

NOTES

Optical Properties of Sulfamic Acid

BY W. M. D. BRYANT

Sulfamic acid, $\text{NH}_2\cdot\text{SO}_3\text{H}$, has been the subject of crystallographic studies at widely different times by at least two experimenters.^{1,2} Only very meager optical data incidental to goniometric observations were reported, and these were inadequate for purposes of identification. Recently M. E. Cupery³ described a new process for industrial scale preparation of pure sulfamic acid and kindly placed some of this substance at the writer's disposal for optical crystallographic examination.

The methods employed in this study were those described in an earlier paper.⁴ The refractive indices and optic axial angles were measured in green monochromatic light (5461 Å.) from the mercury arc. Due to the weak dispersion optic axial angles in white light were not appreciably different. The observed optical data are tabulated.

Refractive indices at $25 \pm 3^\circ$: $\alpha = 1.553$; $\beta = 1.563$; $\gamma = 1.568$ all ± 0.003 .

Optic axial angle: $2H_a = 65 \pm 1^\circ$; $2H_0 = 120 \pm 5^\circ$; $2V = 64^\circ$ (calculated from $2H_a$ and $2H_0$ by the tangent relation); $2V = 63^\circ$ (calculated from $2H_a$ and β).

Dispersion: weak, indeterminate.

Optical character: negative.

Crystal system: orthorhombic bipyramidal, according to both Fock and Jaeger. However, these investigators each used a different setting, so that the crystallographic *b*- and *c*-axes are transposed in their respective treatments.

Crystal habit: tablets and compact prisms from cold aqueous solution; large lozenge-shaped plates on cooling hot aqueous solution; the fused material is glassy.⁵

Optical orientation: the optic axial plane coincides with the principal pinacoid, which is 001 according to Jaeger or 010 according to Fock. The obtuse bisectrix apparently coincides with the *a*-axis for both settings.

The only numerical optical constant found in the earlier literature is the optic axial angle re-

(1) A. Fock, *Z. Krist.*, **14**, 531 (1888); E. Raschig, *Ann.*, **241**, 177 (1887).

(2) F. M. Jaeger, *Verslag Akad. Wetenschappen, Amsterdam*, [1] **35**, 68 (1926).

(3) M. E. Cupery, *Ind. Eng. Chem.*, **30**, 627 (1938).

(4) W. M. D. Bryant, *THIS JOURNAL*, **60**, 1394 (1938).

(5) The writer is indebted to Dr. Cutler D. West (private communication) for a measurement of the refractive index of the amorphous phase obtained on cooling molten sulfamic acid. The value reported, n_D^{25} 1.5048, was measured on an Abbe refractometer using the pure Lamotte product.

ported by Fock¹ as $2E = \text{circa } 85^\circ$. $2E$ calculated from the present $2H_a$ value is about $109 \pm 2^\circ$. Since no indications of a second crystal modification of sulfamic acid have been obtained to date, it is believed that Fock's $2E$ value is erroneous.

AMMONIA DEPARTMENT

E. I. DU PONT DE NEMOURS AND CO., INC.

WILMINGTON, DELAWARE

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A Method of Coupling Organic Radicals by Means of the Grignard Reagent; A Correction

BY JOHN H. GARDNER AND LIONEL JOSEPH

In a paper of this title published in 1929¹ the statement was made that when iso- and *s*-butylmagnesium bromides were allowed to react with silver bromide, there is formed a mixture from which no pure compound could be isolated. In connection with some other work in progress in this Laboratory, some results were obtained which led us to doubt the correctness of this statement. Consequently, the experiments were repeated using more effective distilling apparatus than was available at the time the earlier work was done. In this way, we obtained the dimethylhexanes which would be expected from the coupling of the radicals in high purity but in rather poor yield. The other products were gases, very likely the corresponding butanes and butenes, although definite proof of their identity has not as yet been obtained. It is thus definitely established that in all cases so far studied of the action of Grignard reagents on silver bromide, there is no rearrangement.

