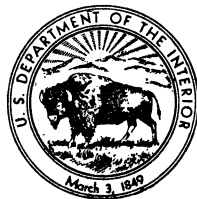


DETERMINATION OF PHENOLS IN COAL TARS  
AND HYDROXYL GROUPS IN COAL  
BY FORMING TRIMETHYLSILYL ETHERS

By Sidney Friedman, Charles Zahn,  
Marvin Kaufman, and Irving Wender



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# DETERMINATION OF PHENOLS IN COAL TARS AND HYDROXYL GROUPS IN COAL BY FORMING TRIMETHYLSILYL ETHERS

By

Sidney Friedman,<sup>1</sup> Charles Zahn,<sup>1</sup> Marvin L. Kaufman,<sup>1</sup> and Irving Wender<sup>1</sup>

---

## *Abstract*

THE BUREAU OF MINES has developed new methods for determining phenols in coal tar oils and the hydroxyl content of coal. The methods are based on the conversion of the hydroxyl group to the trimethylsilyl ether group by hexamethyldisilazane. Complex mixtures of high-boiling phenols were analyzed by low-ionizing voltage mass spectrometry before and after their conversion to trimethylsilyl ethers. Lower boiling phenols were analyzed by gas-liquid chromatography of their trimethylsilyl ethers. The hydroxyl content of coals was determined by first forming the trimethylsilyl ethers, and then either analyzing for added silicon gravimetrically or determining the added trimethylsilyl content by infrared spectroscopy. A sample of coal weighing not more than 10 milligrams can be analyzed for hydroxyl content by infrared spectroscopy of the trimethylsilylated coal. The hydroxyl oxygen content of 29 coals and 10 vitrains is reported. The preparations of new trimethylsilyl ethers of various types of phenols are described.

## *Introduction*

Recent interest in upgrading of coal by converting it into valuable chemicals and specialty fuels created three main areas of research and development by the Bureau of Mines at Pittsburgh (Pa.) as follows:

1. The exploration and development of new technological processes using coal as a raw material.
2. The development of new methods for analyzing coal and coal products with rapidity, accuracy, and specificity.
3. The conduct of basic research on the constitution of coal from the standpoint of the physical and chemical behavior of coal. This area of investigation is in keeping with the premise—the more that is learned about the nature of coal, the more can coal be utilized to the best advantage.

This report reviews related previous work and describes studies by the Bureau of Mines on (1) the development of new methods for analyzing phenols, (2) the development of a specific method for the determination of phenolic hydroxyl groups in coal, and (3) the preparation and properties of trimethylsilyl derivatives of individual phenols. Information obtained from the experimental preparations served, in part, as the basis for the new methods of identifying and analyzing phenols as their trimethylsilyl ethers.

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A. G. Sharkey, Jr., supervisory research physicist; and Peter Pantages, physical science technician. The last three persons are with the Bureau of Mines, Pittsburgh Coal Research Center.

## ANALYSIS OF PHENOLS IN MIXTURES

Coal-conversion processes such as hydrogenation of coal or low-temperature carbonization yield large amounts of tar acids (phenols). Whether the tar acids are used as such or converted into other products, the investigator or technologist generally prefers to know the structural types of compounds present instead of merely the total content of monohydric or polyhydric phenols. Until recently, procedures for specific identification of phenolic constituents necessitated a laborious separation of individual compounds. The procedures usually entailed various chemical and physical operations, and frequently they provided only an approximation of the amount of certain of the higher boiling compounds present in the original oil. Typical of the approach previously employed in these laboratories is the work of Woolfolk, Orchin, and Dull (82).<sup>2</sup> The work of Dean, White, and McNeil (16) is a good example of the application of various physical and chemical methods for the separation and identification of individual compounds in coal tar. Dean and others compared some of their analyses with those performed on the same sample at the Bureau of Mines by means of the newer low-ionizing voltage mass-spectrometric technique.

Coal tar contains a host of phenolic compounds, for example, work at the Bureau of Mines indicated the presence of 84 compounds in a wide-boiling tar acid fraction (bp 231°–331° C) (44). Sy and Lejeune list 58 polyalkylphenols found in coal tar as well as the methods used to separate them (72).

Success with the mass-spectrometric analyses of alcohols as their trimethylsilyl ethers (49, 86) led to the mass-spectrometric examination of the trimethylsilyl ether of phenol. The spectrum of this trimethylphenoxysilane exhibited a distinctive identifiable pattern as did those for the trimethylsilyl ethers of aliphatic alcohols (66). The conversion of phenols to trimethylsilyl derivatives was found to be especially useful for the mass-spectrometric analysis of unfractionated coal tar acids (65, 67, 68).

Exploratory studies on the gas-liquid chromatographic behavior of trimethylsilyl arylethers indicated that conversion of phenols to trimethylsilyl derivatives also facilitates their separation by gas-liquid chromatography and thereby provides a convenient method for ana-

lyzing mixtures of low-boiling phenols (51). The utility of such ethers for gas-chromatographic analysis was confirmed by Grant (30).

### MASS SPECTROMETRY

Very little can be deduced from the usual mass-spectrometric run about molecular weights or types of compounds present in high boiling fractions. A nondistinctive spectrum is obtained which results primarily from the occurrence of many compounds having similar fragmentation spectra, and from rearrangements producing ions corresponding to the molecular weight of lower members of a homologous series. A low-ionizing voltage technique, however, can be employed to obtain the true molecular weight distribution. This technique depends on the use of electrons of low energy to produce selective ionization. Production of fragment ions generally requires several volts more energy than for molecular ions. The ionizing voltage, therefore, is adjusted to eliminate fragment ions, and a spectrum is obtained consisting only of molecule ions, thus providing the molecular weights of the constituents.

On applying the low-ionizing voltage technique to tar acid fractions from hydrogenation of lignite and also to those from low-temperature tar, the Bureau observed that wide-boiling fractions of tar acids can be characterized by correlating the spectrum of the original tar acid sample with the spectrum of the same phenolic fraction after its conversion to the trimethylsilyl derivatives (65, 67, 68).

Apparently a definite correlation exists between the sensitivities of the phenols and their trimethylsilyl derivatives. Sensitivity coefficients indicate that as little as 0.1 volume-percent of many phenolic compounds present in tar acid fractions probably can be detected in spectra of both the original and the derivative material. Formation of trimethylsilyl derivatives permits identification of various phenolic types in the presence of neutral material. Certain structural types forming identical homologous series of identical mass can be identified in the trimethylsilyl ether derivative spectrum; for example, dihydric phenols, such as resorcinol, and alkoxyphenols, such as guaiacol. Results obtained with a 10-com-

<sup>2</sup> Italicized numbers in parentheses refer to items in the list of references at the end of this report.

ponent synthetic blend as shown in table 1. Reasonable values have been obtained for several major types of compounds found in tar acid fractions; these results indicate that at least a semiquantitative interpretation of spectra is valid for tar acid fractions.

TABLE 1.—*Analysis of synthetic mixture of phenols by low-ionizing voltage mass spectrometry, volume-percent*

Compound	As phenols	As trimethylsilyl ether derivatives	Known composition (%)
<i>m</i> -Cresol	30.3	28.6	31.3
<i>m</i> -Ethylphenol	22.2	22.1	21.1
3-Ethyl-5-methylphenol	5.9	6.1	5.9
Resorcinol	10.1	12.7	12.1
2-Methylresorcinol	4.7	5.1	5.1
5-Indanol	8.3	7.6	8.2
1-Naphthol	5.7	5.5	5.5
5-Acenaphthenol	11.6	11.2	9.9
<i>m</i> -Phenylphenol			
1-Pyrenol	1.2	1.1	.9

<sup>1</sup> Both compounds have molecular weight of 170; weighted sensitivity used.

## GAS-LIQUID CHROMATOGRAPHY

Fitzgerald (21) recommended that a phenolic mixture should be chromatographed first on a nonpolar stationary phase since this type of liquid phase tends to retain ortho-substituted compounds and to elute them along with higher-boiling unsubstituted phenols. Such fractions should be collected and then chromatographed on a polar stationary phase, which elutes ortho-substituted phenols before the unsubstituted phenols. Use of a polar phase alone did not produce satisfactory results. Fitzgerald concluded that the most satisfactory pair of stationary phases was Apiezon L<sup>3</sup> and a commercial detergent of the sodium dodecylbenzene sulfonate type. Fitzgerald later assayed the tar acids in lower boiling fractions of a tar from the Lurgi pressure gasification of a brown coal (22). Phenol, cresols, some xylenols and ethylphenols were analyzed satisfactorily but not the higher-boiling phenols. The *m*- and *p*-cresols and the 2,4- and 2,5-xylenols were not separated.

Janák and Komers (39, 40) tested a variety of nonpolar and polar stationary phases (including sugars) for the chromatographic behavior of different phenols from the standpoint of the role of interaction by hydrogen bonding as well as the effects of steric hindrance.

<sup>3</sup> Reference to specific commercial products and equipment in this report does not imply endorsement of the products or equipment by the Bureau of Mines.

Karr and others (42, 43) analyzed a mixture of low-temperature tar phenols, boiling up to 234° C, by gas chromatography on di-*n*-octyl phthalate at 160° C. These phenols were analyzed also by the earlier method of fractional distillation followed by infrared spectroscopy. This work indicated that such mixtures of phenols could be analyzed more readily by gas chromatography supplemented by infrared analysis of certain unresolved gas-chromatographic fractions.

Kreyenbuhl and Weiss (46) analyzed known mixtures of phenols on columns of Apiezon L or of silicone grease, and applied their experiences to the quantitative analysis of 9 phenolic fractions (bp 74.5°–130° C at 10 mm) obtained from a coal-hydrogenation product.

Paterson (61) separated *m*- and *p*-cresol on a mixed stationary phase composed of 3 to 5 percent phosphoric acid and 5 percent tricresylphosphate on Chromosorb as a support. Brooks (9) observed that a phosphate ester gives good separations on acid-washed Celite. He tested several types of these esters and found that the 2,4-xylene phosphate ester effects the best separation of *m*-cresol from *p*-cresol, and 2,4-xylene from 2,5-xylene.

Payn (62) reported on the use of di-*n*-octyl sebacate as a liquid phase for the rapid gas-chromatographic control analysis of refined tar acids. Separation of *o*-ethylphenol and the 2,4- and 2,5-xylenols was only partial; the separation of 2,3-xylene and 3,5-xylene admittedly was poor.

Grant (31) investigated the utility of the capillary column for the analysis of coal tar fractions. By using a 15-meter capillary column (with tri-*o*-cresyl phosphate at 100° C), he was able to separate, in 20 minutes, a mixture of phenol, *o*-cresol, *m*- with *p*-cresol, 2,4- and 2,5-xylene.

Prior to many of these investigations, work in the laboratories of the Bureau of Mines demonstrated that conversion of phenols to trimethylsilyl ethers afforded a useful technique for altering the nature of the solute-liquid phase interaction (51). This treatment is superior to the conversion of phenols to their methyl ethers, not only because the trimethylsilyl reaction is much more quantitative, but also because such compounds as 2,5-xylene and 3,5-xylene are separable as their trimethylsilyl ethers. Carruthers, Johnstone, and Plimmer (12) were unable to separate the methyl ethers of 2,5-xylene and 3,5-xylene by gas chromatography. By comparing the chromatogram of the trimethylsilyl ethers of mixed tar acids with the chromatogram of the original mixed tar acids, Grant (30) was able to analyze for each of the low-boiling tar acids except for 3,5-dimethylphenol and *m*-ethylphenol.



