in a Dry Ice–acetone-bath there was added 100 mg. of acepleiadylene and the resulting mixture was stirred in the cold for the three hours. The mixture was then allowed to warm to room temperature and stirring was continued for an additional three hours. The solution was then diluted to a volume of 200 ml. with water and extracted with methylene chloride. After the methylene chloride extracts had been washed with aqueous bicarbonate and water, they were dried and concentrated to give a dark solid residue. This was taken up in a 20% methylene chloride in hexane solution and chromatographed over alumina. From the eluate there was isolated 36.7 mg. of deep red crystals. These were recrystallized from a methylene chloride–hexane mixture and yielded dark red needles, m.p. 162–170°. Further recrystallization did not sharpen the melting point. The infrared spectrum of these crystals showed absorption bands at 6.58, 7.54 and 7.65 μ as expected for a nitro group.[12] The maxima and log ϵ values for the ultraviolet and visible spectrum of nitroacepleiadylene are 556 (3.20), 510 (3.42), 476 (3.42), 400 (3.53), 324 (4.35), 312 (4.40) and 250 mμ (4.30).

Anal. Calcd. for $C_{16}H_9NO_2$: C, 77.72; H, 3.67; N, 5.67. Found: C, 77.55; H, 4.01; N, 5.53.

After elution of the red needles of nitroacepleiadylene, a 50% methylene chloride–hexane solution was passed over the column and from the eluate there was isolated 16 mg. of black crystals, m.p. 210–212°. Satisfactory characterization of this material could not be made although its infrared spectrum showed absorption typical of the nitro group.

Nitration of Acepleiadiene.—A 100-mg. sample of acepleiadiene was nitrated following the same procedure described previously for pleiadiene and acepleiadylene. From the methylene chloride–hexane eluate from the chromatogram there was isolated 17 mg. of a yellow solid melting above 300°. Its infrared spectrum showed absorption at 6.57, 7.45 and 7.56, indicating the presence of a nitro group. Its ultraviolet absorption spectrum showed a broad maximum at 390 mμ (log ϵ 3.62) with no further absorption at longer wave lengths. This would suggest the presence of a substituted nitronaphthalene as the absorbing system. This is in agreement with the possibility that this product is a dimer of the Diels–Alder type.

Anal. Calcd. for $C_{32}H_{22}N_2O_4$: C, 77.09; H, 4.45; mol. wt., 498. Found: C, 77.61; H, 4.98; mol. wt. (Rast camphor), 456.

ROCHESTER, NEW YORK

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

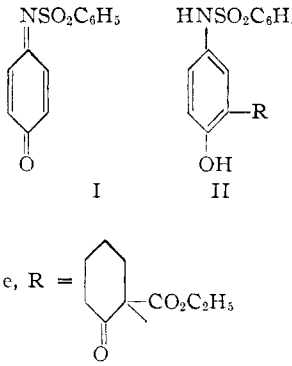
Quinone Imides. XXXIX. Adducts of Quinone Monoimides and Conversion of Active Methylene Adducts to Benzofurans

BY ROGER ADAMS AND LEROY WHITAKER[1]

RECEIVED JUNE 13, 1955

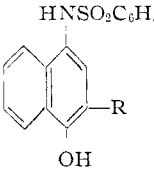
Hydrazoic acid, benzenesulfinic acid and several active methylene compounds have been added to *p*-quinonemonobenzenesulfonimide. The latter adducts are converted by means of acid to benzofuran derivatives. 1,4-Naphthoquinonemonobenzenesulfonimide adds the same reagents and, unlike the benzene analog, also reacts with piperidine, morpholine and aniline to give crystalline adducts.

The addition of active methylene compounds to quinone diimides[2] and the conversion of the adducts to indoles by treatment with acids[3] have been reported. Active methylene compounds have now been added to quinone monoimides and the adducts have been converted to benzofurans by treatment with acids. Acetylacetone, acetoacetanilide and the ethyl esters of acetoacetic acid, benzoylacetic acid, cyclohexanone-2-carboxylic acid and malonic acid were allowed to react with *p*-quinonemonobenzenesulfonimide (I) to form the substituted phenols IIa–IIf. All these products except IIf were obtained in good yield.



a, R = $CH(COCH_3)_2$
b, R = $CHCONHC_6H_5$ | $COCH_3$
c, R = $CHCO_2C_2H_5$ | $COCH_3$
d, R = $CHCO_2C_2H_5$ | COC_6H_5
f, R = $CH(CO_2C_2H_5)_2$
g, R = $SO_2C_6H_5$
h, R = N_3
i, R = NH_2
j, R = $NHCOCH_3$

No isolable products resulted from the following reactions: I with dimedone, nitromethane, dibenzoylmethane and the ethyl esters of acetylsuccinic acid, cyclopentanone-2-carboxylic acid, cyanoacetic acid, methylmalonic acid, propionylmalonic acid, α,α'-dimethyl-β-ketoglutaric acid and thiolacetic acid; *p*-quinonemonomethanesulfonimide with acetylacetone, acetoacetanilide and ethyl acetoacetate; 1,4-naphthoquinonemonobenzenesulfonimide with diethyl malonate. 3-(4-Benzenesulfonamido-1-hydroxynaphthalene-2)-2,4-pentanedione (IIIa) was obtained in an impure state from the reaction of acetylacetone with 1,4-naphthoquinonemonobenzenesulfonimide.