Experimental

Reaction of Iso- and *s*-Butylmagnesium Bromides with Silver Bromide.—To an ethereal solution of 1 mol of the Grignard reagent in a flask provided with a mechanical stirrer and two reflux condensers, and cooled in an ice-salt bath, there was added a slight excess of silver bromide, with continual stirring. The mixture was stirred in the cooling bath for a half hour and then for an hour at the boiling point. After the addition of very dilute hydrochloric acid, the organic products were separated by steam distillation, dried over calcium chloride and distilled through a 70-cm. Vigreux column. In both cases, after

(1) J. H. Gardner and P. Bergstrom, *THIS JOURNAL*, **51**, 3375 (1929).

the ether had distilled, the distillation curve rose sharply and the hydrocarbon fraction was collected over an approximately 5° range. The products were boiled for an hour over metallic sodium to remove any alkyl halide and redistilled. There was thus obtained from isobutylmagnesium bromide, 20 g. (37.5%) of 2,5-dimethylhexane, b. p. (755 mm.) 107–108.5°, d_{20}^4 0.6911, n_D^{21} 1.3922. Egloff² gives b. p. (760 mm.) 109.3°, d_{20}^4 0.6949, n_D^{20} 1.39295 as the preferred values. Similarly, from *s*-butylmagnesium bromide, there was obtained 7.5 g. (13%) of 3,4-dimethylhexane, b. p. (757 mm.) 116–117°, d_{22}^4 0.7199, n_D^{26} 1.4040. Egloff² (p. 54) gives as the preferred values, b. p. (760 mm.) 117.8°, d_{20}^4 0.7195, n_D^{20} 1.4045.

(2) G. Egloff, "Physical Constants of Hydrocarbons," Vol. I, Reinhold Publishing Company, New York, 1939, p. 53.

DEPARTMENT OF CHEMISTRY
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Morpholine Condensations

BY CHESTER B. KREMER, M. MELTSNER AND
L. GREENSTEIN

In the course of researches dealing with the condensation of secondary amino alcohols with *o*- and *p*-chloronitrobenzenes, we also investigated the condensing ability of the secondary amine, morpholine. The products obtained have been described by others in a recent article,¹ but were prepared in a manner somewhat different from ours. We are therefore recording our procedures and at the same time including data for one compound as yet unreported.

The general method of procedure was to reflux molar quantities of morpholine and the chloronitrobenzene in the presence of anhydrous sodium carbonate for approximately four hours. The reaction mixture was then steam distilled to rid it of unreacted material. A dark oil, slowly solidifying, remained in the distillation flask in the run with *o*-chloronitrobenzene, an orange-red solid remaining in the case of the para compound. These were recrystallized from benzene: N-(*o*-nitrophenyl)-morpholine, light orange product, m. p. 40–41°; N-(*p*-nitrophenyl)-morpholine, yellow in color, m. p. 149–150°.

Another method used in preparing N-(*p*-nitrophenyl)-morpholine was as follows: 1.0 g. of phenylmorpholine was added to 4 cc. of concentrated sulfuric acid and 4 cc. of concentrated nitric acid added dropwise. The reaction mixture turned red and foamed violently. When the reaction was complete, the mixture was poured

(1) R. H. Harradence and F. Lions, *J. Proc. Roy. Soc. N. S. Wales*, **70**, 406–412 (1937).

onto ice and finally filtered. The filtrate yielded orange crystals of the desired product.

Reduction of the nitro compounds with tin and hydrochloric acid yielded the previously reported N-(*p*-aminophenyl)-morpholine² and the new compound, N-(*o*-aminophenyl)-morpholine, m. p. 98–98.5°; calculated N, 15.73; found, 15.87.

N-(*o*-Aminophenyl)-morpholine can be purified by sublimation, yielding beautiful white platelets. In the pure state the compound is quite stable, but when somewhat impure discolors fairly rapidly on standing.

The present work proves that the compound formed in treating *o*-chloronitrobenzene with diethanolamine is not N-(*o*-aminophenyl)-morpholine as had been tentatively advanced³ in a previous publication.

(2) H. A. Lubs, U. S. Patent 2,004,763 (1935).

(3) Meltsner, *et al.*, *This Journal*, **59**, 2660 (1937).

