



product analogous to *N*-benzyl-*p*-toluenesulfonamide, formed by the migration of a benzyl group, was found. The absence of this compound is not surprising since methyl groups are known to be less prone to migration than benzyl groups.

The *p*-toluenesulfonamide isolated accounted for only 16% of the sulfur originally present. Subsequent hydrolysis of the black residue gave an additional 2.7% of *p*-toluenesulfonamide and suggests the presence of polymers of the *p*-toluenesulfonamide-formaldehyde type.

Further work on the resolution and rearrangements of aminimides is in progress.

### Experimental<sup>10</sup>

***N,N*-Dimethyl-*N'*-*p*-toluenesulfonylhydrazine (V).**—Pure *p*-toluenesulfonyl chloride (45 g.) was added slowly to *unsym*-dimethylhydrazine<sup>11</sup> (28 g.) at 0° with vigorous stirring. The resulting solution was stirred until a thick paste was formed. The paste was dissolved in 95% ethanol (110 ml.), the solution filtered, cooled and water added until the solution became turbid. After standing at 0° for 24 hours the resulting crude *N,N*-dimethyl-*N'*-*p*-toluenesulfonylhydrazine (13.3 g.) (27%) was filtered. Two recrystallizations from 95% ethanol gave a solid melting at 79–81°.

*Anal.* Calcd. for C<sub>9</sub>H<sub>11</sub>SO<sub>2</sub>N<sub>2</sub>: C, 50.45; H, 6.55; N, 13.08. Found: C, 50.13; H, 6.52; N, 12.55.

***N,N,N*-Trimethyl-*N'*-*p*-toluenesulfonylhydrazonium iodide (VI).**—A solution of *N,N*-dimethyl-*N'*-*p*-toluenesulfonylhydrazine (9.3 g.) in methyl iodide (40 ml.) was refluxed for 22 hours. The pale yellow crystals formed were washed four times with 10-ml. portions of absolute ethanol and dried over phosphorus pentoxide for 24 hours, yield 10.2 g. (64%), m.p. 156–157° dec.

*Anal.* Calcd. for C<sub>10</sub>H<sub>17</sub>SO<sub>2</sub>N<sub>2</sub>I: C, 33.71; H, 4.81; I, 35.63. Found: C, 33.95; H, 4.87; I, 35.76.

**Trimethylamine-*p*-toluenesulfonimide (VII).**—*N,N,N*-Trimethyl-*N'*-*p*-toluenesulfonylhydrazonium iodide (9 g.) was triturated with 10% sodium hydroxide (20 ml.) and the resulting white solid filtered. Recrystallization three times from absolute ethanol followed by drying for 24 hours gave a solid (5 g.) (87%) melting at 175–176°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>16</sub>SO<sub>2</sub>N<sub>2</sub>: C, 52.61; H, 7.06. Found: C, 52.27; H, 7.16.

Freezing point depression in water pointed to very little dissociation of the hydrate.

Sample in 10 g. of H <sub>2</sub> O	Freezing point depression, °C.	
	Found	Calcd.
0.0952 g.	–0.079	–0.078
0.0953 g.	–0.082 g.	–0.078 g.

**Trimethylamine-*p*-toluenesulfonimide Hydrate.**—Trimethylamine-*p*-toluenesulfonimide (VII) when recrystallized from water gave white needles which after drying in a vacuum desiccator over phosphorus pentoxide for 24 hours melted at 171–172°.

*Anal.* Calcd. for C<sub>10</sub>H<sub>18</sub>SO<sub>2</sub>N<sub>2</sub>: C, 48.77; H, 7.37. Found: C, 48.57; H, 7.24.

Recrystallization of trimethylamine-*p*-toluenesulfonimide (VII) from methanol gave white crystals melting at the same point as the starting material (174–175°) and had the composition of this material. No evidence for the formation of a methyl alcoholate was found.

**Reactions of Trimethylamine-*p*-toluenesulfonimide (VII).**  
1. **Reduction.**—A mixture of trimethylamine-*p*-toluenesulfonimide (1.5 g.), zinc dust (6.5 g.), water (20 ml.) and acetic acid (5 ml.) was refluxed for 3 hours, cooled and filtered. The filtrate was made basic and steam distilled until 150 ml. of distillate had been collected. Acidification with hydrochloric acid followed by evaporation to dryness gave a solid which after one recrystallization from ethanol and ether and one from ethyl acetate melted at 275° dec. and proved to be trimethylamine hydrochloride.

(10) Melting points are corrected.

(11) A. H. Blatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 211.

The residual solution from the steam distillation was acidified with hydrochloric acid and extracted six times with 20-ml. portions of chloroform. Removal of the chloroform gave *p*-toluenesulfonamide (0.25 g.) melting at 136–137° after one crystallization from water. A mixture with an authentic sample melted at the same point.

