of ethanol. Water was added to incipient turbidity. After 20 hr at O', 5.42 g of slightly colored but nearly pure VI, mp 50- 51°, was collected by filtration. Addition of water to the mother liquor gave a second crop (0.25 g, mp 46-48°), total yield  $79\%$ . The combined material was dissolved in hexane and the solution passed through a short column of silica gel. Evaporation of the eluate and crystallization of the residue from aqueous ethanol gave 4.75 g of colorless prisms: mp 53-54'; ir 1585, 1322, 1195, 1160, 1070, 965, 755, and 685 (strong), 1625, 1300, 1025, 1000,  $925$ , and  $770 \text{ cm}^{-1}$  (medium).

*Anal.* Calcd for C1oH,f,N02: C, 78.87; H, 5.23; N, 4.84. Found: C, 78.75; H, 5.29; N, 5.02.

 $\textbf{Phenyl}$  0-Ethylbenzohydroximate (VII).—O-Phenylbenz hydroximoyl chloride (1.00 g, 4.3 mmol) was dissolved in 20 ml of ethanol and thallium $(I)$  ethoxide  $(1.07 g, 4.3 mmol)$  was added. The mixture was heated under reflux for  $4 \text{ hr}$ , thallium(I) chloride filtered off, and the filtrate evaporated. The residue was dissolved in ethyl acetate-hexane  $(1:1)$  and the solution passed through a short column of silica gel. Evaporation of the eluate and crystallization of the residue from aqueous ethanol gave 550 mg **(53%)** of flat prisms: mp 43-44'; ir 1590, 1320, 1215, 755, and 695 (strong), 1629, 1575, 1300, 1155, 1105, 1075, 1025, 955, 930, and  $770 \text{ cm}^{-1}$  (medium).

*Anal.* Calcd for  $C_{15}H_{15}NO_2$ : C, 74.62; H, 6.27; N, 5.81. Found: C, 74.60; H, 6.24; N, 5.88.

Reaction of IBenzohydroxamic Acid with Thionyl Chloride and **Thallium(I) Phenoxide.**—To a suspension of  $1.37$  g (0.01 mol) of benzohvdroxamic acid in 150 ml of cold anhydrous ether was added  $1.30$  g (0.011 mol) of thionyl chloride. The resulting clear solution was stirred for 1 hr at 0° and evaporated (bath temperature 20'), and the residual syrup dissolved in 100 ml of dry, cold benzene. Thallium(1) phenoxide (2.97 g, 0.01 mol) was added (slight exothermic reaction) and the mixture stirred at room temperature for 2 hr. Filtration and evaporation of the filtrate gave a syrup which crystallized upon trituration with ethyl acetate-petroleum ether to give  $250$  mg  $(23\%)$  of triphenyl isocyanurate, mp  $275^{\circ}$  (lit.<sup>11</sup> mp  $275^{\circ}$ ).

Addition of more petroleum ether to the mother liquors gave 180 mg (6%) of impure phenyl benzohydroxamate, mp 120°, mmp (with pure 11) 130'. The yield of this material was not increased when the reaction of benzohydroxamic acid with thionyl chloride and thallium $(I)$  phenoxide was carried out at lower temperatures.

Thermolysis of Phenyl O-Phenylbenzohydroximate (VI).-Compound VI (1.00 g) was placed in a small round-bottom flask equipped with a condenser and immersed into a Wood's metal bath at 180". The reaction mixture, which immediately started to boil violently, was maintained at 180' for 30 min and then cooled to room temperature. The partly crystalline product was dissolved in ethyl acetate-methanol  $(1:1)$  and the solution left at *0'* for 20 hr. Filtration then gave **15** mg of 2,4,6-triphenyl-l,3,5-triazine (VIII), mp 231-232' *(m/e* 309) (lit.12 mp 230'). Evaporation of the filtrate and chromatography of the residue on a silica gel column [eluent, hexane-ethyl acetate  $(5:1)$ ] gave benzonitrile  $(250 \text{ mg})$  (containing a little VI and VIII), phenol (80 mg), and 170 mg of a mixture **of** at least three different, unidentified compounds.