LABORATORIES OF ORGANIC CHEMISTRY
THE CITY COLLEGE
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NEW YORK, N. Y.

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Hydrogen and Deuterium Exchange between Nitramide and Water

BY V. K. LA MER AND SEYMORE HOCHBERG

On the basis of measurements of the decomposition rate of proto-nitramide dissolved in mixtures of H₂O and D₂O, La Mer and Greenspan¹ suggested two mechanisms for the decomposition. The first assumed that only one H of nitramide exchanges promptly on being dissolved in D₂O; the second that both H atoms of nitramide exchange promptly.

On the basis of the data then available it was impossible to decide whether the decomposing substrate was HDN₂O₂ or D₂N₂O₂ when proto-nitramide is dissolved in D₂O.

We now present evidence based upon two independent procedures that both H atoms are exchanged promptly for D atoms in a solvent of high deuterium content, and that the rate-determining step in D₂O involves D₂N₂O₂.

I. Decomposition Rate of D₂N₂O₂.—Deutero-nitramide was prepared by the reaction of potassium nitrocarbamate with 99% D₂O and SO₃. On reaction of this nitramide with water (0.01 *N* hydrochloric acid) the observed rate constant, based upon manometric measurement² of

(1) La Mer and Greenspan, *Trans. Faraday Soc.*, **197**, XXXIII, Part 0, 1266 (1937).

(2) Greenspan, La Mer and Liotta, *This Journal*, **59**, 1606 (1937).

the nitrous oxide formed, is $k^* = 387 \times 10^{-5}$ min.⁻¹ (decadic logs) at 35°, in excellent agreement with Baughan and Bell's³ $k^* = 386 \times 10^{-5}$ min.⁻¹ obtained for proto-nitramide in H₂O.

Partially deuterized nitramide prepared from 48% D₂O and sulfur trioxide yielded $k^* = 125.5 \times 10^{-5}$ min.⁻¹ at 24.84° in 0.01 *N* hydrochloric acid in H₂O. La Mer and Greenspan¹ obtained $k^* = 126.6 \times 10^{-5}$ min.⁻¹ under the same conditions for proto-nitramide in H₂O.

II. Direct Exchange.—Proto-nitramide was dissolved in D₂O (temp., approx. 5°). The nitramide produced by exchange was extracted with ether (dried over sodium) by the freezing method of Marlies and La Mer.^{4,5} The exchange and extraction required less than one hour.

To ensure the complete removal of possible traces of deuterio-solvent, the nitramide was kept over phosphorus pentoxide for one week. It was then decomposed by gentle heating in the presence of a trace of anhydrous sodium carbonate. The liberated water was redistilled and the density determined by the falling drop method.⁶

The following results show that the deuterium content of the nitramide approximated the deuterium content of the water from which it had been extracted.

Mole fraction of D in the solvent water in which exchange takes place	0.28	0.87	0.97
Mole fraction of D in the water from the decompn. of the extracted nitramide	.25	.65	.94

There is no point in calculating an exchange constant because, due to the method of extraction, the equilibrium temperature and the equilibrium concentration of D₂O cannot be held constant. Since deuterio-nitramide decomposes in water at the same rate as proto-nitramide and since deuterio-nitramide containing more than one atom of D per molecule may be extracted from a solution of proto-nitramide in D₂O, it is evident that both atoms of hydrogen in nitramide exchange with D₂O before decomposition occurs.

DEPARTMENT OF CHEMISTRY
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(3) Baughan and Bell, *Proc. Roy. Soc. (London)*, **A894**, 158, 464-478 (1937).

(4) Marlies and La Mer, *THIS JOURNAL*, **57**, 2008 (1935).

(5) Marlies, La Mer, and Greenspan, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., Vol. 1, p. 72.

(6) Hochberg and La Mer, *Ind. Eng. Chem., Anal. Ed.*, **9**, 291 (1937).

Ferric Chloride as a Condensing Agent

BY W. M. POTTS AND R. J. DOBSON

A further investigation¹ of anhydrous ferric chloride as a condensing agent in the alkylation of benzene has been carried out using butyl alcohols.

