

bicarbonate, which removed only a trace of material; sodium hydroxide extraction removed most of the product, which gave a ferric chloride test and the ultraviolet spectrum given above.

B. Of the Dehydrogenation Product.—Fraction 3 (183 mg.), which had the benzofuran spectrum, although it did not appear to be as pure as some other fractions, was ozonized as above; the sodium hydroxide-soluble fraction (2–4 mg.) gave the ultraviolet spectrum reported above, and showed infrared bands at 3.31, 3.41, 5.89 and 6.12 μ , identical with the model compound.

Hydrogenation Experiments. A. 3,5-Dimethylbenzofuran.²²—Reduction of 5.7 g. of this material (n_D^{20} 1.5458) in ethanol with Raney nickel and hydrogen at 2 atm. for 48 hr. gave 4.4 g. of product after distillation; b.p. 100–104° (24 mm.), n_D^{20} 1.5269; ultraviolet absorption, 228 (3.64); 287 (3.48). This product is presumably 3,5-di-

(22) R. L. Shriner and J. Anderson, *THIS JOURNAL*, **61**, 2705 (1939), showed that 2-substituted benzofurans could be reduced catalytically with Raney nickel at low temperature and pressure.

methyl-2,3-dihydrobenzofuran, which has not been described very thoroughly.²³

B. Of the Dehydrogenation Product.—The product (50 mg.) was hydrogenated under the above conditions, and also at 100° and 40 atm. of hydrogen, but appeared from its ultraviolet spectrum and the color in concentrated sulfuric acid, to be unchanged. The reduction experiments appeared to remove some selenium-containing impurity, because the product after attempted reduction, smelled much more like 3,5-dimethylbenzofuran. The failure of the dehydrogenation product to reduce is perhaps to be expected if it has a large group in the 3-position.

Acknowledgment.—We are indebted to Dr. J. R. Schenck, Dr. R. D. Coghill and Dr. D. W. MacCorquodale of Abbott Laboratories for their interest and assistance in this problem.

(23) German Patent 501,723 (C. A., **24**, 4793 (1930)); J. B. Nieder and E. A. Storch, *THIS JOURNAL*, **55**, 4549 (1933).

ROCHESTER, NEW YORK

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

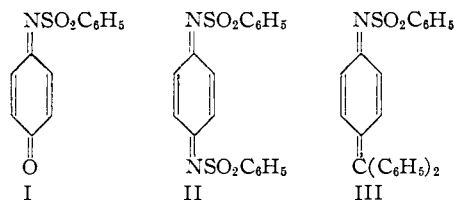
Quinol Imides and *o*-Quinone Imide Diacetates. I. Conversion of 4-Benzenesulfonamidotriphenylmethane to 4-Benzohydril-*o*-quinonediacetate-1-benzenesulfonimide

BY ROGER ADAMS, E. J. AGNELLO AND RICHARD S. COLGROVE¹

RECEIVED APRIL 23, 1955

4-Benzenesulfonamidotriphenylmethane is oxidized by lead tetraacetate in glacial acetic acid to give two compounds, the chief one 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide and the secondary one 2-benzenesulfonamido-5-benzohydril-*p*-benzoquinone. The structures, the addition reactions and the mechanism of formation and reactions of these two compounds are discussed. The 3-methyl derivative of 4-benzenesulfonamidotriphenylmethane gives upon oxidation an analogous compound which adds reagents; the entering groups are probably *para* to the methyl group in all cases.

Previous studies have shown that *p*-quinone-monobenzenesulfonimide (I)² and *p*-quinone-dibenzenesulfonimide (II)³ are stable compounds which exhibit many of the reactions of *p*-quinones. Since fuchsonebenzenesulfonimide (III) is closely related structurally to I and II, it has been the subject of investigation in order to compare its properties with those of its oxygen congener, fuchsone.

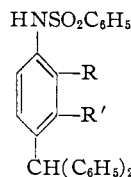


4-Benzenesulfonamidotriphenylmethane (IVa) used as the raw material in attempts to synthesize III was prepared by the following sequence of reactions: condensation of benzohydril and acetanilide in refluxing glacial acetic acid, hydrolysis of the acetylamino group with 30% sulfuric acid followed by benzene sulfonation of the amino group in pyridine solution. Quinone imides generally are prepared by oxidation of the corresponding amides with lead tetraacetate in either acidic or neutral solvents. Upon oxidation of IVa with two or more

(1) An abstract of a thesis submitted by Richard S. Colgrove to the Graduate College of the University of Illinois, 1954, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; University of Illinois Fellow, 1950–1951; Minnesota Mining and Manufacturing Co. Fellow, 1951–1952; American Cyanamid Co. Fellow, 1952–1953.

(2) R. Adams and J. H. Looker, *THIS JOURNAL*, **73**, 1145 (1951).

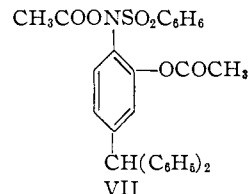
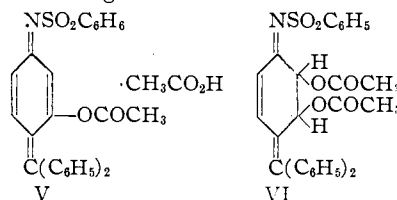
(3) R. Adams and A. S. Nagarkatti, *ibid.*, **72**, 4601 (1950).



- a, R' = R = H
b, R' = OCOCH₃; R = H
c, R' = H; R = CH₃
d, R' = H; R = OCOCH₃
e, R' = OH; R = H
f, R' = H; R = OH

IV

mole equivalents of lead tetraacetate in glacial acetic acid the formation of III was anticipated. Instead, two compounds resulted, the chief one of which had the empirical structure of III with two moles of acetic acid added. Three possible formulas for this compound first were proposed as shown in V, VI and VII, but all proved to be untenable on various grounds.



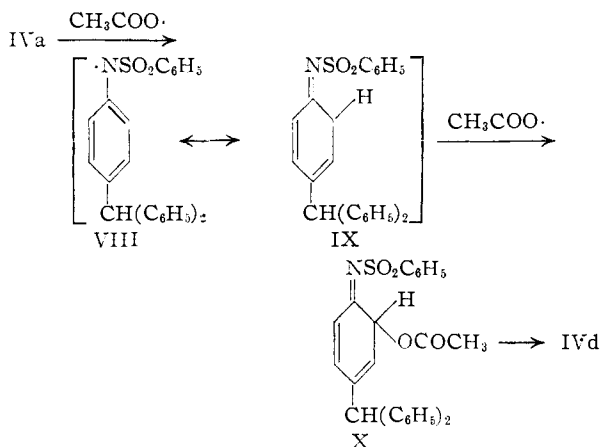
Structure V could be formed by oxidation of IVa to III followed by 1,4-conjugate addition of acetic acid⁴ to give structure IVb. Compound IVb,

(4) R. Adams and D. S. Acker, *ibid.*, **74**, 3657 (1952).

upon oxidation, might yield the corresponding imide which is indicated in V as crystallizing with a mole of acetic acid. The properties of the product, however, make this structure unacceptable. It can be crystallized from large volumes of acetone-water or benzene-petroleum ether (b.p. 80–110°) and always is recovered unchanged. A water-acetone solution of the product is neutral to litmus and could not be titrated with sodium hydroxide using phenolphthalein as an indicator. The infrared spectrum shows no bands characteristic of the hydroxyl or carbonyl group of a carboxyl function.

Structure VI and related structures conceivably could be formed by attack of lead tetraacetate on a double bond of III.⁵ However, the normal ester carbonyl band at 1740 cm.⁻¹ in the infrared spectrum is absent. Moreover, when the homologous product IVc was oxidized under similar conditions, an imide with only one combined equivalent of acetic acid resulted.

Compound VII could be formed by abstraction of a hydrogen atom from the nitrogen of IVa by an acetoxy radical to give structure VIII.⁶ The main contributing resonance structure (IX) has a free electron in the α -position which upon pairing with another acetoxy radical would give the unstable dihydrobenzenoid structure X. The latter structure would be converted to IVd by a prototropic shift.

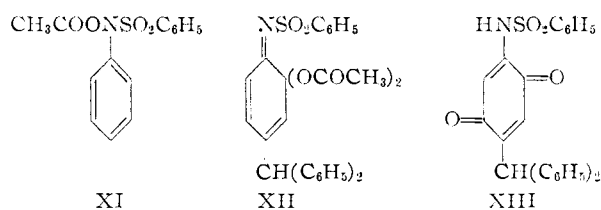


Abstraction of a hydrogen from the nitrogen of IVd and combination with an acetoxy radical would result in VII. The ring acetoxy group of VII is of the vinyl ester type and the band for the carbonyl would be expected in the range 1754–1786 cm.⁻¹. Actually a band was found at 1755 cm.⁻¹. The position of the other carbonyl band in the acetoxy group on the nitrogen atom, unknown at the time, might have fallen at such a position as to be superimposable on the ring acetoxy band. A strong band might then result. As a model compound for determining the position of the N-acetoxycarbonyl band, N-acetoxybenzenesulfonanilide (XI) was prepared. It was formed from phenylhydroxylamine by benzenesulfonation in absolute ethanol followed by acetylation with isopropenyl acetate. The carbonyl band in this product is at 1802 cm.⁻¹, thus ruling out VII as a possible structure.

