Benzaldehyde *n*-Butylhydrazone.—A 20% aqueous solution of barium hydroxide octahydrate was mixed with an equimolar quantity of *n*-butylamine oxalate,[19] and the precipitate was removed by filtration. The filtrate was distilled and the last fractions were saturated with sodium hydroxide and extracted with ether. The extracts were mixed with a quantity of benzaldehyde equal to the number of moles of *n*-butylamine oxalate originally used. The solution was dried over sodium sulfate. After the ether had been evaporated, the residue was distilled and the fraction boiling at 114–118° (1.2 mm.) was collected. The yield was 11%; ultraviolet λ_{max} 222, 289 mμ (a_M 7850, 11,200).

Anal. Calcd. for $C_{11}H_{16}N_2$: C, 74.93; H, 9.15. Found: C, 74.65; H, 9.03.

IOWA CITY, IOWA

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[19] G. Gever and K. Hayes, *J. Org. Chem.*, **14**, 813 (1949).

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

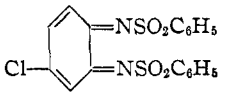
Quinone Imides. XLIII. The Reactions of *o*-Quinonedibenzenesulfonimides

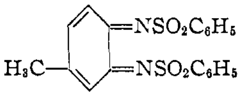
BY ROGER ADAMS AND EDWIN L. DEYOUNG[1]

RECEIVED SEPTEMBER 4, 1956

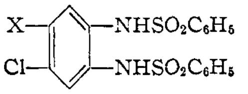
4-Chloro- and 4-methyl-*o*-quinonedibenzenesulfonimide add hydrazoic acid, benzenesulfinic acid and acetylacetone to give presumably the 5-substituted *o*-phenylenedibenzenesulfonamides. The constitution of the hydrazoic acid products was determined by reduction and hydrolysis to the substituted triamines which were synthesized by unequivocal methods. Dimers of the two diimides were formed by the action of nitromethane or cyclopentadiene.

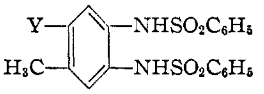
The syntheses of several substituted *o*-quinonedibenzenesulfonimides and their reactions with hydrogen chloride have been reported in a previous paper.[2] When 4-chloro- and 4-methyl-*o*-quinonedibenzenesulfonimide (I and II, respectively) were treated with hydrogen chloride, the major product in each case was the 5-chloro adduct (III and IV).


I


II

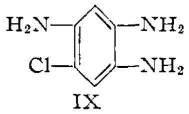
Other addition reactions to *o*-quinonedibenzenesulfonimides have now been studied.

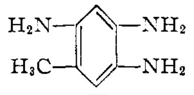

III, X = Cl
V, X = N_3
VII, X = NH_2
XI, X = $SO_2C_6H_5$
XIII, X = $CH(COCH_3)_2$


IV, Y = Cl
VI, Y = N_3
VIII, Y = NH_2
XII, Y = $SO_2C_6H_5$
XIV, Y = $CH(COCH_3)_2$
XV, Y = CH_2COCH_3

The starting materials (I and II), prepared by lead tetraacetate oxidation of the corresponding *o*-phenylenedibenzenesulfonamides,[2] were obtained in good yields and in sufficient purity for use in all addition reactions.

Addition of an aqueous solution of sodium azide to glacial acetic acid solutions of I and II afforded the 5-azido adducts V and VI in good yields. The structures of these adducts were established by reduction of the azido groups to the corresponding amino compounds (VII and VIII), followed by hydrolysis of the resulting disulfonamides to the free triamines IX and X. Structures IX and X were synthesized by unequivocal methods and the products were identical in melting point and spectra with those derived from the azido compounds.


IX


X

Compound IX was made by the following sequence of reactions: 3-chloroacetanilide, 3-chloro-4,6-dinitroacetanilide, 3-chloro-4,6-dinitroaniline,[3] 2-chloro-1,4,5-benzenetriamine. For comparison, 5-chloro-1,2,3-benzenetriamine was prepared by the following steps: 4-chloroaniline, 4-chloroacetanilide, 4-chloro-2,6-dinitroacetanilide, 4-chloro-2,6-dinitroaniline,[4] 5-chloro-1,2,3-benzenetriamine.