IIIa, R = $CH(COCH_3)_2$
b, R = $N(CH_2)_5$
c, R = $N(CH_2CH_2)_2O$
d, R = NHC_6H_5
e, R = $SO_2C_6H_5$

The additions were effected successfully in dioxane using sodium methoxide as the catalyst. The addition of the catalyst caused the reaction mixture to turn dark. The speed and degree of decolorization usually could be used as a measure of the success of the reaction. The desired adduct was obtained from only one addition that did not decolorize and then in a yield of only 18%. Tar formation

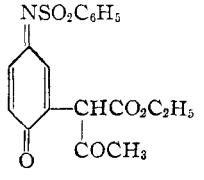
(1) An abstract of a thesis submitted by Leroy Whitaker to the Graduate College of the University of Illinois, 1955, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Eastman Kodak Company Fellow, 1952–1954; American Cyanamid Company Fellow, 1954–1955.

(2) R. Adams, *et al.*, THIS JOURNAL, **74**, 5557, 5872 (1952); **75**, 3403 (1953); **76**, 2763 (1954).

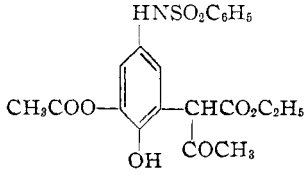
(3) R. Adams and W. P. Samuels, Jr., *ibid.*, **77**, 5375 (1955).

and reduction of the monoimides were the primary reactions that occurred in the unsuccessful additions.

Oxidation of IIc by lead tetraacetate in acetic acid led not to the expected quinone imide IV, but instead to the acetoxy derivative V. Compound IV was probably the primary reaction product to which acetic acid is added to give V. The position occupied by the acetoxy group was not ascertained, but the infrared spectrum indicated that the compound probably had the 1,2,3,5-configuration. A study conducted in this Laboratory of the infrared spectra of *p*-phenylenedibenzenesulfonamides and *p*-benzenesulfonamidophenols containing substituents in the 2,6- or 2,5-positions as established by chemical means revealed that the spectra of the 2,6-disubstituted compounds show the presence of a band between 900 and 850 cm.$^{-1}$, while in the spectra of the 2,5-disubstituted compounds this band is shifted to a position between 850 and 800 cm.$^{-1}$. The spectrum of V showed the presence of a band at 877 cm.$^{-1}$, probably indicative of the 1,2,3,5-configuration, but the complexity of the region between 900 and 800 cm.$^{-1}$ makes the assignment of such configuration uncertain.

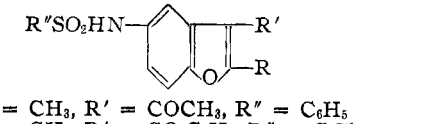


IV

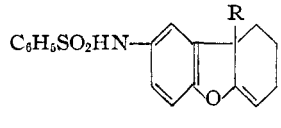


V

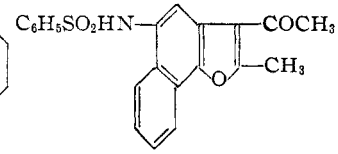
When a suspension of IIa, IIc, IIe or IIIa in constant boiling hydrochloric acid was heated under reflux the respective benzofurans VIa, VIb, VII or VIII were obtained. Treatment of IIc with 70% sulfuric acid also resulted in the formation of VIb, but when concentrated sulfuric acid was used an amorphous solid resulted. The conversion of IIa to VIa proceeds spontaneously; a sample of IIa that had been standing at room temperature for approximately one year was found to have lost water to form VIa almost quantitatively. Compound VIII could also be prepared without isolation of the intermediate by pouring an acetone solution of the oily residue obtained by the evaporation of the solvent from the addition of acetylacetone to 1,4-naphthoquinonemonobenzenesulfonimide over a mixture of ice and hydrochloric acid.



VIa, R = CH_3, R′ = $COCH_3$, R″ = C_6H_5
b, R = CH_3, R′ = $CO_2C_2H_5$, R″ = C_6H_5
c, R = CH_3, R′ = CO_2H, R″ = C_6H_5
d, R = R″ = C_6H_5, R′ = $CO_2C_2H_5$
e, R = CH_3, R′ = CH_2CO_2H, R″ = C_6H_5
f, R = R″ = CH_3, R′ = $COCH_3$