(5) O. Dimroth and R. Schweizer, *Ber.*, **56**, 1375 (1923).

(6) W. A. Waters in Gilman's "Organic Chemistry," Vol. IV. John Wiley and Sons, Inc., New York, N. Y., 1953, p. 1185.

A formula which is compatible with the spectroscopic evidence and is supported by an abundance of chemical evidence is shown in XII. The product accompanying it might then have structure XIII.



When XII is reduced with sodium hydrosulfite or hydrogen in the presence of a platinum catalyst the product is IVd, a molecule whose infrared spectrum indicates the presence of an NH band and a vinyl-type ester carbonyl band. The reaction may involve direct hydrogenolysis of one of the *gem*-diacetate linkages in the allyl position to give X which would undergo a prototropic shift to IVd.⁷ Another possible pathway from XII involves reduction of the carbon-nitrogen double bond followed by loss of acetic acid to give IVd. The formation of XII, the major product isolated from the oxidation of IVa with lead tetraacetate, may be explained in the following manner. Abstraction of a hydrogen atom from IVd would give resonance structures analogous to VIII and IX, which upon combination with an acetoxy radical would result in XII.

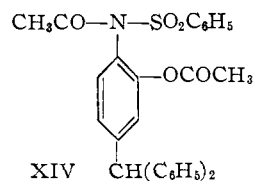
The symmetrically disposed acetoxy groups in XII result in one intensified carbonyl band in the infrared absorption spectrum at 1755 cm.⁻¹. This is in good agreement with the band found in propylidene diacetate at 1761 cm.⁻¹.⁸ The carbon-nitrogen double bond band at 1577 cm.⁻¹ may be abnormally strong compared to other quinone imides because of the enhancing effect of the α -acetoxy groups. The ultraviolet absorption spectrum shows bands λ_{max} 207 m μ , ϵ_{max} 50×10^3 ; and λ_{max} 288 m μ , ϵ_{max} 5.08×10^3 .

Oxidation of IVd under the same conditions that were used to oxidize IVa to XII and XIII gave in one run XII and in another XIII as the only isolable products. The evidence indicates that IVd is a probable intermediate in the conversion of IVa to XII and XIII by means of lead tetraacetate.

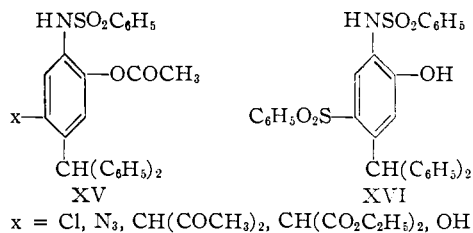
Compound IVb, the position isomer of structure IVd, was synthesized by condensation of benzohydroxyl with *m*-acetamidophenyl acetate followed first by hydrolysis and then in succession by benzenesulfonation and acetylation. Excess acetic anhydride in the last step gave the corresponding N-acetyl derivative of IVb. The preparation of IVd by a similar series of reactions from *o*-acetamidophenyl acetate failed on account of the very low yield in the initial condensation. Acetylation of IVd with acetic anhydride and pyridine afforded 3-acetoxy-N-acetyl-4-benzenesulfonamidotriphenylmethane (XIV) in excellent yield. The non-identity of the N-acetyl derivative of IVb with XIV is indicative that structure IVd is correct for the compound made from IVa by the reactions previously mentioned.

(7) H. E. Burdick and H. Akins, *THIS JOURNAL*, **56**, 438 (1934).

(8) R. S. Rasmussen and R. R. Brattain, *ibid.*, **71**, 1073 (1949).



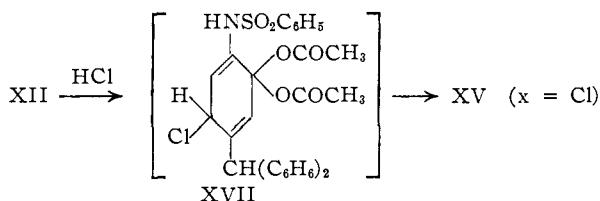
The reactions of XII resemble closely those of a quinone diimide. When treated with hydrogen chloride in chloroform 3-acetoxy-4-benzenesulfonamido-*x*-chlorotriphenylmethane (XV, $x = \text{Cl}$) results. In a similar manner, the compound adds hydrazoic acid to give the corresponding azido derivative (XV, $x = \text{N}_3$) and benzenesulfonic acid to give a phenyl sulfone in which the acetoxy group is hydrolyzed, 4-benzenesulfonamido-*x*-benzenesulfonyl-3-hydroxytriphenylmethane (XVI).



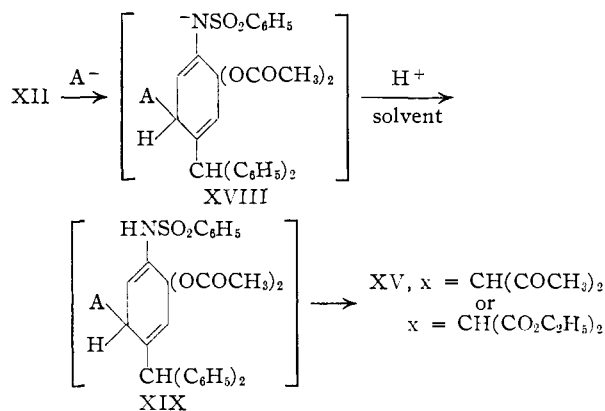
Heating with water and acetone results in the introduction of a hydroxyl group; XV, $x = \text{OH}$. Acetylacetone and diethyl malonate add readily in presence of sodium methoxide to give excellent yields of products; XV, $x = \text{CH}(\text{COCH}_3)_2$ or $\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$. Addition of thiophenol, cyclopentadiene and phenol failed to give adducts which could be isolated.

In the infrared spectrum of compound XV ($x = \text{OH}$) there is an OH band similar to that found in IVe and not to that in IVf, thus supporting its assignment to the position *para* to the acetoxy and *meta* to the benzenesulfonamido group. Both IVe and IVf were synthesized by unequivocal methods.

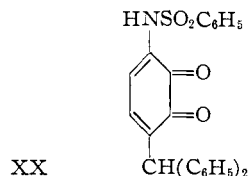
A possible mechanism by which acidic reagents such as hydrogen chloride may convert compound XII to benzene derivatives with the entering group *para* to the acetoxy is 1,4-conjugate addition to provide compound XVII, which upon 1,4-elimination of acetic acid and rearrangement will be converted to XV ($x = \text{Cl}$).



The addition of diethyl malonate or acetylacetone is catalyzed by small amounts of a base. The first step is probably the addition of an anion to the polarized form of XII to give XVIII. This base XVIII combines with a proton from the solvent or from the triethylammonium cation derived from the catalyst to give XIX. By a 1,4-elimination of acetic acid and rearrangement, the stable aromatic compound XV ($x = \text{CH}(\text{COCH}_3)_2$ or $\text{CH}(\text{CO}_2\text{C}_2\text{H}_5)_2$) is formed.

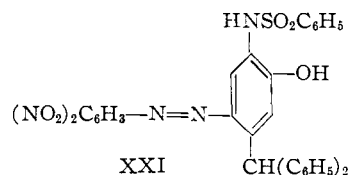


Structure XIII was assumed for the secondary product on the basis of the physical and chemical properties of the compound. Its empirical formula differs from that of III only by addition of two atoms of oxygen. The infrared spectrum shows an NH band but no OH band. A quinone structure is indicated and indeed a *p*-quinone XIII rather than the analogous *ortho* derivative XX.



The product is yellow and not the usual orange or red found in *o*-quinones. The infrared carbonyl bands appear in 1651 and 1670 cm^{-1} . The carbonyl frequency in ketones is lowered normally 20–50 cm^{-1} by conjugation.⁹ Since each carbonyl is in conjugation with two α,β -carbon-carbon double bonds, the carbonyl bands would be anticipated in the range 1650–1670 cm^{-1} , which is in good agreement with the observed bands. On the other hand, the carbonyls in XX are each conjugated with only a single α,β -carbon-carbon double bond and since γ,δ -unsaturation has little additional effect the carbonyl bands in such a molecule would be expected in the range 1675–1700 cm^{-1} .

