

tion of sulfuric acid, it has been reported¹ that this reagent will not effect such a ring closure for the simplest β -arylpropionic acid, hydrocinnamic acid, to yield α -hydrindone.

By varying the conditions for the reaction of hydrocinnamic acid in sulfuric acid it has been found possible to obtain a very pure product rapidly and conveniently although in only moderate yield.

The concentration of acid was varied from 15% fuming to 85% sulfuric acid, the time of heating from one minute to three hours and the reaction temperature from 100 to 160°. Optimum conversion was obtained by using 5% fuming sulfuric acid at 140° for five minutes. In each case the sulfuric acid (20 cc.) was heated to the desired temperature in an oil-bath, the hydrocinnamic acid (5 g., m. p. 49–50°) added with stirring and, at the end of the specified time, the reaction mixture poured over cracked ice (100–150 g.). The α -hydrindone was extracted with two 25-cc. portions of benzene. After drying over sodium sulfate, the benzene was removed by evaporation on a steam plate, leaving a pale yellow oil which crystallized on cooling to room temperature, maximum yield 1.2 g. (27%), m. p. 40–41°. A mixture of these crystals with the starting material was liquid at room temperature. The identity of the product was established further by preparation of the 2,4-dinitrophenylhydrazone, m. p. 254–255°. No starting material was isolated in any case.

The addition of boron fluoride or aluminum chloride to the sulfuric acid lowered the yield considerably.

(1) Von Miller and Rohde, *Ber.*, **23**, 1887 (1890).

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Some Schiff Base Hydrochlorides. A Test for Arylamines¹

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In the course of certain studies,³ a very simple color test was devised for the estimation of sulfanilamide and other arylamines. The test is not

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(3) H. D. Ratish, J. G. M. Bullowa; J. B. Ames and J. V. Scudi, *J. Biol. Chem.*, **128**, 297 (1939).

as sensitive (1 part in 200,000) as diazotization procedures,^{4,5} but its simplicity has made it useful in following various concentrates in a semi-quantitative way. Recently the Ehrlich reagent has been more rigorously standardized⁶ for the determination of sulfanilamide, although the reaction mechanism was left in doubt. It was therefore decided to record our observations.

The test consists in adding 1 cc. of 10% hydrochloric acid to 5 cc. of a 1% solution of cinnamaldehyde in alcohol followed by 5 cc. of a 2–4 mg. % solution of the arylamine. A yellow color is instantly formed. This is stable for several days, but unstable to alkali. Other aldehydes may be used, but not benzaldehyde. Toluenesulfonamide does not give the test. The sensitivity is increased ten-fold by performing the test in absolute alcohol in the presence of concentrated sulfuric acid.

The color producing substances were shown to be the somewhat labile hydrochlorides of the Schiff bases of sulfanilamide and sulfapyridine. These were converted to the free bases. In accord with the finding of Dimroth and Zoeppritz⁷ and Moore and Gale,⁸ the color appears to be produced by the halochromic effect of the acid upon the Schiff base. The compounds reported are not submitted as crystalline derivatives for the characterization of the arylamine, but as evidence of the mechanism of the color development.

Experimental

Schiff Base Hydrochlorides.—These were prepared essentially by the method of Dimroth and Zoeppritz⁷ with the exception that one mole of cinnamaldehyde was dissolved in alcohol prior to addition to the arylamine in dilute hydrochloric acid. Yields of 85–95% of the products were precipitated instantly as golden-orange plates. The cinnamylidene sulfanilamide hydrochloride, melting at 203–205° dec., was recrystallized with some hydrolysis from dilute hydrochloric acid. Calculated for $C_{16}H_{14}O_2N_2S \cdot HCl$: Cl, 11.01. Found: Cl, 11.35.

The cinnamylidene sulfapyridine hydrochloride was too labile to be crystallized. Washed with a minimal amount of alcohol and ether, the product melted at 178–180° dec. Calculated for $C_{20}H_{17}O_2N_3S \cdot HCl$: N, 10.52; Cl, 8.90. Found: N, 10.15; Cl, 9.65.

Free Bases.—Crystallization of cinnamylidene sulfanilamide hydrochloride from water gave 70–80% yields of the base, m. p. 213–215° dec. The melting point was unchanged when mixed with an authentic sample,⁹ although

(4) E. K. Marshall, Jr., *J. Biol. Chem.*, **122**, 263 (1938).

(5) J. V. Scudi, *ibid.*, **122**, 539 (1939).

(6) A. E. A. Werner, *Lancet*, **1**, 1095 (1938).

(7) O. Dimroth and R. Zoeppritz, *Ber.*, **35**, 984 (1902).

(8) F. J. Moore and R. D. Gale, *THIS JOURNAL*, **30**, 394 (1908).

(9) W. H. Gray, G. A. H. Buttle and D. Stephenson, *Biochem. J.*, **31**, 724 (1937).

it was depressed when mixed with a sample of the hydrochloride. Recrystallized from dilute hydrochloric acid, the free base gave the hydrochloride along with hydrolysis products. The cinnamylidene sulfapyridine hydrochloride was dissolved in cold 2% sodium hydroxide, and precipitated by neutralizing with acetic acid; pale yellow needles, m. p. 208–210° dec. The melting point was depressed by mixing with the hydrochloride. Calculated for $C_{20}H_{17}O_2N_3S$: N, 11.57. Found: N, 11.32.