### Separation of Phenols as Trimethylsilyl Ethers

The relative retentions of 15 trimethylsilyl ethers of various phenols on Dow Corning 550 silicone oil and di-*n*-butyl tetrachlorophthalate at 125° C are given in table 2. The order of elution from both liquid phases is similar for the monoalkylphenyl trimethylsilyl ethers; the cresol derivatives, at least, are eluted in the order of boiling point, *o*-194°-195° C, *m*-196°-197° C, *p*-198°-199° C. For dialkyl compounds, the larger deviations in relative retentions are in the direction of greater relative retentions on di-*n*-butyl tetrachlorophthalate. These differences in behavior can be interpreted in terms of steric factors and charge transfer interaction with the tetrachlorophthalate (52, 53), if a parallel orientation for the two interacting aromatic rings is assumed. Thus, the trimethylsilyl ethers of 2,3-dimethylphenol and 2,6-dimethylphenol have larger relative retentions on di-*n*-butyl tetrachlorophthalate, whereas the trimethylsilyl ether of 3,5-dimethylphenol, in which no two adjacent positions on the aromatic ring are free of substituents (75), has about the same relative retention on di-*n*-butyl tetrachlorophthalate and silicone oil, D.C. 550.

TABLE 2.—Relative retentions of the trimethylsilyl ethers of phenols at 125° C (51)

Trimethylsilyl ether of	D.C. 550 Silicone oil	Di- <i>n</i> -butyl tetrachlorophthalate
Phenol.....	1.2 1.00	1.3 1.00
<i>o</i> -Cresol.....	1.59	1.68
<i>m</i> -Cresol.....	1.71	1.75
<i>p</i> -Cresol.....	1.84	1.89
<i>o</i> -Ethylphenol.....	2.36	2.34
<i>m</i> -Ethylphenol.....	2.80	2.81
<i>p</i> -Ethylphenol.....	3.05	3.10
2,3-Dimethylphenol.....	3.3	3.75
2,4-Dimethylphenol.....	2.77	3.01
2,5-Dimethylphenol.....	2.48	2.69
2,6-Dimethylphenol.....	3.06	3.55
3,4-Dimethylphenol.....	3.61	3.89
3,5-Dimethylphenol.....	2.86	2.85
2,4,6-Trimethylphenol.....	5.33	6.07
1-Hydroxy-2-methoxybenzene (Guaiacol).....	3.23	3.48

<sup>1</sup> Retention volume of air taken as zero. Corrected retention volume per gram of liquid phase is, respectively:

<sup>2</sup> 330 ml/g at column temperature.

<sup>3</sup> 447 ml/g at column temperature.

Separation of a 3.3 $\mu$ l. sample of trimethylsilyl ethers resulting from treatment of a commercial cresol mixture with an excess of hexamethyldisilazane is illustrated in figure 1.

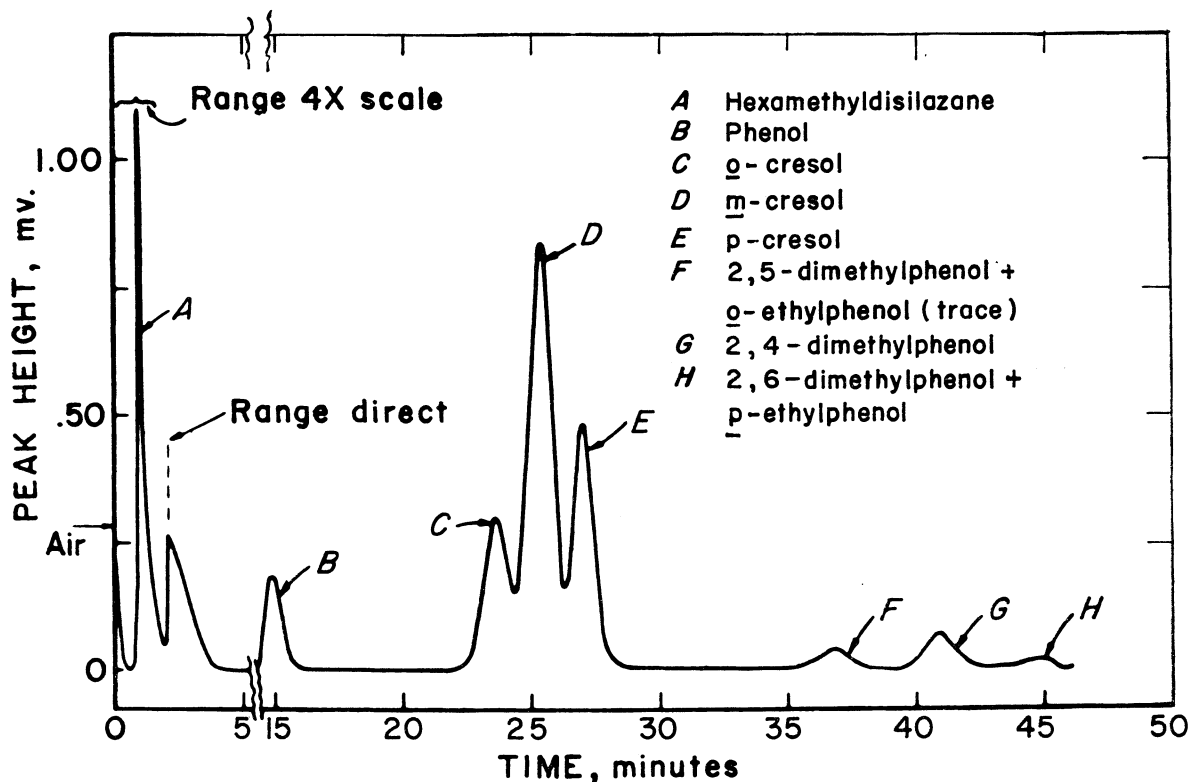


FIGURE 1.—Separation of a Cresol Mixture Treated With Hexamethyldisilazane. Column 0.5 x 365.8 cm. Flow 153.2 ml/min of He  $\Delta$ P 896 mm. Atm Pressure 736 mm. 34 g Packing Containing 12 pct (w/w) Silicone Oil on 42 to 48 Mesh Firebrick, Column Temperature 125° C.

Identification of constituents producing peaks with the D.C. 550 silicone oil column was possible from supplementary data obtained on the di-*n*-butyl tetrachlorophthalate column. Quantitative analysis should be possible by calibration relative to the phenol peak and normalization, or through the addition of an internal standard, preferably a hydroxyl compound, to the original cresol mixture.

The extent of conversion to trimethylsilyl ethers of a mixture originally containing 40 percent<sup>4</sup> of 2,4,6-trimethylphenol was checked by mass-spectroscopic analysis after 16 hours of reflux with hexamethyldisilazane (not catalyzed with hydrochloric acid). Less than 0.2 volume-percent of unchanged trimethylphenol was found in the mixture.

Tests with the silicone oil column revealed that aqueous phenol concentrations as low as 0.2 percent are readily detected by gas chromatography of the solution after treatment with hexamethyldisilazane,  $(\text{CH}_3)_3\text{SiNHSi}(\text{CH}_3)_3$ . The water is converted to hexamethyldisiloxane,  $(\text{CH}_3)_3\text{SiOSi}(\text{CH}_3)_3$ , and trimethylsilylanol,  $(\text{CH}_3)_3\text{SiOH}$ , (49, 86); these compounds are eluted very rapidly from the column, well before the trimethylsilyl ether of phenol.

## Experimental

### MATERIALS

The trimethylsilyl ethers of the phenols were prepared by the procedure described in a later section of this report. The di-*n*-butyl tetrachlorophthalate liquid phase was prepared (54), and the gas chromatograph was constructed in the Bureau's laboratory (53) at Pittsburgh. Samples were measured and introduced into the chromatograph by a modified microsyringe (50).

### PRETREATMENT OF FIREBRICK

Two 200-gram batches of 42 to 48 mesh firebrick were elutriated with water to remove fines. The residue was treated with six batches of 10 percent sodium hydroxide solution at room temperature, elutriated with water to remove additional fines, transferred to a Buchner funnel fitted with acid-hardened filter paper, washed with flowing distilled water until the filtrate was neutral, and finally dried in an electric oven for 100 hours at 135° to 140° C. After resieving, the yields were 152 and 162 grams, respectively, of 42 to 48 mesh firebrick. The products were combined before use.

### PREPARATION OF SILICONE OIL COLUMN

A 12-foot (1/4-inch outer diameter) U-shaped stainless steel tube was filled, by the aid of a vibrator, with 34 grams of packing containing

12 percent silicone oil, D.C. 550, on the NaOH-treated 42 to 48 mesh firebrick. A 1/8-inch layer of dry firebrick was added to the top of each limb, and finally a small plug of glass wool was added.

### PREPARATION OF DI-*N*-BUTYL TETRACHLOROPHTHALATE COLUMN

A 12-foot U-shaped stainless steel tube was filled, as described previously, with 33 grams of packing containing 10 percent di-*n*-butyl tetrachlorophthalate on NaOH-treated 42 to 48 mesh firebrick.

### CRESOL MIXTURE (fig. 1)

A 4-ml mixture of 90.2 percent of U.S.P. cresol and 9.8 percent of toluene (as solvent) was refluxed with 9 ml of hexamethyldisilazane for 12 hours (51). The product was analyzed on the silicone oil column operated at 125° C. The flow of the helium carrier gas was 153.2 ml/min;  $\Delta P$  was 896 mm, and the atmospheric pressure was 736 mm.

### 2,4,6-TRIMETHYLPHENOL MIXTURE (51)

A 3-ml mixture of 40.24 percent 2,4,6-trimethylphenol, 13.34 percent phenol, 4.00 percent *p*-ethylphenol, 25.09 percent *m*-cresol (mp 10°–12° C), 12.48 percent 2,6-xyleneol, and 4.84 percent toluene was refluxed with 6 ml of hexamethyldisilazane for 16 hours.

### PHENOL AND WATER MIXTURE (51)

A 0.7-ml mixture consisting of 99.66 percent water, 0.18 percent phenol, and 0.16 percent amyl alcohol was refluxed with 8.5 ml of hexamethyldisilazane for 15 hours.

## OTHER NEW METHODS OF SEPARATION AND ANALYSIS OF PHENOLS

Karr and others (44) extended Golumbic's procedure for countercurrent distribution of phenols (28, 29) to the separation of high-boiling tar fractions. (Countercurrent distribution is in effect an automatic multistage fractionation.) The presence of 84 individual compounds was demonstrated in tar acid fractions (bp 231°–331° C) from a low temperature bituminous coal tar. Karr concluded that countercurrent distribution in combination with ultraviolet and infrared spectroscopy is especially useful for analysis of complex mixtures of high-boiling phenols. Supplementing the countercurrent distribution of a highly complex tar acid mixture with an analysis by the newly developed low-ionizing voltage mass spectrometry might be more informative, because a molecular weight distribution can be directly obtained.

<sup>4</sup> Percentage data refers to percent by weight unless otherwise stated.

# DETERMINATION OF THE HYDROXYL CONTENT OF COALS AND VITRAINS BY FORMATION OF TRIMETHYLSILYL ETHERS

## EARLIER METHODS

The various methods used for the determination of hydroxyl groups in coal have been reviewed previously (4, 17, 77). More recently, comparisons of some of these methods have been made (32, 33).

Potential uncertainties are present in each of the methods that were based on conventional procedures. Methylation by either dimethyl sulfate, in the presence of base (84), or by diazomethane (4), gives low values, presumably due to incomplete reaction. The method of ion-exchange, which uses barium hydroxide (8, 38, 47, 73), may give rise to hydrolysis products, but in high rank coals, the functional groups appear to be inaccessible to the reagent. Potentiometric titration in ethylenediamine (6, 7, 55, 63, 78) not only determines the acidic hydroxyl but also will include quinones and acidic nonhydroxylic hydrogen groups. Results by this method are difficult to reproduce. Several acetylation procedures have been used, as well as different methods for estimation of the extent of reaction (4, 8, 11, 19, 37, 56-58, 83). Inherent uncertainties in acetylation values include possible acetylation of nitrogen-containing systems and failure to react with hindered or hydrogen-bonded hydroxyl groups. Determination of hydroxyl groups in coal through formation of their trimethylsilyl ethers (25, 26) seems to be a method that does not suffer from the uncertainties mentioned.