Photolysis of Phenyl  $O$ -Phenylbenzohydroximate (VI).--Compound VI  $(2.00 g)$  was dissolved in hexane (500 ml) and irradiated with 3000-A light (Rayonet photochemical reactor) for **3** hr. Some insoluble brown material was filtered off and the filtrate irradiated for an additional **4** hr. Filtration gave a second crop of hexane-insoluble material, total yield 400 mg.18 Evaporation of the filtrate gave a syrup which was separated on a silica gel column into VI11 (12 mg), unreacted starting material (740 mg, containing a little benzonitrile), benzonitrile (50 mg), phenol (350 mg), 40 mg of a solid, recrystallized from water to give an

(11) A. W. Hofmann, Be?., **18,** 3217 (1885).

(12) A. Pinner, ibid., **28,** 1611 (1889).

amide (5 mg, mp  $215-220^{\circ}$ ),<sup>14</sup> and 45 mg of an unidentified aromatic compound (no OH, NH, CO).

(14) **Its** ir spectrum showed **NH** absorption at **3340 om-1,** strong bands at **1655** (amide I) and **1545** em-1 (amide **II),** and additional bands at 1590, 1510, 825, and **726** cm-1, suggesting the presence of phenyl groups. It has been shown [J. R. Cox, Jr., and **M. F.** Dunn, Tetrahedron Lett., 985 (1963)] that *N*-acetyl-O,*N*-diphenylhydroxylamine rearranges spontaneously to **4-** (and **2-) hydroxy-4'-acetylaminobiphenyl.** It **seems**  reasonable to suggest, therefore, that VI may have rearranged first by **a**  Chapman-type rearrangement to phenyl **N-phenylbenaohydroxamate,**  which subsequently underwent a further rearrangement to 4'-benzovlaminohydroxybiphenyl according to the following scheme.



**4'-Benzoylamino-4-hydroxybiphenyl** melts at **284O** [L. C. Raiford and E. **P.**  Clark, *J.* Amer. Chem. *Soc.,* **48,** 483 (1926)l; **our** compound could be the unknown 2-hydroxy **isomer.** 

**Registry** No.-11, 4380-77-2; V, 26630-25-1; VI, 26630-26-2; VII, 26630-27-3.

## Tautomerism **in 1,5=Dianilino-4,8-naphthoquinones**

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While studying a number of **1,5-bis(alkylamino)-4,8**  naphthoquinones, $\frac{1}{x}$  we noted that the absorption spectra of the dianilide (1) was solvent dependent (Figure 1 and



Table I). In polar, associating solvents, the absorption at 661 nm of the dianilide is of maximum intensity and decreases with decreasing solvent associating ability. Conversely, the band at  $\sim 560$  nm (broad) increases in intensity. The alkyl-substituted aminonaphthoquinones, however, have a limited dependence of the electronic spectrum upon solvent, the effects being in the range considered normal (for example,  $\epsilon_0$  shifting from  $2.42$  to  $2.28 \times 10^3$  between ethanol and pyridine).<sup>1</sup>

Dahne and Paul discussed the strong solvent dependency of the electronic spectra of 1,8-diamino-2,7-naphthoquinones.2 They attributed the solvent effect to mesomerism from the quadrapolar nature of the mole-

<sup>(13)</sup> This material was insoluble in water, but it could be dissolved in hot benzene and precipitated again upon addition of petroleum ether to give a dark red powder, mp 140–150° dec. Its ir spectrum showed a medium strong absorption band at 1650 cm<sup>-1</sup>. Its nmr spectrum (in DMSO-*ds*) showed onl appears to be diphenoquinone, which is known to be unstable and to decompose *at* 165' **[R.** Willstatter and L. Kalb, ibid., *88,* 1235 **(1905)l.** It also liberated iodine from an acidic potassium iodide solution, a characteristic reaction of diphenoquinone.

<sup>\*</sup> To whom correspondence should be addressed, Harvard University.

<sup>(1)</sup> *S. hl.* Bloom and G. Dudek, Tetrahedron, **88,** 1267 (1970).

<sup>(2)</sup> S. Dahne and H. Paul, **Chem.** Ber., **97, 1625** (1964).



