water was carefully added. The mixture was poured onto about 150 g. of ice and then 250 ml. of an hydrochloric acid solution was added. The solution was concentrated by evaporation on a steam-bath.

A 1-l. round-bottom, two-necked flask was fitted with an addition funnel and a condenser set for distillation. A trap containing hydrochloric acid was connected to the receiver. The solution of hydrochlorides was added to a hot solution of 140 g. of sodium hydroxide in 60 ml. of water in this flask. Liquid was distilled until the temperature reached 100°. The distillate was saturated with sodium hydroxide and the evolving gases passed through the hydrochloric acid trap. No hydrazine layer separated. The solution was further degassed by 0.25 hr. boiling after completion of the saturation. The dried hydrochlorides from the trap weighed 41 g.

Ammonia was identified as ammonium chloride, dimethylamine as the benzenesulfonamide and trimethylamine as the picrate. Solubility separations with *n*-butyl alcohol–chloroform indicated that the presence of methylamine could be in no more than trace quantities.

The quantitative distribution of the amines reported above was calculated from the titration of the chloroform soluble and insoluble hydrochlorides with standard silver nitrate.

The values of the basic dissociation constants reported in Table I were obtained from the hydrogen ion concentrations measured during the potentiometric titrations to determine the equivalent weights. The dielectric constants were obtained by a beat frequency method in an apparatus loaned by Prof. W. C. Fernelius.

STATE COLLEGE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, FACULTY OF SCIENCE, FOUAD I UNIVERSITY]

Experiments with Derivatives of Quinone Imides

BY AHMED MUSTAFA AND MOHAMED KAMEL

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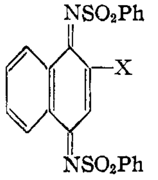
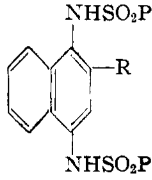
1,4-Naphthoquinone dibenzenesulfonimide (Ia) reacts with Grignard reagents to give the corresponding 2-substituted naphthalene-1,4-dibenzenesulfonamides IIa–IIe together with naphthalene-1,4-dibenzenesulfonamide (II, R = H). Ib, IIIa, IIIb and IV are readily reduced by Grignard reagents to the corresponding di-amides. The mixture (Mg + MgI_2) and lithium aluminum hydride effect the reduction of quinone imides (Ia, Ib, IIIa, IIIb and IV) to the corresponding di-amides. The action of diphenyldiazomethane on Ia and IIIa and the action of 9-diazofluorene on Ia led to the formation of the corresponding cyclopropane derivatives VIII, IX and X, respectively, probably *via* the formation of XI in the case of VIII.

Grignard reagents react with substituted and unsubstituted quinones to give mixtures resulting from 1,4-addition, from addition to carbonyl group, and from reduction.[1]

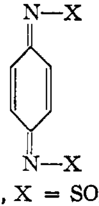
Quinone imides resemble quinones in many of their reactions.[2] We have investigated the action of Grignard reagents on quinone imides.[3] When the yellow 1,4-naphthoquinonedibenzenesulfonimide (Ia) is treated with methyl-, ethyl-, *n*-propyl-, *n*-butyl- and phenylmagnesium halides, the corresponding 2-substituted naphthalene-1,4-dibenzenesulfonamides (IIa–IIe, respectively) are obtained together with the reduction product of Ia, namely, naphthalene-1,4-dibenzenesulfonamide (II, R = H). The addition of the Grignard reagents is presumably 1,4 followed by rearrangement, since the 2-substituted naphthalene-1,4-dibenzenesulfonamides (IIa–IIe) are obtained.



