

TABLE III
 SOLUBILITY OF DIBORANE IN DIETHYL ETHER

T°, K	Initial B_2H_6 , moles/100 g. solvent	0.706	0.110	0.184	K_1^a average
273	Total press., atm.	1.47	1.90	3.70	0.057
	B_2H_6 press.	1.24	1.68	3.49	
	K_1	0.055	0.064	0.051	
283	Total press., atm.	1.82	2.16	4.02	.052
	B_2H_6 press.	1.46	1.81	3.68	
	K_1	0.047	0.059	0.049	
293	Total press., atm.	2.22	3.22	4.64	.041
	B_2H_6 press.	1.67	2.68	4.13	
	K_1	0.041	0.040	0.043	
303	Total press., atm.	2.70	3.85	5.48	.036
	B_2H_6 press.	1.89	3.06	4.73	
	K_1	0.036	0.035	0.038	
313	Total press., atm.	3.33	4.63	6.48	.032
	B_2H_6 press.	2.17	3.50	5.40	
	K_1	0.032	0.031	0.033	
323	Total press., atm.	4.07	5.52	7.60	.028
	B_2H_6 press.	2.48	3.96	6.11	
	K_1	0.028	0.027	0.029	

^a $K_1 = S/P$ (moles $B_2H_6/100$ g. ether—atm.).

 TABLE IV
 SOLUBILITY OF DIBORANE IN TETRAHYDROFURAN

T°, K	Initial B_2H_6 , moles/100 g. solvent	0.0779	0.148	0.145	0.248	0.255	0.324	K_2^a average
280	Total press., atm.		0.198	0.218	0.333	0.401	0.899	0.42
	B_2H_6 press.		.113	.133	.250	.325	.828	
	K_2		.44	.40	.49	.44	.35	
293	Total press., atm.	0.266	0.368	0.381	0.667	0.830	1.819	.29
	B_2H_6 press.	.100	.215	.227	.530	.694	1.691	
	K_2	.25	.32	.30	.33	.30	0.24	
303	Total press., atm.	0.402	0.619	0.633	1.137	1.477	2.910	.22
	B_2H_6 press.	.147	.388	.398	0.931	1.272	2.716	
	K_2	.20	.23	.23	0.25	0.22	0.18	
313	Total press., atm.	0.566	0.967	1.033	1.885	2.230	4.545	.17
	B_2H_6 press.	.196	.626	0.691	1.579	1.925	4.255	
	K_2	.18	.18	0.17	0.19	0.18	0.14	
323	Total press., atm.			1.461	2.874	3.386	6.380	.14
	B_2H_6 press.			0.967	2.429	2.942	5.967	
	K_2			0.14	0.15	0.14	0.12	

^a $K_2 = S/P^{1/2}$ (moles $B_2H_6/100$ g. tetrahydrofuran—atm.^{1/2}).

The solubility of diborane in diethyl ether is slightly greater than predicted by Raoult's law but is proportional to pressure. In tetrahydrofuran the solubility of diborane is much greater than perfect solution predictions, and solubility increases as the square root of diborane pressure.

TABLE V

 COMPARISON OF SOLVENT PROPERTIES OF DIETHYL ETHER
 AND TETRAHYDROFURAN AT 25°

	Solubility in ether, g. solute/100 g. solvent	Solubility in tetrahydrofuran, g. solute/100 g. solvent
B_2H_6	1.1 ^a	8.1 ^a
$LiBF_4$	1.9	71
$LiBH_4$	3 ^a	28
LiF	0.05	0.6

^a Calcd. from Tables III and IV. Diborane at 1 atm., 20°.

(2) H. I. Schlesinger, *et al.*, Final Report, Navy Contracts No. N173 S-9058 and N173 S-9820.

This suggests that diborane is present in tetrahydrofuran solution as the complex $C_4H_8O:BH_3$. Heats of solution of -2800 cal./mole in ether and -4900 cal./mole in tetrahydrofuran were obtained from the change in equilibrium constants with temperature. These values should be given only qualitative significance.