Figure 1.—The electronic spectra of 1,5-dianilino-4,8-naphthoquinone. For clarity, only the extremes of the solvent effect are shown.

TABLE I ELECTRONIC SPECTRAL DATA

Compd	Solvent	$\lambda_{nm}$	$\epsilon \times 10^4$	$\lambda_{nm}$	$\epsilon \times 10^4$
ı	CH <sub>a</sub> OH	620 $(s)^a$	1.52	660	2.20
	CHCl <sub>3</sub>	625	1.51	667	2.14
	$\rm{C_2H_5OH}$	625	1.55	661	2.14
	CH <sub>3</sub> SOCH <sub>3</sub>	625	1.38	667	1.81
	$\rm C_5H_5N$	628	1.37	671	1.75
	$CH_3COCH_3$	628	1.35	668	1.63
	$_{\rm CCL}$	624	1.31	668	1.59
	$\rm{C_6H_{12}}$	618	1.21	663	1.26
3	CHCI.	620	1.51	673	2.38
	$_{\rm CCL}$	620(s)	1.44	673	1.94

 $a (s) =$  shoulder.

cule. However, the behavior of the dianilide is more like that of systems<sup>3</sup> such as 2-(N-methylacetimidoyl)-1-naphthol **(2). A** band at **420** nm in **2** decreases in intensity with decreasing solvent association and a weak band at *380* nm, also observed as a shoulder, increases.



The solvent dependency of **2** has been ascribed to the tautomeric shift of the proton from nitrogen to oxygen  $(2a \leftrightharpoons 2b)$ . Confirmation of this equilibrium was obtained through the proton magnetic resonance spectrum of the  $^{15}N$ -substituted compound.<sup>3</sup> In nonexchanging compounds, such as amides, the 15NH spin coupling is about 88-99 HZ which decreases as the residence time of the proton on the nitrogen decreases.

Accordingly, the <sup>15</sup>N analog of 1 was synthesized using  $99\%$  <sup>15</sup>N-enriched aniline. In chloroform solution, the **l5IYH** spin coupling is **76.5** Hz at **27"** (Table 11) and only 62.0 Hz in carbon tetrachloride solution. These <sup>15</sup>NH spin couplings are appreciably smaller than the value of  $88-90$  Hz frequently measured.<sup>3,4</sup> The chemical shift of the NH is at **6** 14.28 ppm, indicative of a strong hydrogen bond. The utilization of pyridine as a solvent little affects the strength of the association.

Although reduced spin couplings may be attributed to intermolecular proton exchange, the strong intermolecular hydrogen bond, the parallel solvent dependent of the electronic spectra, and the normal behavior



<sup>*a*</sup> From tetramethylsilane as reference. <sup>*b*</sup> Labeled with <sup>15</sup>N.  $\cdot$  Spin coupling in Hz.

of the alkyl substituted compound suggest the presence of a keto-enol tautomeric process. The existence of a keto-enol equilibrium is verified by the parallel solvent dependency of the electronic spectra.

The tautomeric shift of the dianilide may involve three species. If the equilibrium involves only a and b,



then the observed  $J_{16}$  will vary between 90 and 45 Hz, while a and c would have  $J_{16}$  varying between 90 and  $0 \text{ Hz.}^5$  If all three forms are present, the quantitative aspects of both the nmr and uv spectra will be complex.

The synthesis of 1,5-bis(4'-ethoxyaniline)-4,8-naphthoquinine **(3)** provides a compound with a negative  $\sigma$ for comparison.6 The ethoxy substituent on the phenyl stabilizes the amino tautomer as the solvent dependency of this derivative is less marked, but an equilibrium is still observable. Regrettably, the insolubility of the compound limited the solvents that could be utilized.

Since derivatives of the dianilinonaphthoquinones are important commercial dyestuffs,<sup>7</sup> these findings suggest the color of the dyes can be markedly affected through a tautomeric shift. The color and intensity of the product would depend strongly upon the material being colored.