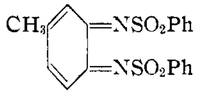
Ia, X = H
Ib, X = Cl



IIa, R = CH_3 IId, R = $n\text{-}C_4H_9$
IIb, R = C_2H_5 IIe, R = C_6H_5
IIc, R = $n\text{-}C_3H_7$



IIIa, X = SO_2Ph
IIIb, X = COPh



IV

Compounds (IIa–IIe) are obviously analogous. The constitution of the 2-ethylnaphthalene-1,4-dibenzenesulfonamide was established by an unequivocal synthesis: 2-ethyl-1-naphthylamine is treated with a diazotized solution of sulfanilic acid and the resulting azo-dye V is reduced, using stannous chloride and hydrochloric acid, to 2-ethylnaphthalene-1,4-diamine dihydrochloride (VI) which is converted to IIb by the action of benzenesulfonyl chloride in pyridine (*cf.* Scheme A).

The structure of 2-methylnaphthalene-1,4-dibenzenesulfonamide (IIa) was determined by synthesis through benzenesulfonation of 2-methylnaphthalene-1,4-diamine dihydrochloride,[4] and by comparison with a sample of this same product kindly furnished by Professor R. Adams, University of Illinois.

Excess methyl- or ethylmagnesium iodides cause decolorization of the benzene solutions of 2-chloro-1,4-naphthoquinonedibenzenesulfonimide, *p*-quinonedibenzenesulfonimide, *p*-quinonedibenzimide and 4-methyl-*o*-quinonedibenzenesulfonimide. Ap-

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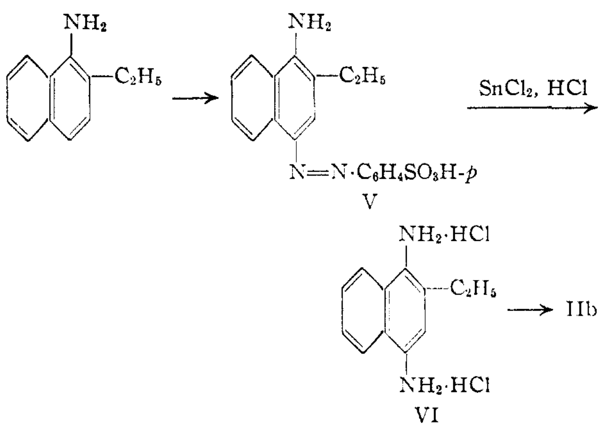
[1] (a) E. Bamberger and L. Blangey (*Ann.*, **384**, 272 (1911)) studied the reaction of methylmagnesium iodide on *p*-xyloquinone, and identified hydroquinone as well as the addition products; (b) A. Fränssen (*Bull. soc. chim.*, **37**, 902 (1925); *ibid.*, **45**, 1030 (1929)) using α-naphthoquinone, isolated a di-addition product and reduction products; (c) the action of phenylmagnesium bromide on a fully substituted *p*-quinone, *e.g.*, duroquinone and 2,3-dimethyl-α-naphthoquinone, gave 1,2- and 1,4-addition products as well as reduction products (L. I. Smith and H. M. Crawford, THIS JOURNAL, **50**, 869 (1928); H. M. Crawford, *ibid.*, **57**, 2000 (1935)); (d) *cf.*, the reduction of tetrachloro- and 4-triphenylmethyl-1,2-benzoquinone by the Grignard reagents to the corresponding catechols (A. Schönberg and N. Latif, *J. Chem. Soc.*, 446 (1952)).

[2] R. Adams and A. S. Nagarkatti, THIS JOURNAL, **72**, 4601 (1950), and later papers from this Laboratory.

[3] A. Mustafa and M. Kamel, *Science*, **117**, 234 (1953).

[4] This experiment was carried out with A. Harhash.

SCHEME A

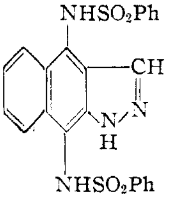


parently no normal addition reactions occur and only the corresponding di-amides could be isolated from the reaction mixtures.

A mixture of magnesium and magnesium iodide, which has been so effective in reduction of azobenzene,[5] benzil[6] and benzophenone-anil[7] to hydrazobenzene, benzoin and benzhydrylaniline, respectively, reduces Ia, Ib, IIIa, IIIb and IV quantitatively to the di-amides. The reaction probably occurs by 1,6-addition of two –MgI groups to the nitrogen atoms.

