[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Nitration of Organosilicon Compounds with Copper Nitrate

BY ROBERT A. BENKESER AND PHILIP E. BRUMFIELD

Phenyltrimethylsilane and benzyltrimethylsilane were successfully nitrated with copper nitrate trihydrate in an acetic anhydride solvent. In the case of the phenyltrimethylsilane there was obtained a 30/40/30 ratio of ortho/meta/para isomers. This would indicate that under the conditions of the experiment the trimethylsilyl group is a *weak* ortho–para director. With benzyltrimethylsilane there was obtained an 80/20 ratio of ortho to para nitro isomers. The copper nitrate reagent seems to have certain advantages in nitrating organosilanes possibly because it affords a relatively non-acidic nitrating medium.

The aromatic carbon–silicon bond in mixed trialkylarylsilanes usually undergoes cleavage rather readily in the presence of acidic reagents.[1] Thus: $(\text{alkyl})_3\text{Si}(\text{aryl}) \xrightarrow{\text{HX}} (\text{alkyl})_3\text{Si-X} + (\text{aryl})\text{-H}$. Possibly because of this tendency to cleave only a few reports have appeared describing the successful nitration of silanes of this type.[1d,2]

Because of the current interest in the electrical effects of a trimethylsilyl group attached to an aromatic nucleus[3] it seemed particularly appropriate to study the nitration of some trimethylsilyl derivatives and to determine the ratio of the isomers formed. Such a study would enable one to determine directly the orienting influence of a trimethylsilyl group.

In order to minimize the loss of the aromatic nucleus during the reaction, a relatively non-acidic nitrating agent was sought. A mixture of copper nitrate[4] in acetic anhydride was found fairly effective in this regard, since by means of this reagent it was possible to nitrate phenyltrimethylsilane and benzyltrimethylsilane without excessive cleavage.

Nitration of Phenyltrimethylsilane.—This compound was nitrated in 65% yield with copper nitrate in acetic anhydride. A mixture of the ortho (30%), meta (40%) and para (30%) nitro-isomers was obtained along with 25% nitrobenzene as cleavage product.

The ortho isomer was easily separated from the reaction product by fractionation at reduced pressure through an efficient column (Todd column with helices packing), since its boiling point at 10 mm. is nine degrees lower than that of the meta–para mixture.

The separation of the meta and para isomers was much more difficult since it is estimated that their boiling points differ by about three degrees at 10 mm. A separation of these two was accomplished by dissolving them in pentane and then cooling this solution in Dry Ice. The para isomer separates as a solid under these conditions and can be filtered off. The filtrate now enriched in meta isomer was again carefully fractionated and the higher boiling fractions again cooled in Dry Ice. By successive treatments of this sort the meta isomer was enriched to the point where it was judged to be 95% pure (see Table II). The solid para isomer can be further purified by crystallization from pentane. The physical constants of these compounds are listed in Table I.

The identification of these isomers was accomplished by cleaving off the trimethylsilyl group with bromine. The bromonitrobenzenes thus obtained were identified by mixed melting points with authentic samples. The ortho nitro isomer was found to undergo bromine cleavage with great difficulty. As a result one hesitates to base its identification on such a comparatively low yield of *o*-bromonitrobenzene. Consequently the ortho nitro compound was reduced to the amine which in turn could be cleaved in 80% yield to 2,4,6-tribromoaniline. The latter product establishes this nitro-isomer as either the ortho or para. However the identity of the para isomer had been previously established by bromine cleavage. It was adjudged to be a solid melting at 39°. Hence by elimination the identity of the ortho isomer was confirmed.

