derivative. A 92.8% yield of the pale yellow oily product (b.p. 175–178° (0.45 mm.)) was obtained. The solid tetrapicrate (m.p. 152–154°) was obtained after recrystallization from methanol and was used for analysis.

Anal. Calcd. for $C_{47}H_{48}N_{16}O_{28}$: C, 43.93; H, 3.77; N, 17.44. Found: C, 43.64; H, 3.81; N, 17.55.

LINCOLN 8, NEBRASKA

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

Quinone Imides. XXVIII. Addition of Active Methylene Compounds to *p*-Quinonedibenzenesulfonimide and its Derivatives

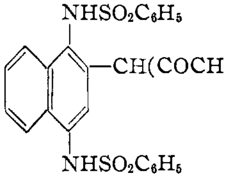
BY ROGER ADAMS AND DALE C. BLOMSTROM[1]

RECEIVED APRIL 11, 1953

p-Quinonedibenzenesulfonimide undergoes the Michael reaction with several active methylene compounds to give monosubstituted *p*-phenylenedibenzenesulfonamides. The corresponding 2-chloro and 2-methyl diimide derivatives also give substituted diamides, which probably have the 2,5-orientation.

Early workers on the reactions of *p*-benzoquinones and naphthoquinones with active methylene compounds obtained highly colored products which were not purified or characterized. More recently Wood, *et al.*,[2] demonstrated that in the presence of ethanolic ammonia, ethyl cyanoacetate, malonitrile and cyanoacetamide add to *p*-benzoquinone to give 2,5-disubstituted hydroquinones in low yields. Smith and co-workers[3] observed that *p*-benzoquinones bearing three substituents add active methylene compounds readily in the vacant position in good yields, and that tetrasubstituted benzoquinones containing methyl groups react by an attack on a methyl group with formation of coumarins.

The succession of reactions which so often occurs when benzoquinones add various reagents is not usually encountered with the quinone diimides. Thus 1,4-naphthoquinonedibenzenesulfonimide in presence of triethylamine as catalyst adds diethyl malonate, ethyl benzoylacetate, acetylacetone and nitroethane to form the monosubstituted diamides as exemplified by the acetylacetone adduct (I).[4] *p*-Quinonedibenzimide also forms similar monoadducts (II).[5]



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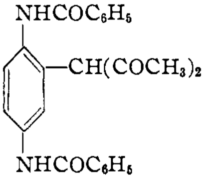
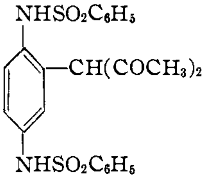


II

This Michael reaction has now been extended to the *p*-quinonedibenzenesulfonimides. *p*-Quinonedibenzenesulfonimide reacted with acetylacetone (III), methone (IV) and the ethyl esters of acetoacetic acid, benzoylacetic acid, malonic acid and cyclopentanone-2-carboxylic acid (V) to form the monosubstituted diamides in good yields.



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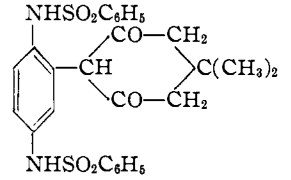

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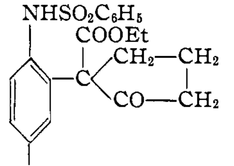

V

2-Chloro- and 2-methyl-*p*-quinonedibenzenesulfonimide likewise reacted with acetylacetone, ethyl acetoacetate and diethyl malonate to give monoadducts with the substitution probably in the 5-position by analogy to other additions to these diimides. Ethyl cyanoacetate, malononitrile, nitromethane, nitroethane and 2-nitropropane failed to give isolable products with any of the three diimides. Tar formation and reduction of the diimides were the primary reactions.