1. Condensation products were not formed with *n*-butyl alcohol and benzene. This agrees with the results reported by Huston and Hsieh² using aluminum chloride and primary alcohols up to and including *n*-hexyl alcohol.

2. *s*-Butyl alcohol gave evidence of a reaction but no product was identified. With aluminum chloride under the same conditions, a 69% yield of *s*-butylbenzene was obtained. Huston and Hsieh² reported a 25-28% yield, while Tzukervanik and Tokareva³ reported a 70% yield. The *s*-butylbenzene was identified by its physical constants and the diacetamino derivative, m. p. 193°.⁴

3. At room temperature, one mole of *t*-butyl alcohol, one mole of ferric chloride and five moles of benzene gave an 82% yield of *t*-butylbenzene. With aluminum chloride under the same conditions a 50% yield of *t*-butylbenzene was obtained. Using two moles of *t*-butyl alcohol, one mole of benzene and one mole of ferric chloride, a 24% yield of mono-*t*-butylbenzene and 64% of 1,4-di-*t*-butylbenzene was obtained. The acetamino derivative of the former melted at 168°.⁴ The latter was identified by the method reported by Potts and Carpenter.¹

Better yields of *t*-butylbenzene were obtained with ferric chloride than with aluminum chloride, but ferric chloride does not effect the condensation of primary and secondary alcohols with benzene. Higher temperatures and larger quantities of ferric chloride lower the yields of *t*-butylbenzene.

(1) Potts and Carpenter, *THIS JOURNAL*, **61**, 663 (1939).

(2) Huston and Hsieh, *ibid.*, **58**, 439 (1936).

(3) Tzukervanik and Tokareva, *J. Gen. Chem. (U. S. S. R.)*, **5**, 764 (1935); *C. A.*, 442 (1936).

(4) Ipatieff and Schmerling, *THIS JOURNAL*, **59**, 1056 (1937).

DEPARTMENT OF CHEMISTRY AND
CHEMICAL ENGINEERING
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α -Hydrindone

BY CHARLES C. PRICE AND FREDERICK M. LEWIS

Although ring closures of many β - and γ -aryl butyric acids to the corresponding cyclic ketones have been accomplished successfully by the ac-

tion of sulfuric acid, it has been reported¹ that this reagent will not effect such a ring closure for the simplest β -arypropionic 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).

NOYES CHEMICAL LABORATORY
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Some Schiff Base Hydrochlorides. A Test for Arylamines¹

BY J. V. SCUDI, H. D. RATISH AND J. G. M. BULLOWA²

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

(1) Presented at the Baltimore meeting of the American Chemical Society, April, 1939.

(2) These studies received financial support from the Littauer Pneumonia Research Fund, from the Metropolitan Life Insurance Company, and from Mr. Bernard M. Baruch, Mr. Bernard M. Baruch, Jr., Miss Belle N. Baruch, and Mrs. H. Robert Samstag.

(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.

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 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	$-\text{CONHNHCOC}_2\text{H}_5\text{CH}_3$	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	$\begin{array}{c} \parallel \\ \text{N}-\text{O}-\text{N} \\ \parallel \end{array}$	
$-(\text{CH}_2)_8\text{CHC}_6\text{H}_5(\text{CH}_2)_4\text{C}_6\text{H}_5$.85	$-\text{CONHNHCOC}_6\text{H}_4\text{Cl}$	3.82
$-(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$.98	$\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}-\text{C}_6\text{H}_5 \end{array}$	4.08
$-(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{CHC}_6\text{H}_5(\text{CH}_2)_2\text{C}_6\text{H}_5$	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) Svirbely 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.

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 ₄ /100 cc. solvent	Wt. % of SiF ₄ 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 ethanolsis of spruce and maple woods,¹ gives rise to typical ethanolsis 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,² α -ethoxypropiosyringone as the *p*-nitrobenzoate (m. p. 141–142°), syringoylacetaldehyde 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,^{1,2} 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).