## DISCUSSION OF THE TRIMETHYLSILYL ETHER METHOD

The method involves treatment of minus 325-mesh whole coal or vitrain sample with hexamethyldisilazane in pyridine, either with or without trimethylchlorosilane.<sup>5</sup> After removal of solvent and reagents, the sample is washed with petroleum ether, dried, and analyzed for silicon. The hydroxyl or hydroxyl oxygen content then can be calculated from the silicon value. The number of trimethylsilyl groups introduced into coal can be determined

<sup>5</sup> In the early work on whole coals, relatively large amounts of trimethylchlorosilane and long reflux periods were used. Later it was learned that coal reacts rapidly with only a trace of trimethylchlorosilane.

also by a new method based on the infrared adsorption of potassium bromide disks containing the treated coal. This spectroscopic method, however, has been applied only to the vitrains.

Figure 2 shows that when the results determined by the trimethylsilyl ether method are compared with those reported for the acetylation procedure of Blom and others, fairly good agreement is obtained for the hydroxyl oxygen contents of similar rank vitrains. These

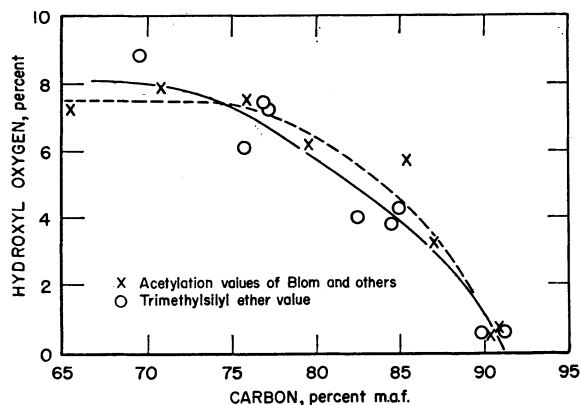


FIGURE 2.—Percent of Hydroxyl Oxygen in Vitrains.

values differ not too greatly from those reported for coals titrated in ethylenediamine (6, 7, 63, 78). This similarity of results is reassuring and instills confidence in the assumption that each of these methods has been measuring essentially the same thing—the hydroxyl content or the phenolic content of coal—since there is no evidence for the presence of nonphenolic hydroxyl groups in any but low-rank coals. The agreement among the different methods implies that no hindered nonacetyltable groups, or any titratable nonphenolic groups are present.

The determination of hydroxyl content of coal by trimethylsilylation is now preferred by the Bureau because of its ease of application and freedom from side reactions. Furthermore, a coal sample weighing not more than 10 milligrams can be analyzed for its content of (phenolic) hydroxyl groups when infrared spectroscopy is used after the trimethylsilyl ether formation.

Experiments with model compounds (see the later section on preparations) indicated that formation of the trimethylsilyl derivatives is quantitative with both hindered and hydrogen-bonded hydroxyl groups; nitrogen-containing functional groups suspected of being present in coal do not react to form trimethylsilyl derivatives (48).<sup>6</sup> The reaction with coal is rapid; the determination of extent of reaction is a direct analysis of the treated coal for silicon content—no hydrolysis step or back-titration is necessary.

The results obtained by the trimethylsilyl ether method appear to be relatively insensitive to interference from oxygen. However, in obtaining the results given in this report, reasonable care was taken to exclude atmospheric oxygen during grinding and refluxing. Some of the early work (25) was not performed with these precautions. The values obtained for identical coals under both sets of conditions, however, checked within the reproducibility of the method. Bubbling dried air through the reaction mixture during reflux did increase the silicon content of the coals, but the values so obtained were not reproducible.

Neither pretreatment with boiling water nor with dilute hydrochloric acid by the procedure of Blom and others (4) changed the hydroxyl values finally obtained, but the acid treatment caused poorer reproducibility than was obtained with untreated coal samples.

Although the standard procedure involved heating the coal or vitrain in the pyridine-hexamethyldisilazane-trimethylchlorosilane mixture at reflux temperature (approximately 115° C), several analyses were made also at 150° C in a stainless steel reaction vessel. Within the reproducibility of the method, the hydroxyl values obtained in the latter process were the same as the values from the standard procedure.

Considerable difficulty was experienced with minus 60-mesh samples; consequently, minus 325-mesh samples were used in all analyses (57). The method seems to be reasonably insensitive to reaction conditions. The only requirements are a sample ground to pass 325-mesh, the use of dry pyridine, and sufficient hexamethyldisilazane to allow complete reaction.

Of the functional groups other than the hydroxyl group suspected of being in coal, only the free carboxyl group reacted with hexamethyldisilazane. In experiments with benzoic acid and naphthoic acid, a mixture of trimethylsilyl ester and the acid amide (formed from the liberated ammonia) was obtained. The comparatively few carboxyl groups in coal probably react similarly to form some tri-

ethylsilyl ester and some amide; the ester would affect the results if present in large amounts, but fortunately, appreciable amounts of carboxyl groups occur only in very low rank coals. The trimethylsilyl esters of the carboxylic compounds are extremely sensitive to moisture.

Having demonstrated the ease with which trimethylsilyl ether formation occurs with the organic hydroxyl groups in coal, it was also necessary to ascertain whether inorganic hydroxyl groups, possibly present in coal mineral matter, would interfere with the determination of phenolic hydroxyl groups by reacting with the reagents used in the procedure. This question was resolved by treating inorganic materials representing the different types of hydroxyl groups that could be present in mineral matter. Calcium hydroxide is an example of a compound containing an inorganic hydroxyl group, and kaolin is a clay mineral often found in coal, which contains chemically bound water of hydration. Under conditions used for trimethylsilyl ether formation of coals, neither substance reacted with the reagents. Therefore, silicon does not add to the mineral matter in coal during the reaction (26).

The stability of the trimethylsilyl ethers of coal is excellent. Storage in a tightly capped sample vial for over a year did not cause any detectable change in the silicon analysis of the trimethylsilyl ether of Pond Creek vitrain. Washing such a sample with petroleum ether (60°–68° C), ethanol, or water had no detectable effect on the silicon content. Refluxing with water for 1 hour gave slight hydrolysis; 72 hours of refluxing effected the hydrolysis of only one-third of the silicon introduced into Bruceton vitrain. This behavior toward water apparently is due to the water-proofing nature of the trimethylsilyl group. Yet, 85 percent of the trimethylsilyl groups were successfully removed by hydrolysis after 1 hour of reflux with the system pyridine-ethanol-water.

## CHEMICAL ANALYSIS OF COALS AND VITRAINS

The identity and ultimate analyses of the coals and vitrains that were studied are listed in tables 3 and 4, respectively. The coals were analyzed for the hydroxyl content through the formation of the trimethylsilyl ethers. The analytical procedure is described later under the subject Gravimetric Analysis for Silicon. The results, calculated as hydroxyl oxygen content and the ratio of hydroxyl oxygen to the total oxygen content, are given in table 5. The analysis for the hydroxyl oxygen content of vitrains is discussed in the following section.

<sup>6</sup> Primary amines will react, while secondary amines form trimethylsilyl derivatives only under special conditions.

## INFRARED SPECTROSCOPY OF THE TRIMETHYLSILYL ETHERS OF COAL

Potassium halide disks have been used previously for quantitative analysis of mixtures (14, 34, 81); the use of disks to study the extent of reaction on cellulose also has been reported (36, 59). Subsequent to the development of the method described in this report, a similar spectroscopic procedure was reported by Durie and Sternhell (19) for acetylated coals. Their extensive treatment of the quantitative aspects of potassium halide disk techniques has verified several observations by the Bureau.

The infrared spectra of coal trimethylsilyl ethers show several distinctive absorption bands due to the Si-CH<sub>3</sub> and Si-O-C groups. In particular, the band at 8.0 $\mu$ , attributed to

Si-(CH<sub>3</sub>)<sub>2</sub> deformations (3, 85), is very intense and has little interference from the absorption due to the coal. A sample of trimethylsilylated Rock Springs vitrain that had given consistent gravimetric silicon analyses was selected for study. A series of potassium bromide disks was made with concentrations varying from one part of the treated coal in 560 parts of potassium bromide to one part in 50. When the optical density of these disks at 8.0 $\mu$  was plotted against concentration of silicon (determined by gravimetric analysis), the resulting points fitted a straight line passing through the origin and having a slope of 1.45 (see fig. 3). The point corresponding to the disk with the greatest concentration (not shown in the figure) was below the line, which indicates a departure from Beer's law at high optical densities.

TABLE 3.—*Identity of coals and vitrains studied*

Item No.	State or country	Seam	Mine	County	Rank <sup>1</sup>
1	North Dakota	Beulah-Zap	Beulah	Mercer	Lignite.
2V	do		Kincaid	Burke	Do.
3	do		do	do	Do.
4	do	Beulah-Zap	Knife River	Mercer	Do.
5	Colorado	Laramie		Weld	Subbituminous.
6	Canada		Red Hot	Edmonton, Alberta	
7	Illinois	No. 6	Little Dog	Macoupin	hvb.
8V	Jugoslavia		Raca <sup>2</sup>		
9	Illinois		Danville <sup>2</sup>	Vermilion	hvc.
10V	do	No. 6	Little John	Knox	hvc.
11	do	No. 7	Harrmattan	Vermilion	hvc.
12	Ohio	Pittsburgh No. 8	Dorothy	Belmont	hvb.
13	Pennsylvania	Middle Kittanning			mvb.
14	Ohio	do		Athens	hvb.
15	Kentucky	No. 11		Hopkins	hvb.
16	do	No. 12		do	hvb.
17	Indiana	No. V	Enos	Pike	hvb.
18	Kentucky	No. 9		Hopkins	hvb.
19	do	No. 11		Muhlenberg	hvb.
20	Indiana	No. V		Knox	hvb.
21	Ohio	Pittsburgh No. 8	Powhatan	Belmont	hvb.
22	Illinois	No. 6	Orient No. 3	Jefferson	hvb.
23	Indiana	No. V			hvb.
23V	Wyoming		Rock Springs	Sweetwater	hvc.
24	do		do	do	hvc.
25	Utah	Sunnyside	Sunnyside No. 1	Carbon	hvb.
26	Illinois	No. 5		Saline	hvb.
27	West Virginia	Pittsburgh		Marion	hvb.
27V	Pennsylvania	do	Bruceton	Allegheny	hvb.
28V	do	do	do	do	hvb.
29V	Kentucky	No. 9	Pond Creek	Muhlenberg	hvb.
30	West Virginia	Powellton			hvb.
31	do	No. 2 Gas Bed	Lady Dunn	Fayette	hvb.
32	do	Sewell	Big Knob No. 1	Randolph	mvb.
33V	Pennsylvania	Fulton		Huntingdon	lvb.
34V	West Virginia	Sewell	Marianna	Wyoming	mvb.
35V	do	Pocahontas No. 3	Buckeye No. 3	do	lvb.
36	Pennsylvania		Dorrance	Luzerne	Anthracite.
	do		Jeddo	do	Do.

<sup>1</sup> Ranks: hvab, high-volatile A bituminous.  
hvb, high-volatile B bituminous.  
hvc, high-volatile C bituminous.  
lvb, low-volatile bituminous.  
mvb, medium-volatile bituminous.

<sup>2</sup> Location.