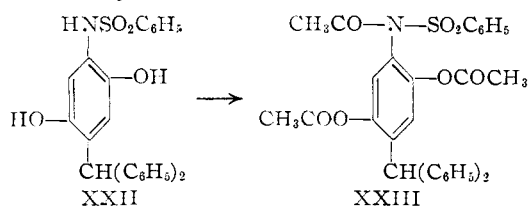
The compound assigned structure XIII reacts with 2,4-dinitrophenylhydrazine to give a product containing an azo grouping. The product probably has structure XXI though the hydroxyl and azo groups may be in the reverse positions. The infrared analysis indicates an NH and OH band (broad) at 3400 cm^{-1} with confirmatory bands present and an N=N band at 1620 cm^{-1} . It has been shown that analogous structures with the hydroxyl and azo groups *ortho* to each other exhibit



(9) H. W. Thompson and P. Torkington, *J. Chem. Soc.*, 640 (1945); R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *THIS JOURNAL*, 71, 1068 (1949); N. H. Cromwell, F. A. Miller, *et al.*, *ibid.*, 71, 3337 (1949).

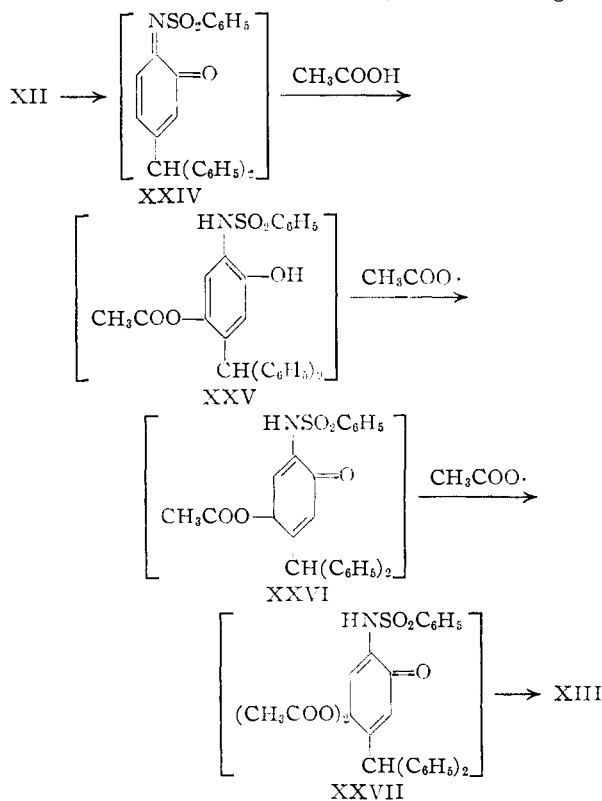
neither OH nor NH bands.¹⁰ As a consequence, structure XX for the quinone is unlikely. The selection of XXI as the more probable orientation of the hydroxyl and azo groups was based on the fact that all the following molecules have a hydroxyl band at 3400 cm^{-1} : 2-benzenesulfonamidophenol, 2-benzenesulfonamide-*p*-cresol and 6-benzenesulfonamido-*m*-cresol.¹¹ The phenol IVe has an OH band at 3415 cm^{-1} while compound IVf has an OH band at 3400 cm^{-1} .

Compound XIII is reduced readily with sodium hydrosulfite in aqueous ethanol to the corresponding hydroquinone XXII which with excess acetic anhydride is converted to the triacetyl derivative XXIII. Compound XXIII has an infrared vinyl ester carbonyl band at 1767 cm^{-1} and an amide



carbonyl band at 1722 cm^{-1} . This is in good agreement with the infrared spectrum of XIV in which the vinyl ester carbonyl band was found at 1769 cm^{-1} and the amide carbonyl band at 1721 cm^{-1} .

Formation of compound XIII from compound XII may be explained by initial loss of acetic anhydride¹² to form XXIV. This product undergoes



(10) S. B. Hendricks, *et al.*, THIS JOURNAL, **58**, 1995 (1936).

(11) Kindly furnished by J. M. Stewart of this Laboratory.

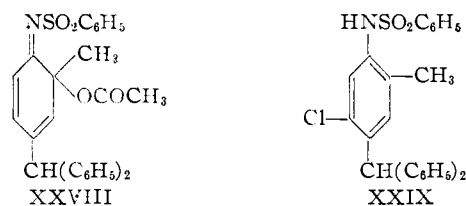
(12) F. C. Whitmore, "Organic Chemistry," Second Edition, Van Nostrand Co., Inc., New York, N. Y., 1951, p. 200.

reaction with acetic acid by a 1,4-conjugate addition process involving the nitrogen followed by re-arrangement to yield XXV.

Abstraction of a hydrogen atom from the phenolic hydroxyl group of compound XXV would give a structure in resonance with XXVI. Combination of XXVI with an acetoxy radical would yield XXVII which would lose acetic anhydride with formation of XIII.

The evidence that in the addition of reagents to XII the entering group occupies the position *para* to the acetoxy group (XV) is supported by the experiments with the methyl analog XXVIII.

Oxidation of 4-benzenesulfonamido-3-methyltriphenylmethane (IVc) with lead tetraacetate in glacial acetic acid took place in a manner analogous to the oxidation of 4-benzenesulfonamidotriphenylmethane to give 3-acetoxy-4-benzenesulfonimido-3-methyl-3,4-dihydrotriphenylmethane (XXVIII) in 71% yield. The infrared spectrum of this compound has the expected normal carbonyl band at 1736 cm^{-1} . The ultraviolet spectrum shows a band λ_{max} 350 $\text{m}\mu$, ϵ_{max} 4.04×10^3 . Reduction converts XXVIII to IVc.

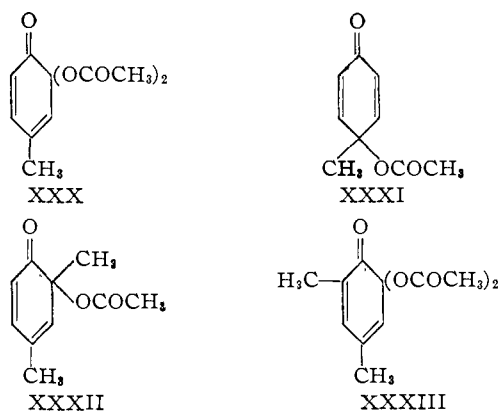


Upon addition of hydrogen chloride to XXVIII a product shown by an unequivocal synthesis to be XXIX results. The synthesis consisted in the condensation of benzohydrol with 2-acetamido-4-chloro-toluene followed by hydrolysis and benzenesulfonation. It is probable that all the addition products of XII have the same orientation.

Compound XII is analogous in structure to the quinols¹³ reported to be formed by the oxidation of certain phenols with lead tetraacetate in acetic acid. The structures of the oxidation products were established by identifying the compounds formed by their reduction and by analysis of ultraviolet spectra. Thus by the oxidation of *p*-cresol, the diacetoxy compound XXX and *p*-quinol acetate XXXI are formed in 28 and 14% yields, respectively. 2,4-Dimethylphenol is oxidized to XXXII in 23% yield and to XXXIII in 2% yield. Other phenols yield analogous products.¹³ The mechanism of formation of the *o*- and *p*-quinols which has been postulated is similar to that proposed in this Communication.

Furthermore, reduction and addition reactions in the two series yield analogous products. Reduction of XII results in IVd, while compound XXX is reduced to 2-acetoxy-*p*-cresol. The Reformatsky reagent from zinc and ethyl α -bromoacetate reacts with introduction of a carboxymethyl group *para* to the position originally holding the two acetoxy

(13) F. Wessely, *et al.*, *Monatsh.*, **81**, 811, 1055 (1950); **83**, 902 (1952); **84**, 124, 291, 425, 969 (1953); **85**, 69, 637 (1954); B. Witkop and S. Goodwin, *Experientia*, **8**, 377 (1952); A. Ebnöther, L. M. Meyer and H. Schmid, *Helv. Chim. Acta*, **35**, 910 (1952). For addition of reagents see F. Wessely, *et al.*, *Monatsh.*, **83**, 1253 (1952); **84**, 655 (1953); A. Siegel and H. Keckers, *ibid.*, **84**, 910 (1953).



groups. This observation is in agreement with the addition reactions of XII to give products with the entering group *para* to the carbon originally holding the two acetoxy groups.

Acknowledgment.—The authors are indebted to Mrs. Lucy Chang, Miss Emily Davis, Mrs. Esther Fett, Mrs. Jean Fortney, Mrs. Katherine Pih and Mr. Joseph Nemeth for the microanalyses, to Mrs. Rosemary Hill, Mrs. Elizabeth Leighly, Miss Helen P. Miklas and Mr. James J. Brader for the determination and interpretation of the infrared absorption spectra and to Miss Gardine Meerman and Mr. E. Reinold Fett for the ultraviolet and visible spectra determinations.