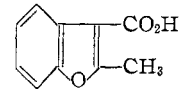


VII, R = $CO_2C_2H_5$
IX, R = H



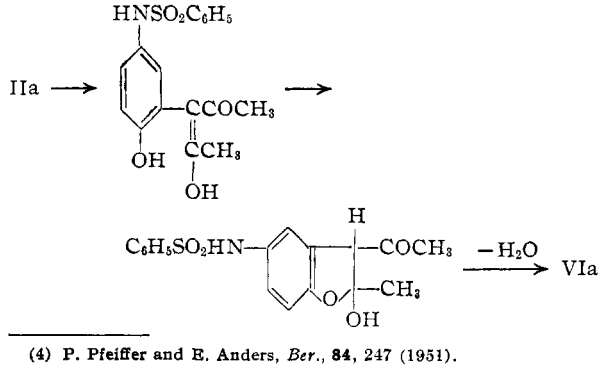
VIII

Certain of the adducts that could not be converted to benzofurans by treatment with acid in a two-phase system were readily converted when acetone or dioxane was added to effect solution. By this procedure IIb and IId were converted to 4-benzenesulfonamido-2-methylbenzofuran-3-carboxylic acid (VIc) and ethyl 5-benzenesulfonamido-2-phenylbenzofuran-3-carboxylate (VId), respectively. Alkaline hydrolysis of VIb also resulted in the formation of VIc. When IIe was treated in this way 2-benzenesulfonamido-7,8,9,9a-tetrahydrodibenzofuran (IX) was formed whereas treatment with constant boiling hydrochloric acid without solvent resulted in the formation of VII. The position of the double bond in the hydrogenated benzene nucleus of compound IX was not positively established. The infrared spectrum of IX permitted the deduction that the double bond was probably not conjugated with the benzene ring. Some of the oily products obtained from the addition reactions were converted to benzofurans when treated with acid in a homogeneous system. 5 - Benzenesulfonamido - 2 - methylbenzofuran-3-acetic acid (VIe) and 3-acetyl-5-methanesulfonamido-2-methylbenzofuran (VIf) were obtained by hydrolysis of the oils from the addition of diethyl acetylsuccinate to I and acetylacetone to *p*-quinonemonomethanesulfonimide, respectively.

X 

The infrared spectrum of 2-methylbenzofuran-3-carboxylic acid[4] (X) was compared with that of VIc. In the spectrum of X there were bands at 1630 and 1098 cm.$^{-1}$. The former band can be attributed to the double bond of the furan ring and the latter to the carbon–oxygen–carbon bonds of the furan ring. There were also bands at 1710, 1248 and 925 cm.$^{-1}$ due to the carboxyl group. The spectrum of VIc showed bands at 1629, 1100, 1687, 1263 and 920 cm.$^{-1}$. This similarity of the spectra reflects the identity of the nuclei in these two molecules.

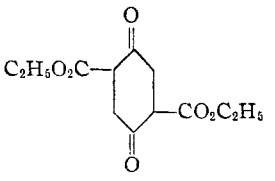
The infrared spectrum of IIa showed the presence of a band at 3540 cm.$^{-1}$, indicating the probable existence of the diacetylmethyl group in the enol form. This is further substantiated by the presence of a broad band in the region of 1600 cm.$^{-1}$, probably due to chelation of the enolized form of IIa. The cyclization therefore probably proceeds through the enol form by the sequence reactions represented below.



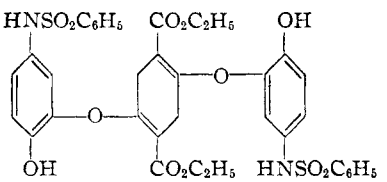
(4) P. Pfeiffer and E. Anders, *Ber.*, **84**, 247 (1951).

The cyclization step involves the addition of a hydroxyl group to an α,β-unsaturated ketone. The subsequent dehydration is merely loss of water from a β-hydroxy ketone. The spontaneous formation of VIa from IIa might well be expected. This reaction would be catalyzed by acid.

The reaction between diethyl succinosuccinate (XI) and I yielded the same product regardless of the proportion of starting materials employed. The analysis indicated that two moles of I react with one mole of XI. The infrared spectrum of the product showed bands at 1717, 1290 and 1195 cm.$^{-1}$ corresponding to those of a conjugated ester. The complexity of the spectrum made it impossible to identify an ether linkage. The assigned structure XII anticipates that the dienol form of XI added to I. Compound XII was not changed by heating with hydrochloric acid or a mixture of acetic and hydrobromic acids.

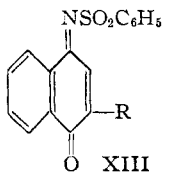


XI



XII

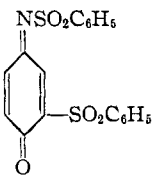
No crystalline products were obtained from the reaction of piperidine or morpholine with I or of morpholine with *p*-quinonemonomethanesulfonimide. Two products resulted from the reaction of piperidine with 1,4-naphthoquinonemonobenzenesulfonimide. One which was white turning pink in the air and for which no method of purification was found was probably 4-benzenesulfonamido-2-piperidino-1-naphthol (IIIb). The other red, crystalline product was identified as 2-piperidino-1,4-naphthoquinone-4-benzenesulfonimide (XIIIa). The reduction of XIIIa gave a white solid that quickly turned pink on exposure to air; it was probably IIIb. Morpholine reacted in a similar manner to piperidine to give a mixture of 4-benzenesulfonamido-2-morpholino-1-naphthol (IIIc) and 2-morpholino-1,4-naphthoquinone-4-benzenesulfonimide (XIIIb). The former was a white compound that slowly turned pink on exposure to air, while the latter was a red compound very similar in appearance to XIIIa. Aniline reacted to give a mixture of 4-benzenesulfonamido-1-naphthol and 2-anilino-1,4-naphthoquinone-4-benzenesulfonimide (XIIIc). Reduction of XIIIc gave the expected 2-anilino-4-benzenesulfonamido-1-naphthol (IIId). This compound was a white crystalline solid that slowly turned pink on exposure to air.