The relative amounts of the meta and para isomers formed in the nitration were determined by a procedure similar to that described by Westheimer[5] for use on nitrated mercurials. Essentially the procedure consisted of cleaving the meta and para isomer mixture with bromine and iron filings to a mixture of *m*- and *p*-bromonitrobenzene. This mixture was then treated with piperidine which reacts preferentially with *p*-bromonitrobenzene. A titration with silver nitrate estimates the bromide ion which corresponds to the amount of para isomer in the mixture. The success of such a determination obviously depends on the quantitative removal of the trimethylsilyl group with bromine. It was found that catalytic amounts of iron filings greatly facilitate this cleavage and help promote its quantitative nature.

Nitration of Benzyltrimethylsilane.—It was possible to nitrate benzyltrimethylsilane with copper nitrate in acetic anhydride in an average yield of 66%. The amount of cleavage, in this case based on the amount of nitrotoluenes recovered, was about 5%. Only the ortho (80%) and para (20%) nitro-isomers are formed in this reaction to any extent. While it is entirely possible that some meta isomer is formed, it can be present in only small amounts since it was not detected in the reaction product. The ortho and para isomers

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(1) (a) F. S. Kipping and L. L. Lloyd, *J. Chem. Soc.*, **79**, 449 (1901); (b) F. S. Kipping and G. Martin, *ibid.*, **95**, 489 (1909); (c) A. R. Steele and F. S. Kipping, *ibid.*, 1431 (1928); (d) F. S. Kipping and N. W. Cusa, *ibid.*, 1088 (1935); (e) H. Gilman and F. J. Marshall, THIS JOURNAL, **71**, 2066 (1949).

(2) (a) F. S. Kipping and J. C. Blackburn, *J. Chem. Soc.*, 2200 (1932); (b) B. N. Dolgov and O. K. Panina, *J. Gen. Chem.*, **18**, 1129 (1948), [*C. A.*, **43**, 1737 (1949)]; (c) R. A. Benkeser, Doctoral Dissertation, Iowa State College, 1947.

(3) J. D. Roberts, E. A. McElhill and R. Armstrong, THIS JOURNAL, **71**, 2923 (1949).

(4) (a) J. B. Menke, *Rec. trav. chim.*, **44**, 141, 269 (1925); (b) G. Bacharach, THIS JOURNAL, **49**, 1522 (1927).

(5) W. J. Klapproth and F. H. Westheimer, THIS JOURNAL, **72**, 4461 (1950).

TABLE I

NITROPHENYLTRIMETHYLSILANES

	B.p., 10 mm., °C.	$n^{20}D$	d^{20}_4	Silicon, % Calcd.	Silicon, % Found	Mol. refraction Calcd.	Mol. refraction Found
o-$NO_2C_6H_4Si(CH_3)_3$	117	1.5321	1.073	14.36	14.04	56.34	56.30
m-$NO_2C_6H_4Si(CH_3)_3$ (95%)	126	1.5239	1.055	14.36	14.42	56.34	56.55
p-$NO_2C_6H_4Si(CH_3)_3$	129	(solid—m.p. 38–39°)		14.36	14.04		
NITROBENZYLTRIMETHYLSILANES							
o-$NO_2C_7H_6Si(CH_3)_3$	125	1.5276	1.045	13.42	13.37	60.90	61.59[a]
p-$NO_2C_7H_6Si(CH_3)_3$	147	1.5423	1.069	13.42	13.08	60.90	61.65[a]

[a] It is perhaps noteworthy that the calculated molecular refraction for benzyltrimethylsilane is reported to be 0.43 unit lower than the observed value (see E. L. Warrick, THIS JOURNAL, **68**, 2457 (1946)).

can be easily separated by careful fractionation, since at 10 mm. they boil 22° apart. Table I lists the physical constants of the o- and p-nitrobenzyltrimethylsilanes.