Experimental

All melting points are corrected.

The infrared spectra were run in Nujol mulls using a Perkin-Elmer model 21 double beam spectrophotometer.

The lead tetraacetate used in all oxidations was recrystallized from glacial acetic acid and dried over phosphorus pentoxide.

In all benzenesulfonations and acetylations pyridine (reagent grade) dried over potassium hydroxide was employed as a solvent.

4-Aminotriphenylmethane Sulfate. Method A.—Although 4-aminotriphenylmethane has been prepared by a number of investigators,¹⁴ none of the methods described is satisfactory. A study of the reaction under many conditions led to the following procedure as superior to any yet published.

To a solution of 92.1 g. of benzohydrol and 67.6 g. of acetanilide in 500 ml. of glacial acetic acid was added 100 g. of concentrated sulfuric acid. The reaction mixture was heated under reflux for 34 hours. The resulting cherry-red solution was poured slowly with stirring into about 4 l. of distilled water containing crushed ice. The cream-colored granular precipitate of crude 4-acetamidotriphenylmethane was removed by filtration and heated under reflux with 2.5 l. of 30% sulfuric acid for 19 hours. The reaction mixture was poured into 9 l. of boiling distilled water and filtered to remove the sulfate of the dicondensatation product. The filtrate upon standing overnight yielded tan needles, which after washing with ether on the filter were white; weight 111.9 g. (72.5%). The average yield of several runs was somewhat lower.

The product was not purified before conversion to the 4-benzenesulfonamidotriphenylmethane which was obtained in practically pure state after one recrystallization in a yield of 70%. From this experiment it was deduced that the crude 4-aminotriphenylmethane sulfate contained only a small percentage of impurities.

Method B.—A solution of 93 g. of polyphosphoric acid in 100 ml. of glacial acetic acid was heated under reflux. To

this refluxing solution was added dropwise a solution of 5.55 g. of benzohydrol and 4.05 g. of acetanilide in 40 ml. of glacial acetic acid. The addition took 30 minutes. After a 21-hour period under reflux the solution was poured into one liter of distilled water containing crushed ice. The crude yellow granular solid was removed by filtration and heated under reflux for 13 hours with 100 ml. of 30% sulfuric acid. The acid solution then was poured into one liter of boiling water and filtered. The filtrate upon standing overnight yielded 4.0 g. (43.5%) of orange-tan needles. The product prepared by this method is colored, while preparation by method A gives a colorless product.

4-Benzenesulfonamidotriphenylmethane.—To a solution of 111.9 g. of 4-aminotriphenylmethane sulfate in one liter of dry pyridine was added a solution of 79.1 g. of benzenesulfonyl chloride in 200 ml. of dry pyridine. The cherry-red solution was heated under reflux for 10 minutes. The resulting yellow-orange solution was allowed to stand overnight at room temperature. After 24 hours the pyridine solution was poured into 1.4 l. of concentrated hydrochloric acid containing crushed ice to give an off-white granular product which became gummy on standing. After recrystallization from ethanol-water (Darco) 102 g. (70.5%) of white platelets resulted. Four recrystallizations from acetic acid-water gave white needles, m.p. 153–154°, with some previous sintering at 152°.

Anal. Calcd. for $C_{26}H_{21}NO_2S$: C, 75.16; H, 5.30; N, 3.51. Found: C, 75.31; H, 5.53; N, 3.32.

Infrared analysis indicated an NH band at 3250 cm^{-1} ; SO_2 bands at 1165 and 1328 cm^{-1} ; monosubstituted benzene bands at 702, 748 and 764 cm^{-1} .

Oxidation of 4-Benzenesulfonamidotriphenylmethane:
(1) **4-Benzohydryl-*o*-quinonediacetate-1-benzenesulfonimide.**—A suspension of 15.5 g. of 4-benzenesulfonamidotriphenylmethane and 35 g. of lead tetraacetate in 200 ml. of glacial acetic acid was stirred at room temperature. The acetic acid turned pale yellow immediately, then gradually orange and finally red over a 30-minute period. Most of the suspended solids went into solution over a 7-hour period. During the next few hours an orange solid separated from solution. After 24 hours the reaction mixture was treated with 10 ml. of ethylene glycol to destroy the excess lead tetraacetate. The suspended orange solid was removed by filtration and washed on the filter with 25 ml. of glacial acetic acid and then with 50 ml. of ether to give, after drying, 6.0 g. (30%) of pale yellow needles. Recrystallization was effected by dissolving in excess warm acetone, filtering, adding water to the cloud point and allowing to cool slowly to room temperature. Pale yellow needles, weighing 5.6 g., resulted after two such crystallizations; m.p. 176–178° dec. The analytical sample was prepared from a smaller scale run. After six recrystallizations from acetone-water, very pale yellow needles, m.p. 178.5–179.5° dec., resulted.

Anal. Calcd. for $C_{26}H_{25}NO_6S$: C, 67.56; H, 4.89; N, 2.72. Found: C, 67.48; H, 4.78; N, 2.84.

Infrared analysis indicated a C=O band at 1755 cm^{-1} , a C=N band at 1577 cm^{-1} .

(2) **2-Benzenesulfonamido-5-benzohydryl-*p*-benzoquinone.**—The isolation and purification of 2-benzenesulfonamido-5-benzohydryl-*p*-benzoquinone from the reaction mixture of a 0.1-mole run is described.

After removal of 4-benzohydryl-*o*-quinonediacetate-1-benzenesulfonimide by filtration, the combined acetic acid filtrate and washings were poured into one liter of water to give an orange gum, which turned red-brown upon standing a few minutes. The gum was taken up in 300 ml. of ether (except for a brown residue of 1.3 g., which proved to be 4-benzohydryl-*o*-quinonediacetate-1-benzenesulfonimide), washed twice with water, thrice with 5% aqueous sodium bicarbonate and twice with water. The resulting red solution was dried over anhydrous magnesium sulfate overnight. The dry ethereal solution was filtered. To the filtrate was added an equal volume of dry benzene (dried over sodium) and the solution was warmed to remove the ether. When the odor of ether was no longer apparent an orange-yellow crystalline product separated and the solution was allowed to cool to room temperature. The crude product weighed 6.6 g. (15.5%). One recrystallization from benzene and two recrystallizations from acetone-water gave yellow needles, m.p. 172.5–174° dec.

Anal. Calcd. for $C_{26}H_{19}NO_4S$: C, 69.91; H, 4.46; N, 3.26. Found: C, 70.11; H, 4.42; N, 3.20.

(14) (a) O. Fischer and L. Roser, *Ann.*, **206**, 155 (1881); (b) O. Fischer and G. Fischer, *Ber.*, **24**, 723 (1891); (c) A. Baeyer and V. Villiger, *ibid.*, **37**, 599 (1904); (d) M. Busch and A. Rinck, *ibid.*, **38**, 1761 (1905); (e) J. B. Shoemith, C. E. Sosson and A. C. Hetherington, *J. Chem. Soc.*, 2221 (1927).

Infrared analysis indicated an NH band at 3250 cm^{-1} ; conjugated C=O bands at 1670 and 1651 cm^{-1} ; conjugate C=C bands at 1610 and 1618 cm^{-1} ; SO₂ bands at 1365 and 1177 cm^{-1} ; monosubstituted benzene bands (normal) 1610, 1092, 745 and 705 cm^{-1} , (SO₂ type) 1590, 1497, 718 and 685 cm^{-1} ; NH bending band at 1455 cm^{-1} probably lowered by hydrogen bonding.

The product should be protected from light since it was observed that on exposure to sunlight for 2 hours the surface of the compound had become orange colored.

After separation of the crude product the benzene filtrate was taken to dryness by a stream of dry air. The resulting red oil could not be induced to crystallize and was not characterized further.

3-Acetoxy-4-benzenesulfonamidotriphenylmethane.—To a suspension of 5.16 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in one liter of boiling 95% ethanol was added 50 ml. of boiling water and 2.0 g. of sodium hydrosulfite in small portions. The boiling was continued for 15 minutes after completion of the addition. The solution was filtered, concentrated to 500 ml., water added to the cloud point and allowed to stand overnight. The white needles were removed by filtration and the filtrate concentrated to give a second crop. The combined crops weighed 3.37 g. (73.6%). Two recrystallizations from 95% ethanol gave white needles, m.p. 178–180° dec.

Anal. Calcd. for C₂₇H₂₃NO₅S: C, 70.88; H, 5.07; N, 3.06. Found: C, 70.98; H, 5.12; N, 2.94.

Infrared analysis indicated an NH band at 3220 cm^{-1} , vinyl ester C=O band at 1772 cm^{-1} , SO₂ bands at 1335 and 1170 cm^{-1} , monosubstituted benzene bands at 698 and 726 cm^{-1} .