The additions were carried out in dioxane solution with a catalytic amount of sodium methoxide. The use of triethylamine as catalyst, so successful in the naphthalene series, led only to the formation of tars, amorphous solids, and *p*-phenylenedibenzenesulfonamide. The successful reactions were rapid; complete decolorization of the diimide solution usually occurred within one minute, in some cases within ten seconds. Products from solutions in which only partial decolorization occurred were contaminated with colored impurities. No purifiable adduct was obtained from reaction mixtures which did not fade but turned red-brown instead. No product could be isolated from the addition of diethyl malonate to *p*-quinonedibenzenesulfonimide at room temperature, but a moderate yield was obtained when the reaction was carried out in dilute solution at 70° with a large excess of diethyl malonate.

3-(2,5-Dibenzenesulfonamidophenyl)-2,4-pentanedione (III) was hydrolyzed to the corresponding acetone derivative (VI). When subjected to

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[1] An abstract of a thesis submitted by Dale C. Blomstrom to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the Degree of Doctor of Philosophy; Cincinnati Chemical Company Fellow, 1950–1951; Standard Oil Company of Indiana Fellow, 1951–1952.

[2] J. H. Wood, *et al.*, THIS JOURNAL, **66**, 1540 (1944).

[3] L. I. Smith and W. J. Dale, *J. Org. Chem.*, **15**, 832 (1950), and many previous papers.

[4] R. Adams and W. Moje, THIS JOURNAL, **74**, 5557 (1952).

[5] R. Adams and D. S. Acker, *ibid.*, **74**, 5872 (1952).

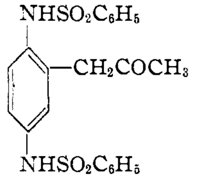
TABLE I

ADDUCTS OF ACTIVE METHYLENE COMPOUNDS AND QUINONE DIIMIDES

Quinone diimide	Active methylene compound	Time for decolorization	Crude yield, %	Pure m.p., °C.	Solv. for recryst.[f]	Empirical formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
p-Quinonedibenzenesulfonimide[a]	Acetylacetone	2–3 min.	95	226–227	A, B–D	$C_{23}H_{22}N_2O_6S_2$	56.77	57.05	4.56	4.76	5.76	5.73
	Methone	Incomplete	76[b]	206–208	B	$C_{26}H_{26}N_2O_6S_2$	59.30	59.49	4.98	4.97	5.32	5.38
	Ethyl acetoacetate	15 sec.	90	171–173	B–D	$C_{24}H_{24}N_2O_7S_2$	55.80	55.94	4.68	4.70	5.42	5.44
	Ethyl benzoylacetate	5 sec.	94	175–176.5	B–D	$C_{29}H_{26}N_2O_7S_2$	60.19	60.14	4.53	4.67	4.84	4.98
	Ethyl cyclopentanone-2-carboxylate[c]	10 sec.	97	190–191	B	$C_{26}H_{26}N_2O_7S_2$	57.55	57.67	4.83	5.09	5.16	5.03
	Diethyl malonate	15 sec.[d]	57[b]	132–133	C–D	$C_{25}H_{26}N_2O_8S_2$	54.93	54.97	4.80	4.54	5.13	5.07
2-Chloro-p-quinonedibenzenesulfonimide[e]	Acetylacetone	1 min.	94	211.5–213	C	$C_{23}H_{21}ClN_2O_6S_2$	53.02	53.27	4.06	4.11	5.38	5.30
	Ethyl acetoacetate	15 sec.	97	198.5–199.5	C, B–D	$C_{24}H_{23}ClN_2O_7S_2$	52.31	52.40	4.21	4.33	5.09	5.02
	Diethyl malonate	Incomplete	62[b]	168.5–170	C	$C_{25}H_{25}ClN_2O_8S_2$	51.67	51.74	4.34	4.41	4.82	4.84
2-Methyl-p-quinonedibenzenesulfonimide[e]	Acetylacetone	1–2 min.	79[b]	216.5–218	A	$C_{24}H_{24}N_2O_6S_2$	57.59	57.44	4.83	5.10	5.60	5.31
	Ethyl acetoacetate	5–10 sec.	95	190–191.5 229–232(dec.)[g]	C	$C_{25}H_{26}N_2O_7S_2$	56.59	56.72	4.94	4.97	5.28	5.33
	Diethyl malonate	Incomplete	82[b]	184–185	C	$C_{26}H_{28}N_2O_8S_2$	55.70	55.65	5.03	4.93	5.00	5.06