The unusual solvent properties of tetrahydrofuran on boron-containing salts are shown in Table V. Solubility of the salts was roughly determined by evaporation of solvent from saturated solutions.

Experimental

Determination of Diborane Solubility.—A tared stainless steel cylinder, equipped with a pressure gage, was filled to approximately one-third capacity with dry solvent and was degassed by repeated freezing and evacuation. The cylinder was reweighed and connected by flexible metal tubing to a steel storage tank containing diborane of purity greater than 99%. Connecting lines were evacuated and small portions of diborane were admitted to the cylinder until the desired equilibrium pressure registered on the gage. The cylinder was again weighed, then submerged in a water-bath of known temperature until an equilibrium pressure was established. After a series of pressure-temperature values had been obtained, the cylinder was placed in a bell jar and dried under vacuum until constant weight had been reached.

A second portion of diborane was then introduced and the above procedure repeated.

Solutions of diborane in ether showed no change in pressure after several days storage. In two weeks, a pressure increase from 2 to 14 lb. and from 28 to 118 lb. had occurred in the two diborane-tetrahydrofuran cylinders.

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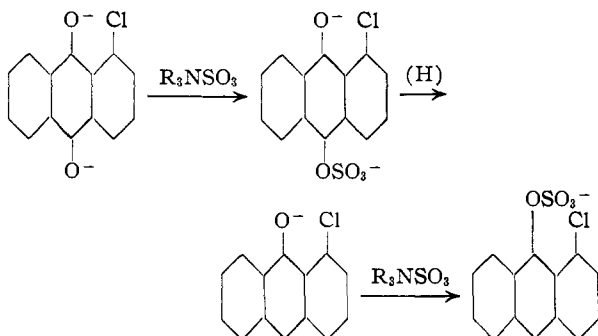
Separation of Mixtures with Triethylamine-Sulfur Trioxide

By WILLIAM B. HARDY AND MARIO SCALERA
 RECEIVED MAY 20, 1952

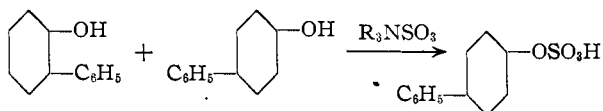
In an earlier paper¹ we have reported that the action of triethylamine-sulfur trioxide on anthrahydroquinones leads to the formation of anthranol sulfuric esters in addition to the expected disulfuric

(1) M. Scalera, W. B. Hardy, E. M. Hardy and A. W. Joyce, *THIS JOURNAL*, **73**, 3094 (1951).

esters. While this side reaction occurs with anthrahydroquinone itself, it was found to be greatly enhanced by the presence of α -substituents in the anthraquinone molecule. The postulation that steric effects accounted for the enhancement of the side reaction by the α -substituent was borne out by the nature of the reduction products. For example, in the esterification of 1-chloroanthraquinone, 1-chloro-9-anthranolsulfuric ester was isolated as the principal reduction product. This is the expected product if the α -substituent hinders the esterification, as can be seen by examination of the equations



In view of these facts, we considered it of interest to determine if this postulated steric effect on the esterification rate would be observable in simple compounds. In order to avoid the tedious measurements which would be involved in the determination of reaction rates, we resorted to the simple expedient of carrying out competitive esterifications on mixtures. Application of the esterification reaction to an equal molecular mixture of *o*- and *p*-phenylphenol in aqueous alkaline medium led to the formation of the sulfuric ester of *p*-phenylphenol in high yield, as



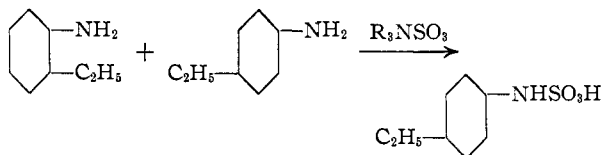
The regenerated material from this ester was of exceedingly high purity. In an independent experiment it was shown that *o*-phenylphenol was esterified in high yield under the same conditions as used for esterification of the mixture, thus demonstrating that the exclusive formation of para isomer from the mixture was simply the result of its greater esterification rate.