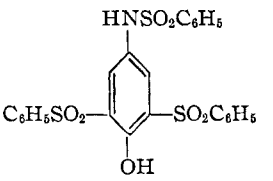
XIII

XIIIa, R = $N(CH_2)_5$
b, R = $N(CH_2CH_2)_2O$
c, R = NHC_6H_5

Benzenesulfinic acid added quite readily to I and the naphthalene analog to give 4-benzenesulfonamido-2-benzenesulfonylphenol (IIg) and 4-benzenesulfonamido - 2 - benzenesulfonyl - 1 - naphthol (IIIe) respectively. The additions were accomplished by adding sodium benzenesulfinate to a hot solution of the monoimide in acetic acid; the benzenesulfinic acid was thus generated *in situ*. Oxidation of IIg by lead tetraacetate in acetic acid led to the expected 2-benzenesulfonyl-1,4-quinone-4-benzenesulfonimide (XIV) to which a second mole of benzenesulfinic acid was added to give 4-benzenesulfonamido-2,6-dibenzenesulfonylphenol (XV). The infrared spectrum of XV showed the presence of a band at 878 cm.$^{-1}$, indicating that the compound probably has the 1,2,3,5-configuration.



XIV



XV

Hydrazoic acid, generated *in situ* by the addition of an aqueous solution of sodium azide to a warm solution of I in acetic acid, was added to I. The product, 2-azido-4-benzenesulfonamidophenol (IIh), decomposed at room temperature in the dark and more rapidly if exposed to light or heat. Reduction of IIh with sodium hydrosulfite gave the unstable 2-amino-4-benzenesulfonamidophenol (IIi) which was acetylated to the stable 2-acetamido-4-benzenesulfonamidophenol (IIj).

Acknowledgment.—The authors are indebted to Mrs. Esther Fett, Mrs. Lucy Chang, Mrs. R. Maria Benassi, Mr. Joseph Nemeth and Mr. R. J. Nesset for the microanalyses and to Mrs. Louise Griffing and Mr. James Brader for determination and interpretation of the infrared spectra.

Experimental

All melting points are corrected.

1,4-Naphthoquinonemonobenzenesulfonimide.—A suspension of 8.4 g. of 4-benzenesulfonamido-1-naphthol[5] and 12.6 g. of lead tetraacetate in 42 ml. of glacial acetic acid was stirred at room temperature. The solution developed a yellow color immediately. After one hour one ml. of ethylene glycol was added and the stirring was continued for 15 minutes. The mixture was cooled in an ice-bath and the imide was removed by filtration and washed with water. Recrystallization from chloroform–cyclohexane gave 5.31 g. (63.2%) of yellow needles, m.p. 152–154° (lit.[5] m.p. 148–149°).

General Procedure for the Addition of Active Methylene Compounds to Quinone Monoimides (See Table I).—To a solution of 0.01 mole of the quinone monoimide and 0.011 mole of the active methylene compound in 50 ml. of dry dioxane was added about 40 mg. of sodium methoxide and the mixture was allowed to stand at room temperature. The product was obtained from the reaction mixture by one of the following procedures.

Procedure A.—The reaction mixture was filtered and the filtrate was concentrated under vacuum on the steam-bath to a volume of about 25 ml. Addition of petroleum ether (b.p. 80–100°) to this solution caused the separation of a tan oil which solidified on cooling.

(5) R. Adams and R. A. Wankel, THIS JOURNAL, **73**, 131 (1951).

TABLE I

ADDUCTS OF ACTIVE METHYLENE COMPOUNDS AND QUINONE MONOIMIDES

Quinone monoimide	Active methylene compd.	Reaction time	Procedure	Crude yield, %	Pure m.p., °C.	Solv. for recryst.[b]	Analyses, % Calcd.	Found
p-Quinonemonobenzenesulfonimide[a]	Acetylacetone	15 min.	A	94	171–173.5 dec.	A-B	C, 58.78 H, 4.92 N, 4.03	C, 58.76 H, 4.66 N, 4.06
	Ethyl acetoacetate	30 sec.	A	94	171 dec.	C	C, 57.29 H, 5.09 N, 3.71	C, 57.25 H, 5.05 N, 3.70
	Ethyl benzoylacetate	5 min.	B	98	197–198 dec.	C	C, 62.85 H, 4.81 N, 3.18	C, 62.82 H, 4.70 N, 3.28
	Acetoacetanilide	2 hr.	B	87	181.5–182	A	C, 62.25 H, 4.75 N, 6.60	C, 62.29 H, 4.96 N, 6.51
	Diethyl malonate	3 d.	C	18	160–162	C	C, 56.01 H, 5.20 N, 3.44	C, 56.02 H, 5.44 N, 3.42
	Ethyl cyclohexanone-2-carboxylate	1 hr.	B	95	175–177	C	C, 60.42 H, 5.55 N, 3.36	C, 60.27 H, 5.70 N, 3.26
	Diethyl acetylsuccinate	20 hr.	A	oil				
p-Quinonemonomethanesulfonimide[a]	Acetylacetone	30 min.	A	oil				
1,4-Naphthoquinonemonobenzenesulfonimide	Acetylacetone	7 d.	D	70	184–186[c]	A		

[a] R. Adams and J. H. Looker, THIS JOURNAL, **73**, 1145 (1951). [b] A, ethyl acetate; B, petroleum ether (b.p. 80–100°); C, ethanol. [c] Impure.