2. **Oxidation.**—A mixture of trimethylamine-*p*-toluenesulfonimide (0.55 g.) and 30% hydrogen peroxide (30 ml.) was allowed to stand for 24 hours. The solution was evaporated to dryness and the resulting oil taken up in ethanol. Partial removal of the ethanol gave a very small amount of *p*-toluenesulfonamide, m.p. 136–137°. Further removal of the solvent followed by an extraction with ethyl acetate gave only the starting material (0.1 g.), m.p. 171–173°.

3. **Reaction with Hydriodic Acid.**—A solution of trimethylamine-*p*-toluenesulfonimide (VII) (1.06 g.) in water (20 ml.) was treated slowly with stirring with hydriodic acid (sp. gr. 1.50) (2 ml.) and the resulting solution after standing for 20 hours was filtered. The *N,N,N*-trimethyl-*N'*-*p*-toluenesulfonylhydrazonium iodide (VI) (1.6 g., 96.1%) formed melted at 159–161° dec.

4. **Reaction with Methyl Iodide.**—A solution of trimethylamine-*p*-toluenesulfonimide (VII) (0.4 g.) and methyl iodide (4 ml.) in absolute ethanol (20 ml.) was refluxed for 20 hours. The reaction flask was protected from moisture with a calcium chloride tube. The solid which was formed (0.116 g.) was recrystallized three times from absolute ethanol and proved to be *N,N,N*-trimethyl-*N'*-*p*-toluenesulfonylhydrazonium iodide (VI). The alcohol filtrate gave a very small amount of starting material together with an oil. The insolubility of the aminimide in non-hydroxylated solvents prevented the use of one of these in this reaction.

5. **Reaction with Ethyl Iodide.**—A solution of trimethylamine-*p*-toluenesulfonimide (VII) (2.0 g.) and ethyl iodide (10 ml.) in absolute ethanol (20 ml.) was refluxed for 24 hours. The small amount of insoluble solid formed proved to be *N,N,N*-trimethyl-*N'*-*p*-toluenesulfonylhydrazonium iodide (VI). From the filtrate the starting material (1.8 g.) was recovered.

6. **Reaction with Benzyl Chloride.**—A solution of trimethylamine-*p*-toluenesulfonimide (1.0 g.) and benzyl chloride (2 ml.) in absolute ethanol (30 ml.) was allowed to stand at room temperature for three weeks. The white solid (0.2 g.) which formed was recrystallized twice from an absolute ethanol-ether solution and melted at 171–173°. A mixture with trimethylamine-*p*-toluenesulfonimide (VII) melted at 120–122°. The product gave a positive Beilstein test for halogen.

*Anal.* Calcd. for C<sub>17</sub>H<sub>23</sub>N<sub>2</sub>SO<sub>2</sub>Cl: C, 57.53; H, 6.53; N, 7.90. Found: C, 57.69; H, 6.21; N, 7.57.

The above product (0.1 g.) was refluxed with zinc dust (0.4 g.), acetic acid (3.5 ml.) and water (10 ml.) for 3 hours. The resulting solution was filtered, made basic and steam distilled. Acidification followed by extraction with chloroform gave a solid melting at 115–117°. Recrystallization from a chloroform-petroleum ether (60–68°) mixture gave *p*-toluenesulfonamide, m.p. 134–135°.

No *p*-toluenesulfonamide was obtained when a similar reduction was carried out with *N*-benzyl-*p*-toluenesulfonamide (1.5 g.). In this example *N*-benzyl-*p*-toluenesulfonamide (1.4 g.) was recovered, m.p. 115–116°.

6. **Pyrolysis.**—Trimethylamine-*p*-toluenesulfonimide (25 g.) was heated in a stream of nitrogen at 185–195° for 7 hours and the volatile products were collected in four traps the first of which was at room temperature, the second in a mixture of Dry Ice and acetone, the third contained concentrated hydrochloric acid and the fourth a solution of 2 *N* hydrochloric acid saturated with 2,4-dinitrophenylhydrazine. The liquid (1 ml.) from the Dry Ice trap upon treatment with ethyl iodide in ether gave trimethylethylammonium iodide (0.2 g.), m.p. 320–322° dec.

The concentrated hydrochloric acid solution upon evaporation gave ammonium chloride, m.p. 325–335°.

*Anal.* Calcd. for NH<sub>4</sub>Cl: N, 26.19. Found: N, 25.94. The hydrochloric acid-2,4-dinitrophenylhydrazine solution gave a trace of formaldehyde-2,4-dinitrophenylhydrazine, m.p. 163–165°.

The oils (4 ml.) from the first trap could not be purified sufficiently to be characterized.

From the black tarry residue (17.0 g.) in the reaction flask *p*-toluenesulfonamide (3.0 g.) was obtained by extrac-

tion with ether and water, respectively. The remainder of the products consisted of a black oil (1.5 g.) and a dark brown, high melting solid (7.5 g.). The latter when refluxed with concentrated hydrochloric acid for 4 hours gave a crystalline brown solid from which *p*-toluenesulfonamide (0.5 g.) could be recovered by extracting with boiling water. The residue from this extraction contained 11.56% sulfur.