Application of the esterification procedure to a mixture of 8-benzamido-1-naphthol and 5-benzamido-1-naphthol in pyridine solution led to esterification of the 1,5-isomer as would be expected based on steric effects. However, in aqueous medium the 1,8-isomer only was esterified. Independent experiments showed that the failure of the reaction to take the expected course was probably due to the low solubility of the 5-benzamido-1-naphthol in the organic phase of the aqueous reaction mixture. Indeed, the 1,5-isomer was not esterified at all under the conditions of aqueous esterification.

The remarkably sharp separation of the components of the *o*- and *p*-phenylphenol mixture made

it of interest to examine the possible suitability of triethylamine-sulfur trioxide as a reagent for the separation of other isomeric compounds or compounds having active hydrogen atoms.

When a mixture of *o*- and *p*-ethylphenol was treated with the sulfating agent in chloroform, a clean-cut separation was obtained with the para isomer being converted to the sulfamic acid in a high state of purity.



The separation of 1-propanol and 2-propanol by means of triethylamine-sulfur trioxide represents a case where two compounds may be separated due to the difference in degree of dissociation of the hydrogen-oxygen bond. Heating a mixture of these two alcohols with the esterification reagent resulted in a good yield of the sulfuric ester of *n*-propanol identified as its benzylisothiuronium salt. That this was a case of selective action on the 1-propanol is demonstrated by an experiment in which 2-propanol was heated with triethylamine-sulfur trioxide under the same conditions and the ester of 2-propanol was readily obtained.

These results were obtained in connection with a broad research program on the esterification of leuco vat dyes by trialkylamine-sulfur trioxide compounds, and sufficient time was not available to explore further this interesting method of separation. However, in addition to being applicable to the separation of isomeric compounds containing amino or hydroxy groups, it is felt that this procedure could be used in many cases where the hydrogen atoms of two compounds show differing reaction rates toward triethylamine-sulfur trioxide.

Experimental

Intermediates.—With the exception of triethylamine- SO_3 ² and the benzamidonaphthols, the intermediates used were commonly available materials. 1-Benzamido-8-naphthol was prepared from peri acid by alkali fusion followed by benzoylation with benzoic anhydride; m.p. 187–189°.³

1-Benzamido-5-naphthol, a new compound, was prepared by the above procedure starting with Eastman Kodak Co. purified 1-amino-5-naphthol hydrochloride. The yield of gray-white solid was 45%. It sintered at 261° and melted at 270–273°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{13}\text{O}_2\text{N}$: C, 77.5; H, 4.90; N, 5.30. Found: C, 77.7; H, 4.84; N, 5.94.

Separation of Phenols. Aqueous Process.—Samples weighing 8.5 g. (0.05 mole) each of *o*-phenylphenol and *p*-phenylphenol were dissolved at 70° in a solution consisting of 4.4 g. (0.11 mole) of sodium hydroxide in 58 cc. of water. Nine and two-tenths grams (0.11 mole) of sodium bicarbonate and 13.8 g. (0.075 mole) triethylamine- SO_3 were added. The mixture was stirred for 3.5 hours at 45–50°. After cooling, the mixture was extracted with ether. The two lower layers were diluted to 125 cc. with water and 30 cc. of 5 *N* sodium hydroxide was added. Addition of sodium chloride to the solution precipitated the sulfuric ester of *p*-phenylphenol in 81% yield, as shown by hydrolysis in acid solution to pure *p*-phenylphenol; m.p. 163–164°. The high purity of this product is demonstrated by the fact that a mixture comprised of 10% *o*-phenylphenol and 90% *p*-phenylphenol softened at 80° and melted at 112–157°.

(2) H. Z. Lecher and W. B. Hardy, *THIS JOURNAL*, **70**, 3789 (1948).

(3) F. Fichter and R. Gageur, *Ber.*, **39**, 3331 (1906).

Working up the filtrates and ether extract yielded 8.2 g. of crude ortho isomer melting at 52–87°.