TABLE 4.—*Ultimate analysis of coals and vitrains*

Item No. <sup>1</sup>	Moisture- and ash-free basis, percent					Ash	Silicon
	Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen		
1	64.15	5.32	0.87	0.46	29.19	6.04	0.27
2	64.96	5.72	.77	.87	27.68	6.78	.45
2V	68.5	5.0	.9	.5	25.1	4.7	.03
3	65.74	5.18	.85	.54	27.68	7.98	1.01
4	66.91	5.48	1.41	.39	25.81	4.22	.93
5	70.75	5.32	1.41	3.39	19.14	10.53	1.36
6	71.94	5.50	1.36	2.71	18.58	8.58	3.13
7	75.06	5.58	1.13	12.14	6.09	12.58	.51
8V	75.7	5.8	1.2	1.5	15.8	.9	.12
9	76.47	5.66	1.38	3.35	13.13	7.42	1.57
10V	77.2	5.9	1.1	1.6	14.2	.4	.07
11	77.42	5.47	1.36	4.18	11.57	4.18	1.42
12	77.48	5.63	1.57	1.06	14.26	6.57	1.40
13	77.52	5.33	1.59	1.07	14.48	6.92	1.53
14	77.94	5.68	1.58	3.70	11.10	5.46	1.26
15	78.00	5.79	1.39	3.71	11.11	10.90	2.98
16	78.15	5.74	1.54	3.82	10.74	9.05	1.98
17	78.32	5.64	1.63	4.47	9.93	11.19	2.72
18	78.37	5.62	1.60	3.56	10.85	7.87	2.11
19	78.79	5.72	1.57	4.37	9.55	7.68	1.47
20	78.84	5.88	1.16	4.83	9.28	8.01	1.40
21	78.87	5.57	1.83	1.47	12.26	7.06	2.03
22	79.11	5.55	1.35	1.82	12.17	14.23	3.48
23	79.31	5.41	1.74	.90	12.64	1.96	.48
23V	76.9	5.8	2.1	.9	14.3	.9	.06
24	79.79	5.73	1.74	1.01	11.72	5.42	1.86
25	80.90	5.62	1.92	1.32	10.24	6.71	1.80
26	82.32	5.70	1.27	3.69	7.02	8.91	1.63
27	82.68	5.51	1.61	1.18	9.02	4.93	1.17
27V	82.5	5.5	1.0	1.2	9.8	2.3	.20
28V	84.5	5.3	1.2	.7	8.3	2.3	.45
29V	84.9	5.0	1.6	.5	8.0	1.5	.21
30	84.93	5.65	1.71	.82	6.89	3.36	.83
31	87.86	5.20	1.17	1.01	4.77	7.52	1.65
32	89.16	4.59	1.45	1.30	3.50	6.60	1.36
33V	89.4	5.2	1.0	.7	3.7	2.3	.16
34V	89.9	4.5	1.5	.6	3.5	2.4	.42
35V	91.2	2.6	1.1	.6	4.5	2.3	.34
36	93.25	2.23	.79	.52	<sup>2</sup> 1.26	3.34	.70

<sup>1</sup> Identity of coal or vitrain is given in table 3.<sup>2</sup> Oxygen by direct determination, all other values by difference.TABLE 5.—*Hydroxyl oxygen content of coals*

Item No. <sup>1</sup>	Hydroxyl oxygen, percent <sup>2</sup>	$\frac{O_{OH}}{\text{total } O}$ , percent	Item No. 1	Hydroxyl oxygen, percent <sup>2</sup>	$\frac{O_{OH}}{\text{total } O}$ , percent
1	4.46	16.3	18	5.61	51.7
2	5.96	23.1	19	5.26	55.1
3	5.85	23.0	20	4.44	47.8
4	4.13	16.0	21	5.34	43.6
5	7.79	40.7	22	2.68	22.0
6	3.51	18.9	23	4.47	35.3
7	1.35	22.2	24	3.56	30.4
9	5.15	39.2	25	4.68	45.6
11	3.81	32.9	26	3.23	46.9
12	5.01	35.2	27	3.45	38.2
13	4.53	31.3	30	3.22	46.7
14	5.21	46.9	31	1.79	37.5
15	5.41	48.7	32	.18	5.1
16	4.78	44.5	36	.18	14.3
17	4.10	41.3			

<sup>1</sup> Identity of coals given in table 3.<sup>2</sup> By gravimetric analysis for silicon before and after the trimethylsilyl ether formation.

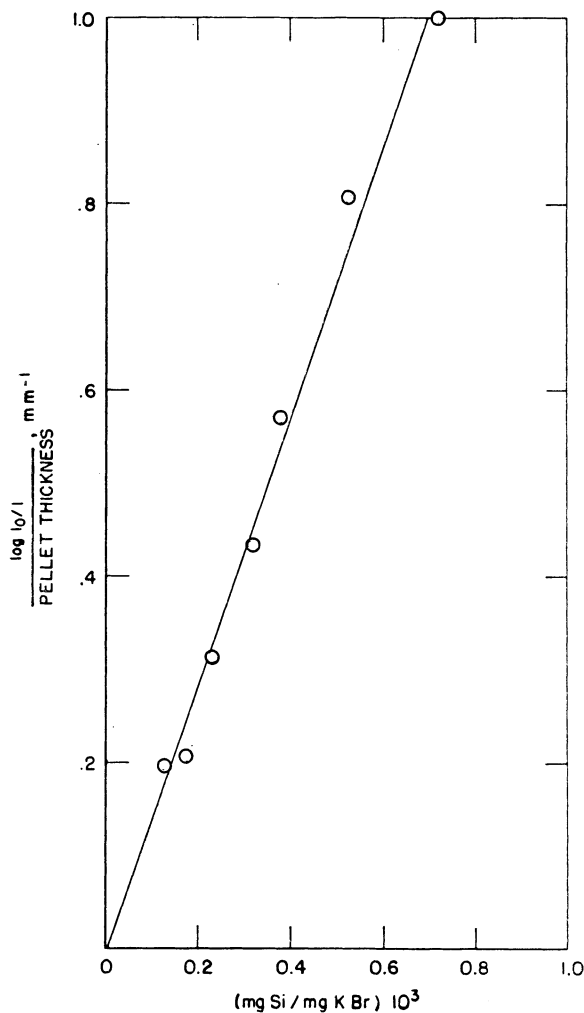


FIGURE 3.—Calibration Curve for Trimethylsilyl Groups at  $8.0\mu$ .

TABLE 6.—Hydroxyl oxygen content of vitrains by gravimetric and infrared analysis

Item No. <sup>1</sup>	Hydroxyl oxygen, percent		$\frac{O_{OH}}{\text{total } O}$ , percent
	Gravimetric <sup>2</sup>	Infrared <sup>2</sup>	
2V-----	<sup>3</sup> 8.8 ± 0.1	6.7	35.1
8V-----	6.1 ± .1	( <sup>4</sup> )	38.6
10V-----	7.2 ± .1	5.8	50.7
23V-----	7.4 ± .2	7.1	52.0
27V-----	4.0 ± .3	4.6	40.8
28V-----	3.8 ± .2	3.5	45.8
29V-----	4.2 ± .2	4.1	52.5
33V-----	1.6 ± .3	1.4	43.2
34V-----	.5 ± .1	.8	14.3
35V-----	.6 ± .1	( <sup>5</sup> )	13.3

<sup>1</sup> Identity of vitrain is given in table 3.

<sup>2</sup> By analysis of the trimethylsilylated vitrain.

<sup>3</sup> Absolute variation.

<sup>4</sup> Insufficient sample remaining for analysis.

<sup>5</sup> See text on infrared spectroscopy.

Disks were then prepared from the trimethylsilylated vitrains, and the silicon contents were determined by use of the experimentally evaluated absorptivity,  $k$ , of 1.45. The corresponding hydroxyl oxygen values are shown in table 6. A close correlation will be noted between the hydroxyl oxygen values obtained in this manner and those determined by gravimetric analysis. Elemental analyses were carried out on several treated vitrains—no chlorine was found; nitrogen content showed little if any increase, which indicated no more than traces of adsorbed pyridine were present. No evidence of pyridine adsorption was observed in the infrared spectra of the treated vitrains. No usable spectrum of the trimethylsilyl ether of anthracite could be obtained because of the high background absorption of anthracite.

The infrared spectra of the treated vitrains, aside from offering a quantitative measure of trimethylsilylation and revealing absence of unreacted hydroxyl groups, also provide circumstantial evidence concerning the possible presence of carbonyl groups. That these groups exist in coal has been suggested on the basis of the intense infrared absorption at  $6.19\text{--}6.25\mu$  (10, 23, 24). Normally, a carbonyl group would not be expected to absorb at this high wavelength; the carbonyl-containing compounds cited as having infrared absorption at this wavelength are all hydrogen-bonded conjugated carbonyl compounds such as hydroxyanthraquinones (10), kojic acid,  $\beta$ -diketones, and 2 hydroxyacetophenone (23, 24). Although all of these compounds absorb at approximately  $6.2\mu$ , each compound has either (1) absorption at a slightly lower wavelength ( $6.0\text{--}6.1\mu$ ), which may be ascribed to the hydrogen-bonded conjugated carbonyl; or (2) two functional groups which absorb at  $6.2\mu$ . This phenomenon is demonstrated by the trimethylsilyl ether derivatives of these compounds. For those compounds absorbing at both  $6.2\mu$  and in the  $6.0\mu$  region, the spectra of the trimethylsilyl ethers show the expected shift of the band near  $6.0\mu$  to a lower wavelength, while the band at  $6.2\mu$  is changed only slightly, if at all. For compounds having two functional groups that absorb at  $6.2\mu$ , the spectra of the trimethylsilyl derivatives show a split band, one part due to the conjugated C=O, the other due to C=C. This condition is true also for the enol ether (80) and enol acetate of acetylacetone (64). Thus, a probability exists that the absorption at  $6.2\mu$  by the hydrogen-bonded conjugated carbonyl compounds is due to the C=C bond with the absorption for C=O occasionally superimposed (5, 15, 18, 80). In each instance the absorption at  $6.2\mu$  is enhanced by an electronegative group ( $-\text{OH}$ ,  $-\text{OSi}(\text{CH}_3)_3$ ,

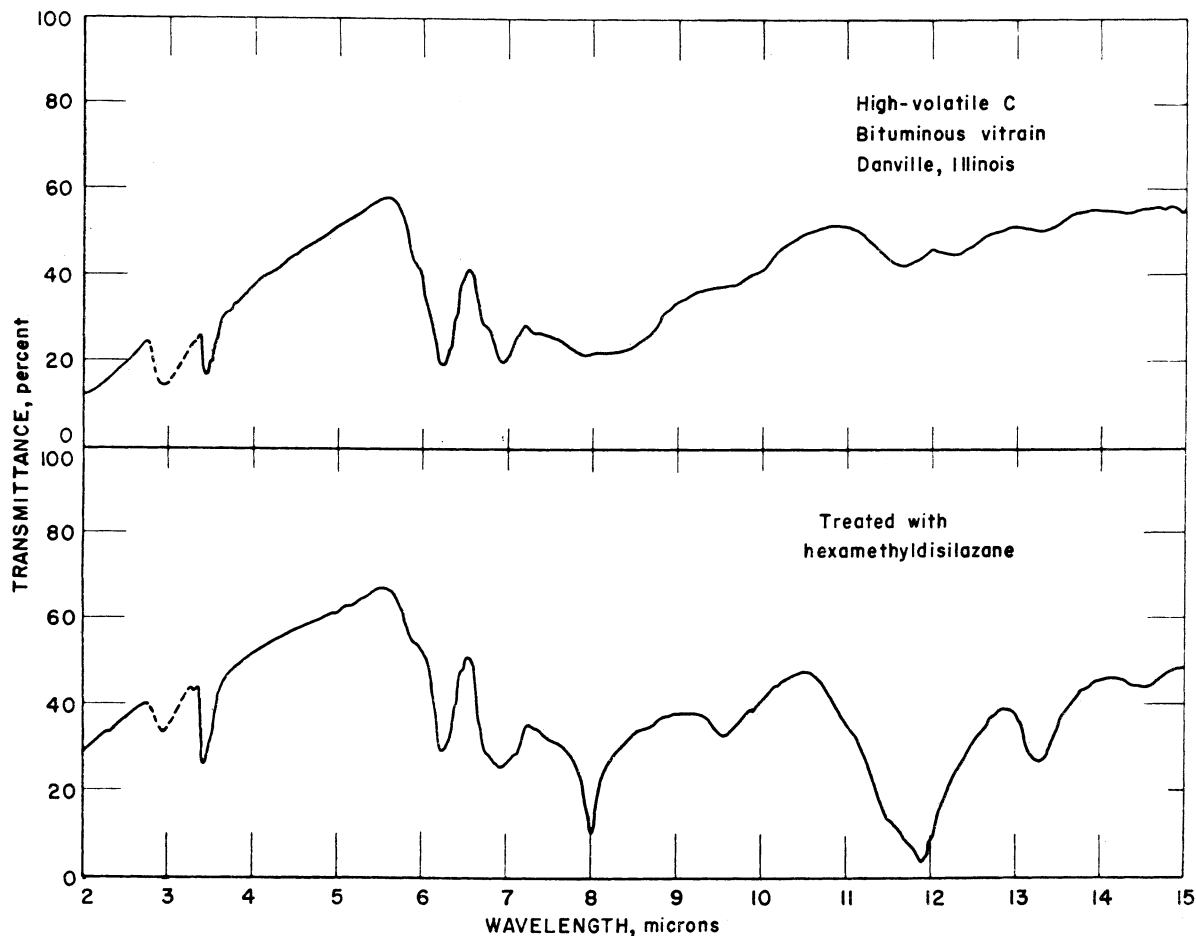


FIGURE 4.—Infrared Spectra of Coal Before and After Treatment With Hexamethyldisilazane.