[a] R. Adams and K. R. Eilar, THIS JOURNAL, **73**, 1149 (1951). [b] Once recrystallized. [c] Kindly furnished by W. H. Middleton of this Laboratory. [d] At 70°. [e] R. Adams and A. S. Nagarakatti, THIS JOURNAL, **72**, 4610 (1950). [f] A, Aqueous dioxane; B, ethyl acetate; C, ethanol; D, cyclohexane. [g] This compound melted at 190–191.5° with evolution of gas; the melt resolidified at once and remelted with decomposition at 229–232°.

strong alkaline hydrolysis the ethyl benzoylacetate and acetoacetate adducts gave the same carboxylic acid (VII). Attempted ketone hydrolysis of the acetoacetate adduct failed to yield a solid product.



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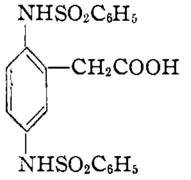
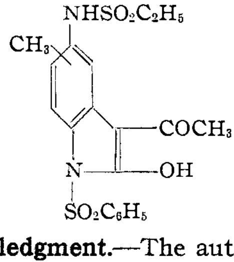


VII

Oxidation of several of these adducts with lead tetraacetate in acetic acid led to the formation of yellow solutions but only amorphous, extremely soluble yellow solids resulted which could not be crystallized.

Several of the adducts melted with the evolution of bubbles. The melt from the adduct of ethyl acetoacetate and 2-methyl-p-quinonedibenzenesulfonimide was the only one to solidify after the reaction. Analysis of this solid product revealed the loss of one mole of ethanol. The analysis and infrared spectrum supported the formulation of the compound as the enol form of an oxindole derivative (VIII). The reaction is analogous to the cyclizations occurring in certain active methylene adducts with substituted p-benzoquinones.[6]



VIII

Acknowledgment.—The authors are indebted to Mr. J. Nemeth, Mrs. Esther Fett and Mrs. Katherine Pih for the microanalyses and to Miss Helen Miklas for the infrared determinations and interpretations.

Experimental

All melting points are corrected.

Addition of Active Methylene Compounds. A. General Procedure (except Diethyl Malonate with p-Quinonedibenzenesulfonimide).—To a solution of 1 g. of the p-quinonedibenzenesulfonimide and 1.1 mole equivalents of the active methylene compound in 50 ml. of dioxane (dried over sodium) was added about 40 mg. of sodium methoxide. After the fading of the yellow color was complete 3 drops of acetic acid was added and the solution was poured slowly into 200 ml. of water with stirring. The white solid product was filtered, washed with water and dried.

B. **Diethyl Malonate with p-Quinonedibenzenesulfonimide.**—To a solution of 1 g. of p-quinonedibenzenesulfonimide in 180 ml. of dry dioxane at 70° were added in quick succession 5 g. (12 mole equivalents) of diethyl malonate and 40 mg. of sodium methoxide. The color faded rapidly. After one minute 3 drops of acetic acid was added and the solution was cooled and poured into 500 ml. of water. The oil was extracted with ether and the ether was extracted with 5% aqueous sodium carbonate. The aqueous extract was acidified and extracted with ether. The oil obtained by evaporation of the ether solution crystallized on standing. One recrystallization from aqueous ethanol yielded 0.81 g. (57%) of a light tan solid.

The attempted addition of ethyl cyanoacetate, malononitrile, nitromethane, nitroethane and 2-nitropropane to the quinone diimides resulted only in the isolation of p-phenylenedibenzenesulfonamides, tars and low-melting amorphous solids. The use of triethylamine as catalyst for the addition of acetylacetone, ethyl acetoacetate and ethyl benzoylacetate to p-quinonedibenzenesulfonimide led to the formation of p-phenylenedibenzenesulfonamide and dark amorphous solids which could not be purified.