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The Directive Influence of the Electric Moment on Substitution in the Benzene Ring

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A few years ago¹ a comparison of the electric moments of the monosubstituted benzene derivatives which direct substitution to the ortho and para positions with those which direct substitution to the meta position resulted in the following rule: *in general, if the electric moment of a monosubstituted benzene derivative is greater than $\sim 2.07D$, the next substituted group will be directed to the meta position; if the moment is less than $\sim 2.07D$, the next group will be directed to the ortho and para positions.*

In Table I there are listed the monosubstituted benzene derivatives whose moments have been determined since 1935. The compounds are divided into two groups depending upon whether

TABLE I

ELECTRIC MOMENTS AND THE OBSERVED ORIENTING INFLUENCE

Ortho-para substitution compound, phenyl	$\mu \times 10^{18}$ e. s. u.	Meta substitution compound, phenyl	$\mu \times 10^{18}$ e. s. u.
$-\text{CH}_3-\text{C}_6\text{H}_5$	0.33	$-\text{CONHNHCOC}_6\text{H}_5$	2.63
$-(\text{CH}_2)_2\text{C}_6\text{H}_5$.45	$-\text{CONHNH}_2$	2.70
$-(\text{CH}_2)_3\text{C}_6\text{H}_5$.48	$-\text{CON}=\text{N}-\text{COC}_6\text{H}_5$	2.85
$-(\text{CH}_2)_4\text{C}_6\text{H}_5$.50	$-\text{COCl}$	3.33
$-(\text{CH}_2)_5\text{C}_6\text{H}_5$.52	$-\text{CONHNHCOC}_6\text{H}_4\text{CH}_3$	3.38
$-(\text{CH}_2)_6\text{C}_6\text{H}_5$.52	$-\text{C}-\text{C}_6\text{H}_5$	3.45
$-(\text{CH}_2)_7\text{C}_6\text{H}_5$.55	$\begin{array}{c} \parallel \\ \text{N}-\text{O}-\text{N} \\ \parallel \\ \text{CONHNHCOC}_6\text{H}_4\text{Cl} \end{array}$	3.82
$-(\text{CH}_2)_8\text{CHC}_6\text{H}_5(\text{CH}_2)_4\text{C}_6\text{H}_5$.85	$\begin{array}{c} \parallel \\ \text{O} \\ \text{CONHNHCOC}_6\text{H}_4\text{Cl} \end{array}$	4.08
$-(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$.98	$-\text{S}-\text{C}_6\text{H}_5$	
$-(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$	1.51	$-\text{SO}_2\text{Cl}$	4.47
$-\text{CHOHCH}_3$	1.55	$-\text{CONHNHCOC}_6\text{H}_4\text{NO}_2$	5.57
$-(\text{CH}_2)_2\text{CH}_2\text{OH}$	1.71		
$-\text{CH}_2\text{COOH}$	1.75		
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}$	1.76		
$-\text{CH}=\text{CHCOOH}$	1.78		
$-\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$	1.78		
$-\text{OOC}_6\text{H}_5$	1.92		
$-\text{CH}=\text{CHCOOCH}_3$	1.93		
1- $\text{C}_{10}\text{H}_7\text{Cl}$	1.51		
2- $\text{C}_{10}\text{H}_7\text{Cl}$	1.65		

(1) Svirebely and Warner, THIS JOURNAL, 57, 655 (1935).

the second substituted group is directed to the ortho and para or to the meta position. An examination of the data shows that in all of these compounds the rule is obeyed. Compounds which contained unsaturated bonds in the monosubstituted group such as the styrenes, diazoaminobenzenes, cinnamyl derivatives, etc., where the side chain is first attacked, have not been included in the table although their moments are listed in the literature.

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The Solubility of Silicon Tetrafluoride in Organic Solvents. Behavior of Such Solutions

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In a search for practical solvents for silicon tetrafluoride, its solubility in a number of organic solvents at room temperature (27–33°) has been determined. Saturated solutions were prepared by circulating the purified gas through the various solvents, contained in an absorption tower or an Orsat pipet, in a closed system at atmospheric pressure until saturation appeared to be attained. The non-aqueous solvents, except absolute ethyl alcohol, were used as purchased without additional purification. The rate at which the gas dissolved seemed to depend largely on the fluidity of the solvent. The concentration of silicon tetrafluoride in the solutions was calculated from the determination of fluorine in weighed samples. The saturated solutions remained clear, showing no precipitation of silica, when allowed to stand overnight out of direct contact with air. The results obtained are given in the table below. Owing to lack of temperature control and the possibility that the more viscous solutions may have been incompletely saturated, the results are regarded as approximate, but of practical value.

The data show that the solubility of silicon tetrafluoride in the homologous series of monohydroxy alcohols decreases definitely and quite regularly with an increase in the number of carbon atoms and for the same number of carbon atoms with an increase in the number of hydroxyl groups. Compounds containing ether groups (diethylene glycol), carbonyl groups (acetone and pyruvic acid), and carboxyl groups (acetic and pyruvic acids) were found not to be very good solvents for silicon tetrafluoride.