$-\text{OC}_2\text{H}_5$ ) on one of the olefinic carbons. However, formation of an ether or ester derivative of such a conjugate chelate carbonyl system, causes a shift to a lower wavelength of at least one band in the  $6.0\text{--}6.2\mu$  region (64, 80). In the trimethylsilylated vitrains, little, if any, such change is observed (fig. 4). Acetylated coals similarly show little change in absorption in the  $6.2\mu$  region (19). Assuming that all hydroxyl groups in coal, whether simple or chelated, are converted to their respective trimethylsilyl ethers during treatment with hexamethyldisilazane, then the absorption at  $6.2\mu$  must be assigned primarily to  $\text{C}=\text{C}$  vibrations, with but a small contribution from carbonyl groups of any kind. The assumption that all hydroxyl groups have been converted to trimethylsilyl ethers in the treated vitrains is valid if behavior in known compounds is considered. Assignment of this intense absorption band to  $\text{C}=\text{C}$  vibrations (principally in systems containing aromatic ether substituents) is reasonable, since such systems normally

absorb at this wavelength with an intensity which varies over a considerable range (3). Even in simple molecules, such as *m*-cresol and anisole, the  $6.2\mu$  absorption is one of the most intense bands in the infrared spectrum.

These considerations refer only to hydrogen-bonded hydroxycarbonyl groups and do not exclude the presence in coal of some as yet unsuggested type of carbonyl group which does absorb at  $6.2\mu$ . Both 3,3',5,5'-tetramethylstilbenequinone and 3,3',5,5'-tetra-*t*-butyl-diphenoquinone have strong absorption bands at  $6.2\mu$ . They also have weak absorption bands at  $6.1\mu$ .

## EXPERIMENTAL

### Formation of the Trimethylsilyl Ethers of Coals

A 5-gram sample of the coal, ground to minus 325-mesh and dried to constant weight in a vacuum oven, was refluxed under nitrogen



in a solution of 5 ml of trimethylchlorosilane and 10 ml of hexamethyldisilazane in 50 ml of dry pyridine. The reflux period was 4 days except where noted later. At the end of this time, the reagents were distilled off under vacuum. The reacted coal was washed with petroleum ether (bp 60°–68° C) to remove the last traces of reagents and was dried in a vacuum oven.

Reflux periods from 1 hour to 8 days were used on one coal. As shown in table 7, the reaction was essentially complete after only 1 hour. With this coal (14.5 percent O) the method gave results reproducible to  $\pm 3$  (relative) percent of the oxygen content, based on the weight of total oxygen in the moisture- and ash-free coal.

TABLE 7.—Effect of time on formation of the trimethylsilyl ethers in coal<sup>1</sup>

Time, hour	Silicon in treated coal, percent	Oxygen as OH in original coal, percent	$\frac{\text{O OH}}{\text{O total}}$ , percent
1-----	8.08	5.07	35.0
4-----	7.97	4.97	34.3
24-----	8.35	5.33	36.8
96-----	7.90	4.60	31.8
96-----	7.57	4.91	33.9
192-----	8.57	5.43	37.5
Average----	8.07	5.05	34.9

<sup>1</sup> No. 13 of table 3.

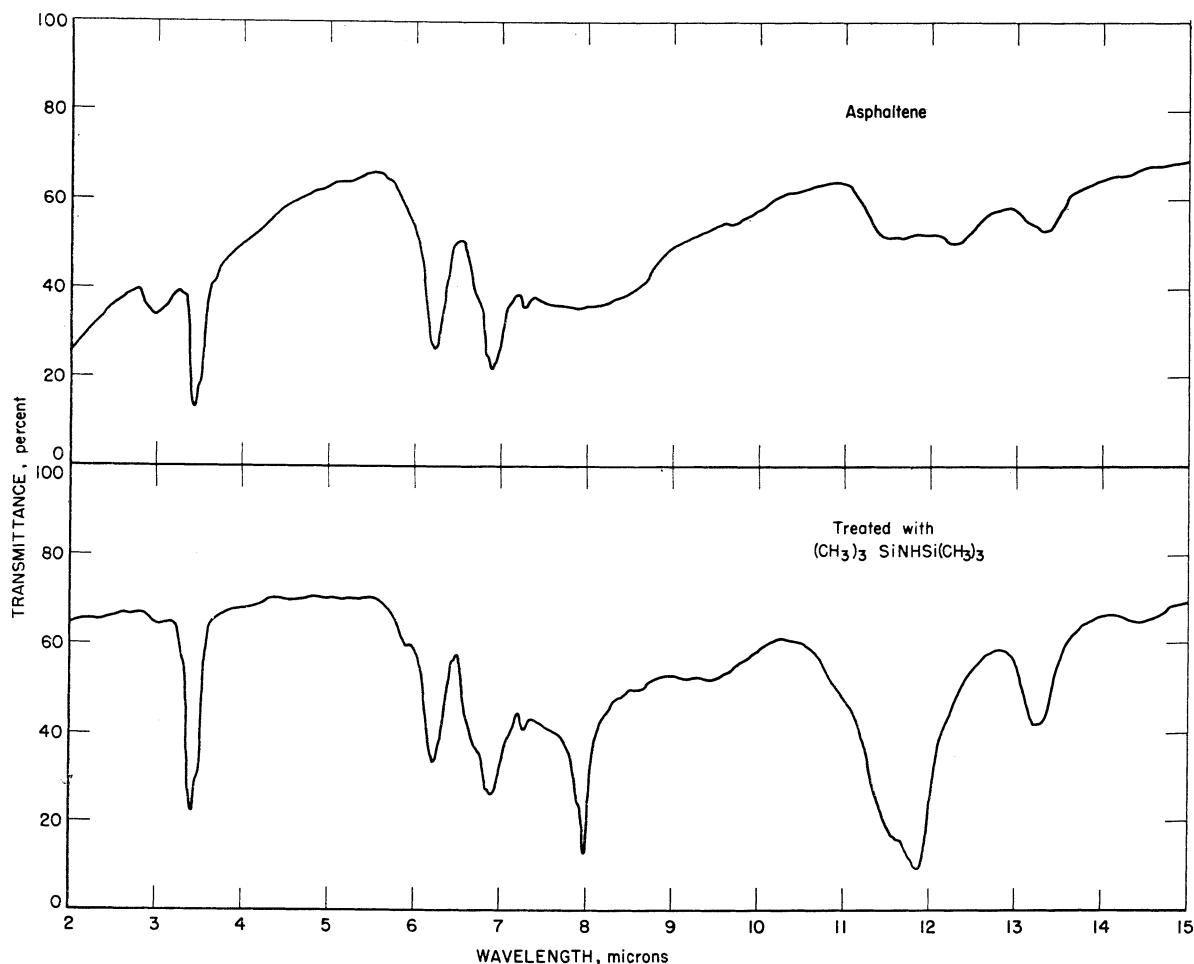


FIGURE 5.—Infrared Spectra of Asphaltene Before and After Treatment With Hexamethyldisilazane.

### Formation of the Trimethylsilyl Ethers of Coal Hydrogenation Asphaltene

To 20 ml of hexamethyldisilazane was added 1 gram of a coal hydrogenation asphaltene and 1 drop of trimethylchlorosilane. The solution was refluxed under nitrogen for 3 days, and the reagents then were removed by distillation under vacuum. The dry residue exhibited some solubility in heptane; therefore, no washing was possible. Instead, the product was dried in a vacuum oven to constant weight. The infrared analyses of the product (fig. 5) indicated that almost all the hydroxyl groups had reacted.

Analysis of the asphaltene before treatment was C, 85.25; H, 7.00; N, 1.15; and O, 6.60 percent.

The treated asphaltene contained 6.21 percent silicon, corresponding to a hydroxyl oxygen content that is equivalent to 64 percent of the oxygen present in the original asphaltene.

### Formation of the Trimethylsilyl Ethers of Vitrains (26)

#### REFLUX METHOD

A 2- to 3-gram sample of vitrain (ground to minus 325-mesh under nitrogen in a stainless steel ball mill containing Borundum balls and dried to constant weight in a vacuum oven) was refluxed under nitrogen in a solution of 20 ml of hexamethyldisilazane and 50 ml of dry pyridine. In most instances, duplicate runs were made with 0.01, 0.2, and 5.0 ml of added trimethylchlorosilane. Since the amount of trimethylchlorosilane used did not have any noticeable effect on the results, the values reported in table 6 are averages of six determinations. Refluxing was carried out overnight (16 hr) to ensure completion of reaction. At the end of this time, the reagents were removed by vacuum distillation. The product was washed with 5 ml parts of petroleum ether (bp 60°-68° C), to remove the last traces of reagents, and was dried in a vacuum oven to constant weight.

#### BOMB METHOD

To a 70 ml stainless steel bomb with a glass liner were added 2 grams of minus 325-mesh vitrain, 20 ml of dry pyridine, 5 ml of hexamethyldisilazane, and 0.25 ml of trimethylchlorosilane. The bomb was then evacuated and heated for 16 hours at 154° C. The product was processed as previously mentioned.

### Attempted Reactions of Hexamethyldisilazane and Trimethylchlorosilane with Inorganic Hydroxyl Compounds

#### CALCIUM HYDROXIDE

To a solution of 5 ml of hexamethyldisilazane and 5 ml of trimethylchlorosilane in 20 ml of dry pyridine was added 1 gram of calcium hydroxide. The mixture was refluxed for 7 hours. The residue was filtered off and washed with petroleum ether, air dried, and then dried further in a vacuum oven. The infrared spectrum of this material was identical with that of the starting calcium hydroxide.

#### KAOLIN

The preceding experiment was repeated with kaolin ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ) instead of the calcium hydroxide. Infrared analysis of the resulting material showed that no reaction occurred with the chemically bound water.

### Infrared Spectroscopy (26)

Infrared spectra were obtained on a Perkin Elmer Model 21 spectrometer. Liquids and low-melting solids were examined as thin films; other solids were examined as potassium bromide pellets.

Quantitative spectra of the vitrain trimethylsilyl ethers were obtained by use of potassium bromide pellets. Best results were obtained by hand grinding the potassium bromide with the powdered vitrain (previously ground to minus 325-mesh) in an agate mortar and pestle for 10 minutes, followed by pelleting in a press. Grinding the vitrain and potassium bromide together for longer periods of time resulted in poor reproducibility of spectra. Concentrations varied from 1 part of sample in 125 parts of potassium bromide, to 1 part in 175 parts, depending on the absorption characteristics of the coal. The potassium bromide pellet spectra showed bands at 8.00 $\mu$  (strong), 9.60 (medium), 11.90 (strong), 13.20 (medium), and 14.50 $\mu$  (weak), as well as the expected coal absorption. The spectra of a high-volatile C bituminous vitrain before and after treatment have already been shown in figure 4. The treated vitrains were also examined as Nujol mulls to check for the absence of hydroxyl absorption at 3 $\mu$ . The mulls indicated absence of hydroxyl absorption at 2.8-3.1 $\mu$ .