A structure proof of o-nitrobenzyltrimethylsilane was accomplished by oxidative cleavage of the compound with hot nitric acid. Practically a quantitative yield of o-nitrobenzoic acid was obtained. This oxidative procedure was adopted when base cleavage gave relatively low yields of o-nitrotoluene.

p-Nitrobenzyltrimethylsilane could be cleaved quite readily with sodium hydroxide, however, to give p-nitrotoluene in 63% yield. A 29% yield of a yellow solid was also isolated from this cleavage mixture melting at 182–183°. It was identified by reduction to an amine which melted at 131–132° (lit. m.p. for p,p'-diamino-1,2-diphenylethane is 131–132°), and by a mixed melting point with an authentic sample of p,p'-dinitro-1,2-diphenylethane. Reportedly this compound can be formed by treating p-nitrotoluene with base,[6] which could explain its formation in our case.

Experimental

Nitration of Phenyltrimethylsilane (Run I).—A mixture of 124.5 g. (1.03 moles of nitrate ion) of copper nitrate ($3H_2O$) and 600 ml. of acetic anhydride was vigorously agitated in an open flask on a water-bath at 16°. The temperature of the reaction solution rose exothermally to about 38° and then subsided gradually. With the nitrating mixture cooled to 30°, 136.2 g. (0.90 mole) of phenyltrimethylsilane[7] (b.p. 168° (747 mm.), $n^{20}D$ 1.4908) was added at a substantially uniform rate over a period of 2 hours. The reaction temperature was maintained between 30–35° during this time. The water-bath temperature was then raised to about 40° and the mixture was stirred at this temperature for about 6 hours. It was then cooled and a cold solution of 120 g. of sodium hydroxide in 300 ml. of water was carefully added. The partially neutralized solution was steam distilled and the acetic acid in the distillate was neutralized by the addition of ammonium hydroxide. After extraction of the distillate with ether the organic layer was dried over calcium chloride. After the ether was removed the residual oil was distilled through a Todd column, using a 5 mm. metal spiral core, 36 inches long and vacuum-jacketed. A manostat was used to maintain a constant pressure of 10 mm. of mercury. The products were collected as follows:

Fraction	Temp.	Grams	Moles	Per cent.
1	53	7.2	0.048	5.3
2	83	27.1	.222	24.7
3	114–117	36.3	.186	20.6
4	122–128	71.6	.367	40.8
		Totals	0.823	91.4

Fraction 1 consisted of unreacted phenyltrimethylsilane, fraction 2 of nitrobenzene, and fractions 3 and 4 of nitrophenyltrimethylsilanes. The total yield of nitrated silanes in this run was 62%. Fraction 3 was shown to be largely o-nitrophenyltrimethylsilane.

Fraction 4 was shown to be a mixture of the meta and para isomers. Upon dissolving this fraction in pentane and cooling in Dry Ice a solid separated, which, upon crystallization from pentane, melted sharply at 38–39° and was shown to be the para isomer by bromine cleavage.

(Run II).—Another run was made similar to that described above using 93 g. (0.62 mole) of the silane, 84.5 g. (0.70 mole of nitrate ion) of copper nitrate ($3H_2O$) and 400 ml. of acetic anhydride. After a reaction time of 6 hours there was obtained 7.5 g. (8%) of unreacted silane, 17.2 g. (23%) of nitrobenzene, 21.7 g. (18%) of o-nitrophenyltrimethylsilane, b.p. 115–117° (10 mm.) and 50.8 g. (42%) of a mixture of m- and p-nitrophenyltrimethylsilane, b.p. 120–130° (10 mm.). The total yield of nitrated silanes was 60%. The physical constants of purified samples of the nitrophenyltrimethylsilane isomers are listed in Table I.

Proof of Structure of Nitrophenyltrimethylsilanes.—Following a procedure described by Kipping,[1d] one-gram portions of fractions believed to be relatively pure in each isomeric nitrophenyltrimethylsilane were placed in sealed tubes with 1 g. of bromine and 2 ml. of water. After being heated at 200° for 6 hours, the organic material was isolated by extraction with benzene and then crystallized from petroleum ether.

