glacial acetic acid and formed yellow crystals, m. p. 199° (cor.). In concentrated sulfuric acid, a straw yellow solution is formed which changes slowly to orange.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2$: C, 57.97; H, 4.32; N, 6.76. Found: C, 58.17; H, 4.22; N, 6.92.

(B).—To a suspension of 70 mg. of finely powdered 2,5-dibenzenesulfonamido-*p*-xylene in 40 ml. of dry ether and 5 mg. of anhydrous sodium sulfate was added 39 mg. of freshly prepared dry silver oxide. The mixture was agitated on a mechanical shaker for fifteen hours then filtered from the silver oxide. Upon evaporation of the ether a yellow solid weighing 10 mg. was obtained. It was crystallized from acetone and melted at 199° (cor.). It was identical with the product formed by oxidation with bromine and pyridine.

Addition of Hydrogen Chloride 2,5-Dimethyl-*p*-quinone Dibenzenesulfonimide: 2,5 - Dimethyl - 3 - chloro - *p*-phenylene Dibenzenesulfonamide.—Dry hydrogen chloride was bubbled into a solution of 8 g. of 2,5-dimethyl-*p*-quinone dibenzenesulfonimide in 200 ml. of dry chloroform. A white crystalline precipitate was deposited and the yellow color of the solution was completely discharged in one hour. The solid was collected by filtration and the filtrate was evaporated to obtain the balance of the material. The product weighed 8.5 g. (quant.). It was purified by crystallization from glacial acetic acid and formed colorless crystals, m. p. 261° (cor.) with darkening at 257–258°. *Anal.* Calcd. for $C_{20}H_{19}N_2O_4S_2Cl$: C, 53.26; H, 4.25. Found: C, 53.06; H, 4.52.

2,5-Dimethyl-3-chloro-*p*-quinone Dibenzenesulfonimide.—A suspension of 4.72 g. of finely powdered 2,5-dimethyl-3-chloro-*p*-phenylenedibenzenesulfonamide in 125 ml. of glacial acetic acid and 4.64 g. of lead tetraacetate was warmed on a water-bath maintained at 70–75°. The solid material went slowly (one hour) into solution which was orange in color. After adding 3–4 ml. of ethylene glycol, and allowing to stand for a few minutes, the solution was cooled, filtered to remove traces of unreacted original compound, then poured onto ice. A yellowish-orange precipitate formed which weighed 4.68 g. (99%). By crystallization from glacial acetic acid, orange crystals resulted, m. p. 152–153° (cor.). In concentrated sulfuric acid, a golden yellow solution is formed which remains unchanged on standing.

Anal. Calcd. for $C_{20}H_{17}N_2O_4S_2Cl$: C, 53.51; H, 3.82; N, 6.24. Found: C, 53.54; H, 3.97; N, 6.14.

2,5-Dimethyl-3,6-dichloro-*p*-phenylenedibenzenesulfonamide.—Into a solution of 3.5 g. of 2,5-dimethyl-3-chloro-*p*-quinone diimide in 150 ml. of chloroform, hydrogen chloride was bubbled. In the course of ten to fifteen minutes, a white solid deposited and the yellow-orange solution became colorless. The product weighed 3.72 g. (94%). It was purified by two crystallizations from glacial acetic acid in which it was only sparingly soluble. It turned dark without melting at about 280°.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S_2Cl_2$: C, 49.49; H, 3.74. Found: C, 49.21; H, 3.90.

Summary

1. *p*-Phenylenedibenzenesulfonamide has been oxidized by a variety of reagents to *p*-quinone dibenzenesulfonimide which is a stable yellow crystalline compound. The di-*p*-toluenesulfonyl and dimethanesulfonyl derivatives of *p*-phenylenediamine, the dibenzenesulfonyl derivatives of 2-methyl-, 2-chloro-, 2,5-dimethyl- and 2,5-dimethyl-3-chloro-*p*-phenylenediamine were equally readily oxidized to stable *p*-quinone diimides. The reactions are essentially quantitative when lead tetraacetate in glacial acetic acid is used as oxidizing agent. The 2,5-dimethyl derivative was oxidized successfully with bromine in pyridine solution.

