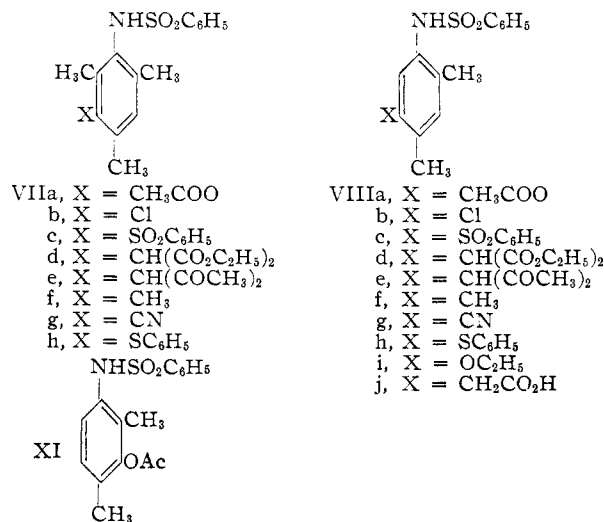
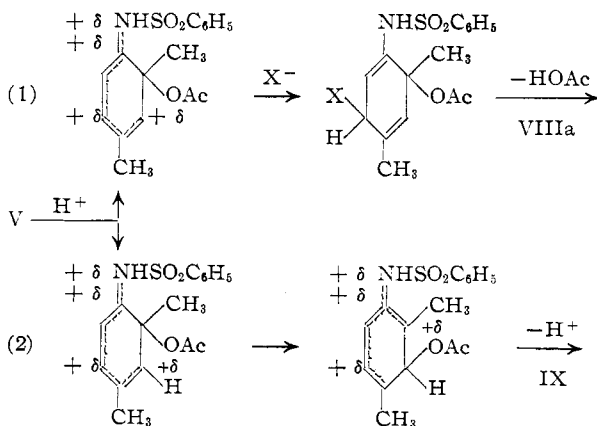


(2) F. Wessely, *et al.*, *Monatsh. Chem.*, **81**, 811 (1950); **81**, 1055 (1950); **83**, 902 (1952); **84**, 291 (1953); **85**, 69 (1954).

owing to reaction of IV with the solvent to produce 3-acetoxy-*N*-benzenesulfonylmesidine (VIIa). Compound VIIa can be formed in good yield by heating IV under reflux in acetic acid for a few minutes. It is also formed at a much slower rate, evidently by an intramolecular rearrangement, by heating under reflux in ethanol. The structure of VIIa was proved by hydrolysis to 3-aminomesitol of which an authentic sample was prepared from 3-nitromesidine by diazotization, decomposition in hot aqueous acid and reduction.



Since the 3- and 5-positions in *N*-benzenesulfonylmesidine are equivalent, the position occupied in the quinol imide acetate IV by the entering group is uncertain. In the case of compound V it was possible to settle this question. When compound V is heated in acetic acid VIIIa is the primary product, but when V is allowed to rearrange by treatment of its solution in dioxane with a small amount of sulfuric acid the product is IX. It may thus be deduced that the normal mode of addition-elimination is represented by reaction scheme 1 while the intramolecular rearrangement follows scheme 2

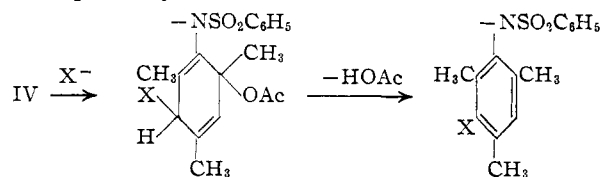


The compounds VIIIa and IX were synthesized by unequivocal routes. Compound VIIIa was made from 2,4-dimethyl-5-nitroaniline by replacement of the amino group by hydroxyl, acetylation, reduction of the nitro group and benzenesulfonation.

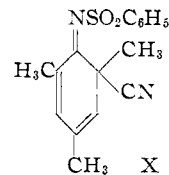
Compound IX was derived from 2-amino-4-nitro-1,3-xylene by the same sequence of operations.