2,5-Dibenzenesulfonamidophenyl-2-propanone (VI).—To 100 ml. of 2.5% aqueous sodium hydroxide heated to 100° was added 0.3 g. of 3-(2,5-dibenzenesulfonamidophenyl)-2,4-pentanedione. Heating was continued for 10 minutes. After treatment with Darco the solution was acidified with dilute hydrochloric acid. The yield of white solid was 0.24 g. (88%). The product was recrystallized from chloroform-cyclohexane, m.p. 165–166°.

Anal. Calcd. for $C_{21}H_{20}N_2O_5S_2$: C, 56.74; H, 4.54; N, 6.30. Found: C, 56.44; H, 4.49; N, 6.32.

2,5-Dibenzenesulfonamido-α-toluic Acid (VII). A.—To 50 ml. of 25% aqueous potassium hydroxide at 100° was added 0.71 g. of ethyl α-(2,5-dibenzenesulfonamidophenyl)-acetoacetate. Heating was continued for 5 minutes. The solution was treated with Darco, filtered and acidified. The gummy product was dissolved in 5% aqueous sodium bicar-

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[6] L. I. Smith and E. W. Kaiser, THIS JOURNAL, **62**, 133 (1940); L. I. Smith and P. F. Wiley, *ibid.*, **68**, 894 (1946).

bonate, and the solution was filtered and acidified. The yield of product after one recrystallization from ethyl acetate–cyclohexane was 0.26 g. (43%). Further recrystallization gave the pure product, m.p. 217–217.5°, with evolution of bubbles.

Anal. Calcd. for $C_{20}H_{18}N_2O_6S_2$: C, 53.80; H, 4.06; N, 6.28. Found: C, 54.01; H, 3.92; N, 6.28.

B.—Hydrolysis of ethyl α-(2,5-dibenzenesulfonamidophenyl)-benzoylacetate in the same manner gave a crude yield of 84% of 2,5-dibenzenesulfonamido-α-toluic acid. The product was recrystallized from acetic acid and from ethyl acetate–cyclohexane, m.p. 215.5–217.5°, with evolution of bubbles. It was identical with the product prepared in A.

Attempted Oxidations of Active Methylene Adducts.—The adducts from *p*-quinonedibenzenesulfonimide and acetylacetone, ethyl benzoylacetate and ethyl cyclopentanone-2-carboxylate were treated with lead tetraacetate in glacial acetic acid. Yellow colors developed readily, but the products obtained by pouring the solutions into water were low-melting amorphous yellow solids which were too soluble in organic solvents to recrystallize. Addition of hydrochloric acid to solutions of the materials produced other uncrystallizable amorphous substances which did not resemble monomeric substituted *p*-phenylenedibenzenesulfonamides.

3-Acetyl-5-benzenesulfonamido-1-benzenesulfonyl-x-methyloxindole.—A test-tube containing 0.39 g. of ethyl α-(2,5-dibenzenesulfonamido-x-methylphenyl)-acetoacetate was heated in an oil-bath at 195° for 10 minutes. The compound melted with evolution of bubbles, then resolidified. Recrystallization of the product from ethyl acetate and from ethanol gave 0.27 g. (76%) of a white solid. The pure compound melted at 238–239°. It gave a blue color with ferric chloride.

Anal. Calcd. for $C_{23}H_{20}N_2O_6S_2$: C, 57.01; H, 4.16; N, 5.78. Found: C, 57.03; H, 4.18; N, 5.70.

The infrared spectrum indicated that the compound existed in the 2-hydroxyindole form. The bands at 1688 and 1625 cm.$^{-1}$ were assigned to a conjugated ketone carbonyl and a conjugated carbon–carbon double bond.