2. *p*-Quinone dibenzenesulfonimide resembles quinone in being readily reduced by various reagents, such as hydrogen in presence of platinum, hydriodic acid, zinc and acetic acid, tin and hydrochloric acid and sulfurous acid to the *p*-phenylenedibenzenesulfonamide. It is also reduced by heating with dilute sulfuric acid or by cold dilute sodium hydroxide.

3. The diimides add readily hydrogen chloride to yield the 2-chloro-*p*-phenylenedibenzenesulfonamides.

4. The diimides oxidize hydrogen bromide to bromine and hydriodic acid to iodine.

URBANA, ILLINOIS RECEIVED MARCH 10, 1950

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

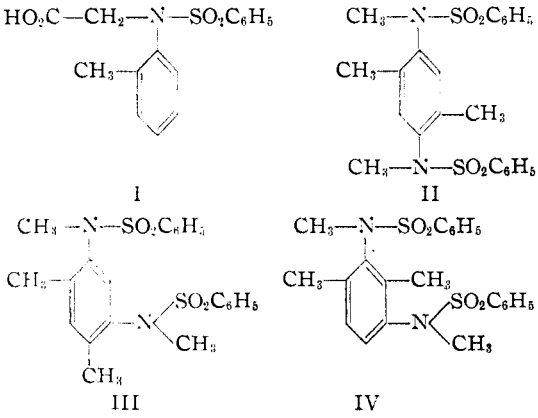
Restricted Rotation in Aromatic Amines. XIII. The Effect of Monosubstitution in the *Ortho* Position

BY ROGER ADAMS AND A. S. NAGARKATTI

In exploring the effect of ring substituents on the restricted rotation of N,N′-disubstituted aromatic amines,[1] various compounds have been synthesized with merely one methyl group *ortho* to the amino group and with two groups, benzenesulfonyl and methyl or carboxymethyl, substituted on the nitrogen.

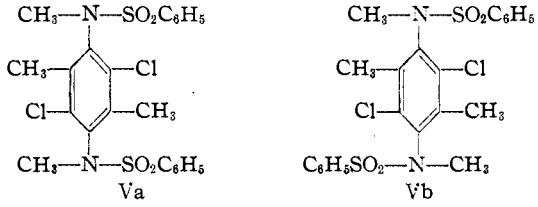
Attempts to resolve N-carboxymethyl *o*-benzenesulfonamidotoluene (I) failed, though in one experiment which could not be repeated, the cinchonidine salt exhibited mutarotation. It was obvious that restriction of the carbon–nitrogen bond is so slight, if any, that minor experimental factors might influence the results. The isolation of *cis* and *trans* forms in molecules with two points of restricted rotation appeared from past experience to offer a more reliable means of determining the presence of restricted rotation in molecules where the restriction was very small since resolution may be avoided. The three diamine derivatives II, III and IV were, therefore prepared. In no case could two isomers be isolated. Excellent yields of single compounds resulted in all cases. It is evident then that the combinations of groups on the nitrogen atoms in I, II, III and IV with a methyl group in the *ortho* position in the ring are not adequate to permit measurable restricted rotation.

(1) For previous papers see Adams and Tjepkema, THIS JOURNAL, **70**, 4204 (1948); Adams, *et al.*, *ibid.*, **71**, 1620 (1949); **72**, 128, 132, 135 (1950).



I II III IV

The derivative of compound II with two chlorines in the vacant positions in the ring (Va and Vb) was readily obtained in two forms as might be anticipated. The lower-melting, presumably Va, is readily converted to Vb when it is melted.



Va Vb

These compounds were synthesized from the corresponding sulfonamides by treatment with ethanolic alkali and the proper halogen compounds. In the case of I, methyl bromoacetate was used and, the ester formed as an intermediate, hydrolyzed to the acid. In all other cases, II–V, methyl iodide was employed.

Experimental

***o*-Benzenesulfonamidotoluene.**—This product was prepared in 92% yield by the method of Willstätter and Pfannensteil.[2]

N-Carbomethoxymethyl *o*-Benzenesulfonamidotoluene.—A solution of 6.2 g. of *o*-benzenesulfonamidotoluene in 60 ml. of absolute ethanol containing 0.6 g. of sodium hydroxide was treated with 3.85 g. of methyl bromoacetate and the mixture refluxed on a steam-bath for six hours. After cooling and filtering from sodium bromide, the ethanol was evaporated and a thick oil resulted. This was dissolved in 250 ml. of ether, the ether solution washed with 5% aqueous sodium hydroxide, dried and the ether removed. The product weighed 5 g. (75%) and boiled at 210° (2 mm.).