Other acids which add to IV and V are hydrogen chloride which produces VIIb and VIIIb, benzenesulfonic acid which produces VIIc and VIIIc, and thiophenol which produces VIIh and VIIIh, respectively. Compound V adds ethanol to produce VIIIi although IV is relatively inert to this reagent. Compound VIIIi was synthesized by another route: conversion of 2,4-dimethyl-5-nitroaniline to 2,4-dimethyl-5-nitrophenol, ethylation, reduction and benzenesulfonation. The structures VIIIb through VIIIh were assigned by analogy.

Quinol imide acetates undergo addition reactions in basic as well as acidic media as shown by the reaction of IV and V with diethyl sodiomalonate, sodioacetylacetone, methylmagnesium iodide and triethylammonium cyanide to produce VIIId-VIIg and VIIIId-VIIIg, respectively. The reactions probably follow the scheme



The reaction of IV with cyanide ion is abnormal to a large degree since the major portion of the product is a molecule in which the acetate ion is replaced by cyanide ion to give a new quinonoid substance probably having structure X. The in-



frared and ultraviolet spectra of the substance show maxima at 1552 cm.<sup>-1</sup> (C=N) and 320 mμ (log ε 3.5) and are intermediate between the values cited above for *o*- and *p*-quinol imide acetates. The over-all appearance of the ultraviolet spectrum resembles that of V much more than that of VI, however, and structure X is more likely than the corresponding *p*-quinonoid structure.

Although the rates of the addition reactions of IV and V have not been compared quantitatively, it can be said that V is definitely the more reactive. Under the conditions used for addition of thiophenol, for example, V reacts exothermically while IV requires several hours standing. A still greater difference is evident in the addition of ethanol which proceeds readily with V but not at all with IV. The lower reactivity of IV may be owing to a combination of steric hindrance and a decrease in the driving force (reduction potential) caused by the release of electrons from the additional methyl group.

The addition reactions of the quinol imide acetates may be applied to the synthesis of otherwise inaccessible compounds. The resultant benzenesulfonanilides may be hydrolyzed to the corresponding amines and the amino groups replaced by hydrogen or other atoms or groups. The active

methylene adducts are exemplified by N-benzenesulfonyl-3-dicarbethoxymethylmesidine (VIII<sub>d</sub>) which may be hydrolyzed to N-benzenesulfonyl-3-carboxymethylmesidine (VIII<sub>j</sub>). Unusual structures may thus be synthesized.

**Acknowledgment.**—The authors are indebted to Mr. J. Nemeth, Mrs. M. Benassi and Mr. R. Nessel for the microanalyses and to Mr. J. Brader and Mrs. L. Griffin for the determination of the infrared spectra.

### Experimental

All melting points are corrected.

**2,4,6-Trimethyl-*o*-quinolbenzenesulfonimide Acetate.**—A solution of 50 g. of benzenesulfonylmesidine and 85 g. (1 mole equiv.) of lead tetraacetate in a mixture of 50 ml. of acetic acid and 800 ml. of chloroform was allowed to stand at 28°. After standing for 24 hours (85% reaction), the mixture was shaken with water and filtered to remove the precipitated lead dioxide. Extraction of the chloroform layer with alkali to remove unreacted sulfonamide and evaporation to dryness gave yellow crystals of the quinol imide acetate. After recrystallization from ethanol the yield was 24 g. (50% based on lead tetraacetate consumed), m.p. 142–143°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>19</sub>NO<sub>4</sub>S: C, 61.24; H, 5.74; N, 4.20. Found: C, 61.15; H, 5.72; N, 4.24.

**2,4-Dimethyl-*o*-quinolbenzenesulfonimide Acetate.**—A solution of 10 g. of N-benzenesulfonyl-2,4-dimethylaniline and 22 g. (1 mole equiv.) of commercial lead tetraacetate in 150 ml. of chloroform was allowed to stand 15 minutes at room temperature and then poured into water. The chloroform layer was separated, washed with water, dried, and concentrated to 20 ml. on the hot-plate. On cooling, the liquor crystallized, and the solid was recrystallized from 35 ml. of ethanol yielding 3 g. (25%) of yellow crystals, m.p. 126–127°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>NO<sub>4</sub>S: C, 60.15; H, 5.36. Found: C, 60.38; H, 5.51.