With o-nitrophenyltrimethylsilane only 0.1 g. (10%) of o-bromonitrobenzene was isolated melting at 41–42° and giving no depression when mixed with an authentic sample. A portion of o-nitrophenyltrimethylsilane was reduced to the amine[8] and 0.5 g. of this amine when treated with bromine in carbon tetrachloride gave 0.3 g. (40%) of 2,4-dibromoaniline, melting point and mixed melting point 76–77°. The reaction of 0.5 g. of o-aminophenyltrimethylsilane with bromine water gave 0.8 g. (80%) of 2,4,6-tribromoaniline (m.p. 118–119°).

With m-nitrophenyltrimethylsilane, 0.5 g. (48%) of m-bromonitrobenzene was isolated, melting at 48–49° and giving no depression when mixed with an authentic sample.

p-Nitrophenyltrimethylsilane gave 0.7 g. (67%) of p-bromonitrobenzene, melting point and mixed melting point 126–127°.

Determination of Meta to Para Ratio for Nitrophenyltrimethylsilane.—Samples of the mixed meta and para isomers of the nitrophenyltrimethylsilanes, as well as purified samples of these isomers were cleaved to the corresponding bromonitrobenzenes. This was accomplished by treating the silane with an excess of bromine and a trace of iron filings for 90 minutes at 100°. The excess bromine was destroyed with aqueous sodium thiosulfate, and the iron bromide and bromosilane produced were hydrolyzed by the addition of aqueous sodium hydroxide. The bromonitrobenzenes thus formed were extracted with a mixture of ether and benzene. The combined extracts were then evaporated to dryness in small glass-stoppered bottles. The residue was treated with 1 ml. of purified piperidine and then placed in an oil-bath at 55° for 44 hours. The reaction mixture was washed into a flask with two 20-ml. portions of water and one 20-ml. portion of 0.1 N sodium carbonate. After extracting the piperidine with 20 ml. of benzene, the bromide ion was ti-

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(6) A. G. Green, A. H. Davies and R. S. Horsfall, *J. Chem. Soc.*, **91–92**, 2076 (1907).

(7) Prepared in 70% yield by adding trimethylchlorosilane to an ethereal solution of phenyllithium.

(8) The preparation and reactions of these silicon amines will be published later.

trated by the Volhard method.[9] The amount of bromide ion was assumed equivalent to the amount of *p*-nitrophenyltrimethylsilane in the original mixture. These results are presented in Table II.

TABLE II

PIPERIDINE CLEAVAGES

Mixed *m*-, *p*-nitrophenyltrimethylsilanes

Wt. sample, g.	*p*-Isomer found, g.	Para, %
	Run I	
0.1000	0.0414	41.4
.1104	.0478	43.5
.0999	.0451	45.1
	Av.	43.3
	Run II	
.1345	.0561	41.7
.1345	.0548	40.8
	Av.	41.2
Purified *m*-nitrophenyltrimethylsilane		
0.1278	0.0062	4.9
.1011	.0067	6.6
	Av.	5.7
Purified *p*-nitrophenyltrimethylsilane		
0.1002	0.0988	98.5

Nitration of Benzyltrimethylsilane.—A mixture of 140.8 g. (1.17 moles of nitrate ion) of copper nitrate ($3H_2O$) and 400 ml. of acetic anhydride was stirred in a three-neck flask maintained in a cold water-bath until the exothermic reaction was virtually completed as evidenced by a decrease in the reaction temperature. One hundred seventy-four and three-tenths grams (1.06 moles) of benzyltrimethylsilane[1e] (b.p. 188° (743 mm.), $n^{20}D$ 1.4932) was added at a substantially uniform rate over a period of 90 minutes, while maintaining a reaction temperature of 30–35°. The temperature of the reaction mixture was raised to about 40° and stirring was continued for 5 hours. The acetic anhydride was hydrolyzed and neutralized by the simultaneous addition of chipped ice and ammonium hydroxide, accompanied by external cooling of the flask in an ice-bath to maintain the temperature of the reaction mixture below 20°. The organic material was extracted from the reaction mixture with ether, the organic extracts dried over sodium sulfate, and the ether distilled off. The residual orange oil was fractionated through a Todd column at 10 mm. pressure. The products were collected as follows:

Fraction	Temperature	Grams	Moles	Per cent.
1	74–96	6.1	0.04	3.9
2	96–124	5.9	.04	3.9
3	125–127	113.4	.50	47.2
4	149–150	31.4	.14	13.2
		Totals	0.72	68.2

A large amount of brown tar remained in the distillation flask. Fraction 1 consisted primarily of recovered benzyltrimethylsilane and Fraction 2 of nitrotoluene. Fraction 3 was essentially pure *o*-nitrobenzyltrimethylsilane as shown by oxidation (described below) to *o*-nitrobenzoic acid and comparison with an authentic sample. Fraction 4 was essentially pure *p*-nitrobenzyltrimethylsilane as shown by basic cleavage to *p*-nitrotoluene (see below). The total yield of nitrated derivatives of benzyltrimethylsilane was 60%. The physical constants of redistilled samples of the nitrobenzyltrimethylsilane isomers are listed in Table I.

Structure Proof of *o*-Nitrobenzyltrimethylsilane.—A mixture of 4.6 g. (0.022 mole) of the lower boiling isomer, 4.5 g. of sodium hydroxide, 30 ml. of water and 10 ml. of ethanol was refluxed for 8 hours. Distillation of the oil isolated from this reaction yielded 1.6 g. (53%) of material boiling 80–81° (6 mm.). Preparation of the acetotoluide from 0.8 g. of this material by a tin reduction and acylation gave 0.2 g. (23%) of *o*-acetotoluide melting at 107–110°.

Another portion (4.0 g.) of the lower boiling isomer was heated at 140° and small portions of nitric acid (d. 1.42) and small crystals of potassium nitrate were added at intervals. After 36 hours the oil layer had disappeared and 3.2 g. (99%) of a solid product melting at 144–146° was obtained after pouring the reaction mixture onto crushed ice. Recrystallization from alcohol–water gave *o*-nitrobenzoic acid, melting point and mixed melting point 145–147°.

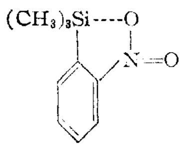
Structure Proof of *p*-Nitrobenzyltrimethylsilane.—A portion (5.8 g.) of the higher-boiling isomer was placed in a flask with 10 ml. of ethanol and 25 ml. of 15% sodium hydroxide. Reaction occurred immediately, with a deep red color forming and a yellow solid precipitating with the evolution of heat. The ether extract gave 2.4 g. (63%) of *p*-nitrotoluene (m.p. 51–52°) which did not depress the melting point of an authentic sample. A residual yellow solid in the reaction mixture, which was insoluble in ether, was extracted with benzene to give 1.0 g. of material melting at 180–182°. A purified sample melted at 182–183° and the reduction product melted at 131–132°. The nitro compound was identified by a mixed melting point with an authentic sample of *p*,*p'*-dinitro-1,2-diphenylethane.[10]

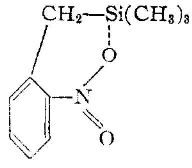
Discussion

Of particular interest is the 30/40/30 ortho/meta/para isomer ratio for the nitration of phenyltrimethylsilane. A purely statistical isomer distribution would lead to a 40/40/20 ratio. If one assumes a decrease in the ortho isomer of 10% because of steric factors, a statistical distribution would demand a 30/47/23 ratio. It is obvious that our results indicate the trimethylsilyl group to be a *very weak* ortho–para director. An exact interpretation of this orientation with regard to the electrical influence of the trimethylsilyl group must await further information concerning the mechanism of nitration by the copper nitrate reagent.