TABLE II

FURANS FROM ACTIVE METHYLENE ADDUCTS

Furan	Adduct	Method	Reaction time, hr.	Crude yield, %	Pure m.p., °C.	Solv. for recryst.[a]	Analyses, % Calcd.	Found
3-Acetyl-5-benzenesulfonamido-2-methylbenzofuran	3-(5-Benzenesulfonamido-2-hydroxyphenyl)-2,4-pentanedione	A	5.5	77	191.5–193.5	A-B	C, 61.99 H, 4.59 N, 4.25	C, 62.09 H, 4.37 N, 4.23
Ethyl 5-benzenesulfonamido-2-methylbenzofuran-3-carboxylate	Ethyl α-(5-benzenesulfonamido-2-hydroxyphenyl)-acetoacetate	A B	3 48	96 96	143–144	C-B	C, 60.16 H, 4.77 N, 3.89	C, 60.39 H, 4.55 N, 3.70
Ethyl 5-benzenesulfonamido-2-phenylbenzofuran-3-carboxylate	Ethyl α-(5-benzenesulfonamido-2-hydroxyphenyl)-benzoylacetate	C	17	92	134.5–135.5	D	C, 65.54 H, 4.54 N, 3.32	C, 65.66 H, 4.50 N, 3.34
5-Benzenesulfonamido-2-methylbenzofuran-3-carboxylic acid	α-(5-Benzenesulfonamido-2-hydroxyphenyl)-acetoacetanilide	C	18	67	254.5 dec.	D	C, 57.99 H, 3.95 N, 4.23	C, 58.20 H, 3.92 N, 4.12
3-Acetyl-5-methanesulfonamido-2-methylbenzofuran	3-(5-Methanesulfonamido-2-hydroxyphenyl)-2,4-pentanedione[b]	C	12	35[c]	171–172	E	C, 53.92 H, 4.90 N, 5.24	C, 54.04 H, 5.33 N, 5.11
3-Acetyl-5-benzenesulfonamido-2-methylnaphtho[1,2-b]furan	3-(4-Benzenesulfonamido-1-hydroxynaphthalene-2-)-2,4-pentanedione	A D	24 14 days	75 65[c]	246–247	D	C, 66.47 H, 4.52 N, 3.69	C, 66.56 H, 4.56 N, 3.64
5-Benzenesulfonamido-2-methylbenzofuran-3-acetic acid	Diethyl 1-acetyl-1-(5-benzenesulfonamido-2-hydroxyphenyl)-succinate[b]	C	24	17[c]	200–201.5 dec.	D	C, 59.10 H 4.41 N, 4.05	C, 59.16 H, 4.32 N, 4.00
Ethyl 2-benzenesulfonamido-7,8,9,9a-tetrahydrodibenzofuran-9a-carboxylate	Ethyl 1-(5-benzenesulfonamido-2-hydroxyphenyl)-2-oxocyclohexane carboxylate	A	6	71	186–188	D	C, 63.14 H, 5.30 N, 3.51	C, 62.85 H, 5.51 N, 3.69
2-Benzenesulfonamido-7,8,9,9a-tetrahydrodibenzofuran	Ethyl 1-(5-benzenesulfonamido-2-hydroxyphenyl)-2-oxocyclohexane carboxylate	C	18	33	191–192.5	D	C, 66.04 H, 5.24 N, 4.28	C, 65.55 H, 5.28 N, 4.26

[a] A, benzene; B, petroleum ether (b.p. 80–100°); C, acetone; D, ethanol; E, dioxane. [b] Oil. [c] Based on the monoimide employed in the addition.

Procedure B.—The reaction mixture was poured into water which caused the product to separate.

Procedure C.—The dioxane was evaporated in a stream of air and petroleum ether was added to the residue. The dark oil which formed was dissolved in acetone and the acetone was allowed to evaporate slowly to give a solid residue.

Procedure D.—The dioxane was evaporated in a stream of air and water was added to the residue to cause the separation of an oil. By dissolving the oil in acetic acid and pouring the solution into water with vigorous stirring a solid product separated.

General Procedure for the Conversion of the Active Methylene Adducts to Benzofurans (See Table II). Method A.—

A suspension of 1.00 g. of the adduct in 50 ml. of constant boiling hydrochloric acid was heated under reflux. After the reaction was complete the mixture was cooled and the product was removed by filtration.

Method B.—A suspension of 1.00 g. of the adduct in 50 ml. of 70% sulfuric acid was allowed to stand at room temperature. After the reaction was complete the mixture was poured over crushed ice. The solid product was removed by filtration.

Method C.—To a solution of 1.00 g. of the adduct in 40 ml. of dioxane or acetone was added 25 ml. of concentrated hydrochloric acid and the mixture was heated under reflux. The solution was concentrated by evaporating the solvent in a stream of air. The product was removed by filtration.