Separation of Naphthols. Aqueous Process.—A mixture consisting of 2.6 g. (0.01 mole) each of 8-benzamido-1-naphthol and 5-benzamido-1-naphthol was dissolved in 10 cc. of water by addition of 4.2 cc. of 5 *N* sodium hydroxide. Addition of 1.7 g. (0.02 mole) of sodium bicarbonate precipitated the naphthols. Then 2.8 g. (0.015 mole) of triethylamine-SO₃ was added. After stirring for six hours at 30°, 10 cc. of 5 *N* sodium hydroxide was added and the triethylamine was extracted with ether. Acidification with 20% acetic acid precipitated 2.6 g. of product identified as being principally 5-benzamido-1-naphthol.

From the filtrate the sulfuric ester of 8-benzamido-1-naphthol was isolated in 81% yield.

Separation of Naphtols. Anhydrous Process.—A mixture consisting of 1.3 g. (0.005 mole) each of 5-benzamido-1-naphthol and 8-benzamido-1-naphthol was placed in 15 cc. of dry pyridine and 1 g. (0.005 mole) of triethylamine-SO₃ was added. The clear brown solution was allowed to stand for 24 hours at room temperature. Ten cc. of water and 5 cc. of 5 *N* sodium hydroxide were added and the organic bases were extracted with ether. The aqueous layer was neutralized with 80% acetic acid and the upper layer was decanted from the oil and clarified. A 50-cc. portion was taken from the total volume of 115 cc. and boiled with hydrochloric acid. The dried product resulting from this hydrolysis weighed 0.3 g. and melted at 233–242°. Thus, the principal product isolated is 5-benzamido-1-naphthol formed in about 53% yield.

Separation of Anilines.—A mixture consisting of 12.1 g. (0.1 mole) each of *o*-ethylaniline and *p*-ethylaniline was placed in 100 cc. of chloroform in a flask fitted with mechanical stirrer and 20.2 g. (0.11 mole) of triethylamine-SO₃ was added. While stirring, the temperature was allowed to rise gradually from 15 to 25° during a five-hour period. The white solid was filtered off at 7° and washed with hexane. It weighed 19.4 g., 64.2% yield, m.p. 101–103°. The identity of this material as the para isomer is shown by the fact that no depression in melting point occurs when it is mixed with an authentic sample of the para isomer. Furthermore, the ortho isomer yields an oil under these conditions.

Separation of Alcohols.—A mixture of 30 g. (0.5 mole) each of 2-propanol and 1-propanol was treated in 125 cc. of chloroform with 97 g. (0.525 mole) of triethylamine-SO₃. The clear solution was allowed to stand at room temperature for two and one-half days. The solvent was then evaporated under reduced pressure so that the liquid temperature did not exceed 40°. Addition of 200 cc. of hexane caused a layer separation and the lower layer weighing 177 g. was separated and cooled. Since crystallization could not be induced, a 3.5-g. (0.01 mole real) aliquot was added to 10 cc. of water containing 2.2 g. of benzylisothiuronium chloride. The vacuum-dried product obtained weighed 2.4 g., a 77.2% yield of the sulfuric ester of 1-propanol as the benzylisothiuronium salt; sintering point 113°, m.p. 115–116°.

Anal. Calcd. for C₁₁H₁₇N₂O₄S₂: C, 43.2; H, 5.6; S, 20.9. Found: C, 43.2; H, 5.8; S, 20.6.

***o*-Phenylphenol Sulfuric Ester.**—A 17-g. (0.1 mole) sample of *o*-phenylphenol was dissolved to a clear solution in 90 cc. of water by addition of 20 cc. of 5 *N* sodium hydroxide. Then 8.4 g. (0.1 mole) of sodium bicarbonate, 5.3 g. (0.05 mole) of sodium carbonate and 28 g. (0.15 mole) of triethylamine-SO₃ were added. The mixture was stirred for three hours at 45–50° to give a two-layer system. The cooled reaction mixture was extracted with ether. The two remaining lower layers were neutralized with dilute hydrochloric acid and again extracted with ether. The aqueous layer was salted to 15% concentration with potassium chloride at 50°, and the white solid was filtered off at 10° and washed with 15% potassium chloride–2% potassium hydroxide solution. The wet cake weighed 68.5 g. One-fourth of this was clarified from 75 cc. of water and re-salted. The dry product weighed 7.6 g., an 83% yield based on the carbon content.