The enhanced stability of the *o*-nitrophenyltrimethylsilane and *o*-nitrobenzyltrimethylsilane toward cleavage is worthy of note. A possible explanation might be the steric requirements of two rather bulky ortho substituents. One might predict that such a situation would render more difficult an attack by a cleaving agent on the carbon atom holding the silicon. Studies now in progress in this Laboratory on the mechanism for elimination of the R_3Si– group from an aromatic nucleus seem to indicate an attack by an electrophilic group on the aromatic carbon atom holding the silicon. If this mechanism is correct, rules of aromatic substitution should hold, which predict that *o*-nitrophenyltrimethylsilane will resist silicon cleavage more than the meta isomer. It would not predict, however, any marked difference between the ortho and para isomers.

Another possibility is that the silicon atom in the ortho isomers has expanded its valence shell by forming a chelated silicon–oxygen bond. Such





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(9) See H. H. Willard and N. H. Furman, "Elementary Quantitative Analysis," D. Van Nostrand Co., Inc., New York, N. Y., 1935, p. 139.

(10) W. H. Rinkenbach and H. A. Aaronson, THIS JOURNAL, 52, 5040 (1930).

a situation is not to be considered impossible since silicon is capable of expending its valence shell and the Si–O bond is a very stable linkage. The possibility of this chelation is now under investigation.

LAFAYETTE, IND. RECEIVED APRIL 24, 1951

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER LABORATORY, LEHIGH UNIVERSITY]

Halogen Reactivities. Certain Heterocyclic Iminohalide Systems[1]

BY THOMAS E. YOUNG[2] AND E. D. AMSTUTZ

Pseudo-first order rate constants have been determined for the reactions of 2-bromopyridine (I), 2-bromoquinoline (II), 2-chloroquinoline (III) and 2-chlorothiazole (IV) with piperidine at various temperatures in the range between 40.00 and 90.00°. The activation energies of these processes have been calculated. The reactions of 2-chloropyrimidine (V) and 2-chlorobenzothiazole (VI) with piperidine have been shown to proceed much more rapidly than the reactions of compounds I to IV, too rapidly, in fact, to permit quantitative rate measurements under similar temperature conditions. Comparison of rate constants calculated at a common temperature of 50.00° establishes the following order of decreasing activity: II > III > IV > I.

Introduction

The present work originated in a desire to discover, if possible some important common basis for the comparison of the various heterocycle systems. After critically surveying the many possible reactions which might be carried out on the various heterocycles for comparative purposes we felt that the most significant results might be obtained by determining the ease of replacement of nuclear halogen by nucleophilic reagents. It was felt that in this way evidence might be obtained as to the relative charge density on the various carbon atoms of the rings.[3]

The reaction rates of the halides of aliphatic and aromatic compounds with nucleophilic halogen-substituting reagents such as hydroxides, alkoxides, ammonia and amines have been widely studied.[4] Analogous kinetic studies of heterocyclic halogen compounds have been just as widely ignored. With the exception of rate constants and activation energy for the ammonolysis of 2-chlorobenzothiazole with liquid ammonia[5] there are no accurate quantitative measurements in this field.

It is the purpose of this paper to present the results of an investigation of the pseudo-unimolecular reaction rates of 2-bromopyridine (I), 2-bromoquinoline (II), 2-chloroquinoline (III) and 2-chlorothiazole (IV) with piperidine. Preliminary experiments have also been made with 2-chloropyrimidine (V) and 2-chlorobenzothiazole (VI), though their reaction rates with piperidine proved to be too rapid for accurate determination.

Experimental

Preparation of Reagents.—Piperidine (VII) was obtained as 98% piperidine from Monsanto Chemical Co.[6] Specifications indicated a maximum of 1% pyridine. Purification was accomplished as follows: one liter of 98% piperidine was refluxed over three successive 100-g. portions of potassium hydroxide pellets for 2 hours for each portion. This partially dried product was made anhydrous and most of the pyridine removed by refluxing with excess sodium metal until the mixture became black with polypyridyls. The product was then distilled through a 50-cm. Widmer column, the fraction boiling at 105.5–105.8° at 760 mm. being collected. This material was stored over sodium wire and redistilled from sodium just prior to use.