The double bond proton-proton spin coupling of 10.0 Hz suggests little bond delocalization (aromaticity) in the system.\* The small change in this value from 10.0 Hz in CDCl<sub>3</sub> to 10.2 Hz in CCl<sub>4</sub> solution indicates the other tautomers have even less bond delocalization than the predominate tautomer a.

This has a possibility of being construed as evidence for elimination of b as an important tautomer. In b one ring should possess a significant degree of aromaticity.

Infrared Spectra.-The infrared spectra of the <sup>15</sup>Nlabeled anilide (1) mas compared with that of the unlabeled compound so the frequencies indicating the

**<sup>(3)</sup>** G. Dudek and E. Dudek, *J.* **Amsr.** *Chem.* Soc., **88, 2407** (1966).

**<sup>(4)</sup> A. J.** Bourn and E. **W.** Randall, *Mol.* Phys., **8,** 567 (1964).

<sup>(5)</sup> Assuming **of** course, that the tautomeric process is rapid on an nmr

time scale. (6) R. **W.** Taft in "Steric Effects In Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 656. Ed., Wiley, New York, N. Y., 1956, p 556.<br>(7) E. Merian, *Chimia*, **13,** 181 (1959).

**<sup>(8)</sup> M. A.** Cooper and *8.* L. Manatt, *J.* **Amer.** *Chem.* **Soc., 91,** 6325 (1969).





nitrogen could be identified. In Table 111 it can be seen that the strong band at  $1537 \text{ cm}^{-1}$  and the one at  $1289 \text{ cm}^{-1}$  shift appreciably upon isotopic substitution and these are the only absorptions observed with appreciable shifts.

## Experimental Section

Spectra were taken as previously described.'

Compound **1** .-To 54 mg **(0.3** mmol) of 1,5-diamino-4,8-naphthoquinone was added **166** mg, **1.2** mmol, of aniline and **1** ml of acetic acid. The solution was gently refluxed for **4** hr and then the solvent was removed. The residue was crystallized from toluene-hexane, wt 86 mg, mp **220-221°.8** 

The <sup>15</sup>N compound was synthesized in the same manner, employing **99.5%** aniline-I6N.

Compound 3.-This compound was synthesized as 1. The material was crystallized from xylene, mp **220-222'.** Anal. Calcd for  $C_{26}H_{24}O_4N_2$ : C, 72.88; H, 5.69; N, 6.54. Found: C, **72.77;** H, **7.53; N, 6.43.** 

Registry **No.** -1,26823-92-7; 3,26823-93-8.

(9) C. Neudeckar, Thesis, Wurzburg, Germany, **1930.** 

## The Reaction of  $\alpha$ -Sulfonyl Carbanions with Carbon Disulfide

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The base-induced reaction of activated methylene groups with carbon disulfide followed by alkylation of



This reaction has now been investigated as a synthetic route to structures of the type  $\text{RSO}_2(\text{R}')\text{C}=\text{C}(\text{SR}'')_2$ and  $(RSO<sub>2</sub>)<sub>2</sub>C=C(SR')<sub>2</sub>$ , starting with the appropriate sulfone or disulfone.

(1) R. Gompper and W. **Topfl,** *Chem. Ber.,* **96, 2861 (1962).** 

**(2) E.** Soderback, Acta *Chem.* Scand., **17, 362 (1963). (3) R.** Gompper, **E.** Kutter, and W. Topfl, *Justus* **Liebigs Ann.** *Chem.,* 

**669, 00** (1962).

(4) A. Thuillier and J. Vialle, *Bull. Soc. Chim. Fr.*, 2182, 2194 (1962). **(5)** D. C. Dittmer, H. E. Simmons, and **R.** D. Vest, *J. Org. Chem.,* **29, 497** (1964).