Compound X was synthesized as follows: *o*-toluidine, 2-amino-4-nitrotoluene, 2-acetylamino-4-nitrotoluene,[5] 2-acetylamino-4,5-dinitrotoluene, 2-amino-4,5-dinitrotoluene,[6] 2,4,5-toluenetriamine. For comparison, 3,4,5-toluenetriamine was synthesized: *p*-toluidine, *p*-acetotoluidide, 4-acetylamino-3,5-dinitrotoluene, 4-amino-3,5-dinitrotoluene,[7] 3,4,5-toluenetriamine.[7]

The addition of benzenesulfinic acid to I and II took place readily. From analogy to the 5-chloro and the 5-azido adducts, and from the C–H absorption in the infrared spectrum, it is probable that the products are the 5-benzenesulfonyl adducts XI and XII. Thiophenol did not add in presence of either an acidic or basic catalyst; only reduction of the imides resulted.

Acetylacetone, catalyzed with sodium methoxide, added to I and II in dioxane solution to give the monoadducts XIII and XIV. While the structures of these adducts were not proven, the entering diacetylmethyl group is probably in the 5-position. Steric factors are likely to inhibit the entry into the 3-position and if the group had entered the 6-position, *ortho* to the benzene and sulfonamido group, the adducts would probably have cyclized to indoles under the influence of acid.[8]

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

[2] R. Adams and C. N. Winnick, THIS JOURNAL, **73**, 5687 (1951).

[3] F. Kehrman and L. Staroyevich, *Helv. Chim. Acta*, **8**, 664 (1925).

[4] M. A. F. Hollemann, *Rec. trav. chim.*, **34**, 208 (1915).

[5] J. B. Cohen and H. D. Dakin, *J. Chem. Soc.*, **81**, 1333 (1902).

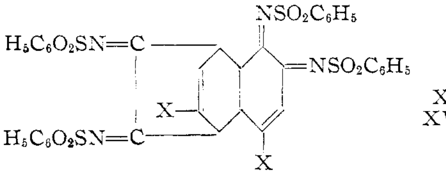
[6] O. L. Brady and P. N. Williams, *ibid.*, **117**, 1138 (1920).

[7] H. Lindemann and H. Krause, *J. prakt. Chem.*, [2] **115**, 264 (1927).

[8] R. Adams and W. P. Samuels, Jr., THIS JOURNAL, **77**, 5375 (1955).

Alkaline hydrolysis of XIV afforded the monoketone XV in 68% yield. The infrared spectrum of this product showed C–H absorption at 863 cm.$^{-1}$, indicating that it was probably the 5-substituted isomer.

Attempted addition of nitromethane in dioxane solution, catalyzed with sodium methoxide, and attempted Diels–Alder additions of cyclopentadiene to I or II, afforded identical crystalline products in each case. Elemental analyses and molecular weight determinations proved the products to be dimers of the starting imides, probably with the structures XVI and XVII, respectively.



XVI, X = Cl
XVII, X = CH_3

A dimer from 3,4-dimethyl-*o*-benzoquinone upon attempted addition of nitromethane[9] and a dimer from *o*-quinonedibenzimide upon attempted addition of *p*-benzoquinone or maleic anhydride[10] have been reported. Structures similar to XVI and XVII were postulated for these dimers.

The proposed structures of these dimers are supported by the infrared spectra. There are no NH bands present; C=N bands are found at 1580 cm.$^{-1}$. An interesting observation is the shift in the infrared absorption band of the conjugated carbon–carbon double bonds in the monomers I and II and the dimers XVI and XVII. In the monomers, the system is completely conjugated, and the absorption frequency of the carbon–carbon double bond is at 1528 cm.$^{-1}$ for I and 1525 cm.$^{-1}$ for II. In the dimers, there is an isolated carbon–carbon double bond. As a consequence of this lack of conjugation, the carbon–carbon double bond frequency is higher, 1662 cm.$^{-1}$ for XVI and 1665 cm.$^{-1}$ for XVII.

The carbon–chlorine absorption band is at 720 cm.$^{-1}$, typical of vinyl chlorides and lower by 30 cm.$^{-1}$ than an aliphatic carbon–chlorine band absorption which is located at about 750 cm.$^{-1}$.[11]

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 the microanalyses.

Experimental

All melting points are corrected.

5-(?)-Benzenesulfonyl-4-chloro-*o*-phenylenedibenzenesulfonamide.—To a solution of 5.0 g. of 4-chloro-*o*-quinonedibenzenesulfonimide[2] in 15 ml. of glacial acetic acid was added 2.14 g. of sodium benzenesulfinate. The mixture was heated to boiling, filtered and cooled. The tan precipitate, which weighed 2.7 g. (40.3%), was purified by recrystallization from ethanol (Darco); white needles, m.p. 187°.