The same product also was formed in 92% yield by reduction of the imide as a suspension in absolute ethanol by means of hydrogen and platinum oxide catalyst.

Oxidation of 3-Acetoxy-4-benzenesulfonamidotriphenylmethane: 2-Benzenesulfonamido-5-benzohydril-*p*-benzoquinone and 4-Benzohydril-*o*-quinonediacetate-1-benzenesulfonimide.—A suspension of 0.70 g. of 3-acetoxy-4-benzenesulfonamidotriphenylmethane and 1.37 g. of lead tetraacetate in 50 ml. of glacial acetic acid was stirred at room temperature for 128 hours. About 2 ml. of ethylene glycol was added to destroy the excess lead tetraacetate and the reaction mixture was poured into 200 ml. of water to give an orange-yellow precipitate which was removed by filtration and air-dried. Three recrystallizations from benzene-petroleum ether (b.p. 80–110°) gave yellow needles, m.p. 173–174° dec., unchanged by further recrystallization. Infrared analysis indicated it was identical with 2-benzenesulfonamido-5-benzohydril-*p*-benzoquinone.

Anal. Calcd. for C₂₅H₁₉NO₄S: C, 69.91; H, 4.46; N, 3.26. Found: C, 69.90; H, 4.48; N, 3.07.

Another run, using 0.92 g. of 3-acetoxy-4-benzenesulfonamidotriphenylmethane and 1.82 g. of lead tetraacetate in 60 ml. of glacial acetic acid with stirring for 98 hours at room temperature, led to a product which after four recrystallizations from acetone-water formed pale yellow needles, m.p. 178–179.5° dec. This proved to be 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonamide as determined by infrared analysis.

3-Acetoxy-N-acetyl-4-benzenesulfonamidotriphenylmethane.—To a solution of 2 g. of 3-acetoxy-4-benzenesulfonamidotriphenylmethane in 20 ml. of dry pyridine was added 0.5 g. of acetic anhydride. After standing at room temperature for 54 hours, the resulting solution was poured into 50 ml. of 1:1 hydrochloric acid (ice). The white precipitate was removed by filtration and recrystallized from glacial acetic acid-water to give 1.56 g. (71.5%) of white crystals. Four recrystallizations from ethanol-water gave a pure product, m.p. 140–141°.

Anal. Calcd. for C₂₉H₂₃NO₆S: C, 69.72; H, 5.04; N, 2.80. Found: C, 69.56; H, 5.21; N, 2.69.

Infrared analysis indicated a vinyl ester C=O band at 1769 cm^{-1} ; an amide C=O band at 1721 cm^{-1} ; SO₂ bands at 1373 and 1180 cm^{-1} ; monosubstituted benzene bands at 763, 749, 728 and 689 cm^{-1} .

3-Acetoxy-4-benzenesulfonamido-*x*-chlorotriphenylmethane.—Hydrogen chloride was passed into a solution of 2.58 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in 200 ml. of dry chloroform (dried over calcium chloride) for 30 minutes. The resulting colorless solution was

evaporated to dryness by a current of dry air to give an oily residue. The oil was taken up in 10 ml. of 95% ethanol and evaporated almost to dryness to give 2.40 g. (97.5%) of white crystals. Three recrystallizations from 95% ethanol (Darco) gave white needles, m.p. 167–169°.

Anal. Calcd. for C₂₇H₂₂ClNO₅S: C, 65.91; H, 4.51; N, 2.85. Found: C, 65.71; H, 4.56; N, 2.86.

Infrared analysis indicated an NH band at 3245 cm^{-1} , vinyl ester C=O band at 1780 cm^{-1} , SO₂ bands at 1337 and 1175 cm^{-1} , monosubstituted benzene at 698 and 753 cm^{-1} .

3-Acetoxy-*x*-azido-4-benzenesulfonamidotriphenylmethane.—To a suspension of 5.2 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in 250 ml. of glacial acetic acid and 50 ml. of acetone was added 3.0 g. of sodium azide. The mixture was agitated manually. The reaction flask was covered with aluminum foil and placed in the dark for 25 hours at room temperature. The resulting solution was poured into one liter of water to give a light tan precipitate, which after drying in a vacuum desiccator over potassium hydroxide-calcium chloride weighed 4.7 g. (94%). Three recrystallizations from benzene-petroleum ether (b.p. 93–97.5°) gave cream-colored needles, m.p. 163–164° dec.

Anal. Calcd. for C₂₇H₂₂N₄O₅S: C, 65.04; H, 4.45; N, 11.24. Found: C, 65.32; H, 4.50; N, 11.39.

Infrared analysis indicated an NH band at 3185 cm^{-1} , vinyl ester C=O band at 1774 cm^{-1} , N₃ band at 2100 cm^{-1} .

4-Benzenesulfonamido-*x*-benzenesulfonyl-3-hydroxytriphenylmethane.—To a suspension of 0.52 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in 25 ml. of glacial acetic acid was added 0.57 g. of sodium benzene sulfinate and 2 drops of concentrated sulfuric acid. The reaction mixture was shaken manually. In 5 minutes the pale yellow color had faded. After 49 hours at room temperature the acid solution was poured into 100 ml. of water. A crude tan product separated from solution weighing 0.48 g. (86%). Four recrystallizations from ethanol-water gave micro-needles, m.p. 276.5–277.5° dec., with some previous sintering at 275°.

Anal. Calcd. for C₃₁H₂₅NO₆S₂: C, 67.01; H, 4.54; N, 2.52. Found: C, 67.15; H, 4.57; N, 2.67.

Infrared analysis indicated an NH and OH doublet band centering at 3320 cm^{-1} , a strong aromatic band at 1592 cm^{-1} probably intensified because of the OH group, SO₂ bands at 1345 and/or 1333 cm^{-1} and 1175 and/or 1138 cm^{-1} ; structure in this region is complex enough to make the presence of two SO₂ groups probable; mono-substituted benzene undoubtedly is present although the substitution region is complex.

3-Acetoxy-4-benzenesulfonamido-*x*-hydroxytriphenylmethane.—A suspension of 0.52 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in 200 ml. of 1:1 acetone-water was heated under reflux for 85 hours. The resulting solution was concentrated to the cloud point, an equal volume of water added and the solution was allowed to stand overnight. The crude product was removed by filtration and air-dried. It weighed 0.44 g. (93.5%). Four recrystallizations from acetone-water gave white micro-needles, m.p. 217–218.5° dec.

Anal. Calcd. for C₂₇H₂₃NO₆S: C, 68.48; H, 4.90; N, 2.96. Found: C, 68.37; H, 4.85; N, 2.90.

Infrared analysis indicated NH bands at 3240 (stretch) and 1524 cm^{-1} (bend); a vinyl ester C=O band at 1773 cm^{-1} ; an OH band at 3420 cm^{-1} ; SO₂ bands at 1375 and 1174 cm^{-1} (probable); monosubstituted benzene bands at 1605, 1500, 739, 725, 699 and 680 cm^{-1} .

3-Acetoxy-4-benzenesulfonamido-*x*-diacetylmethyltriphenylmethane.—To a solution of 1.04 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in 60 ml. of dry dioxane (dried over sodium and distilled) was added 0.44 g. of acetylacetone and 0.04 g. of sodium methoxide as catalyst. After standing at room temperature for 36 hours the solution was poured into 200 ml. of water. The white precipitate which weighed 1.05 g. (94%) was recrystallized four times from ether-petroleum ether (b.p. 37–39°) as white needles, m.p. 206.5–207.5°.

Anal. Calcd. for C₃₂H₂₉NO₆S: C, 69.17; H, 5.26; N, 2.52. Found: C, 69.26; H, 5.13; N, 2.55.

Infrared analysis indicated an NH band at 3220 cm^{-1} ; vinyl ester C=O at 1773 cm^{-1} ; SO₂ bands at 1332, 1177 and/or 1185 cm^{-1} ; a broad band at 1650–1550 cm^{-1} probably due to chelated enol form of ketone carbonyls.

3-Acetoxy-4-benzenesulfonamido-*x*-dicarboethoxymethyltriphenylmethane.—From a solution of 0.52 g. of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide in 100 ml. of dry dioxane (dried over sodium and distilled) and a solution of 2.0 g. of diethyl malonate in 50 ml. of dry dioxane with 0.04 g. of sodium methoxide as catalyst, 0.46 g. (74%) of product resulted (see previous preparation). The reaction time was 7.5 hours. One recrystallization from ethanol-water and two recrystallizations from ether-petroleum ether (b.p. 37–39°) gave white needles, m.p. 156–157.5° dec.

Anal. Calcd. for $C_{34}H_{33}NO_8S$: C, 66.32; H, 5.40; N, 2.28. Found: C, 66.50; H, 5.52; N, 2.19.