Lithium aluminum hydride, which reduces *p*-benzoquinone and phenanthraquinone to the corresponding hydroquinones,[8] also reduces Ia, Ib, IIIa, IIIb and IV to the di-amides. There is probably a resemblance between the action of the Grignard reagents and lithium aluminum hydride.[9]

Action of Diazomethane Derivatives on *p*-Quinone Imides.—Diazomethane and its derivatives have been added to various *p*-quinones to give substituted pyrazoles.[10a] Recently, Adams and Moje[10b] found that the addition of ethereal diazomethane solution to a chloroform solution of Ia gave the corresponding pyrazole (VII).

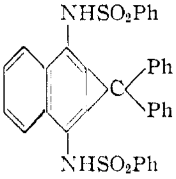


VII

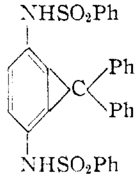
We have found that Ia and IIIa react with a benzene solution of diphenyldiazomethane and Ia reacts, similarly, with a benzene solution of 9-diazofluorene, with evolution of gas, to give the cyclopropane derivatives VIII, IX and X, respectively, probably *via* the formation of XI in the case of VIII.

For similar formation of a cyclopropane ring, the action of diphenyldiazomethane on 9-methylenefluorene,[11] methyleneanthrone[12] and the action of 9-diazofluorene on acenaphthylene[13] may be cited.

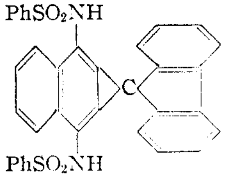
Compound VIII, illustrative of this group, is colorless, dissolves in ethanolic potassium hydroxide and has the correct molecular weight. It does not have the isomeric structure 2-diphenylmethylnaphthalene - 1,4 - dibenzenesulfonamide (XII), for the latter was synthesized by the action of benzhydrol on Ia and is not identical.[14]



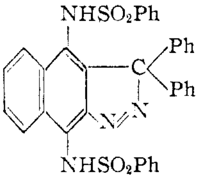
VIII



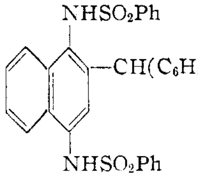
IX



X



XI



XII

Experimental

Action of Grignard Reagents on 1,4-Naphthoquinonedibenzenesulfonimide (Ia).—The following exemplifies the procedure. To a Grignard solution (prepared from 0.9 g. of magnesium, 7.5 g. of ethyl iodide in 50 ml. of ether) was added a solution of 1 g. (Ia)[2] in dry benzene (50 ml.); a colorless precipitate formed at once. The water was removed from the reflux condenser and the ether was evaporated from the reaction mixture, which then was heated for three hours on a steam-bath. After the mixture had stood overnight at 25°, it was poured slowly into 100 ml. of saturated aqueous ammonium chloride solution, and the reaction mixture was extracted with ether. The insoluble solid A in the ether–benzene mixture was collected by filtration and the ether–benzene mixture was dried over sodium sulfate, filtered and evaporated. The solid that remained was crystallized and identified as IIb. A was recrystallized from glacial acetic acid and identified as naphthalene-1,4-dibenzenesulfonamide (II, R = H) (m.p. and mixed m.p.) (yield *ca.* 0.18 g.).

The 2-substituted naphthalene-1,4-dibenzenesulfonamides (IIa–IIe) listed in Table I were similarly prepared (IIe crystallized with one molecule of benzene of crystallization). They give an orange color with concentrated sulfuric acid; IIe gives a green color. They dissolve in warm aqueous sodium hydroxide solution to give colorless solutions. In general, they are soluble in hot benzene, or chloroform, but are sparingly soluble in light petroleum (b.p. 40–60°).