*Anal.* Calcd. for  $C_7H_9SO_2N$ : S, 18.7. Calcd. for  $C_8H_9SO_2N$ : S, 17.6.

7. *pH* Measurements.—A solution of trimethylamine-

*p*-toluenesulfonimide (0.00419 *M*) in conductivity water gave, under nitrogen, an initial *pH* measurement of 6.72. After standing for 15 hours the reading increased to 7.90. The solution upon evaporation to dryness gave the original material.  $K_b$  for the aminimide taking the ionization of water into account is given by the expression

$$K_b(H^+)^3 + (K_bC_B + K_w)(H^+)^2 - K_wK_b(H^+) - K_w^2 = 0$$

$$K_b = 1.51 \times 10^{-10}; \text{ dissociation} = 0.061\%$$

IOWA CITY, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

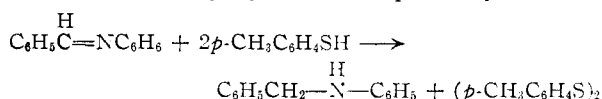
## Reduction of Some Conjugated Azomethine Systems by Aryl Thiols

BY HENRY GILMAN, J. LEWIS TOWLE AND ROBERT K. INGHAM

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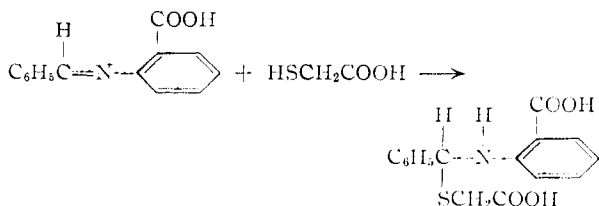
*p*-Thiocresol was found to be without effect on cyclic anils such as pyridine, quinoline, isoquinoline and benzothiazole. However, acridine was reduced to biacridan and acridan by this thiol. An interesting reaction with aryl thiols is the reduction of the carbon-carbon double bond in benzalquinaldine and benzallepidine to form 2-( $\beta$ -phenylethyl)-quinoline and 4-( $\beta$ -phenylethyl)-quinoline, respectively.

It has been shown<sup>1</sup> that *p*-thiocresol has a reducing action on the azomethine grouping in benzalaniline and also in benzophenone-anil, forming benzylaniline and benzhydylaniline, respectively

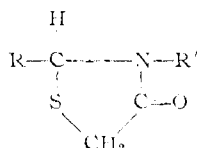


In a similar reaction with *p*-thiocresol, azobenzene was converted to hydrazobenzene.<sup>1</sup>

More recently, Stacy and Morath<sup>2</sup> have found that  $\beta$ -thionaphthol did not react with benzalaniline, and that benzalanthranilic acid, instead of being reduced, formed addition products with *p*-thiocresol, thiophenol and a number of thiols in the alkyl series.



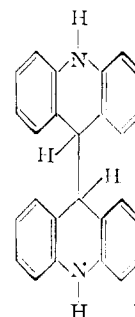
Frequently, when employing an ester of thioglycolic acid or the free acid, the addition to the azomethine grouping is followed by intramolecular condensation to give a 2,3-disubstituted-4-thiazolidone.<sup>3,4</sup>



The unique reduction of benzalaniline and benzophenone-anil with *p*-thiocresol suggested the possibility of using thiols as preferential reductants for the azomethine grouping where the latter is part

of a ring system, as in quinoline or in pyridine. From the results of a number of attempted reductions with a variety of anils (see Table I), it appears that the reaction is not generally applicable to this class of compounds.

Pyridine, quinoline, isoquinoline, 2-phenylquinoline, 2-(*p*-dimethylaminophenyl)-7-methylquinoline and benzothiazole were not acted upon by *p*-thiocresol under our experimental conditions. Acridine was found to undergo reduction to biacridan (I), and in one experiment acridan was isolated as one of the products. The yields varied appreciably with the conditions employed. That steric factors may be significant in this type of reaction was indicated when 9-(*o*-iodophenyl)-acridine<sup>5</sup> was recovered in quantitative amount in one attempted reduction.



The net effect of the reduction of acridine to acridan is the addition of two atoms of hydrogen to the terminal atoms of a conjugated azomethine system. The azomethine grouping is important in this reaction; anthracene, with a similar conjugated system but lacking the azomethine grouping, is not reduced under our conditions (although certain other methods of reduction are successful for both molecules).

The success of this reaction with acridine led to the investigation of several other compounds containing a conjugated azomethine system. It was

(5) The authors are indebted to Dr. C. Gardner Swain for a supply of 9-(*o*-iodophenyl)-acridine.

- (1) H. Gilman and J. B. Dickey, *THIS JOURNAL*, **52**, 4573 (1930).  
 (2) G. W. Stacy and R. J. Morath, *ibid.*, **74**, 3885 (1952).  
 (3) A. R. Surrey, *ibid.*, **69**, 2911 (1947).  
 (4) H. D. Troutman and L. M. Long, *ibid.*, **70**, 3436 (1948).