar quinol imide acetates[2]; the C=N group represented by a single band at 1544 cm.$^{-1}$, and the acetoxyl group by bands at 1737 and 1245 cm.$^{-1}$.

Upon attempted addition of hydrogen chloride to compound XIX in chloroform solution, the rearranged acetoxy compound XX resulted. This same product was obtained by treatment of an acetic acid solution of XIX with one drop of concentrated sulfuric acid at room temperature. The infrared spectrum of XX indicated the presence of an acetate of the vinyl ester type by bands at 1760 and 1215 cm.$^{-1}$.

Acknowledgment.—The authors are indebted to Mrs. Louise Griffing and Mr. James Brader for the determination and interpretation of the infrared absorption spectra, and to Mrs. R. Maria Benassi, Mrs. Ruby Ju, Mrs. Lucy Chang and Mr. Joseph Nemeth for microanalyses.

Experimental

All melting points are corrected.

2,4-Dimethyl-1-*p*-toluenesulfonamidonaphthalene.—1,3-Dimethylnaphthalene was prepared according to the directions of Evans and Smith,[6] and then nitrated and reduced to 1-amino-2,4-dimethylnaphthalene by the methods of Adams and Gibbs.[7] A pyridine solution of 19.5 g. of 1-amino-2,4-dimethylnaphthalene with 23.8 g. of *p*-toluenesulfonyl chloride was permitted to stand for an hour then poured into ice and hydrochloric acid. The product weighed 37.0 g. (86.5%). It was purified by recrystallization from ethanol (Darco); white needles, m.p. 191–192°.

Anal. Calcd. for $C_{19}H_{19}NO_2S$: C, 70.02; H, 5.88; N, 4.31. Found: C, 70.10; H, 5.60; N, 4.29.

(6) R. E. Evans and J. C. Smith, *J. Inst. Petroleum*, **37**, 80 (1951).

(7) R. Adams and H. H. Gibbs, THIS JOURNAL, **79**, 170 (1957).

2,4-Dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide Acetate.—To a solution of 10.0 g. of 2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene in 300 ml. of chloroform was added 15.0 g. of lead tetraacetate and the mixture was stirred under reflux for 2 hours. The solution was then filtered from lead salts, and the excess solvent evaporated *in vacuo*. Upon trituration of the remaining dark brown sirup with 15 ml. of methanol, the mass set to orange crystals. The yield was 9.5 g. (81%). The compound was purified by recrystallization from methanol (Darco); yellow prisms, m.p. 159–160°.

Anal. Calcd. for $C_{21}H_{21}NO_4S$: C, 65.82; H, 5.52; N, 3.67. Found: C, 65.92; H, 5.47; N, 3.86.

The infrared spectrum indicated the presence of a singly conjugated C=N group by a band at 1677 cm.$^{-1}$. The presence of the acetate group was indicated by bands at 1733 and 1246 cm.$^{-1}$.

3-Chloro-2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene.—A stream of dry hydrogen chloride was passed through a solution of 2.0 g. of 2,4-dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 30 ml. of chloroform for 35 minutes. The reaction mixture was allowed to remain at room temperature for one hour, and the chloroform was then evaporated in an air stream. The white residue weighed 1.7 g. (90.4%). It was purified by recrystallization from ethanol (Darco); white needles, m.p. 226–227°.

Anal. Calcd. for $C_{19}H_{18}ClNO_2S$: C, 63.46; H, 5.04; N, 3.89. Found: C, 63.84; H, 5.08; N, 3.76.

The infrared spectrum showed the C–Cl group by an absorption band at 704 cm.$^{-1}$.

3-Bromo-2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene.—To a suspension of 2.0 g. of 2,4-dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 40 ml. of glacial acetic acid was added 10 ml. of 48% aqueous hydrobromic acid, and the mixture was heated for 2 hours on the steam-bath. Upon cooling, a red solid precipitated which weighed 1.0 g. (47.5%). The compound was purified by recrystallization from ethanol (Darco); white needles, m.p. 220°.

Anal. Calcd. for $C_{19}H_{18}BrNO_2S$: C, 56.51; H, 4.48; N, 3.46. Found: C, 57.01; H, 4.60; N, 3.21.

The infrared spectrum showed the C–Br bond by an absorption band at 704 cm.$^{-1}$.