Anal. Calcd. for $C_{16}H_{17}NO_4S$: C, 60.17; H, 5.36. Found: C, 60.50; H, 5.66.

N-Carboxymethyl *o*-Benzenesulfonamidotoluene.—A solution of 2.87 g. of N-carbomethoxymethyl *o*-benzenesulfonamidotoluene in 50 ml. of glacial acetic acid was heated on a steam-bath for ten hours with 10 ml. of concentrated sulfuric acid in 40 ml. of water. Upon cooling, crystals separated. These weighed 2.57 g. (90%). The product was purified by crystallization from benzene, m. p. 157° (cor.).

Anal. Calcd. for $C_{15}H_{15}NO_4S$: C, 58.95; H, 4.95. Found: C, 59.18; H, 5.12.

Attempted Resolution of N-Carboxymethyl *o*-Benzenesulfonamidotoluene.—A mixture of a solution of 1 g. of N-carboxymethyl *o*-benzenesulfonamidotoluene in 10 ml. of acetone and a solution of 0.98 g. of cinchonidine in 130 ml. of acetone was shaken at room temperature. The salt deposited in five minutes. The product weighed 1.96 g. (99%). It was dissolved in 650 ml. of hot ethyl acetate and the solution cooled. The crystals which separated weighed 0.412 g. Evaporation of the filtrate was effected by passing a current of air over its surface. After removal of 100 ml. of ethyl acetate at a time, successive fractions of salt were collected. Each fraction had the same rotation. The salt formed white feathery crystals, m. p. 211° (cor.) with decomposition.

Anal. Calcd. for $C_{15}H_{15}NO_4S \cdot C_{19}H_{22}N_2O$: C, 68.08; H, 6.21. Found: C, 68.19; H, 6.26.

Rotation: 0.10 g. made up to 10 ml. with chloroform at 32° gave α_D −0.762; *l*, 1; $[\alpha]^{32}D$ −76.2°.

2,4-Dibenzenesulfonamido-*m*-xylene.—To a solution of 6 g. of 2,4-diamino-*m*-xylene[3] in 40 ml. of pyridine was cautiously added a solution of 12.5 ml. of benzenesulfonyl chloride in 10 ml. of pyridine. After standing overnight, the mixture was poured into ice and hydrochloric acid. The sticky product solidified in a short time. It was dissolved in 5% aqueous sodium hydroxide, warmed with Darco, the solution filtered and poured into ice and hydrochloric acid. The product weighed 14.7 g. (80%) and was purified by crystallization from ethanol, m. p. 189° (cor.).

Anal. Calcd. for $C_{20}H_{20}N_2O_4S_2$: C, 57.68; H, 4.84; N, 6.73. Found: C, 57.49; H, 5.04; N, 6.82.

N,N′-Dimethyl-2,4-dibenzenesulfonamido-*m*-xylene.—To a solution of 3.8 g. of 2,4-dibenzenesulfonamido-*m*-xylene in 40 ml. of ethanol was first added 0.87 g. of sodium hydroxide in a saturated aqueous solution and then 2.84 g. of methyl iodide. The mixture was refluxed on a water-bath and after two hours 2 ml. of methyl iodide was added and refluxing continued for one hour more. Upon standing in a refrigerator overnight, crystals separated. More were obtained from the filtrate by evaporation. The product weighed 3.73 g. (92%) and was purified by crystallization from ethanol, m. p. 169–170° (cor.).

Anal. Calcd. for $C_{22}H_{24}N_2O_4S_2$: C, 59.39; H, 5.39. Found: C, 59.60; H, 5.41.

4,6-Dibenzenesulfonamido-*m*-xylene.—This product was prepared from 4,6-diamino-*m*-xylene[3] in a similar manner to that used for 2,4-dibenzenesulfonamido-*m*-xylene. The yield was 85%. The product was purified from glacial acetic acid, m. p. 180–181° (cor.). Morgan and Clayton[4] report m. p. 176°.