Infrared analysis indicated an NH band at 3250 cm^{-1} , vinyl ester C=O at 1777 cm^{-1} , C=O bands at 1737 and 1713 cm^{-1} , SO₂ bands at 1300 and 1165 cm^{-1} .

2-Benzenesulfonamido-5-benzohydrilhydroquinone.—To a boiling solution of 1.00 g. of 2-benzenesulfonamido-5-benzohydril-*p*-benzoquinone in 100 ml. of 95% ethanol and 50 ml. of distilled water was added in small portions 0.5 g. of sodium hydrosulfite. The initial red-orange color was discharged in 2 minutes. The resulting colorless solution was filtered, concentrated to the cloud point, diluted with an equal volume of distilled water and allowed to stand overnight. The crude dry product weighed 0.83 g. (83%). Three recrystallizations from ether-petroleum ether (b.p. 37–39°) and a final recrystallization from ether gave white needles, m.p. 195.5–196.5°.

Anal. Calcd. for $C_{28}H_{21}NO_4S$: C, 69.58; H, 4.91; N, 3.25. Found: C, 69.47; H, 5.01; N, 3.43.

Infrared analysis indicated OH bands at 3455 (str.) and 3300 cm^{-1} (med.); NH bands at 3125 (str.) and 3055 cm^{-1} (wk.); SO₂ bands at 1172, 1310 and/or 1325 cm^{-1} ; monosubstituted benzene bands at 752 and 702 cm^{-1} .

2,5-Diacetoxy-*N*-acetyl-4-benzenesulfonamidotriphenylmethane.—To a solution of 0.70 g. of 2-benzenesulfonamido-5-benzohydrilhydroquinone in 20 ml. of dry pyridine was added 0.35 g. of acetic anhydride. It was shaken and allowed to stand at room temperature for 19 hours. The basic solution was poured into 200 ml. of 1:1 hydrochloric acid (ice) to give a tan precipitate. The crude product was recrystallized from acetone-water to give white crystals which weighed 0.60 g. (94%). Four recrystallizations from acetone-water gave white platelets, m.p. 190–191.5°.

Anal. Calcd. for $C_{31}H_{27}NO_7S$: C, 66.77; H, 4.88; N, 2.51. Found: C, 66.93; H, 4.74; N, 2.48.

Infrared analysis indicated a vinyl ester C=O band at 1767 cm^{-1} , an amide C=O band at 1722 cm^{-1} , SO₂ bands at 1355 and 1165 cm^{-1} , a monosubstituted benzene band at 705 cm^{-1} .

2(5)-Benzenesulfonamido-5(2)-benzohydril-4-(2,4-dinitrophenylazo)-phenol.—To a solution of 0.5 g. of 2-benzenesulfonamido-5-benzohydril-*p*-benzoquinone in 20 ml. of 95% ethanol was added a freshly prepared ethanolic solution of 0.4 g. of 2,4-dinitrophenylhydrazine.¹⁵ Upon standing overnight a dark red precipitate had formed, weight 0.55 g. (77.5%). Four recrystallizations from ethanol-water gave dark red needles, m.p. 231–232.5° dec. with some sintering at 229°.

Anal. Calcd. for $C_{31}H_{23}N_5O_7S$: C, 61.08; H, 3.80; N, 11.49. Found: C, 61.21; H, 3.86; N, 11.38.

Infrared analysis indicated an NH and OH band at 3400 cm^{-1} , broad and tapering; an NH (bend) band at 1515 cm^{-1} ; a C–N (stretch) band at 1370 cm^{-1} ; a C–O (stretch) band at 1246 cm^{-1} ; N=N (stretch) band at 1620 cm^{-1} ; C–N=N–C (stretch) band at 940 cm^{-1} ; conjugate NO₂ bands at 1537 (asym.) and 1343 cm^{-1} (sym.); SO₂ bands at 1343 and 1180 cm^{-1} ; benzene ring C–C (stretch) at 1607, 1575 and 1515 cm^{-1} ; monosubstituted benzene bands at 687 and 753 cm^{-1} ; monosubstituted benzene (S-substituted) bands at 723 and 696 cm^{-1} ; 1,2,4-trisubstituted benzene bands at 834 and 864 cm^{-1} , strong due to isolated CH (wag) of 1,2,4,5-tetrasubstituted benzene.

4-Benzenesulfonamido-3-methyltriphenylmethane.—A 5-g. quantity of 4-amino-3-methyltriphenylmethane sulfate¹⁶ was heated with an excess of 15% aqueous sodium hy-

droxide. After cooling, the free base was extracted with ether and dried over Drierite. The residue obtained by evaporation of the ether was dissolved in 35 ml. of pyridine and a solution of 2.6 g. of benzenesulfonyl chloride in 10 ml. of pyridine was added. The resulting red solution was heated on a steam-cone for 4 hours. The product, isolated in the usual way, weighed 4.9 g. (80%) after crystallization from ethanol. Three recrystallizations from ethanol gave white prisms, m.p. 147–148°.

Anal. Calcd. for $C_{26}H_{23}NO_2S$: C, 75.52; H, 5.61; N, 3.39. Found: C, 75.50; H, 5.82; N, 3.40.

Infrared analysis indicated an NH band at 3259 cm^{-1} .

3-Acetoxy-4-benzenesulfonimido-3-methyl-3,4-dihydrotriphenylmethane.—A suspension of 1 g. of 4-benzenesulfonamido-3-methyltriphenylmethane and 3 g. of lead tetraacetate in 35 ml. of glacial acetic acid was stirred for 48 hours at room temperature. After destroying the excess lead tetraacetate with ethylene glycol, the mixture was poured into 250 ml. of water. Crystallization of the amorphous solid from 1:1 acetone-water yielded 0.8 g. (71%) of pale yellow crystals. Three recrystallizations from acetone-water gave pale yellow needles, m.p. 149–150° dec.

Anal. Calcd. for $C_{28}H_{26}NO_4S$: C, 71.31; H, 5.34; N, 2.97. Found: C, 71.34; H, 5.43; N, 3.08.

Infrared analysis indicated a normal ester C=O band at 1736 cm^{-1} and a C=N band at 1560 cm^{-1} .

The product was reduced to 4-benzenesulfonamido-3-methyltriphenylmethane by treatment with sodium hydrosulfite in aqueous ethanol as described for the reduction of 4-benzohydril-*o*-quinonediacetate-1-benzenesulfonimide.

Treatment of the imide with 1% aqueous sodium carbonate, or 1% aqueous sodium hydroxide or an aqueous ethanolic sodium bicarbonate solution failed to remove acetic acid. A suspension of the imide in 5% aqueous sodium hydroxide solution, after standing overnight, yielded 50% unchanged imide. The filtrate upon acidification with acetic acid gave a white amorphous solid which was not characterized further.

A sample of the imide, heated for 13 hours at 138° at 0.1 mm. pressure, lost only 0.8% as compared to a theoretical loss of 12.7% for a molecule of acetic acid.

4-Benzenesulfonamido-2-chloro-5-methyltriphenylmethane. Method A.—A solution of 2.2 g. of 3-acetoxy-4-benzenesulfonimido-3-methyl-3,4-dihydrotriphenylmethane in 100 ml. of dry chloroform was treated with dry hydrogen chloride for 3 hours. The solvent was removed *in vacuo* on a steam-cone and a small amount of ethanol was added to the residue. The product crystallized on scratching and weighed 1 g. (48%). Two recrystallizations from ethanol gave white needles, m.p. 163.5–164.5°.

Anal. Calcd. for $C_{26}H_{22}ClNO_2S$: C, 69.71; H, 4.95; N, 3.13. Found: C, 69.77; H, 5.21; N, 3.32.

Infrared analysis indicated an NH band at 3268 cm^{-1} .

Method B.—A mixture of 3 g. of 2-acetamido-4-chlorotoluene¹⁷ and 3 g. of benzohydril was heated with 3.3 g. of concentrated sulfuric acid in 50 ml. of glacial acetic acid for 24 hours. The solid obtained by pouring the mixture into excess sodium bicarbonate solution was heated for 24 hours with 25% sulfuric acid. After diluting with water and cooling, the thin white needles which formed were removed by filtration and washed with ether and then petroleum ether; yield 3.7 g. (63%).

A solution of 3.7 g. of this salt in 75 ml. of pyridine was heated on a steam-cone with 2.2 g. of benzenesulfonyl chloride for 3 hours. The product, isolated in the usual manner and recrystallized from ethanol, weighed 2 g. (45%). By melting point and infrared spectrum it proved to be identical with the product formed in method A.