A series of pellets of varying concentration was made from one sample of coal trimethylsilyl ether that gave consistently reproducible results when analyzed by the standard gravimetric procedure for silicon. By use of the absorption

band at  $8.0\mu$ , which is characteristic for trimethylsilyl groups, there was prepared a calibration curve (fig. 3) that correlates absorption and relative amount of trimethylsilyl groups. Since the data fit a straight-line plot, it was possible to obtain an absorption coefficient for the trimethylsilyl group at  $8\mu$ . The value obtained was  $k=1.45$ , where  $k$ =absorptivity= $A/Cl$ , and

$$A = \text{absorbance}$$

$$C = \frac{\text{mg Si}}{\text{mg KBr}}$$

$$l = \text{pellet thickness, mm}$$

A straight line approximating the absorption of the untreated coal was chosen as the base line and the absorbance was determined by measuring peak height.

### Gravimetric Analysis for Silicon (26)

Approximately 0.2 gram of sample was ignited in a Parr bomb containing an excess of sodium peroxide. The cooled bomb cup was leached in a nickel beaker, and the solution was made slightly acid with hydrochloric acid, and transferred immediately to a 400-ml beaker. To this material was added 5 ml of nitric acid and 100 ml of 70 percent perchloric acid. The mixture was heated to heavy fuming, allowed to cool, diluted with water, boiled for several minutes to evaporate free chlorine, and filtered through No. 41 H What-

man paper to collect the silica. The silica was washed first with dilute hydrochloric acid and then with water until neutral. The filter was ignited in a platinum crucible at about  $1,000^\circ\text{C}$  to constant weight and the residue was reported as silica. For a coal sample, the residue was fumed with hydrofluoric acid to volatilize the silica, which was reported as the loss on volatilization.

### Calculation of the Hydroxyl Content (26)

Either the hydroxyl or hydroxyl oxygen content of a coal or vitrain can be calculated from the silicon analyses of the treated sample and of the untreated sample by use of the appropriate formula given below.

$$\frac{b}{100} = \frac{a + 0.3889 X}{100 + X}$$

Therefore

$$X = \frac{100(b-a)}{38.89-b}$$

where  $X$  = percent of  $\text{SiC}_3\text{H}_8$  in treated sample  
 $a$  = percent of Si in untreated coal  
 $b$  = percent of Si in treated coal

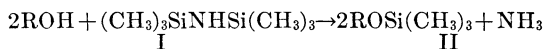
$$\frac{\text{Si}}{\text{SiC}_3\text{H}_8} = \frac{28.06}{72.15} = 0.3889$$

$$\text{percent OH} = \frac{17 X}{72.15} = 0.2356 X$$

$$\text{percent O as OH in raw sample} = \frac{16 X}{72.15} = 0.222 X.$$

## PREPARATION OF THE TRIMETHYLSILYL ETHERS OF PHENOLS

Speier (70) shows that hexamethyldisilazane (I) reacts quantitatively with hydroxyl groups according to the following equation:



Hexamethyldisilazane (I) was first used at the Bureau of Mines for the quantitative determination of hydroxylated compounds in the analysis of mixtures of Fischer-Tropsch alcohols by mass spectrometry of their trimethylsilyl ethers (II), (49, 86). The mixture of trimethylsilyl ethers was more easily and rapidly analyzed than the original alcohol mixtures because of the characteristic mass spectra of trimethylsilyl ethers.

This reaction proceeds with equal facility with simple phenolic compounds, such as phenol, resorcinol, and 1-naphthol, which prompted

an investigation (25, 26) to determine the ability of reagent I to react with hydroxyl groups present in hydrogen-bonded hydroxycarbonyl compounds, such as 1,5-dihydroxyanthraquinone (III of fig. 6). Hydrogen-bonded quinone groupings, as in compound III, have been postulated to exist in coal (10). This compound is reported to form a dimethyl ether only under severe reaction conditions (1)—when its dipotassium salt is heated with dimethyl sulfate at 140° C. However, it forms a bis(trimethylsilyl) ether (IV) readily on refluxing in hexamethyldisilazane; the reaction is essentially quantitative.

1,4- and 1,8-dihydroxyanthraquinones, as well as the hydrogen-bonded ketophenol 2,4-dihydroxyacetophenone (V), also react readily to form trimethylsilyl ethers.

The compound 6,11-dihydroxynaphthacene-5,12-quinone has been reported to undergo acetylation to the extent of 90 percent, and methylation to the extent of 5 percent (4). The bis(trimethylsilyl) ether is formed quantitatively.

Purpurin, 1,2,4-trihydroxyanthraquinone, forms a diacetate (32) when treated with acetic anhydride under the conditions normally used for acetylating coal (4); it forms a tris(trimethylsilyl) ether when refluxed with hexamethyldisilazane.

Work at the Bureau of Mines (26) has demonstrated that the highly hindered 2,6-di-*t*-butylphenol (VI) will react quantitatively with hexamethyldisilazane in the presence of trimethylchlorosilane and pyridine to form a stable trimethylsilyl ether (VII). Reported attempts to form other derivatives of compound VI indicated the necessity of forming the sodium salt first before any reaction will take place (13, 71), and that the derivatives formed in this way are para substitution products and not true phenol esters. Therefore, reaction of a hindered phenol with hexamethyldisilazane apparently represents a convenient and quantitative method for the formation of a derivative.

Finch and Post (20) treated 1-naphthol, 2-naphthol, and several dihydroxynaphthalenes with either dimethyldichlorosilane or trimethylchlorosilane, in the presence of pyridine, to prepare a series of 10 methylsiloxynaphthalenes in good yields.

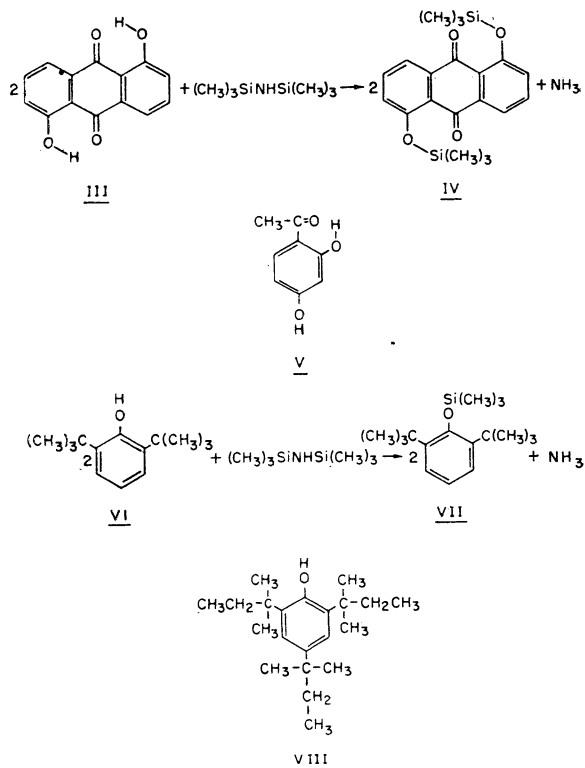


FIGURE 6.—Typical Structures of Hindered Phenols That React With Hexamethyldisilazane.

Success with the trimethylsilyl ether formation of both hydrogen-bonded and hindered phenols indicated that a method for determining the hydroxyl groups in coal (25) might be developed by using the reaction system hexamethyldisilazane-trimethylchlorosilane-pyridine. Choice of pyridine as a solvent was based on its effectiveness as a solvent for coal and the discovery that its presence was necessary for reaction with hindered phenols, such as 2,6-di-*t*-butylphenol. At that time the pyridine system was believed capable of forming trimethylsilyl ethers of any phenol. Subsequently (27) a study of 2,4,6-tri-*t*-butylphenol, 2,4,6-tri-*t*-amylphenol (VIII of fig. 6), and 2,6-di-*t*-butyl-4-methylphenol revealed that substituents in the para position of hindered phenols markedly impede the formation of trimethylsilyl ethers in the pyridine solvent.<sup>7</sup>

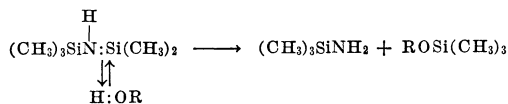
The reaction of the hydroxyl group to form the trimethylsilyl ether offers an excellent means for introducing a protecting group that can be removed by hydrolysis. The ease with which trimethylsilyl ethers are formed is dependent on the solvents used; the ease with which they are hydrolyzed is equally solvent dependent. The simple alcoholic and phenolic trimethylsilyl ethers are sensitive to moisture; water alone can hydrolyze these ethers. In practice, ethanol is added to serve as a mutual solvent to speed up the reaction. Alcoholic hydrochloric acid is required for the hydrolysis of the trimethylsilyl ether of 2,6-di-*t*-butylphenol and of the more unreactive 2,4,6-tri-*t*-butylphenol, which requires special conditions for preparation of its trimethylsilyl ether.

Some complex tar acid mixtures (phenols) and lignins do not give satisfactory results when treated with the combination of hexamethyldisilazane, trimethylchlorosilane, and pyridine. Conceivably, an acid-catalyzed (HCl or NH<sub>4</sub>Cl) polymerization, or some other reaction of sensitive compounds, such as indenols, is involved. The trimethylsilyl ethers of these tar acid mixtures can be obtained by refluxing first with hexamethyldisilazane alone from 4 to 8 hours then adding the trimethylchlorosilane and pyridine, and continuing the reflux. The initial reaction with hexamethyldisilazane presumably stabilizes or protects the sensitive compounds from the trimethylchlorosilane.

## DISCUSSION

The following simple electronic scheme for the reaction of a phenol and hexamethyldisilazane

(70) probably does not hold for the highly hindered phenols.



Although most phenols will react readily with hexamethyldisilazane itself, di-*t*-butylphenol requires the presence of pyridine and trimethylchlorosilane, but tri-*t*-butylphenol does not respond even to the latter conditions. At first, the presence of a base stronger than pyridine was considered necessary to cause reaction of the tri-*t*-butylphenol. Therefore, piperidine was substituted for the pyridine, but reaction still did not take place.

A further attempt was made to form the trimethylsilyl ether of the tri-*t*-butylphenol by a recently published procedure that has been successful on carbohydrate derivatives (35). This method, which uses trimethylchlorosilane and pyridine as reagents and a two-phase solvent system of hexane and formamide, was unsuccessful in our application.

Dimethylformamide, which is neither strongly basic nor strongly acidic, has many applications as a solvent for ionic reactions that fail in other solvents. This property is due primarily to the ability to keep ionic species in solution and the relatively high dielectric constant, which facilitates charge separation necessary for intermediates in some ionic reactions. When used as a solvent for the reaction between hexamethyldisilazane and tri-*t*-butylphenol, dimethylformamide proved to be singularly successful. One possible explanation is that at some stage in the reaction ionic resonance involving charge distribution at the ortho or para positions of the benzene ring is involved. When the para position is vacant, as in 2,6-di-*t*-butylphenol, the charge is free to reside at the para position and be solvated (for example, by pyridine) relatively easily. When no free ortho or para position is available, resonance stabilization becomes more difficult (especially when the substituents are electronegative alkyl groups), and a solvent with dielectric constant higher than that of pyridine is needed to facilitate solvation of this charge. A similar interpretation has been proposed recently to explain the difference in behavior of disubstituted benzenes in different solvents (74). Since trimethylsilyl ether formation probably involves some intermediate having mesomeric charge separation, it is not unreasonable to assume that ionic charges become resonance distributed through the pi orbitals of the benzene ring at some intermediate stage of the reaction. A more detailed

<sup>7</sup> At elevated temperature (150° C), 2,4,6-tri-*t*-amylphenol formed a trimethylsilyl ether in poor yield.

hypothesis concerning the role of solvent or reagent is not possible with the limited information available at present.