Method D.—To a solution of 0.0067 mole of the quinone monoimide and 0.007 mole of the active methylene compound in 50 ml. of dry chloroform was added 3 drops of triethylamine and the mixture was allowed to stand at room temperature. The chloroform was evaporated in a stream of air and the oily residue was dissolved in acetone. The acetone solution was poured over a mixture of ice and hydrochloric acid. A dark oil separated; this oil solidified on standing.

Ethyl α-(3-Acetoxy-5-benzenesulfonamido-2-hydroxyphenyl)-acetoacetate (V).—A suspension of 1.89 g. of ethyl α-(5-benzenesulfonamido-2-hydroxyphenyl)-acetoacetate and 2.30 g. of lead tetraacetate in 50 ml. of glacial acetic acid was stirred at room temperature. The solution became yellow immediately. After 18 hours the yellow color had faded and a white precipitate had formed. To this mixture was added 0.50 ml. of ethylene glycol and the stirring was continued for 5 minutes. The mixture was cooled and filtered. The yield of white crystals was 1.00 g. (45.8%). Recrystallization from ethanol gave small, white crystals, m.p. 193–195° dec.

Anal. Calcd. for $C_{20}H_{21}NO_8S$: C, 55.16; H, 4.86; N, 3.22. Found: C, 55.48; H, 5.02; N, 3.01.

Diethyl 3,6-Dihydro-2,5-bis-(5-benzenesulfonamido-2-hydroxyphenoxy)-terephthalate (XII).—To a solution of 2.47 g. of *p*-quinonemonobenzenesulfonimide and 2.56 g. of diethyl succinosuccinate[6] in 25 ml. of dry chloroform was added 40 mg. of sodium methoxide. The color began to fade immediately and a precipitate formed. After one hour the mixture was filtered to remove the tan solid that had separated; yield 3.15 g. (84%) (fraction A). Fraction A was recrystallized from dioxane to give white crystals, m.p. 269–270° dec.

Anal. Calcd. for $C_{36}H_{34}N_2O_{12}S_2$: C, 57.59; H, 4.56; N, 3.73. Found: C, 57.52; H, 4.84; N, 3.53.

The original chloroform solution was evaporated to give 1.20 g. (46.8%) of a yellow solid which was recrystallized from ethyl acetate; m.p. 125.5–128.5°. It proved to be unchanged diethyl succinosuccinate.

2-Piperidino-1,4-naphthoquinone-4-benzenesulfonimide (XIIIa).—A solution of 1.99 g. of 1,4-naphthoquinonemonobenzenesulfonimide and 0.60 g. of piperidine in 30 ml. of chloroform was allowed to stand at room temperature. The solution developed a dark, red color. After 21 hours the mixture was filtered to remove 0.66 g. of pink solid, m.p. 161–166° (fraction A). The chloroform solution was evaporated in a stream of air and 30 ml. of ethanol was added to the oily residue. A dark-red, crystalline material separated and was removed by filtration; yield 1.32 g. (fraction B). The ethanol solution was evaporated, leaving 0.45 g. of a red solid which was the same material as fraction B. After one recrystallization from chloroform–cyclohexane, it was combined with fraction B and recrystallized from the same solvent pair; m.p. 174.5–176°; total yield 1.77 g. (69.7%).

Anal. Calcd. for $C_{21}H_{20}N_2O_3S$: C, 66.27; H, 5.30; N, 7.36. Found: C, 65.91; H, 5.31; N, 7.20.

No satisfactory method for purification of fraction A was found.

4-Benzenesulfonamido-2-piperidino-1-naphthol (IIIb).—A solution of 0.75 g. of sodium hydrosulfite in 5 ml. of water was added to a suspension of 0.50 g. of 2-piperidino-1,4-naphthoquinone-4-benzenesulfonimide in 10 ml. of ethanol. To the mixture, after boiling for about 10 minutes until all the red solid was gone, was added 10 ml. of ethanol. The inorganic salts were separated from the hot mixture by filtration and water was added to the filtrate. Upon cooling a white solid separated which formed a dark tar when heated to 161°. It quickly turned red when exposed to air. No good method of purification was found.

2-Morpholino-1,4-naphthoquinone-4-benzenesulfonimide (XIIIb) and 4-Benzenesulfonamido-2-morpholino-1-naphthol (IIIc).—A solution of 0.61 g. of morpholine and 1.99 g. of 1,4-naphthoquinonemonobenzenesulfonimide in 30 ml. of chloroform was allowed to stand at room temperature. After 48 hours the mixture was filtered to remove 0.32 g. of pink solid (fraction A). Fraction A could not be purified. The chloroform was evaporated and the oily residue was extracted twice with hot ethanol. A white, crystalline material remained; yield 0.75 g. (29.3%) (fraction B). The ethanol extracts were evaporated to dryness, leaving a red solid; yield 1.40 g. (54.9%) (fraction C).

Fraction B was recrystallized from chloroform to give white crystals which slowly turned pink on exposure to air; m.p. 201–202°. This material was identified as 4-benzenesulfonamido-2-morpholino-1-naphthol.

Anal. Calcd. for $C_{20}H_{20}N_2O_4S$: C, 62.48; H, 5.25; N, 7.29. Found: C, 62.90; H, 5.50; N, 7.18.