Anal. Calcd. for $C_{24}H_{19}ClN_2O_6S_3$: C, 51.22; H, 3.48; N, 4.98. Found: C, 51.44; H, 3.33; N, 4.80.

5-(?)-Benzenesulfonyl-4-methyl-*o*-phenylenedibenzenesulfonamide.—By a procedure similar to that just described, the product from sodium benzenesulfinate and 4-methyl-*o*-quinonedibenzenesulfonimide was obtained in 66% yield and purified by recrystallization from ethanol (Darco); white needles, m.p. 194–195°.

Anal. Calcd. for $C_{25}H_{22}N_2O_6S_3$: C, 55.35; H, 4.08; N, 5.17. Found: C, 55.21; H, 4.30; N, 4.87.

5-Azido-4-methyl-*o*-phenylenedibenzenesulfonamide.—To a solution of 2.0 g. of 4-methyl-*o*-quinonedibenzenesulfonimide in 100 ml. of glacial acetic acid was added a solution of 0.49 g. of sodium azide in 6 ml. of water. After stirring for 15 minutes, the solution was poured into 200 ml. of water. The white precipitate, which weighed 1.5 g. (72%), was purified by recrystallization from a 1:1 ethyl acetate–petroleum ether (b.p. 90–110°) solvent pair; pale yellow needles, m.p. 151–152° dec.

Anal. Calcd. for $C_{19}H_{17}N_5O_4S_2$: C, 51.60; H, 3.87; N, 15.78. Found: C, 51.92; H, 3.95; N, 15.65.

5-Azido-4-chloro-*o*-phenylenedibenzenesulfonamide.—By an identical procedure 4-chloro-*o*-quinonedibenzenesulfonimide and sodium azide gave 68% yield of product which was purified by recrystallization from a 1:1 ethyl acetate–petroleum ether (b.p. 90–110°) solvent pair; pink needles, m.p. 124° dec.

Anal. Calcd. for $C_{18}H_{14}ClN_5O_4S_2$: C, 46.75; H, 3.05; N, 15.10. Found: C, 46.71; H, 2.54; N, 15.94.

5-Amino-4-methyl-*o*-phenylenedibenzenesulfonamide.—To a solution of 1.5 g. of 5-azido-4-methyl-*o*-phenylenedibenzenesulfonimide in 100 ml. of boiling 2% aqueous sodium hydroxide, was added 3.0 g. of sodium hydrosulfite over a period of 30 minutes. The solution was heated under reflux for one hour and then filtered, cooled and acidified to give a white precipitate which weighed 1.0 g. (71%). The compound was purified by recrystallization from ethanol; white needles, m.p. 205–206°.

Anal. Calcd. for $C_{19}H_{19}N_3O_4S_2$: C, 54.63; H, 4.58; N, 10.08. Found: C, 54.82; H, 4.57; N, 9.79.

5-Amino-4-chloro-*o*-phenylenedibenzenesulfonamide.—By a similar reduction procedure 5-azido-4-chloro-*o*-phenylenedibenzenesulfonamide gave a 92% yield of product, which was purified by recrystallization from ethanol (Darco); white crystals, m.p. 216–217° dec.

Anal. Calcd. for $C_{18}H_{16}ClN_3O_4S_2$: C, 49.35; H, 3.69; N, 9.61. Found: C, 49.80; H, 3.85; N, 9.81.

2,4,5-Toluenetriamine. Method A.—Hydrolysis of 3.0 g. of 5-amino-4-methyl-*o*-phenylenedibenzenesulfonamide was effected by the method of Snyder.[12] The crude triamine was isolated as the trihydrochloride in 7% yield. The free triamine was obtained by dissolving the amine hydrochloride in water, neutralizing with 5% aqueous sodium carbonate, and evaporating to dryness. The residue was extracted with 10 ml. of boiling benzene and cooled. The pink crystals were purified by recrystallization from benzene; m.p. 140° dec.

Method B.—Reduction of 1.0 g. of 2-amino-4,5-dinitrotoluene[6] was effected in 100 ml. of glacial acetic acid with platinum oxide catalyst. The 0.9 g. (72%) of the amine trihydrochloride was purified by recrystallization from glacial acetic acid. The free amine was generated by dissolving the trihydrochloride in water and neutralizing the solution with 5% aqueous sodium carbonate. It was purified by recrystallization from benzene; white crystals, m.p. 140° dec.

Anal. Calcd. for $C_7H_{11}N_3$: C, 61.34; H, 8.07; N, 30.60. Found: C, 61.45; H, 7.96; N, 30.40.