URBANA, ILLINOIS

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

Quinone Imides. XXIX. Addition of Hydrazoic Acid and Phenols to *p*-Quinonedibenzenesulfonimide and its Derivatives

By Roger Adams and Dale C. Blomstrom[1]

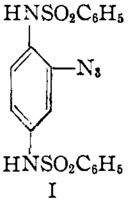
Received April 13, 1953

By alternate addition of hydrazoic acid and oxidation with lead tetraacetate, the following sequence of reactions results: *p*-quinonedibenzenesulfonimide → 2-azido diamide → 2-azido diimide → 2,x-diazido diamide → 2,x-diazido diimide. 2-Chloro-*p*-quinonedibenzenesulfonimide gives two products: 2,x-diazido diamide and an azidochloro diamide, isomeric with the azidochloro diamide obtained by the addition of hydrogen chloride to the 2-azido diimide. 2-Methyl-*p*-quinonedibenzenesulfonimide yields merely the x-azido-2-methyl diamide. Triethylamine catalyzes the addition of phenol, *o*-cresol and *m*-cresol to give substituted biphenyls. The use of *p*-cresol results in reduction of diimide to diamide.

The addition of hydrazoic acid to *p*-benzoquinone was first reported by Oliveri-Mandala and Calderaro,[2] who isolated 2-azidohydroquinone as the product. Fully halogenated quinones were found to react with hydrazoic acid by displacement of halogen by azide groups rather than by addition. Thus, treatment of chloranil with an appropriate amount of sodium azide in ethanol or acetic acid yielded the azidotrichloro-, 2,5-diazido-3,6-dichloro- and tetraazido-*p*-quinones.[3,4] Reaction of hydrazoic acid with 2,3-dichloro-1,4-naphthoquinone gave 2,3-diazido-1,4-naphthoquinone.[4]

When hydrazoic acid was added to 1,4-naphthoquinonedibenzenesulfonimide, 2-azido-1,4-naphthalenedibenzenesulfonamide resulted.[5] Oxidation of this compound with lead tetraacetate yielded the 2-azido diimide, to which another molecule of hydrazoic acid added to form the 2,3-diazido diamide.

The reactions of *p*-quinonedibenzenesulfonimides with hydrazoic acid have now been studied. The addition of sodium azide to a suspension of *p*-quinonedibenzenesulfonimide in glacial acetic acid afforded 2-azido-*p*-phenylenedibenzenesulfonamide (I) in good yield. Reduction of I with sodium hydrosulfite or with hydrogen over platinum oxide catalyst yielded 2-amino-*p*-phenylenedibenzenesulfonamide (II), which was identical with the amine obtained by hydrosulfite reduction of the known 2-nitro-*p*-phenylenedibenzenesulfonamide. Oxidation of I with lead tetraacetate gave the 2-azido diimide (III) to which a second molecule of hydrazoic acid added readily to form 2,x-diazido-*p*-phenylenedibenzenesulfonamide (IV). Upon reduction of IV with sodium hydrosulfite the corresponding diamine (V) was formed. The diazide (IV) was oxidized with lead tetraacetate to the blood-red crystalline 2,x-diazido diimide (VI).



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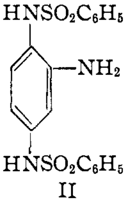

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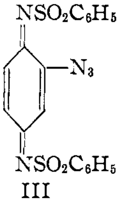

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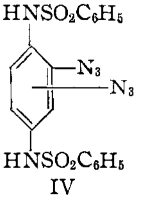

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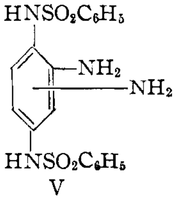

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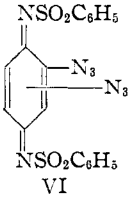

VI

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[1] An abstract of a thesis submitted by Dale C. Blomstrom to the Graduate College of the University of Illinois, 1953, in partial fulfillment of the requirements for the degree of Doctor of Philosophy; Cincinnati Chemical Company Fellow, 1950–1951; Standard Oil Company of Indiana Fellow, 1951–1952.

[2] E. Oliveri-Mandala and E. Calderaro, *Gazz. chim. ital.*, **45I**, 307 (1915); **45II**, 120 (1915).

[3] A. Korczynski, *Bull. soc. chim.*, [4] **35**, 1186 (1924).

[4] K. Fries and P. Ochwat, *Ber.*, **56**, 1291 (1923).

[5] R. Adams and W. Moje, This Journal, **74**, 5560 (1952).