5-Acetoxy-4-benzenesulfonimido-2-chloro-5-methyl-4,5-dihydrotriphenylmethane.—This product was synthesized by the oxidation with lead tetraacetate of 4-benzenesulfonamido-2-chloro-5-methyltriphenylmethane following the procedure for the oxidation of the corresponding unchlorinated amide to the imide. The product was obtained in 63% yield. It was purified from 1:1 acetone-water; pale yellow needles, m.p. 178–179.5° dec.

Anal. Calcd. for $C_{28}H_{24}ClNO_4S$: C, 66.46; H, 4.78; N, 2.77. Found: C, 66.43; H, 4.85; N, 2.96.

(15) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," Third Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 171.

(16) H. A. Iddles and W. L. Hartop, Jr., *THIS JOURNAL*, **72**, 4589 (1950).

(17) H. Goldschmidt and M. Hönig, *Ber.*, **19**, 2438 (1886); L. C. Raiford, *Am. Chem. J.*, **46**, 452 (1911).

Infrared analysis indicated an ester C=O band at 1745 cm^{-1} and a C=N band at 1563 cm^{-1} .

Treatment with sodium hydrosulfite, as described for the unchlorinated imide, gave the corresponding amide.

N-Benzenesulfonyl-N-phenylhydroxylamine.—This product was made from N-phenylhydroxylamine¹⁸ (m.p. 81.5–83°) by benzenesulfonation according to the method of Piloty¹⁹ (m.p. 120–121°).

The infrared analyses follows: N-phenylhydroxylamine, NH band at 3240 cm^{-1} ; OH band at 3120 cm^{-1} ; an NH (bend) band at 1525 cm^{-1} ; OH (bend) band at 793 cm^{-1} probably; N–O (stretch) band at 925 cm^{-1} probably; monosubstituted benzene bands at 1605, 1500, 1160, 1092, 1025, 748 and 690 cm^{-1} . N-Benzenesulfonyl-N-phenylhydroxylamine, OH band at 3370 cm^{-1} ; N–O (stretch) band at 993 cm^{-1} ; SO₂ bands at 1350 and 1175 cm^{-1} ; monosubstituted benzene bands at 1597, 1590, 1492, 685 and 727 cm^{-1} .

N-Acetoxybenzenesulfonanilide.—A solution of 10 g. of N-benzenesulfonyl-N-phenylhydroxylamine and 0.04 g. of *p*-toluenesulfonic acid in 50 ml. of dry thiophene-free benzene (dried over sodium) was heated to 65° (solution temperature) by means of an oil-bath. To the preheated solution was added, over a one-hour period, 4.37 ml. of isopropenyl acetate. Acetone formed in the reaction was removed by fractional distillation using a 30-cm. Vigreux column. After removal of the acetone (ca. 3 hours) the reaction mixture was cooled to room temperature, treated with aqueous potassium carbonate (Darco) and filtered. The brown filtrate upon addition of petroleum ether (b.p. 80–110°) gave a red oil. The solvent was removed by a stream of dry air; the resulting oil was covered with petroleum ether (b.p. 30–60°) and evaporated to dryness to yield a red gum; weight 9.5 g. (81%). The crude product was taken up in chloroform, treated with Darco, filtered and petroleum ether (b.p. 37–39°) added to give a tan precipitate. Three recrystallizations from chloroform–petroleum ether (b.p. 37–39°) gave white micro-prisms, m.p. 105–106.5°.

Anal. Calcd. for C₁₄H₁₃NO₄S: C, 57.71; H, 4.50; N, 4.81. Found: C, 57.78; H, 4.52; N, 4.83.

Infrared analysis indicated an ester (N-substituted) C=O band at 1802 cm^{-1} ; a C–O (stretch) band at 1180 cm^{-1} ; SO₂ bands at 1371 and 1191 cm^{-1} ; monosubstituted benzene bands at 776, 735, 711 and 693 cm^{-1} .

When the reaction was carried out on a 0.005-mole basis using concentrated sulfuric acid as a catalyst, the yield of tan product was very low.

Attempts to prepare the compound by acetylation of N-benzenesulfonyl-N-phenylhydroxylamine with acetic anhydride were unsuccessful.

***m*-Acetamidophenyl Acetate.**—To a solution of 61.9 g. of sodium hydroxide in 150 ml. of water was added slowly, with stirring, 50.2 g. of *m*-aminophenol hydrochloride. The basic solution was cooled in an ice-bath and to it was added 500 g. of crushed ice. To the cooled solution was added all at once with thorough stirring 87.8 g. of acetic anhydride. The resulting white precipitate was removed by filtration. The filtrate was made basic with 50% aqueous sodium hydroxide and cooled in an ice-bath. To the cool basic solution was added acetic anhydride until the pH was 6–7. A light tan precipitate formed which was removed by filtration. The resulting filtrate was made basic again and treated with acetic anhydride but yielded no precipitate and therefore was discarded. The combined fractions of crude product were dried and recrystallized from benzene–petroleum ether (b.p. 80–110°) (Darco) to yield 59.5 g. (89.5%) of white plates, m.p. 99.5–100.5° (lit.²⁰ 101°).

The reaction of *m*-aminophenol with refluxing acetic anhydride¹⁷ gave in lower yield a product which was more difficult to purify.

Condensation of *m*-Acetamidophenyl Acetate and Benzohydrol. **4-Acetamido-2-acetoxytriphenylmethane.**—To a solution of 9.21 g. of benzohydrol and 9.66 g. of *m*-acetamidophenyl acetate in 200 ml. of glacial acetic acid was added 17.4 g. of benzenesulfonic acid dissolved in 50 ml. of glacial acetic acid. The mixture was heated under reflux for 106 hours. The resulting yellow solution was poured into one liter of water containing one kg. of ice. The pH

was adjusted to 6 with 10% aqueous sodium hydroxide which caused formation of a light tan precipitate. The crude product was removed by filtration, washed with water and pressed dry with a rubber dam (suction). After drying *in vacuo* over potassium hydroxide–calcium chloride the crude light tan product weighed 14.0 g. (78%), m.p. 79.5–80.5° with sintering at 75.5°.

The product also could be prepared by the use of sulfuric acid in glacial acetic acid. Benzenesulfonic acid is a more satisfactory reagent.

4-Amino-2-hydroxytriphenylmethane Sulfate.—A suspension of 3.59 g. of crude 4-acetamido-2-acetoxytriphenylmethane in 500 ml. of 1.06% sulfuric acid was heated under reflux. After 8 hours the resulting solution was filtered to remove some dark resinous material and the filtrate was allowed to stand overnight. The white needles, which separated on standing, were removed by filtration, washed with ether and air-dried; weight 1.87 g. (57.5%), m.p. 182–185° dec. with preliminary sintering.

The product gave a positive phenol test (blue color) with phosphomolybdic acid and aqueous ammonia in ethereal solution. It was benzenesulfonated without further purification.

4-Benzenesulfonamido-2-hydroxytriphenylmethane.—To a solution of 1.87 g. of 4-amino-2-hydroxytriphenylmethane sulfate in 15 ml. of dry pyridine was added a solution of 1.10 g. of benzenesulfonyl chloride in 10 ml. of dry pyridine. The resulting red solution was heated under reflux for 5 minutes to give an amber solution which was allowed to stand overnight at room temperature. The reaction mixture was poured into 100 ml. of 1:1 hydrochloric acid (ice). The white precipitate of crude product was recrystallized from acetic acid–water (Darco) to yield 1.6 g. (66.9%) of white needles. Two more recrystallizations from acetic acid–water gave white needles, m.p. 194–195° with sintering at 193.5°.

Anal. Calcd. for C₂₆H₂₁NO₃S: C, 72.26; H, 5.10; N, 3.37. Found: C, 72.22; H, 5.37; N, 3.38.

Infrared analysis indicated an NH band at 3240 cm^{-1} ; OH band at 3415 cm^{-1} ; SO₂ bands at 1165 and 1319 cm^{-1} ; monosubstituted benzene bands at 702, 748 and 754 cm^{-1} .

Acetylation of 4-Benzenesulfonamido-2-hydroxytriphenylmethane. **2-Acetoxy-N-acetyl-4-benzenesulfonamidotriphenylmethane.**—To a solution of 1.0 g. of 4-benzenesulfonamido-2-hydroxytriphenylmethane in 20 ml. of dry pyridine was added 0.25 g. of acetic anhydride. The mixture was shaken manually and allowed to stand at room temperature for 19 hours. The pyridine solution was poured into 200 ml. of 1:1 hydrochloric acid (ice) to give a white precipitate; 0.55 g. (90%). One recrystallization from glacial acetic acid–water and three recrystallizations from ethanol–water gave white needles, m.p. 175–177°.

Anal. Calcd. for C₂₉H₂₅NO₅S: C, 69.72; H, 5.04; N, 2.80. Found: C, 69.54; H, 5.22; N, 2.67.