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

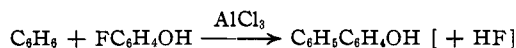
BY ARTHUR W. WESTON¹ AND C. M. SUTER

Recently it was found² 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).

considerable amount. This was phenolic in nature and in an impure condition melted at 153–156°. It has now been determined that the same substance results from heating *p*-fluorophenol with benzene and aluminum chloride. When purified it melted at 163.5–164° and upon oxidation gave a high yield of benzoic acid. No depression of the melting point occurred when a sample of the unknown was mixed with *p*-hydroxybiphenyl. Hence



p-fluorophenol must react as shown and the *p*-hydroxybiphenyl obtained in the deëthylation of *p*-fluorophenetole also results from this reaction.

Attempts to extend the reaction in various directions have been without success. Because aromatic fluorine may be under some conditions

replaced by chlorine,³ it seemed possible that *p*-chlorophenol was an intermediate in the reaction. However, *p*-chlorophenol showed no activity toward benzene in the presence of aluminum chloride. None of the corresponding hydroxybiphenyl was isolated when *p*-fluorophenol and aluminum chloride were heated with toluene or chlorobenzene.

By heating a mixture of 3 g. of *p*-fluorophenol, 7 ml. of benzene and 7 g. of aluminum chloride under reflux for two and one-half hours there was obtained about 1 g. of *p*-hydroxybiphenyl, m. p. 164°. The 51 g. obtained in the deëthylation of *p*-fluorophenetole² corresponds to 13% of the *p*-fluorophenol reacting with the benzene.

(3) Bacon and Gardiner, *J. Org. Chem.*, **3**, 281 (1938).

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COMMUNICATIONS TO THE EDITOR

SYNTHETIC AND NATURAL ANTIHEMORRHAGIC COMPOUNDS

Sir:

In our last communication [THIS JOURNAL, **61**, 1923 (1939)] the reported antihemorrhagic activity of 2-methyl-1,4-naphthoquinone was a minimum assay result. The total comparative activity of this compound is given in Table I. It is by no means as active as vitamin K [Ansbacher and Fernholz, *ibid.*, **61**, 1924 (1939)] or as low in activity as reported by Thayer, *et al.*, [*ibid.*, **61**, 1932 (1939)] and would seem to provide an effective, cheap, synthetic substitute for vitamin K. This compound, like phthiocol and others, is capable of maintaining the prothrombin level of chick blood at a normal value when sufficient is given.

We have purified or synthesized and tested a number of naphthoquinones and related compounds (Table I). Assays were conducted and results expressed as noted previously [*ibid.*, **61**, 1923 (1939)]. Entirely negative results were obtained with 1,4-benzoquinone, naphthalene, 1,4-naphthoquinone, anthraquinone, 1,2-dihydroxyanthraquinone, and hydrolapachol at levels of 100 mg. or more per kg. of diet. Thayer, *et al.*,

[*ibid.*, **61**, 1932 (1939)] have reported some activity in 1,4-naphthoquinone. Fieser, *et al.*, [*ibid.*, **61**, 1925 (1939)] have indicated activity in lomatiol, lapachol and hydrolapachol. We have previously found lomatiol and lapachol to be inactive [*ibid.*, **61**, 1923 (1939)]. These other workers employ assay methods which require only twenty-four hours or less but which are, in our experience, likely to give misleading results.

TABLE I
ANTIHEMORRHAGIC ACTIVITY OF NAPHTHOQUINONES

Substance	Level fed per kg. of diet, mg.	Activity in terms of cc. of ref. standard per g. ^a
2-Methyl-1,4-naphthoquinone	10	> 2400
2-Methyl-1,4-naphthoquinone	2.5	5150
2-Hydroxy-1,4-naphthoquinone	75	139
Phthiocol	20	287
Phthiocol ethyl ether	15	100
Phthiocol octadecyl ether	20	95
Phthiocol phytol ether	20	< 50
Phthiocol monoacetate	15	420
Phthiocol triacetate	15	192
Alfalfa concentrate	0.5	> 53600
Alfalfa concentrates ^b	0.2 to 0.3	63000

^a Standard hexane extract of dried alfalfa representing 1 g. per cc. ^b From preliminary assays of alfalfa preparations (E. A. Doisy, P. Karrer).