Synthesis of 2-Ethylnaphthalene-1,4-dibenzenesulfonamide (IIb).—1-Amino-2-ethyl-4-*p*-sulfophenylazo-naphthalene (V) and 2-ethylnaphthalene-1,4-diamine dihydrochloride (VI) were prepared by the same procedure followed by Veldstra and Wiardi[15] in the synthesis of 1-amino-2-methyl-4-*p*-sulfophenylazo-naphthalene and 2-methylnaphthalene-1,4-diamine dihydrochloride, respectively.

From 3.5 g. of 1-amino-2-ethylnaphthalene sulfate[16] and a suspension of diazobenzenesulfonic acid (obtained by diazotization of 5 g. of sulfanilic acid) is obtained 7 g. of V, m.p. above 350°, yield *ca.* 85%.

VI was obtained as colorless crystals, m.p. 288–290° (with decomposition). It is soluble in water, alcohol and is crystallized from dilute hydrochloric acid, yield *ca.* 82%.

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[5] W. E. Bachmann, THIS JOURNAL, **53**, 1524 (1931).

[6] M. Gomberg and W. E. Bachmann, *ibid.*, **49**, 2584 (1927).

[7] W. E. Bachmann, *ibid.*, **53**, 2672 (1931).

[8] R. F. Nystrom and W. G. Brown, *ibid.*, **70**, 3738 (1948).

[9] *Cf.* A. Mustafa, *J. Chem. Soc.*, 2435 (1952).

[10] (a) H. von Pechmann, *Ber.*, **28**, 855 (1895); *ibid.*, **32**, 2292 (1899); L. F. Fieser and M. A. Peters, THIS JOURNAL, **53**, 4080 (1931); E. Bergmann and F. Bergmann, *J. Org. Chem.*, **3**, 125 (1938); (b) R. Adams and W. Moje, THIS JOURNAL, **74**, 5560 (1952).

[11] H. Wieland and O. Probst, *Ann.*, **530**, 277 (1937).

[12] A. Mustafa and M. K. Hilmy, *J. Chem. Soc.*, 1434 (1952).

[13] A. Schönberg, A. Mustafa and N. Latif, THIS JOURNAL, **75**, 2267 (1953).

[14] See R. Möhlau and V. Klopfer, *Ber.*, **32**, 2146 (1899).

[15] H. Veldstra and P. W. Wiardi, *Rec. trav. chim.*, **62**, 84 (1943).

[16] G. Levy, *Ann. chim.*, **9**, 5 (1938).

TABLE I

2-SUBSTITUTED NAPHTHALENE-1,4-DIBENZENESULFONAMIDES (II)

Solvents: A, chloroform–light petroleum (b.p. 40–60°); B, benzene–light petroleum; C, glacial acetic acid.

						Analyses, %											
						Carbon		Hydrogen		Nitrogen		Sulfur		Active H		Mol. wt.	
	R	M.p., °C.	Solvent for crystn.	Yield, %	Formula	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
IIa	Methyl	234	A	30	$C_{23}H_{20}O_4N_2S_2$	61.1	61.0	4.4	4.2	6.2	6.0	14.2	14.1	0.44	0.43	452	445
IIb	Ethyl	195	A or C	75	$C_{24}H_{22}O_4N_2S_2$	61.8	61.6	4.7	4.6	6.0	5.8	13.7	13.6	.43	.43	466	459
IIc	*n*-Propyl	185	A	65	$C_{25}H_{24}O_4N_2S_2$	62.5	62.4	5.0	4.9	5.8	5.7	13.3	13.0	.42	.41	480	469
IId	*n*-Butyl	194	B or C	60	$C_{26}H_{26}O_4N_2S_2$	63.2	63.0	5.3	5.3	5.6	5.5	12.9	12.5	.41	.41	494	487
IIe	Phenyl	220	B or C	65	$C_{28}H_{22}O_4N_2S_2$[a]	68.9	68.8	4.7	4.6	4.7	4.5	10.8	10.7	.33	.32	...	...