Recrystallization of fraction C from ethanol gave red crystals of 2-morpholino-1,4-naphthoquinone-4-benzenesulfonimide, m.p. 193–194.5°.

Anal. Calcd. for $C_{20}H_{18}N_2O_4S$: C, 62.81; H, 4.75; N, 7.36. Found: C, 63.05; H, 4.81; N, 7.33.

2-Anilino-1,4-naphthoquinone-4-benzenesulfonimide (XIIIc).—A solution of 1.99 g. of 1,4-naphthoquinonemonobenzenesulfonimide and 0.65 g. of aniline in 30 ml. of chloroform was allowed to stand at room temperature. After 60 hours the red mixture was filtered to remove the crystals that had separated, and these crystals were washed with chloroform. The yield of this material was 0.79 g. (39.7%) (fraction A).

Fraction A was recrystallized from acetic acid; white crystals, m.p. 202–204°. A melting point of a mixture with 4-benzenesulfonamido-1-naphthol showed no depression.

Anal. Calcd. for $C_{16}H_{13}NO_3S$: N, 4.68. Found: N, 4.56.

The chloroform washings were added to the original filtrate and the solution was concentrated. Addition of cyclohexane caused a dark-red precipitate to separate. The yield was 1.57 g. (60.3%) (fraction B). Recrystallization of fraction B from ethanol gave bright red needles, m.p. 175–176°. This material was identified as 2-anilino-1,4-naphthoquinone-4-benzenesulfonimide.

Anal. Calcd. for $C_{22}H_{16}N_2O_3S$: C, 68.02; H, 4.15; N, 7.21. Found: C, 68.02; H, 4.14; N, 7.06.

2-Anilino-4-benzenesulfonamido-1-naphthol (IIId).—To a suspension of 0.50 g. of 2-anilino-1,4-naphthoquinone-4-benzenesulfonimide in 50 ml. of ethanol and 10 ml. of water was added 1.00 g. of sodium hydrosulfite and the mixture was heated for 10 minutes. The mixture was filtered while hot and water was added to the filtrate. The white solid was removed by filtration; yield 0.48 g. (96%). The product slowly turned pink on exposure to air. Recrystallization from ethanol in an atmosphere of nitrogen gave white crystals, m.p. 184–185°.

Anal. Calcd. for $C_{22}H_{18}N_2O_3S$: C, 67.67; H. 4.65; N, 7.18. Found: C, 68.09; H, 5.11; N, 7.07.

4-Benzenesulfonamido-2-benzenesulfonylphenol (IIg).—To a solution of 1.00 g. of *p*-quinonemonobenzenesulfonimide in 30 ml. of boiling glacial acetic acid was added 1.31 g. of sodium benzenesulfinate. The yellow color of the solution was discharged immediately. The hot solution was diluted with 80 ml. of water and cooled which caused the product to separate. The yield was 1.49 g. (94.9%). Recrystallization from ethanol gave white flakes, m.p. 170–171°.

Anal. Calcd. for $C_{18}H_{15}NO_5S_2$: C, 55.51; H, 3.88; N, 3.60. Found: C, 55.86; H, 3.99; N, 3.47.

2-Benzenesulfonyl-1,4-quinone-4-benzenesulfonimide (XIV).—To a mechanically stirred suspension of 0.50 g. of 2-benzenesulfonamido-4-benzenesulfonylphenol in 20 ml. of glacial acetic acid was added 0.68 g. of lead tetraacetate. After 30 minutes 5 drops of ethylene glycol was added and the stirring was continued for 10 minutes. The solution was cooled and pale-orange needles separated. The yield was 0.41 g. (82%). Recrystallization from acetic acid gave orange needles, m.p. 162.5–163.5°.

(6) N. Green and F. B. LaForge, THIS JOURNAL, **70**, 2287 (1948).

Anal. Calcd. for $C_{18}H_{13}NO_5S_2$: C, 55.80; H, 3.38; N, 3.62. Found: C, 56.11; H, 3.46; N, 3.88.

4-Benzenesulfonamido-2,6-dibenzenesulfonylphenol (XV).—A solution of 0.15 g. of sodium benzenesulfinate in 2 ml. of water was added to a warm solution of 0.20 g. of 2-benzenesulfonyl-1,4-quinone-4-benzenesulfonimide in 10 ml. of glacial acetic acid. The solution was diluted with 10 ml. of water and cooled. The white product was removed by filtration. The yield was 0.26 g. (96.3%). After recrystallization from acetic acid the product melted at 200°.

Anal. Calcd. for $C_{24}H_{19}NO_7S_3$: C, 54.43; H, 3.62; N, 2.65. Found: C, 54.62; H, 3.68; N, 2.64.

The 4-Benzenesulfonamido-2-benzenesulfonyl-1-naphthol (IIIe).—To a solution of 1.00 g. of 1,4-naphthoquinonemonobenzenesulfonimide in 30 ml. of boiling glacial acetic acid was added 1.00 g. of sodium benzenesulfinate. The color of the solution was quickly discharged. On cooling 1.32 g. (90%) of white, crystalline product separated. Recrystallization from acetic acid gave white needles, m.p. 204.5°.