Anal. Calcd. for $C_{20}H_{20}N_2O_4S_2$: C, 57.68; H, 4.84. Found: C, 57.73; H, 4.86.

N,N′-Dimethyl-4,6-dibenzenesulfonamido-*m*-xylene.—Prepared like the analogous 2,4-derivative, the product was obtained in 95% yield. It was purified from ethanol, m. p. 202–202.5° (cor.). Morgan and Clayton[4] report m. p. 196–197°.

Anal. Calcd. for $C_{22}H_{24}N_2O_4S_2$: C, 59.39; H, 5.39. Found: C, 59.44; H, 5.52.

N,N′-Dimethyl-2,5-dibenzenesulfonamido-*p*-xylene.—From 2,5-dibenzenesulfonamido-*p*-xylene by the procedure just described, a 92% yield of product resulted. It was purified by recrystallization from glacial acetic acid, m. p. 236° (cor.).

Anal. Calcd. for $C_{22}H_{24}N_2O_4S_2$: C, 59.39; H, 5.39. Found: C, 59.59; H, 5.67.

N,N′-Dimethyl-2,5-dibenzenesulfonamido-3,6-dichloro-*p*-xylene.—A solution of 2 g. of 2,5-dibenzenesulfonamido-3,6-dichloro-*p*-xylene[5] in 30 ml. of ethanol, containing 0.2 g. of sodium hydride and 5 ml. of water, was refluxed with 0.6 ml. of methyl iodide. After four

(2) Willstätter and Pfannensteil, *Ber.*, **38**, 2244 (1905).

(3) Adams and Nagarkatti, THIS JOURNAL, **72**, 1831 (1950); see also Grevingk, *Ber.*, **17**, 2422 (1884); Morgan, *J. Chem. Soc.*, **81**, 86 (1902).

(4) Morgan and Clayton, *J. Chem. Soc.*, **89**, 1054 (1906).

(5) Adams and Nagarkatti, THIS JOURNAL, **72**, 4601 (1950).

hours, during which crystals were deposited, the solution was filtered hot. The filtrate was evaporated gradually with filtration of the solution from the crystals from time to time. The results were as follows: Fraction I, 0.675 g., m. p. 292–293°; fraction II, 0.320 g., m. p. 210° (not sharp); fraction III, 0.280 g., m. p. 210° (not sharp); fraction IV, 0.300 g., m. p. 210° (not sharp); fraction V, 0.250 g., m. p. 195° (not sharp); fraction VI, 0.260 g., m. p. 190° (not sharp).

Fraction I was recrystallized from glacial acetic acid, m. p. 292–293° (cor.).

Anal. Calcd. for $C_{22}H_{22}N_2O_4Cl_2S_2$: C, 51.46; H, 4.32; N, 5.46. Found: C, 51.49; H, 4.28; N, 5.67.

Fraction V was refractionated and the more soluble part crystallized thrice from ethanol, m. p. 203–204° (cor.).

Anal. Calcd. for $C_{22}H_{22}N_2O_4Cl_2S_2$: C, 51.46; H, 4.32; N, 5.46. Found: C, 51.62; H, 4.52; N, 5.53.

This lower-melting isomer after melting solidified at 205–206° and melted again at 290–292°. A larger quantity of product heated for one hour above its melting point was then recrystallized from glacial acetic acid and proved to be the higher melting form. To observe satisfactorily the melting point of the lower-melting form, it was found desirable to preheat the bath to 195° and introduce the melting point tube with only a small quantity of product present.

Summary

1. N-Carboxymethyl-*o*-benzenesulfonamidotoluene could not be resolved. *Cis* and *trans* isomers could not be obtained from N,N′-dimethyl-2,4-dibenzenesulfonamido-*m*-xylene, N,N′-dimethyl-2,6-dibenzenesulfonamido-*m*-xylene, and N,N′-dimethyl-2,5-dibenzenesulfonamido-*p*-xylene. It appears that merely one methyl group in the benzene ring *ortho* to the amino group is inadequate to restrict the C–N rotation when the nitrogen atom is substituted with the groups indicated.

