

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.

FROM THE MEDICAL SERVICE AND THE  
DEPARTMENT OF PATHOLOGY  
HARLEM HOSPITAL, DEPARTMENT OF HOSPITALS  
NEW YORK, N. Y. RECEIVED MAY 18, 1939

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

BY W. J. SVIRBELY

A few years ago<sup>1</sup> 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	$-\text{CONHNHCOC}_2\text{H}_5\text{CH}_3$	3.38
$-(\text{CH}_2)_6\text{C}_6\text{H}_5$	.52	$-\text{C}-\text{C}-\text{C}_6\text{H}_5$	3.45
$-(\text{CH}_2)_7\text{C}_6\text{H}_5$	.55	$\begin{array}{c} \parallel \\ \text{N}-\text{O}-\text{N} \\ \parallel \\ \text{CONHNHCOC}_2\text{H}_5\text{CH}_3 \end{array}$	3.82
$-(\text{CH}_2)_8\text{CHC}_6\text{H}_5(\text{CH}_2)_4\text{C}_6\text{H}_5$	.85	$-\text{CONHNHCOC}_2\text{H}_5\text{CH}_2\text{Cl}$	4.08
$-(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$	.98	$\begin{array}{c} \parallel \\ \text{O} \\ \text{S}-\text{C}_6\text{H}_5 \end{array}$	4.47
$-(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$	1.51	$-\text{SO}_2\text{Cl}$	4.47
$-\text{CHOHCH}_3$	1.55	$-\text{CONHNHCOC}_2\text{H}_5\text{NO}_2$	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) Svirbely and Warner, THIS JOURNAL, 57, 655 (1936).

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.

CHEMISTRY LABORATORY  
THE UNIVERSITY OF MARYLAND  
COLLEGE PARK, MD. RECEIVED JULY 24, 1939

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

BY GRADY TARBUTTON, E. P. EGAN, JR., AND S. G. FRARY

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.

TABLE I  
SOLUBILITY OF SILICON TETRAFLUORIDE AT ROOM TEMPERATURE (27-33°) AND TOTAL PRESSURE OF 750-760 MM.

Solvent	G. SiF <sub>4</sub> /100 cc. solvent	Wt. % of SiF <sub>4</sub> in soln.
Methyl alcohol, absolute	..	32.8
Methyl alcohol, 94% by wt.	..	39.0
Ethyl alcohol, absolute	57.2	36.4
Ethyl alcohol, 96.1% by wt.	60.8	37.8
Ethyl alcohol, 95% (U. S. P.)	61.4	38.1
Ethyl alcohol, 94.3% by wt.	61.5	38.1
Ethyl alcohol, 92.6% by wt.	63.4	38.8
Ethyl alcohol, 91.0% by wt.	63.9	39.0
Isopropyl alcohol, 98%	39.4	28.2
n-Butyl alcohol, 98% (U. S. P.)	30.4	23.4
Amyl alcohols (fusel oil)	20.9	17.3
Glycol, c. p.	..	26.2
Diethylene glycol, c. p.	..	17.6
Glycerol, c. p.	..	5.7
Acetone, c. p. anhyd.	3.2	3.1
Acetic acid (glacial)	1.1	1.1
Pyruvic acid, tech. (38-45%)	..	4.4

In addition to these quantitative data, it was found that silicon tetrafluoride is sparingly soluble in benzene and trichloroethylene, and insoluble in carbon tetrachloride at room temperature.

On the addition of 9% by weight of water to the saturated solution in 95% alcohol (U. S. P.), a gelatinous precipitate of hydrated silica was formed. However, when the original solution was subjected to vacuum distillation at room temperature, silicon tetrafluoride was evolved until a solution containing approximately 26.5% of the gas remained, which corresponds to a mole ratio of alcohol to silicon tetrafluoride of approximately 6:1. On adding an equal volume of water to the residual solution from the vacuum distillation, no precipitate formed, possibly because the silicon tetrafluoride had combined chemically with the ethyl alcohol. Subsequent addition of a soluble barium salt precipitated 95% of the fluorine as pure barium fluosilicate. This reaction offers a convenient method for preparing barium fluosilicate of high purity.

When saturated solutions in glycol were distilled in a vacuum at room temperature, 50 and 100°, the residual solutions contained fluorine equivalent to 26.2, 24.5, and 2.8% silicon tetrafluoride, respectively; on addition of water to them, a precipitate was formed in each case.

The above information is of interest in that such solutions in organic solvents may furnish the basis for the synthesis of organic fluorine compounds as well as a means of preparing pure fluorine salts. However, the authors do not plan

to pursue the investigation further and, therefore, wish to relinquish the problem to others who may be interested in it.

TENNESSEE VALLEY AUTHORITY  
DEPARTMENT OF CHEMICAL ENGINEERING  
WILSON DAM, ALABAMA RECEIVED MAY 8, 1939

### Occurrence of the Syringyl Radical in Plant Products

BY EINAR WEST, A. S. MACINNES, JOSEPH L. MCCARTHY AND HAROLD HIBBERT

It has now been shown that treatment of jute fiber, rye straw and corn stalks with a 2% solution of hydrogen chloride in anhydrous ethanol, according to the method described for the ethanolysis of spruce and maple woods,<sup>1</sup> gives rise to typical ethanolysis products, namely, ethanol lignin and a mixture of volatile oils. The yields of ethanol lignin and volatile oils are of the same order of magnitude as those obtained from spruce and maple woods. The presence of the syringyl radical has been established in the volatile oils from each of these fibers. Thus, following the procedures previously described,<sup>2</sup>  $\alpha$ -ethoxypropiosyringone as the *p*-nitrobenzoate (m. p. 141-142°), syringoylacetalddehyde as the mono-semicarbazone (m. p. 207-208°), and syringaldehyde as the 2,4-dinitrophenylhydrazone (m. p. 235-235.5°), were isolated. Mixed melting points with authentic specimens showed no depression.

These, and previous results with hard woods,<sup>1,2</sup> would seem to point to the presence of syringyl derivatives in the lignin constituents of all angiosperms, for example as indicated in corn and rye (monocotyledons) and in jute and maple (dicotyledons).

(1) Brickman, Pyle, McCarthy and Hibbert, *THIS JOURNAL*, **61**, 868 (1939).

(2) Hunter, Cramer and Hibbert, *ibid.*, **61**, 516 (1939); Pyle, Brickman and Hibbert, *ibid.*, **61**, 2198 (1939).

DIVISION OF INDUSTRIAL AND CELLULOSE CHEMISTRY  
MCGILL UNIVERSITY  
MONTREAL, CANADA RECEIVED JUNE 30, 1939

### Reaction of *p*-Fluorophenol with Benzene and Aluminum Chloride

BY ARTHUR W. WESTON<sup>1</sup> AND C. M. SUTER

Recently it was found<sup>2</sup> that in the deethylation of *p*-fluorophenetole with aluminum chloride in benzene solution a by-product was obtained in

(1) Sharp and Dohme Post-Doctorate Fellow 1938-1939.

(2) Suter, Lawson and Smith, *THIS JOURNAL*, **61**, 163 (1939).