## CONCLUSIONS

Simple phenols react readily with trimethylchlorosilane. Hydroxycarbonyl compounds usually react with hexamethyldisilazane, but some require the combination of hexamethyldisilazane, trimethylchlorosilane and pyridine. Hindered phenols, such as 2,6-di-*t*-butylphenol, also require the three reagents. Hindered trialkylphenols, with alkyl groups in the 2,4,6-positions, will not react to form trimethylsilyl ethers even with the combination of hexamethyldisilazane, trimethylchlorosilane, and pyridine, but will react in the system hexamethyldisilazane and dimethylformamide. Lignin and complex mixtures of tar acids do not always give the desired products when treated with the combination of hexamethyldisilazane, trimethylchlorosilane, and pyridine. A two-stage procedure is more effective; first, refluxing with hexamethyldisilazane, then adding pyridine and trimethylchlorosilane and continuing the refluxing.

## EXPERIMENTAL

### Materials

Trimethylchlorosilane, Dow Corning technical grade, was distilled through a 12-plate glass-helix-packed column. Hexamethyldisilazane was prepared by bubbling ammonia through a solution of trimethylchlorosilane in petroleum ether (48), or was obtained by purchase. Pyridine was dried over anhydrous calcium sulfate (Drierite) before use. Dimethylformamide was found to be satisfactory when used as supplied by the manufacturer.

### Reaction of Simple Phenols With Trimethylchlorosilane in Petroleum Ether

#### PREPARATION OF TRIMETHYLSILYL ETHER OF PHENOL (TRIMETHYLSILOXY- BENZENE)

To 37.4 grams (0.4 mole) of phenol was added 54.5 grams (0.5 mole) of trimethylchlorosilane. After 7 hours of refluxing, 50 ml of petroleum ether (bp 60°–68° C) was added. The solution was heated at reflux for another 4 hours and then distilled. After stripping, a total of 56.6 grams of material, bp 166°–178° C,  $n_D^{20}$  1.4907–1.4850, was recovered. This product was distilled through a 2-foot Podbielniak column to give 2 grams of material, bp 112°–174° C,

and 27.0 grams of material, bp 174°–181.9° C. Much of the latter was an azeotrope, bp 175.5° C,  $n_D^{20}$  1.5060. The yield was 20.5 grams of pure trimethylsilyl phenyl ether product, bp 181.9°–182.4° C (742 mm),  $n_D^{20}$  1.4782. Mass-spectrometric analysis of the phenol-phenyl ether azeotrope indicated an approximate composition by weight of 39.5 percent phenol and 60.5 percent trimethylsilyl phenyl ether (48).

Trimethylsilyloxybenzene was also prepared by refluxing 25 grams of phenol with 55 ml of trimethylchlorosilane for 24 hours. Infrared analysis of the distilled product indicated the refined product was essentially the pure trimethylsilyl ether of phenol.

#### PREPARATION OF BIS(TRIMETHYL- SILYL) ETHER OF RESORCINOL (1,3-BIS(TRI- METHYLSILOXY)BENZENE (48))

A mixture of 11.0 grams of resorcinol (0.1 mole), 32.7 grams (0.3 mole) trimethylchlorosilane, and 25 ml petroleum ether (bp 90°–100° C) was refluxed for 24 hours. The flask reflux temperature rose from 64° to 92° C. After stripping off petroleum ether and trimethylchlorosilane, distillation gave 19.4 grams (76.4 percent yield) of product, bp 237°–240° C,  $n_D^{20}$  1.4760. Precision fractionation of a part of this material gave a pure product, bp 154°–155° C/100 mm,  $n_D^{20}$  1.4748.

Calculated for  $C_9H_{14}OSi$ : C 56.6, H 8.7.

Found: C 57.0, 56.9, H 8.7, 8.7.

#### PREPARATION OF TRIMETHYLSILYL ETHER OF 1-NAPHTHOL

1-Trimethylsilyloxynaphthalene was prepared by a procedure similar to that used for resorcinol (48).

Calculated for  $C_{13}H_{16}OSi$ : C 72.2, H 7.5, Si 13.0.

Found: C 72.4, 72.3, H 7.6, 7.5, Si —, 13.0.

### Reaction of Hydroxyanthraqui- nones with Hexamethyldisil- azane and Trimethylchloro- silane in Pyridine

#### PREPARATION OF BIS(TRIMETHYL- SILYL) ETHER OF 1,5-DIHYDROXYANTHRA- QUINONE (26)

To 15 ml of hexamethyldisilazane was added 2.5 grams of 1,5-dihydroxyanthraquinone (recrystallized, mp 280°–284° C) and 1 drop of trimethylchlorosilane. The mixture was refluxed for 24 hours. Hexamethyldisilazane and other relatively volatile substances were removed by distillation under vacuum to leave

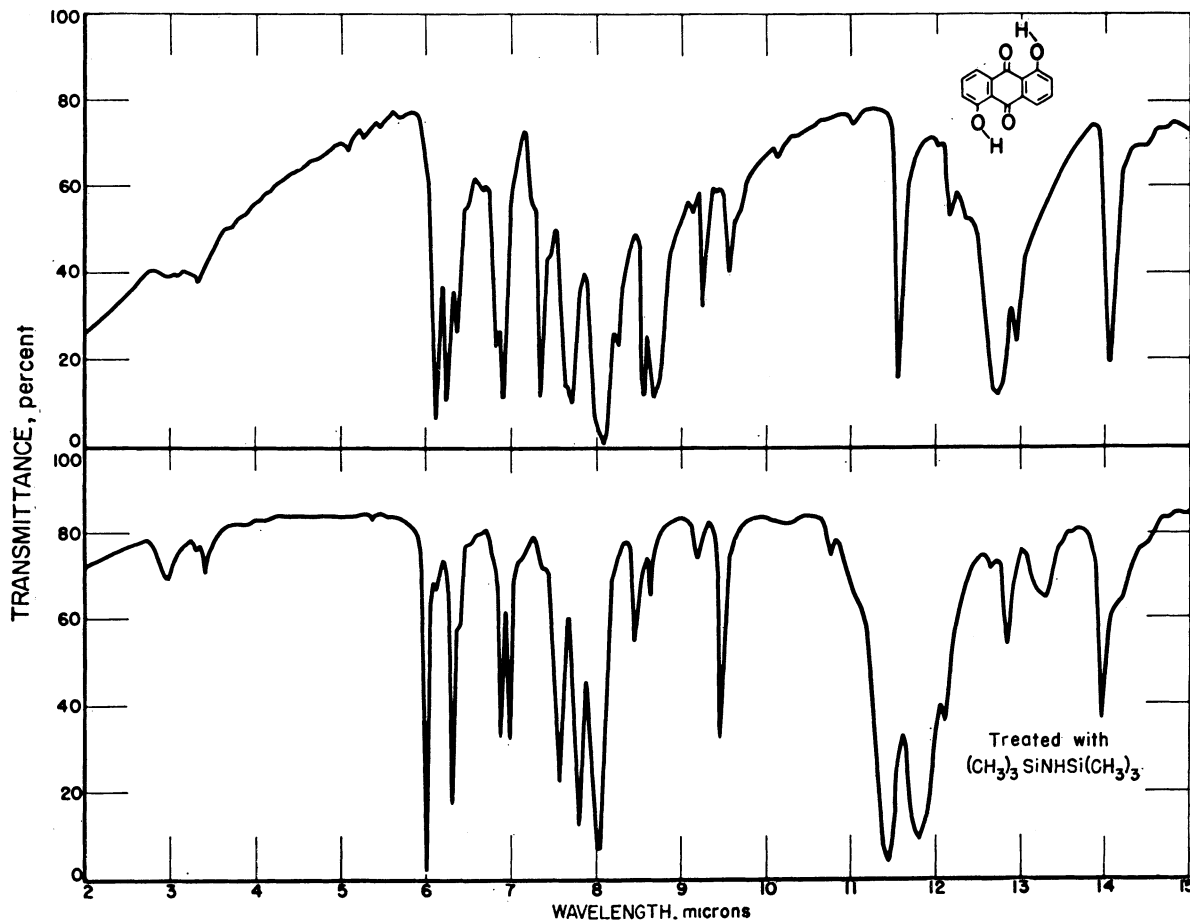


FIGURE 7.—Infrared Spectra of 1,5-Dihydroxyanthraquinone and its Trimethylsilyl Ether.

2.6 grams of solid, which on recrystallization from petroleum ether (bp 60°–68° C) gave orange crystals, mp 133°–142° C. The infrared spectrum of the refined product (fig. 7) showed absorption bands at 8.0, 9.45, 11.80, 13.25, and 14.5 $\mu$ , all of which are common to phenyl trimethylsilyl ether. In addition, the band at 12.70 $\mu$ , found in the hydroxyanthraquinones, was absent, and the 6.12 $\mu$  and 6.23 $\mu$  bands, which were present in the spectrum of the 1,5-dihydroxyanthraquinone due to hydrogen-bonded carbonyl and aromatic absorptions, were shifted to 6.0 $\mu$  and 6.3 $\mu$  in the bis(trimethylsilyl) ether.

Calculated for  $C_{20}H_{24}O_4Si_2$ : C 62.46, H 6.29, Si 14.61.

Found: C 62.81, H 6.45, Si 14.60.

#### PREPARATION OF TRIMETHYLSILYL ETHERS OF OTHER HYDROXY-ANTHRAQUINONES (26)

In a similar manner, 1,4-dihydroxyanthraquinone and 1,8-dihydroxyanthraquinone were converted to the bis(trimethylsilyl) ethers—mp 92°–99° C and 98.8°–101° C, respectively; and

1,2,4-trihydroxyanthraquinone was converted to the tris(trimethylsilyl) ether, mp 81°–86.5° C.

#### PREPARATION OF BIS(TRIMETHYLSILYL) ETHER OF 2,4-DIHYDROXYACETOPHENONE

2,4-Dihydroxyacetophenone (0.5 g) was converted to the trimethylsilyl ether by the same procedure used for the preceding experiment. Infrared absorption at 7.95, 9.97, 10.10, 11.8, and 13.25 $\mu$  indicated the formation of the trimethylsilyl ether. The hydroxyl absorption at 3.0 $\mu$  was absent, as was the phenol absorption at 12.70 $\mu$ . The bands at 6.12 and 6.22 $\mu$  in the starting material, due to the hydrogen-bonded carbonyl and aromatic absorption, were replaced by bands at 5.98, 6.10, and 6.25 $\mu$  in the ether. The spectra are shown in figure 8.