The two amines prepared by these different methods were shown to be identical by melting point and infrared spectra determinations.

2-Chloro-1,4,5-benzenetriamine. Method A.—Hydrolysis of 5-amino-4-chloro-*o*-phenylenedibenzenesulfonamide was effected in a manner similar to the 4-methyl analog. The yield of the crude amine trihydrochloride was 4%. The free amine was generated and purified by recrystallization from benzene; white crystals, m.p. 115–120° dec.

Method B.—Reduction of 1.0 g. of 3-chloro-4,6-dinitroaniline[3] in glacial acetic acid with platinum oxide catalyst gave 0.86 g. (70%) of the amine trihydrochloride, which was purified by recrystallization from glacial acetic acid. The free amine, generated by dissolving the amine hydro-

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[9] L. Horner and K. Sturm, *Ann.*, **597**, 1 (1955).

[10] R. Adams and J. W. Way, THIS JOURNAL, **76**, 2763 (1954).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., London, 1954, p. 271.

[12] H. R. Snyder and R. E. Heckert, THIS JOURNAL, **74**, 2006 (1952).

chloride in water and neutralizing with 5% aqueous sodium carbonate, was purified by recrystallization from benzene; white needles, m.p. 118° dec.

Anal. Calcd. for $C_6H_8ClN_3$: C, 45.76; H, 5.12; N, 26.61. Found: C, 45.46; H, 5.12; N, 26.68.

The amines prepared by these two methods were shown to be identical by melting point and infrared spectra determinations.

3,4,5-Toluenetriamine.—Reduction of 4-amino-3,5-dinitrotoluene[7] in a similar manner afforded the triamine, which was purified by recrystallization from benzene; white needles, m.p. 105° (lit.[7] m.p. 105°).

This triamine was not identical with the amine prepared from II and hydrazoic acid.

5-Chloro-1,2,3-benzenetriamine.—Reduction of 4-chloro-2,6-dinitroaniline[4] in a similar manner gave the amine, which was purified by recrystallization from benzene; tan needles, m.p. 115° dec.

Anal. Calcd. for $C_6H_8ClN_3$: C, 45.76; H, 5.12; N, 26.61. Found: C, 45.46; H, 5.12; N, 26.68.

This triamine was not identical with the amine obtained by reduction of the product from I and hydrazoic acid.

4-Methyl-5(?)-(3-pentanedione-2,4)-*o*-phenylenedibenzenesulfonamide.—To a solution of 5.0 g. of 4-methyl-*o*-quinonedibenzenesulfonamide in 40 ml. of dioxane was added 1.87 g. of acetylacetone and about 40 mg. of sodium methoxide. After remaining at room temperature for one week, the reaction mixture was poured into 300 ml. of petroleum ether (b.p. 30–60°) to give an orange solid which weighed 2.5 g. (40%). The compound was purified by recrystallization from ethanol (Darco); white needles, m.p. 197–198°.

Anal. Calcd. for $C_{24}H_{24}N_2O_6S_2$: C, 57.70; H, 4.82; N, 5.60. Found: C, 57.99; H, 5.12; N, 5.57.

In the infrared spectrum an absorption band at 1610 cm.$^{-1}$ indicated the presence of a carbonyl group as a chelated, enolized diketone.

4-Chloro-5(?)-(3-pentanedione-2,4)-*o*-phenylenedibenzenesulfonamide.—By a procedure similar to that used for the corresponding methyl compound, acetylacetone was added to 4-chloro-*o*-quinonedibenzenesulfonimide. The product was obtained in only 16% yield. It was purified by recrystallization from ethanol (Darco); white needles, m.p. 180–181°.

Anal. Calcd. for $C_{23}H_{21}ClN_2O_6S_2$: C, 53.06; H, 4.07; N, 5.38. Found: C, 52.99; H, 4.02; N, 5.32.

In the infrared spectrum an absorption band at 1610 cm.$^{-1}$ indicated the presence of a carbonyl group as a chelated, enolized diketone.

4-Methyl-5(?)-(1-propanone-2)-*o*-phenylenedibenzenesulfonamide.—A solution of 3.0 g. of 4-methyl-5(?)-(3-pentanedione-2,4)-*o*-phenylenedibenzenesulfonamide in 200 ml. of 5% aqueous sodium hydroxide was boiled for 15 minutes. At the end of this time, the solution was filtered, cooled, and acidified with concentrated hydrochloric acid to give a white precipitate which weighed 2.0 g. (66%). The compound was purified by recrystallization from methanol; white needles, m.p. 125–126°.