3-Acetoxy-2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene. Method A.—A solution of 1.0 g. of 2,4-dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 30 ml. of glacial acetic acid was heated under reflux for 30 minutes. The solution was cooled, and the acetic acid removed *in vacuo*. The product, weighing 1.0 g. (quant.), was purified by recrystallization from ethanol (Darco); white needles, m.p. 226–227°.

Method B.—To a solution of 1.0 g. of 2,4-dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 30 ml. of ethanol was added 2 drops of concd. sulfuric acid and the mixture was heated under reflux for 1.5 hours. The ethanol was removed in an air stream and the resulting white residue recrystallized from ethanol (Darco) to give 0.6 g. (60%) of product. Further recrystallization from ethanol gave white needles, m.p. 226–227°. This compound was identical with that prepared by method A.

Anal. Calcd. for $C_{21}H_{21}NO_4S$: C, 65.82; H, 5.52; N, 3.67. Found: C, 65.60; H, 5.69; N, 3.63.

The infrared spectrum showed the C=O bands of the vinyl ester type at 1749 and 1224 cm.$^{-1}$.

2,4-Dimethyl-3-hydroxy-1-*p*-toluenesulfonamidonaphthalene.—To 25 ml. of a 10% methanolic potassium hydroxide solution was added 1.0 g. of 3-acetoxy-2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene and the reaction mixture was heated under reflux for 5 hours. The reaction mixture was then poured into 100 ml. of water and acidified with concentrated hydrochloric acid to give a white precipitate which weighed 0.8 g. (90%). The compound was purified by recrystallization from ethanol (Darco); white needles, m.p. 205–206°.

Anal. Calcd. for $C_{19}H_{19}NO_3S$: C, 66.86; H, 5.61; N, 4.11. Found: C, 66.60; H, 5.49; N, 4.04.

Absorption bands at 3500 and 1321 cm.$^{-1}$ in the infrared spectrum indicated the presence of a phenolic hydroxyl group.

2-Acetoxy-1-cyano-2,4-dimethyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene.—To a solution of 3.83 g. of 2,4-dimethyl-*o*-naphthoquinol-*p*-toluenesulfonimide acetate in 85 ml. of benzene was added 3 ml. of hydrogen cyanide (not anhydrous) and 1 ml. of triethylamine. The reaction mixture was allowed to remain at room temperature for 24 hours, at the end of which time colorless crystals had precipitated from the solution. These were separated by filtration, and the filtrate evaporated to 25 ml. and poured into 250 ml. of petroleum ether (b.p. 90–110°) to give a second crop of white crystals. The total yield was 3.9 g. (95%). The compound was purified by recrystallization from ethanol (Darco); white needles, m.p. 186–187°.

Anal. Calcd. for $C_{22}H_{22}N_2O_4S$: C, 64.44; H, 5.39; N, 6.83. Found: C, 64.21; H, 5.42; N, 6.67.

Treatment of 2-Acetoxy-1-cyano-2,4-dimethyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene with Base.—A solution of 0.5 g. of 2-acetoxy-1-cyano-2,4-dimethyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene in 25 ml. of 10% methanolic potassium hydroxide was heated under reflux for 2 hours. Cooling the solution, and acidifying with concentrated hydrochloric acid gave 0.23 g. (59%) of a white solid which was purified by recrystallization from ethanol, m.p. 190–191°. The product was 2,4-dimethyl-1-*p*-toluenesulfonamidonaphthalene.

Treatment of 2-Acetoxy-1-cyano-2,4-dimethyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene with Concentrated Sulfuric Acid.—To 15 g. of concd. sulfuric acid cooled to 0°, was added 1.0 g. of 2-acetoxy-1-cyano-2,4-dimethyl-1-*p*-toluenesulfonamido-1,2-dihydronaphthalene and the reaction mixture was kept at 0° for 3 hours. At the end of this time, it was poured onto 30 g. of ice to give a yellow precipitate, which was separated by filtration and dried. The filtrate was extracted with four 50-ml. portions of ether, the ether extracts were dried and evaporated to give 0.1 g. of white solid. The yellow solid was extracted with 20 ml. of boiling 5% aqueous sodium carbonate. The sodium carbonate extracts were acidified with concentrated hydrochloric acid to give 0.25 g. of white crystals. The two crops of white crystals were combined; total yield 0.35 g. (84%). They were recrystallized from 1:1 ethanol–water to give white needles, m.p. 137–139°. This was *p*-toluenesulfonamide.