Anal. Calcd. for $C_{22}H_{17}NO_5S_2$: C, 60.12; H, 3.90; N, 3.19. Found: C, 59.80; H, 4.01; N, 3.04.

2-Azido-4-benzenesulfonamidophenol (IIh).—A solution of 1.00 g. of sodium azide in 4 ml. of water was added to a warm solution of 1.50 g. of *p*-quinonemonobenzenesulfonimide in 30 ml. of acetic acid. After 5 minutes the solution was colorless and it was poured into 80 ml. of water contained in a flask wrapped with aluminum foil to prevent light from striking the product. When the mixture was cooled white needles separated weighing 1.67 g. (94.9%). The product decomposed on standing at room temperature and the decomposition was accelerated by light or heat. The product was recrystallized by dissolving in ethanol at room temperature, adding water to the cloud point and cooling. White needles were obtained, m.p. 121–122.5° dec. Because of the instability of the product it was not analyzed.

2-Acetamido-4-benzenesulfonamidophenol (IIj).—A solution of 6.0 g. of sodium hydrosulfite in 30 ml. of water was added to a solution of 1.00 g. of 2-azido-4-benzenesulfonamidophenol in 30 ml. of 5% aqueous sodium hydroxide. The resulting yellow solution was heated to boiling for 10 minutes, diluted with water and made slightly acidic with dilute hydrochloric acid. A white solid separated and was removed by filtration. The yield was 0.76 g. (83.5%), m.p. 165–168°. Attempts to purify this amine resulted in colored solutions from which colored solids were obtained. The crude material was therefore acetylated directly.

To a solution of 1.00 g. of crude 2-amino-4-benzenesulfonamidophenol in 100 ml. of 5% aqueous hydrochloric acid was added slowly a 5% aqueous solution of sodium hydroxide until the mixture became slightly turbid. The turbidity was removed by the addition of a few milliliters of hydrochloric acid. A few chips of ice were added, followed by 10 ml. of acetic anhydride. The mixture was shaken vigorously and a solution of 10 g. of sodium acetate in 100 ml. of water was introduced. On cooling white crystals separated. The yield was 1.03 g. (78.1%). Recrystallization from acetone–chloroform gave small, white crystals, m.p. 242–242.5° dec.

Anal. Calcd. for $C_{14}H_{14}N_2O_4S$: C, 54.89; H, 4.61; N, 9.15. Found: C, 54.73; H, 4.22; N, 8.86.

URBANA, ILLINOIS

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

Restricted Rotation in Aryl Amines. XVIII. Effect of Remote Substituents on the Stability of Optically Active N-Benzenesulfonyl-N-carboxymethyl-3-benzylmesidine

BY ROGER ADAMS AND K. R. BROWER

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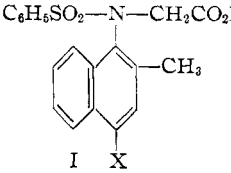
In a series of optically active compounds having *m*-substituted benzyl groups in the 3-position of N-benzenesulfonyl-N-carboxymethylmesidine it was found that variation of the substituent caused no significant variation in the rate of racemization.

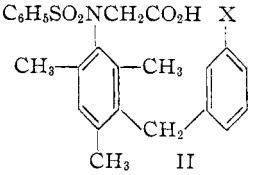
Previous papers in this series have reported that variation of the 4-substituent in optically active N-benzenesulfonyl-N-carboxymethyl-1-amino-2-methylnaphthalenes (I) produces variations in the rate of racemization, amounting in the most extreme case to a factor of twenty.[1,2] The half-lives of the nitro compound (X = NO_2), the amino compound (X = NH_2) and the unsubstituted compound were 0.42, 9.7 and 4.9 hr., respectively.



The effect has been explained on the basis of variations in the resonance stabilization of the coplanar transition state by the *para* substituent,[1,2] but there is no assurance that other factors such as inductive and field effects are not involved.

The purpose of the present investigation has been to determine the susceptibility of the racemization reaction to substituents too well isolated from the reaction center to contribute any but field effects. For this purpose compounds having *m*-substituted benzyl groups attached to the 3-position of N-benzenesulfonyl-N-carboxymethylmesidine (II) have been prepared and studied.

From the table below it is seen that variation of the substituent causes remarkably little variation in the half-lives of the compounds of the present series.



X	Half-life, hr.
H	11.5 ± 0.2
CH_3	11.3 ± .4
Br	12.8 ± .3
CN	12.1 ± .2
CH_3O	12.3 ± .2

The synthesis of the benzyl, *m*-methylbenzyl, *m*-bromobenzyl and *m*-nitrobenzyl derivatives was effected by benzylation of mesitylene with the appropriate benzyl chloride, followed by nitration, reduction and introduction of the benzenesulfonyl and carboxymethyl groups on the amino nitrogen in that order. The nitration of the *m*-nitrobenzylmesitylene provided the dinitro compound with one nitro group in the mesitylene ring and the other on the benzyl group. Selective catalytic reduction

(1) R. Adams and R. H. Mattson, THIS JOURNAL, **76**, 4925 (1954).
(2) R. Adams and K. V. Y. Sundstrom, *ibid.*, **76**, 5474 (1954).