(6) **K.** A. Jensen and L. Henriksen, *Acta Chem. Scand.,* **89, 1107 (1968).** 

The expected product, **l,l-di(methylsulfony1)-2,2**  di(methylmercapto)ethene (1), was isolated in  $11.5\%$ yield when di(methylsulfony1)methane was treated with carbon disulfide in dimethyl sulfoxide in the presence of potassium tert-butoxide, followed by methylation. The structure of **l** was demonstrated by reduc-

$$
\begin{array}{ccc} \text{(CH$_3$SO$_2$)_2$CH$_2$} & \xrightarrow{\text{KO-tert-Bu}} & \xrightarrow{\text{1. CS$_2$}} & \text{(CH$_3$SO$_2$)_2$C=C(SCH$_3$)_2\\ & & & 1\\ \text{KO-tert-Bu} & \xrightarrow{\text{CH$_3$}} & \text{(CH$_3$SO$_2$)_2$CHCH$_3$} & \xrightarrow{\text{NaBH$_4$}}\\ \text{DMSO} & & \text{2} & & \end{array}
$$

tion of the double bond with simultaneous desulfurization of the mercaptal unit by treatment with the sodium borohydride-nickelous chloride system.' The resulting **1,l-di(methylsulfony1)ethane (2)s** was identical with an authentic sample prepared by methylation of di(methy1 sulfonyl)methane. An attempt to extend this sequence to di(p-tolylsulfony1)methane led only to methylated starting material,  $1.1$ -di( $p$ -tolylsulfonyl) ethane.

Treatment of the monosulfones benzyl phenyl sulfone  $(3a)$ , benzyl p-tolyl sulfone  $(3b)$ , and methyl p-tolyl sulfone (3c) in a like manner afforded products  $4a-c$  in 30, 50, and  $2.5\%$  yields, respectively.



Reduction of 4a and 4b with sodium borohydride in diglyme produced the  $\alpha$ -methyl benzyl sulfones, 5a and 5b, which were prepared independently by methylation of the benzyl sulfones.

the benzyl suffones.

\n4a or 4b 
$$
\xrightarrow{\text{NaBH}}
$$
 RSO<sub>2</sub>CHCH<sub>3</sub>  $\xrightarrow{\text{RO-tert-Bu}}$   $\xrightarrow{\text{RO-tert-Bu}}$   $\xrightarrow{\text{R}} \xrightarrow{\text{R'}}$ 

\n5a, R = Ph; R' = Ph  
\nb, R = p-CH<sub>3</sub>Cl<sub>3</sub>I; R' = Ph

Application of the reaction sequence to benzyl phenyl sulfoxide gave a material whose spectral characteristics were in accord with **l-phenyl-l-(phenylsulfinyl)-2,2 di(methy1mercapto)ethene** *(6).* The initial product *6* 

$$
\begin{array}{r}\n\text{PhSO} \\
\text{PhSOCH}_2\text{Ph} \xrightarrow{\text{KO-tert-Bu} \quad 1. \text{ C}\text{S}_2} \text{PhSO} \\
\hline\n\text{DMSO} \quad \frac{1. \text{ C}\text{S}_2}{2. \text{ CH}_31} \quad \text{Ph} \\
\text{Ph} \\
\text{Ch} \\
\text
$$

 $PLCO$ 

decomposed to a pungent black oil which was not further investigated.

Oxidation of **1** with hydrogen peroxide in glacial acetic

\n acid produced 
$$
\text{di}(\text{methylsulfonyl})\text{methane.}\n \quad \text{This result}
$$
\n

\n\n $\text{CH}_3\text{SO}_2\text{b}C = C(\text{SCH}_3)_2 \cdot \frac{\text{H}_2\text{O}_2}{\text{HOAe}} \cdot (\text{CH}_3\text{SO}_2)\cdot \text{CH}_2$ \n

is analogous to that of oxidation of  $1,1,2,2$ -tetra $(p$ -tolylmercapto) ethene<sup>9</sup> and 1-nitro-2,2-di (methylmercapto)ethene.<sup>10</sup> The products of the oxidation reactions

**(7)** W. **E.** Truce snd **E'.** M. Perry, *J. Org. Chem.,* **80, 1316 (1965).** 

*(8)* D. T. Gibson, *J. Chem. SOC.,* **2640 (1031).** 

(9) W. **E. Truce** and B. Groten, *J. Org. Chem.,* **27, 128 (1962).** 

**(10) K. A.** Jensen, 0. Buchsrdt, and C. Lohse, *Acta Chem.* Scand., **ai, 2797 (1967).**