**3-Acetoxy-N-benzenesulfonylmesidine.** A.—A solution of 0.5 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 20 ml. of glacial acetic acid was heated under reflux for 30 minutes. The yellow color of the starting material disappeared during the first few minutes of this time. Evaporation to dryness in vacuum and recrystallization from ethanol gave 0.3 g. (60%) of white crystals, m.p. 167–168°.

*Anal.* Calcd. for C<sub>17</sub>H<sub>19</sub>NO<sub>4</sub>S: C, 61.24; H, 5.74; N, 4.20. Found: C, 61.15; H, 5.72; N, 4.24.

B.—A solution of 0.3 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 4 ml. of ethanol was heated under reflux for 36 hours during which time the yellow color faded, but did not entirely disappear. On cooling, white crystals separated and were recrystallized from ethanol, m.p. 169–170°. A melting point of a mixture with the product of method A showed no depression, and the infrared spectra were identical.

**Hydrolysis of 3-Acetoxy-N-benzenesulfonylmesidine: *m*-Aminomesitol.** A.—A solution of 2.0 g. of acetoxy-N-benzenesulfonylmesidine in 15 g. of cold concentrated sulfuric acid was allowed to stand 5 hours. The solution was poured on ice, filtered from a small amount of precipitate, and neutralized with aqueous ammonia. A crystalline precipitate separated and was recrystallized from ethanol-water mixture. The yield was 1.0 g. (87%), m.p. 134–136°.

*Anal.* Calcd. for C<sub>8</sub>H<sub>13</sub>NO: C, 71.49; H, 8.66; N, 9.26. Found: C, 71.45; H, 8.64; N, 9.21.

B.—A solution of 10 g. of 3-nitromesidine in 200 ml. of 10% sulfuric acid was diazotized at 0° by addition of 4.0 g. of sodium nitrite in 20 ml. of water. The diazonium salt solution was then poured slowly into 200 ml. of boiling dilute sulfuric acid solution. After standing 15 minutes at 100° the mixture was cooled, and the dark, oily product was taken up in ether and extracted with aqueous alkali. Acidification gave 6.0 g. of crude phenolic substance which was hydrogenated at low pressure over Raney nickel catalyst. The product was recrystallized from ethanol-water mixture

to give 4.0 g. (36%) of 3-aminomesitol, m.p. 136–137°. A melting point of a mixture with the hydrolysis product described above showed no depression, and the infrared spectra were identical.

**5-Acetoxy-N-benzenesulfonyl-2,4-dimethylaniline.** A.—A solution of 0.5 g. of 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate in 5 ml. of acetic acid was heated at 100° for 15 minutes. The mixture was poured into water, and the precipitate was recrystallized from ethanol yielding 0.3 g. (60%) of white crystals, m.p. 138–150°. Several further crystallizations from ethanol gave a small amount of substance, m.p. 160–161°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>NO<sub>4</sub>S: C, 60.15; H, 5.36. Found: C, 60.37; H, 5.43.

The crude material is undoubtedly contaminated with a substantial amount of the 3-acetoxy compound formed by rearrangement.

B.—A crude preparation of 2,4-dimethyl-5-nitrophenol<sup>4</sup> from 20 g. of 2,4-dimethyl-5-nitroaniline was dissolved in 30 ml. of acetic anhydride and heated under reflux for 2 hours. The mixture was distilled, and a 7.0-g. fraction, b.p. 140–150° (1 mm.), was collected. The distillate was dissolved in 50 ml. of pyridine and hydrogenated over Raney nickel catalyst at low pressure. After filtration, 7.0 g. of benzenesulfonyl chloride was added, and the mixture was poured into water. The precipitated product was recrystallized from ethanol, yielding 8.0 g. of sulfonamide, m.p. 161–162°. A melting point of a mixture with the product of method A showed no depression, and the infrared spectra were identical.