[a] Analysis corresponds to IIe with one molecule of benzene of crystallization; on drying in vacuum at 80° for five hours, it melts at 224–225°, and gives the following analysis: C, 65.3; H, 4.2; N, 5.4; S, 12.3. Calcd. for $C_{28}H_{22}O_4N_2S_2$: C, 65.4; H, 4.3; N, 5.4; S, 12.4.

Anal. Calcd. for $C_{12}H_{16}N_2Cl_2$: N, 10.8; Cl, 27.4. Found: N, 10.6; Cl, 27.0.

IIb was obtained by treating 2.1 g. of VI in 20 ml. of dry benzene with 3.5 g. of benzenesulfonyl chloride and 3 ml. of pyridine, as described by Adams and Wankel[2] for the preparation of naphthalene-1,4-dibenzenesulfonamide (II, R = H). The resulting colorless solid was recrystallized from chloroform–light petroleum (b.p. 40–60°), m.p. 195° (m.p. and mixed m.p. with a sample of (IIb) obtained by the action of ethylmagnesium iodide on (Ia), gave no depression); yield *ca.* 81%.

2-Methylnaphthalene-1,4-dibenzenesulfonamide (IIa) was prepared, similarly, by the action of 3.5 g. of benzenesulfonyl chloride, 3 ml. of pyridine on 2 g. of 2-methylnaphthalene-1,4-diamine dihydrochloride[16] in 20 ml. of benzene as described in the case of IIb. IIa is obtained as colorless crystals from chloroform–light petroleum, m.p. 234° (not depressed when admixed with a sample prepared by the action of methylmagnesium iodide on Ia), yield *ca.* 75%.

Action of Methyl- and Ethylmagnesium Iodide on Quinone Imides.—A 30-ml. lot of dry benzene solution of 1 g. of each of Ib,[2] IIIa,[2] IIIb[2] and IV[2] was added to methylmagnesium iodide solution (prepared from 0.9 g. of magnesium, 3.6 g. of methyl iodide and 50 ml. of ether); the reaction mixture was refluxed on a steam-bath for three hours, allowed to stand overnight at 25°, and worked out as usual. The corresponding di-amides were obtained, in all cases in an almost quantitative yield. Identification was carried out by m.p. and mixed m.p. with authentic specimens.

Action of ($Mg + MgI_2$) Mixture on Quinone Imides.—To the colorless mixture of 1 g. of magnesium, 4 g. of iodine in 20 ml. of dry ether and 20 ml. of dry benzene, was added 1 g. of each of Ia, Ib, IIIa, IIIb and IV. The reaction mixture was refluxed on a steam-bath for three hours and kept aside overnight. The mixture was hydrolyzed by means of ice in saturated aqueous ammonium chloride solution. The ether–benzene solution gave on concentration, colorless crystals, which on recrystallization proved to be the corresponding di-amides (m.p. and mixed m.p.). Yield is almost quantitative.

Action of Lithium Aluminum Hydride on Quinone Imides.—The action of lithium aluminum hydride on Ia, Ib, IIIa, IIIb and IV was carried out in solvents dried over sodium. To 0.7 g. of pulverized lithium aluminum hydride (from New Metals and Chemicals Ltd., London) was added 50 ml. of ether. After 15 minutes a 30-ml. benzene solution of 1 g. of each of the above quinone imides was added in portions. The reaction mixture was refluxed for three hours and then set aside overnight at room temperature. After treatment with cold aqueous ammonium chloride solution, the ethereal solution was dried and evaporated. The reaction products were recrystallized and proved to be the corresponding di-amides (m.p. and mixed m.p.). Yield is almost quantitative.