Infrared analysis indicated a vinyl ester C=O band at 1774 cm^{-1} , an amide C=O band at 1711 cm^{-1} , monosubstituted benzene bands at 703 and 723 cm^{-1} , SO₂ bands at 1175 and 1330 cm^{-1} , no NH band.

The product also could be formed by the action of acetic anhydride in the presence of a trace of sulfuric acid. When the acetylation was carried out in absolute ether using acetic anhydride and a sulfuric acid catalyst, only unreacted starting material was obtained.

4-Amino-3-hydroxytriphenylmethane Sulfate.—To a solution of 7.59 g. of *o*-acetamidophenyl acetate²¹ and 7.24 g. of benzohydrol in 150 ml. of glacial acetic acid was added 4.0 g. of concentrated sulfuric acid. After heating under reflux for 101 hours the resulting yellow solution was poured into one liter of water containing 1 kg. of ice to give a semi-solid light tan precipitate. After standing 1 hour the crude product was removed by filtration and washed with water. The crude gummy product was heated under reflux with 500 ml. of 1.06% sulfuric acid for 6 hours. The resulting solution was filtered to remove a brown-orange gum, concentrated to 100 ml. and allowed to stand overnight. The resulting light tan needles were removed by

(18) O. Kamm, "Organic Syntheses," Coll. Vol. I, Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 445.

(19) O. Piloty, *Ber.*, **29**, 1564 (1896).

(20) M. Ikuta, *Am. Chem. J.*, **15**, 42 (1893).

(21) R. Mendola, G. H. Woolcott and E. Wray, *J. Chem. Soc.*, **69**, 1323 (1896); E. Bamberger, *Ber.*, **36**, 2050 (1903). The product is also readily formed by adding acetic anhydride to an ice cold solution of *o*-aminophenol hydrochloride in a 10% aqueous sodium hydroxide solution.

filtration and washed with ether to give after drying 0.42 g. (3.5%) of white needles, m.p. 182–186° dec.

The crude product was benzenesulfonated without further purification.

4-Benzenesulfonamido-3-hydroxytriphenylmethane.—To 0.42 g. of 4-amino-3-hydroxytriphenylmethane sulfate in 10 ml. of dry pyridine was added 0.25 g. of benzenesulfonyl chloride. The mixture was heated under reflux for 3 minutes and allowed to cool to room temperature spontaneously. After 30 hours the reaction mixture was poured into 20 ml. of 1:1 hydrochloric acid (ice) to give a dark oil which solidified on standing several hours. The yield of tan product

was 0.45 g. (83.5%). Three recrystallizations from ethanol-water (Darco) gave white micro-needles, m.p. 147–148° with some previous sintering at 146°.

Anal. Calcd. for $C_{25}H_{21}NO_3S$: C, 72.26; H, 5.10; N, 3.37. Found: C, 72.27; H, 5.06; N, 3.16.

Infrared analysis indicated NH bands at 3260 (stretch) and 1524 cm^{-1} (bend); C–N (stretch) band at 1235 cm^{-1} ; an OH band at 3400 cm^{-1} ; C–O (stretch) bands at 1343 and 1235 cm^{-1} ; SO_2 bands at 1322 and 1162 cm^{-1} ; monosubstituted benzene bands at 752, 724, 700 and 679 cm^{-1} .

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Mercuration of Certain Aromatic Compounds^{1,2}

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A quantitative investigation of the classical mercuration of *p*-toluidine, benzoic acid, nitrobenzene, and benzenesulfonic acid is reported. The mercury compounds were converted to the corresponding bromine derivatives and determined cryoscopically for *p*-toluidine, by infrared spectroscopy for the latter three compounds. The mercuration of *p*-toluidine goes almost exclusively *ortho* to the amino group; benzoic acid averaged *o*:*m*:*p* 57:25:18. The *meta* and *para* isomers have not been reported previously. The results of the mercuration of nitrobenzene agree substantially with those in the literature, *o*:*m*:*p* 53:32:15. Both the *ortho* and *para* isomers were found from the mercuration of benzenesulfonic acid, as well as the previously reported *meta* derivative, the approximate ratio being *o*:*m*:*p* 24:61:15.

Aromatic mercuration has been reported by many investigators as giving anomalous orientation effects.⁵ Thus, mercuration of benzoic acid was reported to give the *ortho* product exclusively,⁶ nitrobenzene principally *ortho* and *para*,^{7,8} toluene substantial quantities of the *meta* isomer,⁹ while phenol was reported as mercurating only in the *ortho* and *para* positions.^{10–12} A report on the mercuration of benzenesulfonic acid indicates that the mercury enters the nucleus in the position *meta* to the sulfonic acid group.¹³

The development of a workable hypothesis for the mechanism of mercuration by the classical method (with mercuric acetate in non-polar solvents) has been handicapped by the lack of quantitative data on the relative amounts of the possible isomers obtained. The chief experimental problem in such work is the difficulty of quantitatively separating the isomers obtained. This has often meant that when but one isomer was reported, others may have been present, but not isolated.

The present work deals with an investigation of the classical mercuration of *p*-toluidine, benzoic acid, nitrobenzene and benzenesulfonic acid. In each case the mercury compounds were converted to the

corresponding bromine derivatives, and compared with known bromine derivatives.¹⁴

The possible bromo isomers in the case of *p*-toluidine were determined cryoscopically, and in the other three instances by infrared spectroscopy. The advantage of this method over previous procedures is that it is not necessary to isolate and purify each of the isomeric products, and greatly reduces the possibility of errors in the actual ratio of isomers.

The purpose of this paper is to provide quantitative data for the study of the mechanism of aromatic mercuration.

Experimental

Materials. Mercuric Acetate.—The mercuric acetate used throughout this investigation was Mallinckrodt analytical reagent grade. *p*-Toluidine: Eastman Kodak white label product was recrystallized from 20% ethanol-water solution, and then vacuum distilled. 3-Bromo-4-acetylaminotoluene: The 3-bromo-4-acetylaminotoluene as well as the corresponding amino compound were obtained from Eastman Kodak Co. The amide was recrystallized to constant melting point (see Table I).

2-Bromo-4-acetylaminotoluene.—The 2-bromo-4-nitrotoluene was prepared by the bromination of *p*-nitrotoluene according to the method of Lucas and Scudder,¹⁵ and melted at 76.5–78.0° (lit. 78°). The reduction of the nitro group was effected by use of a 50% alcohol solution of ammonium sulfide, and the resulting amine dissolved in ether and dried. The ether solution was treated with dry hydrogen chloride gas and a yellow amine salt precipitated out. This was converted to the amide by acetic anhydride, and recrystallized from methanol.

o-, *m*- and *p*-Bromobenzoic Acids.—Eastman Kodak Co. *o*-, *m*- and *p*-bromobenzoic acids were recrystallized twice from methanol.

o-, *m*- and *p*-Bromonitrobenzene.—Eastman Kodak Co. *o*- and *p*-bromonitrobenzene were recrystallized twice from ethanol, using Nuchar in the first recrystallization. *m*-

(14) That the replacement of the acetoxymercuri group by halogen occurs without rearrangement has been widely accepted; cf. ref. 13, Chapter III, pp. 67–73; M. Kharasch and L. Chalkley, Jr., *THIS JOURNAL*, **43**, 607 (1921); A. Bernardi, *Gazz. chim. ital.*, **56**, 337 (1926).

(15) H. J. Lucas and N. F. Scudder, *THIS JOURNAL*, **50**, 245 (1928).

(1) Presented at the 124th National Meeting of the American Chemical Society, Chicago, Ill., September 10, 1953.

(2) From the dissertation of Martin S. Frant, submitted in partial fulfillment of the requirements for the Ph.D. degree at Western Reserve University, February, 1953.

(3) Cliffdate Products Corp., Cleveland, Ohio.

(4) Gallowhur Chemical Corp., Ossining, N. Y.

(5) K. A. Kobe and T. F. Doumani, *Ind. Eng. Chem.*, **33**, 170 (1941).

(6) O. Dimroth, *Ann.*, **446**, 148 (1925).

(7) W. J. Klapproth and F. H. Westheimer, *THIS JOURNAL*, **72**, 4461 (1951).

(8) J. Jurgens, *Rec. trav. chim.*, **45**, 61 (1926).

(9) S. Coffey, *J. Chem. Soc.*, **127**, 1029 (1925).

(10) F. C. Whitmore, *THIS JOURNAL*, **43**, 619 (1921).

(11) O. Dimroth, *Ber.*, **35**, 2039 (1902).

(12) L. Vecchiotti, *Gazz. chim. ital.*, **44**, 34 (1914).

(13) F. C. Whitmore, "Organic Compounds of Mercury," Chemical Catalog Co. (Reinhold Publ. Corp.), New York, N. Y., 1921, p. 194.