**3-Acetoxy-N-benzenesulfonyl-2,4-dimethylaniline.** A.—A solution of 0.5 g. of 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate in 5 ml. of purified dioxane containing one drop of concentrated sulfuric acid was allowed to stand at room temperature. After two minutes the yellow color of the starting material had faded, and the mixture was poured into water. The precipitate was recrystallized from ethanol, yielding 0.3 g. (60%) of the sulfonamide, m.p. 163–164°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>17</sub>NO<sub>4</sub>S: C, 60.15; H, 5.36. Found: C, 60.43; H, 5.47.

B.—A solution of 40 g. of 2,6-dimethyl-3-nitrophenol<sup>5</sup> in 100 ml. of acetic anhydride was heated under reflux for 2 hours and distilled at reduced pressure. A light yellow oil, b.p. 172–175° (15 mm.), was obtained in the amount of 45 g. (84%).

*Anal.* Calcd. for C<sub>10</sub>H<sub>11</sub>NO<sub>4</sub>: C, 57.39; H, 5.30. Found: C, 57.27; H, 5.02.

A solution of 4.0 g. of the acetate in 30 ml. of pyridine was hydrogenated over Raney nickel catalyst at low pressure. After filtration the solution was reacted with 4.0 g. of benzenesulfonyl chloride and poured into water. The precipitated oil was taken up in ether, washed with dilute hydrochloric acid, and evaporated. The residue was crystallized by addition of 10–15 ml. of ethanol to give 1.5 g. (22%) of crude sulfonamide. After recrystallization from ethanol, the product melted at 162–163°, and a mixture with the product of method A did not show a depressed melting point. The infrared spectra were also identical.

**N-Benzenesulfonyl-2,4-dimethyl-5-ethoxyaniline.** A.—A solution of 0.3 g. of 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate in 4 ml. of ethanol was heated at reflux overnight. The solution became colorless, and on cooling, white crystals were obtained which were recrystallized from the same solvent, m.p. 180–181°.

*Anal.* Calcd. for C<sub>16</sub>H<sub>19</sub>NO<sub>3</sub>S: C, 62.93; H, 6.27; N, 4.59. Found: C, 63.00; H, 6.41; N, 4.49.

B.—A solution of 15 g. of crude 2,4-dimethyl-5-nitrophenol and 5 g. of sodium hydroxide in a mixture of 100 ml. each of ethanol and water was ethylated by adding 14 g. of ethyl bromide and heating at reflux for 1.5 hours. Extraction of the non-acidic material with ether gave, after evaporation, 7 g. of black oil. The oil was distilled in vacuum and 3 g. of distillate, b.p. 135–145° (0.7 mm.) was collected. This oil was dissolved in 25 ml. of methanol and hydrogenated over platinum catalyst. The solution was filtered, evaporated and benzenesulfonated by treatment with 3.5 g. of benzenesulfonyl chloride and 30 ml. of 5% aqueous sodium carbonate. The sulfonamide was

(4) E. Bamberger and E. Reber, *Ber.*, **40**, 2267 (1907).

(5) K. Auwers and T. Markovits, *ibid.*, **41**, 2338 (1908).

recrystallized twice from ethanol to yield 4.0 g. (65%), m.p. 181–182°. A melting point of a mixture with the product of method A showed no depression and the infrared spectra were identical.

**N-Benzenesulfonyl-3-chloromesidine.**—A solution of 1.0 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 20 ml. of chloroform was saturated with hydrogen chloride. In one minute the yellow color disappeared, and after 5 minutes the solution was evaporated to dryness. The white residue was recrystallized from a mixture of ethanol and water and weighed 0.8 g. (90%), m.p. 163–164°. The melting point of a mixture with an authentic sample, m.p. 163–164°, showed no depression.

When the quinol imide acetate is dissolved in ethanol and 48% aqueous hydrobromic acid was added, bromine was immediately set free. Similarly, iodine was liberated from hydrogen iodide.