2-Bromopyridine (I) was prepared in 60% yield by diazotization of 2-aminopyridine (Reilly Coal Tar product) using the method of Craig.[7] Purified 2-bromopyridine had b.p. 98.2–99.0° at 27.5 mm., n^{20}_{D} 1.5704 (lit.[8] b.p. 91–92° at 24 mm., n^{20}_{D} 1.5713).

2-Bromoquinoline (II).—Five grams of carbostyril (m.p. 199–200°, Eastman Kodak Co.) was placed in a 50-ml. standard taper flask fitted with an air condenser protected by a calcium chloride tube. Twenty-two grams of phosphorus oxybromide was added and the mixture heated on an oil-bath at 150–155° for four hours. The solution was cooled to room temperature, and 25 ml. of water added to decompose the excess phosphorus oxybromide. The resulting clear red solution was neutralized by addition of solid sodium bicarbonate, then made definitely basic by the addition of 10 ml. of 10% sodium hydroxide. The rose colored solid which separated was filtered off, dissolved in 50 ml. of ether, treated with one gram of Darco, and filtered. The resulting solution was evaporated leaving a residue of 5.80 g. (80.9%) of crude 2-bromoquinoline m.p. 42–44°. This material was distilled at 163–163°/16.5 mm. to yield a white product m.p. 47.0–49.0° (lit.[9] m.p. 48.4–48.8°).

2-Chloroquinoline (III) (Eastman Kodak, "White Label" product) was distilled at 90.0–91.4° (2 mm.), m.p. 35.2–36.4° (lit.[10] m.p. 37–38°).

2-Chlorothiazole (IV) was obtained in 66.4% yield from 2-aminothiazole (Matheson Co.) using the diazotization procedure of Ganapathi and Venkataraman.[11] This material had b.p. 34.0–34.5° (10 mm.), n^{20}_{D} 1.5503.

2-Chlorobenzothiazole (VI) (Eastman Kodak product) was purified by distillation, b.p. 90.0–91.5° at 4 mm.; n^{20}_{D} 1.6398.

2-Chloropyrimidine (V).—This material was prepared from 2-pyrimidone and 2-pyrimidone hydrochloride by pro-

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[1] Taken from the M.S. Thesis of T. E. Young, June, 1950.

[2] Dept. of Chemistry, University of Illinois, Urbana, Ill.

[3] It might appear at first that a study of hydrogen replacement by electrophilic reagents would yield information of a more practical nature. Electrophilic reagents are much more limited in their application however since they frequently add to heterocyclic systems of lower aromaticity, sometimes bring about ring opening and generally are ineffective in attacking certain ring positions. It is true however that the results of such a study could be stated in terms of relative electron density and it is possible that the relative densities so determined would not, in all cases, parallel those determined by the nucleophilic reagent method.

[4] For a most recent example see Berliner, Quinn and Edgerton, THIS JOURNAL, **72**, 5305 (1950).

[5] Lemons, Anderson and Watt, *ibid.*, **63**, 1953 (1941); **64**, 467 (1942).

[6] We gratefully acknowledge the kindness of the Monsanto Chemical Co. in supplying us with large quantities of piperidine.

[7] Craig, THIS JOURNAL, **56**, 231 (1934).

[8] den Hertog and Wibaut, *Rec. trav. chim.*, **51**, 381 (1932).

[9] Jansen and Wibaut, *ibid.*, **56**, 699 (1937).

[10] Friedlander and Ostermaier, *Ber.*, **15**, 333 (1882).

[11] Ganapathi and Venkataraman, *Proc. Ind. Acad. Sci.*, **22A**, 343 (1945); *C.A.*, **40**, 4059 (1946).