Anal. Calcd. for $C_{22}H_{22}N_2O_5S_2$: C, 56.43; H, 4.83; N, 6.12. Found: C, 56.55; H, 5.10; N, 6.12.

In the infrared spectrum a carbonyl group was indicated by an absorption band at 1710 cm.$^{-1}$.

Dimerization of 4-Methyl-*o*-quinonedibenzenesulfonimide. Method A. To a solution of 5.0 g. of 4-methyl-*o*-quinonedibenzenesulfonimide in 50 ml. of dioxane was added 1.32 g. of nitromethane and about 40 mg. of sodium methoxide. After remaining at room temperature for 2 weeks, the reaction mixture was poured into 400 ml. of petroleum ether (b.p. 30–60°) to give an orange amorphous solid which weighed 2.5 g. (50%). The compound was purified by recrystallization from ethanol (Darco); orange crystals, m.p. 145°.

Method B.—To a solution of 1.5 g. of 4-methyl-*o*-quinonedibenzenesulfonimide in 100 ml. of chloroform was added 2 ml. of freshly distilled cyclopentadiene. After remaining at room temperature for 3 days, the chloroform was evaporated, leaving 1.0 g. (67%) of an orange residue. The compound was purified by recrystallization from ethanol; orange crystals, m.p. 145°.

Anal. Calcd. for $C_{38}H_{32}N_4O_8S_4$: C, 57.00; H, 4.03; N, 6.98; mol. wt., 800. Found: C, 56.74; H, 4.05; N, 6.86; mol. wt. (ebullioscopic), 847.

The infrared spectra of the dimers prepared by these two different methods were identical.

In the infrared spectrum the carbon–carbon double bond was indicated by an absorption band at 1665 cm.$^{-1}$.

Dimerization of 4-Chloro-*o*-quinonedibenzenesulfonimide. Method A.—By an identical procedure, 4-chloro-*o*-quinonedibenzenesulfonimide was dimerized with nitromethane. The product formed in 50% yield. It was purified by recrystallization from ethanol (Darco); orange crystals, m.p. 186°.

Method B.—4-Chloro-*o*-quinonedibenzenesulfonimide was dimerized with cyclopentadiene as described for the 4-methyl analog. The product was formed in 33% yield. It was purified by recrystallization from ethanol (Darco); orange crystals, m.p. 186°.

Anal. Calcd. for $C_{36}H_{26}Cl_2N_4O_8S_4$: C, 51.37; H, 3.11; N, 6.64; mol. wt., 841. Found: C, 51.24; H, 3.34; N, 6.51, mol. wt. (ebullioscopic), 762.

The infrared spectra of the dimers prepared by these two different methods were identical. In the infrared spectrum the carbon–carbon double bond was indicated by an absorption band at 1663 cm.$^{-1}$; the carbon–chlorine bond by an absorption band at 720 cm.$^{-1}$.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY]

Reaction of β-Pinene with Dienophiles

BY RICHARD T. ARNOLD[1] AND JOHN S. SHOWELL[2]

RECEIVED AUGUST 30, 1956

β-Pinene has been found to react at 140° with a series of dienophiles including maleic anhydride, dimethyl maleate, dimethyl fumarate and methylenemalonic ester to form 1–1 adducts. In the three cases leading to the formation of a new asymmetric center, the 1–1 adduct consisted of a binary mixture of diastereoisomers in which one of these predominated. The adduct from β-pinene and methylenemalonic ester was synthesized independently. The data are consistent with a concerted mechanism involving a six-membered cyclic transition state.

Subsequent to the discovery by Alder and coworkers[3] that allylbenzene reacts thermally with maleic anhydride to form cinnamylsuccinic anhydride, many publications have appeared[4–7] which

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[1] Alfred P. Sloan Research Associate.

[2] Alfred P. Sloan postdoctorate Research Associate.

[3] K. Alder, F. Pascher and A. Schmitz, *Ber.*, **76**, 27 (1943).

[4] K. Alder and Dorfmann, *ibid.*, **85**, 556 (1952), and previous papers.

[5] C. J. Albisetti, N. G. Fisher, M. J. Hogsed and R. M. Joyce, THIS JOURNAL, **78**, 2637 (1956), and earlier papers.

[6] C. S. Rondestvedt and A. H. Filbey, *J. Org. Chem.*, **19**, 548 (1954).

[7] R. T. Arnold and J. F. Dowdall, THIS JOURNAL, **70**, 2590 (1948).