**N-Benzenesulfonyl-5-chloro-2,4-dimethylaniline.**—A solution of 2.0 g. of 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate in 15 ml. of chloroform was saturated with hydrogen chloride and the yellow color disappeared immediately. The solution was evaporated, and the residue, after recrystallization from petroleum ether (b.p. 80–110°), weighed 1.0 g. After two recrystallizations from ethanol, the product was pure, m.p. 151–152°.

*Anal.* Calcd. for  $C_{14}H_{14}ClNO_2S$ : C, 56.85; H, 4.77. Found: C, 57.19; H, 4.70.

**3-N-Dibenzesulfonylmesidine.**—A solution of 0.5 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate and 0.5 g. of benzenesulfonic acid in 5 ml. of ethanol was allowed to stand overnight. White crystals separated and were recrystallized from ethanol, m.p. 192–193°, yield 0.3 g. (50%).

*Anal.* Calcd. for  $C_{21}H_{21}NO_4S$ : C, 60.69; H, 5.10. Found: C, 60.91; H, 6.25.

**N-Benzenesulfonyl-3-carboxymethylmesidine.**—A solution of 10 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 200 ml. of 10% aqueous potassium hydroxide was boiled under reflux for 2.5 hours. The solution was cooled and acidified with carbon dioxide and no precipitate appeared. Acidification with concentrated hydrochloric acid caused precipitation of a white solid which was separated by filtration, dried, and heated to 160°. The liquid product solidified on cooling and was recrystallized from ethanol, m.p. 218–220°.

*Anal.* Calcd. for  $C_{17}H_{19}NO_4S$ : C, 61.24; H, 5.74. Found: C, 61.11; H, 5.54.

**N-Benzenesulfonyl-5-dicarbethoxymethyl-2,4-dimethylaniline.**—A suspension of 1.0 g. of 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate and 1.5 g. of the sodium salt of diethyl malonate in 25 ml. of dry ether was shaken for a few minutes and the yellow color of the starting material disappeared. The product was worked up as described above to give 1.0 g. (77%) of sulfonamide, m.p. 145–146°.

*Anal.* Calcd. for  $C_{21}H_{23}NO_6S$ : C, 60.13; H, 6.01. Found: C, 60.03; H, 6.26.

**N-Benzenesulfonyl-3-(diacetylmethyl)-mesidine.**—A solution of 0.5 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate and 1.0 g. of acetylacetone in 6 ml. of ethanol was heated and 0.2 g. of potassium hydroxide added. An exothermic reaction resulted and the yellow color disappeared. The mixture was acidified with acetic acid, poured into water, and filtered. The solid was purified by recrystallization from ethanol; m.p. 260° dec.

*Anal.* Calcd. for  $C_{20}H_{23}NO_4S$ : C, 64.31; H, 6.21. Found: C, 64.44; H, 6.20.

**N-Benzenesulfonyl-5-(diacetylmethyl)-2,4-dimethylaniline.**—A solution of 0.5 g. of 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate and 1.0 g. of acetylacetone in 6 ml. of ether was treated with 0.2 g. of sodium methoxide, whereupon an exothermic reaction occurred and the yellow color disappeared. The mixture was acidified with acetic acid, evaporated, washed with water and recrystallized from ethanol to yield 1.0 g. (85%) of sulfonamide, m.p. 189–190°.

*Anal.* Calcd. for  $C_{19}H_{21}NO_4S$ : C, 63.49; H, 5.89. Found: C, 63.46; H, 5.93.

**N-Benzenesulfonyl-2,3,4,6-tetramethylaniline.** A.—To a solution containing 4 mole equiv. of methylmagnesium iodide (20 g. of methyl iodide and 4 g. of magnesium) was added a solution of 10 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 40 ml. of warm benzene. The yellow color disappeared and a homogeneous solution resulted. After decomposing unreacted Grignard reagent with water and acetic acid the organic layer was extracted 6 times with aqueous alkali. Acidification of the extracts gave 7.0 g. (80%) of crude sulfonamide which after repeated recrystallization from ethanol gave 1.2 g. of white crystals, m.p. 175–177°.