2. N,N′-Dimethyl-2,5-dibenzenesulfonamido-3,6-dichloro-*p*-xylene was obtained in *cis* and *trans* forms.

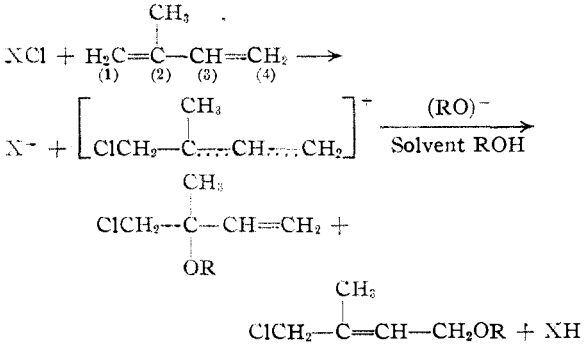
URBANA, ILLINOIS RECEIVED MARCH 17, 1950

[CONTRIBUTION FROM THE DIVISION OF ORGANIC CHEMISTRY OF THE ORTHO RESEARCH FOUNDATION]

The Reaction of Isoprene with *t*-Butyl Hypochlorite in Hydroxylic Solvents

BY WILLIAM OROSHNIK AND ROBERT A. MALLORY

According to the prevailing ionic theory, the hypochlorination of isoprene would be expected to proceed by electrophilic initiation at carbon-1, as follows[1,2]



The intermediate carbonium ion can react at either carbon-2 or carbon-4, producing a pair of isomers. The literature, however, is at variance as to whether a 1,4-adduct can actually be obtained. Petrov,[3] who observed only 1,2-adducts, questioned the validity of the claim of Ingold and Smith[4] that the 1,4-bromohydrin can be obtained in this reaction. An isoprene chlorohydrin obtained through the action of *t*-butyl hypochlorite and water has been described in a German patent. Although no indication was made as to its structure, comparison with the product obtained in the present work showed it to be a 1,2-adduct.

The present work was prompted by a need for the 1,4-chlorohydrin of isoprene in a synthesis of vitamin A.[6] The hypochlorination method used was the elegant one discovered by Harford[7] and extended by Irwin and Hennion[8] wherein *t*-butyl hypochlorite is added to a solution of olefin in a reactive solvent. It was found in the present study that this reagent reacted smoothly with isoprene in glacial acetic acid to give two easily-fractionated isomers, which were shown to be 1,2- and 1,4-adducts by the reactions shown.

The non-allylic nature of the chlorine in I, its facile rearrangement to IV, and its conversion to III, left no doubt as to its structure. In establishing the structure of the 1,4-isomer, the terminal character of the chlorine and acetoxyl groups was first demonstrated by conversion to the diacetate V, and thence to tiglic aldehyde.[9] Catalytic dehalogenation of IV, followed by hydrogenation, gave isoamyl acetate, thereby establishing the exact position of the acetoxyl group in IV. Although VI analyzed very poorly, the alcohol obtained from it by alcoholysis gave the correct derivatives for prenol.[10] Conclusive confirmation of the structure of IV was furnished by the excellent yield of chloroacetone upon ozonolysis.

Upon extension of the reaction to the homolo-

(1) P. D. Bartlett and D. S. Tarbell, THIS JOURNAL, **58**, 466 (1936); G. Williams, *Trans. Far. Soc.*, **37**, 749 (1941).

(2) P. D. B. de La Mare, E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 18 (1948).

(3) A. Petrov, *J. Gen. Chem. (U. S. S. R.)*, **13**, [6] 481 (1943).

(4) C. K. Ingold and H. G. Smith, *J. Chem. Soc.*, 2752 (1931).

(5) German Patent 590,432.

(6) W. Oroshnik, THIS JOURNAL, **67**, 1627 (1945).

(7) C. G. Harford, U. S. Patent 2,054,814, 2,107,789, 2,207,983.

(8) C. F. Irwin and G. F. Hennion, THIS JOURNAL, **63**, 858 (1941).

(9) A. F. Shepard and J. R. Johnson, *ibid.*, **54**, 4388 (1932).

(10) The name prenol has been suggested for γ,γ-dimethylallyl alcohol by E. Späth and J. Bruck to indicate its derivation from isoprene: *Ber.*, **71**, 2709 (1938).