The remaining yellow solid was purified by chromatography on alumina. Elution with a 1:1 ethyl acetate–chloroform solvent pair afforded 0.22 g. (24%) of a yellow solid. The compound was purified by recrystallization from a 1:1 chloroform–cyclohexane solvent pair to give yellow needles, m.p. 250°. It proved to be 1,1′-dicyano-4,4′-dimethyl-2,2′-dinaphthobenzyl ether.

Anal. Calcd. for $C_{28}H_{20}N_2O$: C, 83.02; H, 5.35; N, 7.46; mol. wt., 376. Found: C, 83.15; H, 5.10; N, 7.41; mol. wt. (ebullioscopic), 395.

The infrared spectrum showed a nitrile band at 2215 cm.$^{-1}$, and an ether band at 1280 cm.$^{-1}$.

4-Methyl-1-*p*-toluenesulfonamidonaphthalene.—To a solution of 4.0 g. of 1-amino-4-methylnaphthalene, prepared according to the method of Lesser,[8] in 30 ml. of pyridine was added 5.3 g. of *p*-toluenesulfonyl chloride. After heating the mixture on the steam-bath for one hour and pouring into 100 ml. of ice and concentrated hydrochloric acid, a brown solid was obtained which weighed 5.3 g. (63%). The compound was purified by recrystallization from ethanol (Darco); white needles, m.p. 166–167°.

Anal. Calcd. for $C_{18}H_{17}NO_2S$: C, 69.48; H, 5.51; N, 4.49. Found: C, 69.68; H, 5.44; N, 4.56.

4-Methyl-*p*-naphthoquinol-*p*-toluenesulfonimide Acetate.—To a solution of 4.5 g. of 4-methyl-1-*p*-toluenesulfonamidonaphthalene in 200 ml. of chloroform was added 7.1 g. of lead tetraacetate and the mixture was stirred under reflux for 2 hours. The solution was filtered from lead salts and the excess solvent evaporated *in vacuo*. The remaining dark brown sirup was triturated with methanol and heated to boiling. The sirup crystallized and the crystals were taken up in more methanol and recrystallized to give 2.9 g. (54%) of tan crystals. The compound was purified by recrystallization from methanol (Darco); cream-colored crystals, m.p. 153–155°.

Anal. Calcd. for $C_{20}H_{19}NO_4S$: C, 65.13; H, 5.18; N, 3.79. Found: C, 65.09; H, 5.33; N, 3.84.

The infrared spectrum indicated the presence of a doubly conjugated C=N bond by a band at 1544 cm.$^{-1}$.

3-Acetoxy-4-methyl-1-*p*-toluenesulfonamidonaphthalene. Method A.—To a solution of 0.5 g. of 4-methyl-*p*-naphthoquinol-*p*-toluenesulfonimide acetate in 10 ml. of glacial acetic acid was added one drop of concentrated sulfuric acid. The reaction mixture was allowed to remain for one hour at room temperature and then poured into 100 ml. of water to give 0.45 g. (95%) of a pink precipitate. The product was purified by recrystallization from ethanol (Darco); white needles, m.p. 205–206°.

Method B.—To a solution of 1.0 g. of 4-methyl-*p*-naphthoquinol-*p*-toluenesulfonimide acetate in 20 ml. of chloroform was passed a stream of hydrogen chloride for 30 minutes. The reaction mixture was allowed to remain at room temperature for one hour at which time the chloroform was evaporated in an air stream. The orange solid resulting was taken up in boiling ethanol and cooled to give 0.45 g. (45%) of white crystals. The compound was purified by recrystallization from ethanol; m.p. 204–205°. The product was identical with that prepared by method A.

Anal. Calcd. for $C_{20}H_{19}NO_4S$: C, 65.13; H, 5.18; N, 3.79. Found: C, 64.94; H, 5.20; N, 3.95.

The infrared spectrum indicated the presence of a vinyl-type acetate by bands at 1760 and 1215 cm.$^{-1}$.

URBANA, ILLINOIS

(8) R. Lesser, *Ann.*, **402**, 12 (1914).