*Anal.* Calcd. for  $C_{16}H_{19}NO_2S$ : C, 66.40; H, 6.62. Found: C, 66.39; H, 6.64.

B.—Isodurene was nitrated, reduced, and benzenesulfonated by previously described methods.<sup>7</sup> The yields of these three steps were 70, 90 and 80%, respectively. After recrystallization from ethanol the product melted at 178–179° and a mixture with the product of method A showed no depression. The infrared spectra were also identical.

**N-Benzenesulfonyl-2,4,5(?)-trimethylaniline.**—Method A above was applied to 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate without modification. The crude sulfonamide weighed 8.0 g. (90%) and was purified by recrystallization from ethanol, m.p. 135–136°.

*Anal.* Calcd. for  $C_{15}H_{17}NO_2S$ : C, 65.41; H, 6.22. Found: C, 65.56; H, 6.17.

**N-Benzenesulfonyl-3-cyanomesidine.**—To a suspension of 12 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate in 25 ml. of ethanol was added 4 g. of hydrogen cyanide and 5 g. of triethylamine. After standing overnight the mixture was filtered, giving 6.0 g. of pale yellow solid and a colorless filtrate which was poured into water and extracted with ether. Extraction of the ether with alkali and acidification of the extract gave 2.0 g. of sulfonamide which was purified by recrystallization from ethanol, m.p. 162–164°.

*Anal.* Calcd. for  $C_{15}H_{15}N_2O_2S$ : C, 63.94; H, 5.38; N, 9.34. Found: C, 64.11; H, 5.25; N, 9.05.

The infrared spectrum shows absorption by  $C\equiv N$  at 2220  $cm^{-1}$  and a general similarity to the spectra of the other 3-substituted benzenesulfonylmesidines.

The pale yellow solid which separated from the original reaction mixture was purified by recrystallization from ethanol; m.p. 156–157°.

*Anal.* Calcd. for  $C_{18}H_{18}N_2O_2S$ : C, 63.94; H, 5.37; N, 9.33. Found: C, 63.74; H, 5.48; N, 9.07.

The infrared spectrum shows absorption by  $C\equiv N$  at 1552  $cm^{-1}$  and  $C=N$  at 2210  $cm^{-1}$ , absence of N–H absorption, and general similarity to the spectra of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate and 4-methyl-*p*-quinol-*p*-benzenesulfonimide acetate except for the absence of absorption by the acetoxy group.

**N-Benzenesulfonyl-3-phenylmercaptomesidine.**—A solution of 0.5 g. of 2,4,6-trimethyl-*o*-quinolbenzenesulfonimide acetate and 0.3 g. of thiophenol in 2 ml. of ethanol was allowed to stand overnight. The color faded and a white precipitate appeared. Recrystallization from ethanol gave 0.5 g. (75%) of sulfonamide, m.p. 174–175°.

*Anal.* Calcd. for  $C_{21}H_{21}NO_2S_2$ : C, 65.79; H, 5.52. Found: C, 65.61; H, 5.76.

**N-Benzenesulfonyl-2,4-dimethyl-5(?)-phenylmercaptaniline.**—The experiment above was repeated with 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetate. The reaction was rapid and exothermic. After recrystallization from petroleum ether (b.p. 80–100°) 0.5 g. (75%) of sulfonimide, m.p. 175–176°, was obtained.

*Anal.* Calcd. for  $C_{20}H_{19}NO_2S_2$ : C, 65.00; H, 5.18. Found: C, 64.89; H, 5.43.

**Hydrogenation of Quinol Imide Acetates.**—Both 2,4,6-trimethyl- and 2,4-dimethyl-*o*-quinolbenzenesulfonimide acetates hydrogenated smoothly in benzene solution over platinum oxide catalyst to give quantitative yields of the parent sulfonamides as shown by the undepressed melting points of mixtures with authentic samples.

URBANA, ILLINOIS

(6) M. J. Gortatowski, Ph.D. Thesis, University of Illinois, 1955.

(7) R. Adams and K. R. Brower, *THIS JOURNAL*, **78**, 663 (1956).