Anal. Calcd. for C₁₂H₉KO₄S: C, 51.4; H, 3.1; S, 11.0; C/S, 12.0. Found: C, 38.5; H, 2.93; S, 8.62; C/S, 11.9.

8-Benzamido-1-naphthol Sulfuric Ester.—A 2.6-g. portion (0.01 mole) of 8-benzamido-1-naphthol was treated with triethylamine-SO₃ in aqueous carbonate solution as

described in the preparation of the ester of *p*-phenylphenol. The product weighed 4.3 g., a yield of 72%.

Under these same conditions 1-benzamido-5-naphthol was recovered unchanged.

Anal. Calcd. for C₁₇H₁₃KO₄NS: C, 53.4; H, 3.19; N, 3.68; S, 8.40; C/S, 17.0; N/S, 1.00. Found: C, 42.2; H, 3.34; N, 2.93; S, 6.57; C/S, 17.0; N/S, 1.03.

***p*-Ethylaniline Sulfamic Acid.**—Six grams (0.049 mole) of *p*-ethylaniline and 9.5 g. (5% excess) of triethylamine-SO₃ were dissolved in 50 cc. of chloroform. After warming at 60° for 15 minutes, the solution was cooled to 10° and the product was filtered off and washed with hexane. The crude dry product weighed 16.0 g. and melted at 75–80°. An 8.0-g. sample recrystallized from 50 cc. of chloroform gave 6.6 g. of white solid melting at 99–102°, an 89% yield as the triethylamine salt of *p*-ethylanilinesulfamic acid.

Anal. Calcd. for C₁₁H₁₂N₂O₃S: C, 55.6; H, 8.6; N, 9.28; S, 10.6. Found: C, 55.7; H, 8.48; N, 9.29; S, 10.8.

Under the same conditions, *o*-ethylaniline failed to yield a solid derivative.

2-Propanol Sulfuric Ester.—Six grams (0.1 mole) of 2-propanol was heated with 18.1 g. (0.1 mole) of triethylamine-SO₃ at a bath temperature of 125° for two hours. Since the viscous reaction mixture could not be crystallized, 4.5 g. (0.019 mole) of the mixture was dissolved in 20 cc. of water and the product was precipitated by addition of 4.0 g. (0.02 mole) of benzylisothiuronium chloride in 16 cc. of water. After recrystallization from water, 1.4 g. of dry product sintering at 141°, m.p. 142–144°, was obtained, a yield of 24%.

Anal. Calcd. for C₁₁H₁₇N₂O₄S₂: C, 43.2; H, 5.6; N, 9.2; S, 20.9. Found: C, 43.3; H, 5.0; N, 9.8; S, 20.7.

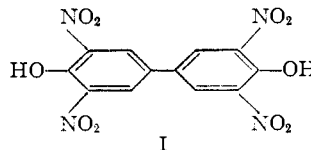
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The Dissociation of 3,3',5,5'-Tetranitro-4,4'-dihydroxydiphenyl in Methanol¹

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RECEIVED MAY 12, 1952

The effect of nitro groups ortho or para to the hydroxyl function of phenols on the acidity of the latter is well known. It was of interest to determine the acidity of a dihydric phenol in which two such arrangements were present in the same molecule, but isolated from each other. Accordingly, the dissociation constant of 3,3',5,5'-tetranitro-4,4'-dihydroxydiphenyl (I) was measured.



The absorption spectrum of I was determined in methanol, in methanol containing hydrogen chloride and in methanol containing sodium methoxide. Several of the curves so obtained are given in Fig. 1. The maximum at 355 μ is taken to represent the undissociated species. A solution $1.87 \times 10^{-4} M$ in I and $1.85 \times 10^{-4} M$ in hydrogen chloride increased the extinction coefficient from 5920 (in neutral methanol) to 6560, but a further increase (tenfold) in the hydrogen chloride concentration had a negligible effect. Curve 1, therefore, represents I in the undissociated form. Addition of in-

(1) Taken in part from the Master of Science thesis of W. J. D., March, 1952.