Action of Diazomethane Derivatives on *p*-Quinone Imides. (a) Diphenyldiazomethane.—One gram of (Ia) in 20 ml. of dry benzene was treated with diphenyldiazomethane[17] (prepared from 1.5 g. of benzophenone hydrazone and 3 g. of yellow mercuric oxide suspended in 30 ml. of dry benzene). The mixture was refluxed for three hours, during which strong evolution of gas was observed. The deep red color faded. The benzene was evaporated off, and the solid residue was washed with cold ether, and finally crystallized from benzene–light petroleum (b.p. 40–60°) as colorless crystals, m.p. 244–245° (red melt). *Anal.* Calcd. for $C_{35}H_{26}O_4N_2S_2$: C, 69.8; H, 4.3; N, 4.7; S, 10.6; active H, 0.33; mol. wt., 602. Found: C, 69.7; H, 4.1; N, 4.6; S, 10.3; active H, 0.31; mol. wt. (Rast), 592. VIII is soluble in hot benzene, but difficultly soluble in cold ethyl alcohol, and gives with concentrated sulfuric acid an olive-green color changing to violet after 15 minutes. It dissolves in alcoholic potassium hydroxide solution with a blue-violet color; yield *ca.* 85%.

Similarly, IX was obtained by the action of diphenyldiazomethane on 1 g. of IIIa as described above. It forms almost colorless crystals from benzene–light petroleum (b.p. 40–60°), m.p. 202° (red melt). *Anal.* Calcd. for $C_{31}H_{24}O_4N_2S_2$: C, 67.4; H, 4.3; N, 5.1; S, 11.6; active H, 0.36; mol. wt., 552. Found: C, 67.3; H, 4.1; N, 5.0; S, 11.3; active H, 0.35; mol. wt. (Rast), 545. IX is easily soluble in hot benzene, chloroform and acetic acid, but difficultly soluble in ether and light petroleum. It dissolves in alcoholic potassium hydroxide solution with a deep green color and gives a reddish-brown color with concentrated sulfuric acid.

(b) 9-Diazofluorene.—To a solution of 1 g. of Ia in 30 ml. of dry benzene, was added 50 ml. of dry benzene solution of 2 g. of 9-diazofluorene.[18] The reaction mixture was refluxed for two hours, whereupon pale-yellow crystals separated. On cooling, the solid contents were filtered off, washed with light-petroleum (b.p. 60–80°) and recrystallized from chloroform as pale-yellow crystals, m.p. 250° (dark brown melt). *Anal.* Calcd. for $C_{35}H_{24}O_4N_2S_2$: C, 70.0; H, 4.0; N, 4.7; S, 10.7; active H, 0.33; mol. wt., 600. Found: C, 70.0; H, 3.8; N, 4.5; S, 10.4; active H, 0.31; mol. wt. (Rast), 588. X is soluble in hot chloroform, but difficultly soluble in alcohol and benzene; it gives a violet-red color with concentrated sulfuric acid. It dissolves in alcoholic potassium hydroxide solution with an intense greenish-blue color.

2-Diphenylmethylnaphthalene-1,4-dibenzenesulfonamide (XII).—The reaction mixture of 0.5 g. of Ia, 0.3 g. of benzhydrol in 5 ml. of glacial acetic acid containing 0.5 ml. of dilute sulfuric acid (1 part sulfuric acid + 19 parts water), was heated on a steam-bath for 10 minutes. On cooling, colorless crystals separated, which were filtered off and recrystallized from acetic acid, m.p. 170°. *Anal.* Calcd. for $C_{35}H_{28}O_4N_2S_2$: C, 69.5; H, 4.6; N, 4.6; S, 10.6; active H, 0.33; mol. wt., 604. Found: C, 69.3; H, 4.6; N, 4.4; S, 10.5; active H, 0.32; mol. wt. (Rast), 595. XII is easily soluble in benzene and alcohol, but difficultly soluble in light petroleum (b.p. 60–80°); it gives an orange color with concentrated sulfuric acid and dissolves in alcoholic potassium hydroxide solution with a violet-blue color; yield, *ca.* 60%.

GIZA, CAIRO, EGYPT

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[17] H. Staudinger and A. Gaule, *Ber.*, **49**, 1897 (1916).

[18] A. Schönberg, W. Awad and N. Latif, *J. Chem. Soc.*, 1368 (1951).