#### PREPARATION OF BIS(TRIMETHYLSILYL) ETHER OF 6,11-DIHYDROXY-NAPHTHACENEQUINONE (26)

A solution of 2.5 grams of 6,11-dihydroxynaphthacenequinone, 5 ml of hexamethyl-

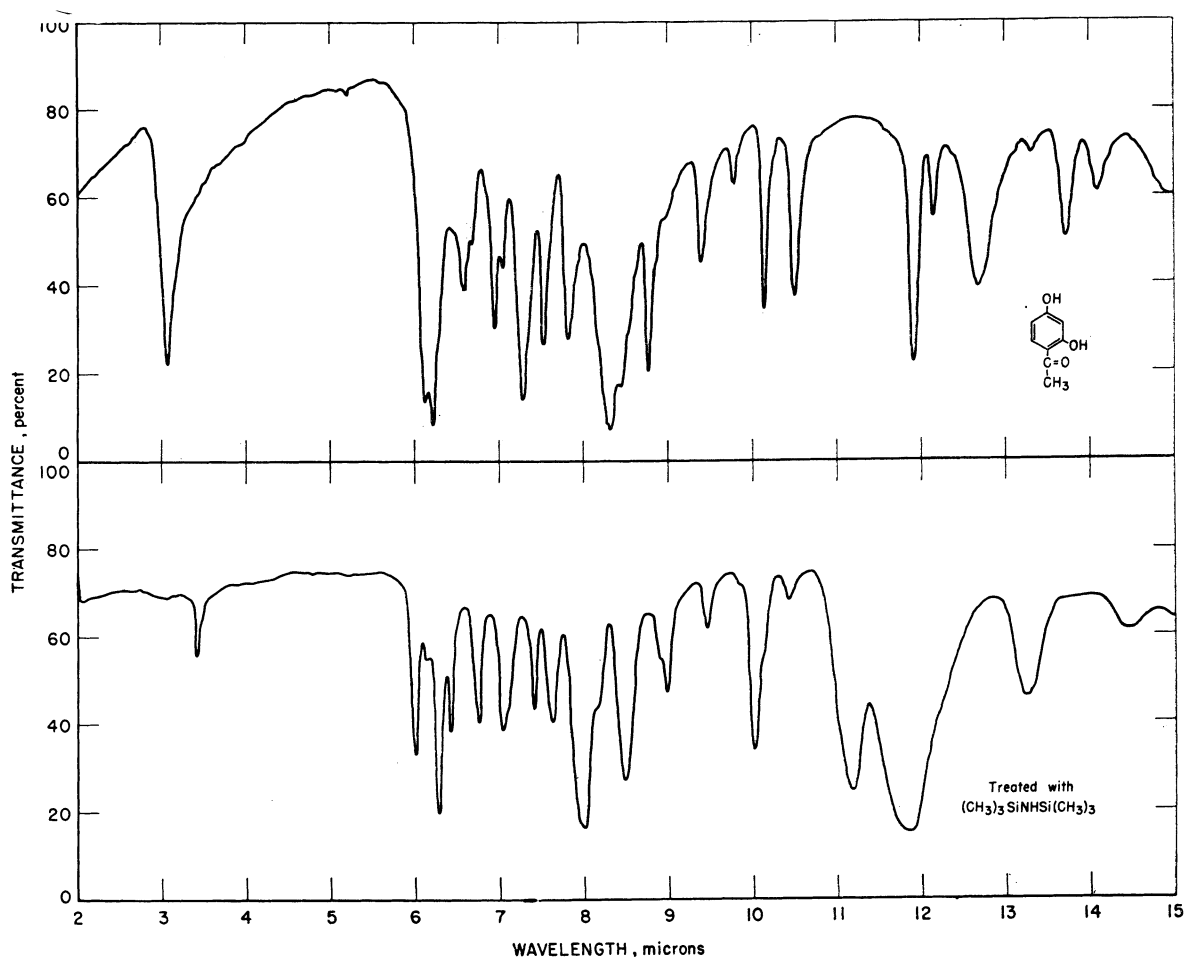


FIGURE 8.—Infrared Spectra of 2,4-Dihydroxyacetophenone and Its Trimethylsilyl Ether.

disilazane, and 10 ml of trimethylchlorosilane in 25 ml of dry pyridine was refluxed for 24 hours. The solvent and reagents were removed by distillation, the last traces being removed under vacuum. The crude product, 3.85 grams was recrystallized from benzene and then from 60°–68° C petroleum ether to yield 2.3 grams of orange crystals, mp 203°–211° C. The infrared spectrum showed absorption bands (at 8.0, 9.72, 11.75, and 13.25 $\mu$ ) that are characteristic of trimethylsilyl ethers of phenols. In addition, the bands at 6.13 and 6.30 $\mu$ , due to the hydrogen-bonded carbonyl and aromatic absorption, were shifted to 6.00 $\mu$  and 6.26 $\mu$  in the ether. The band at 14.5 $\mu$  was obscured by skeletal absorption.

Calculated for  $C_{24}H_{26}O_4Si_2$ : C 66.23, H 6.03, Si 12.93.

Found: C 66.71, H 6.19, Si 12.31.

An attempt to prepare the ether by using hexamethyldisilazane and one drop of trimethylchlorosilane in the absence of pyridine was unsuccessful. The starting material was recovered unchanged.

### Reaction of Disubstituted Hindered-Phenols with Hexamethyldisilazane and Trimethylchlorosilane in Pyridine

#### PREPARATION OF TRIMETHYLSILYL ETHER OF 2,6-DI-*t*-BUTYLPHENOL (26)

A 10-gram sample of 2,6-di-*t*-butylphenol was refluxed for 24 hours with 5 ml of hexamethyldisilazane and 10 ml of trimethylchlorosilane in 25 ml of dry pyridine. Ammonium chloride sublimed into the condenser, and the color of the solution changed from a pale yellow to light pink during the refluxing. The solvent and unchanged reagents were removed by distillation under vacuum to leave 10.3 grams of straw-colored crystals that were recrystallized from petroleum ether (bp 60°–68° C). A second recrystallization gave colorless crystals, mp 109°–110° C.

Calculated for  $C_{17}H_{30}SiO$ : C 73.31, H 10.86, Si 10.09.

Found: C 73.30, H 10.90, Si 10.10.



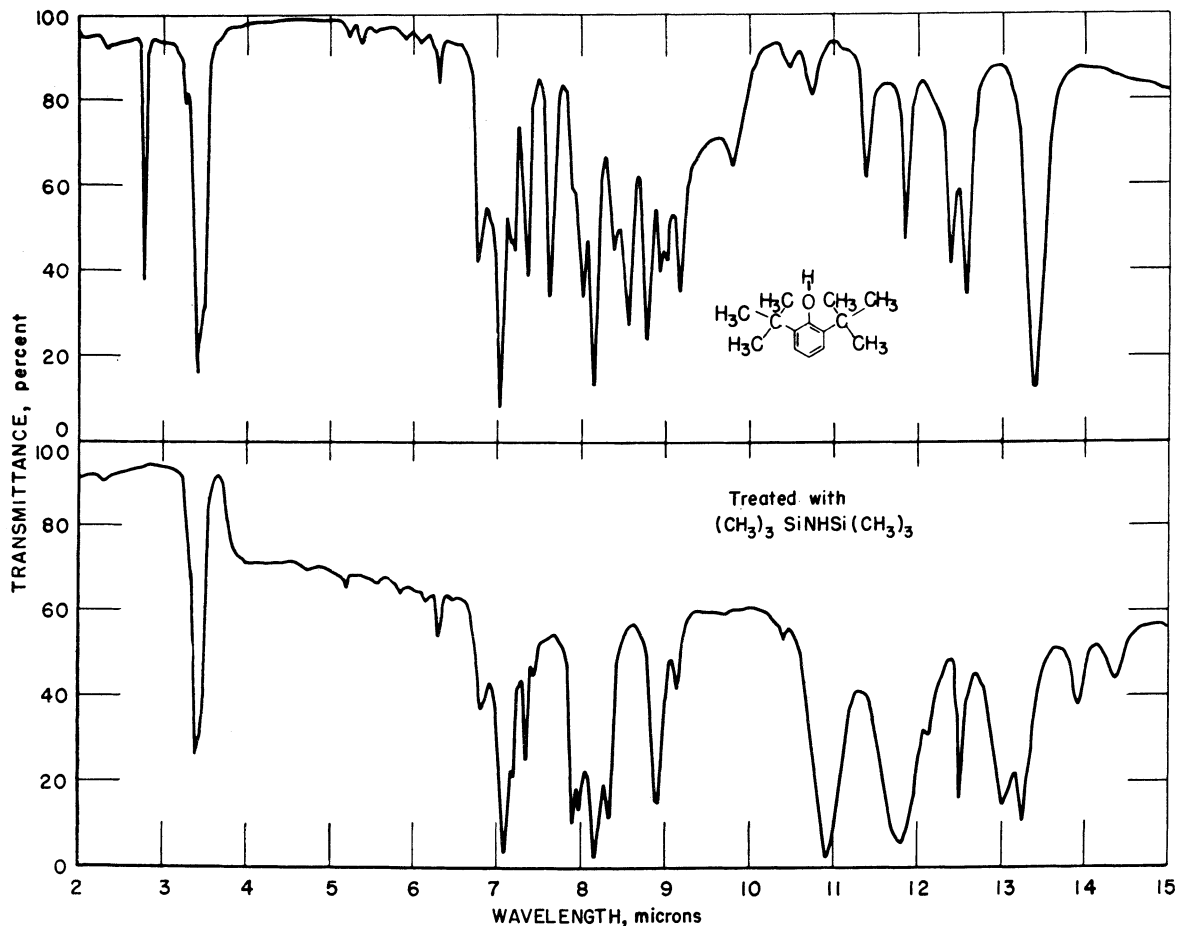


FIGURE 9.—Infrared Spectra of 2,6-di-*t*-butylphenol and Its Trimethylsilyl Ether.

The infrared spectrum (fig. 9) showed the complete disappearance of the hydroxyl band at  $2.75\mu$  and the presence of bands (at 8.0, 11.8, 13.25, and  $14.5\mu$ ) which were found in the previously prepared phenyl trimethylsilyl ethers. Other changes also occurred in the spectrum due to skeletal vibrations.

Attempts were made to prepare this trimethylsilyl ether by use of (1) hexamethyldisilazane and trimethylchlorosilane without pyridine, (2) trimethylchlorosilane and pyridine without hexamethyldisilazane, and (3) hexamethyldisilazane and pyridine with only a drop of trimethylchlorosilane as catalyst. All were unsuccessful; a trace of the ether was found after the use of system (3).

#### REACTION OF 2,4,6-TRI-*t*-AMYLPHENOL WITH HEXAMETHYLDISILAZANE AND TRIMETHYLCHLOROSILANE IN PYRIDINE

(1) The previous procedure, which was used for the preparation of the trimethylsilyl ether of 2,6-di-*t*-butylphenol, was repeated with 2,4,6-tri-*t*-amylphenol. The mixture was refluxed

for 8 days. The infrared spectrum of the product indicated only slight reaction.

(2) Three runs were conducted in a small stainless steel bomb with 2 grams of the 2,4,6-tri-*t*-amylphenol, 5 ml each of trimethylchlorosilane and hexamethyldisilazane, and 20 ml of pyridine. The conditions and results for the runs were as follows:

Run	Time, hour	Temp., ° C	Phenol in product, percent
1-----	5	150	81
2-----	7	200	88
3-----	44	150	73

The percentage of unaltered phenol was determined by infrared analysis of the material remaining after removal of the solvent and unchanged reagents.

(3) In a 1-liter bomb, 25 grams of the 2,4,6-tri-*t*-amylphenol was heated to  $150^\circ\text{C}$  for 30 hours with 5 ml of trimethylchlorosilane and

10 ml of hexamethyldisilazane in 300 ml of pyridine. The solvent and low-boiling material were distilled off, and the residue chromatographed on alumina in a 500 ml burette. The initial petroleum-ether eluate gave 1.27 grams of material, which, according to infrared analysis, consisted of 37 percent of the phenol and 63 percent of the trimethylsilyl ether. The second petroleum ether fraction contained 6.15 grams of material, 20 percent of which was the trimethylsilyl ether. Subsequent fractions contained mostly unchanged phenol.

The first two fractions were rechromatographed on alumina that had been activated overnight in an oven at 140° C. This operation gave a much sharper separation. The early fractions were found by infrared analysis to be free of phenol; the phenol was not released from the column until benzene was used as an eluent. The trimethylsilyl ether was analyzed by a mass spectrometer using a low-ionizing voltage technique. The spectra showed a very definite parent peak at 376 mass units, corresponding to the trimethylsilyl ether of 2,4,6-tri-*t*-amylphenol. The absence of other ethers of lower molecular weight phenols (for example, di-*t*-amylphenol) could not be confirmed by this method.

### Reaction of Trisubstituted Hindered-Phenols with Hexamethyldisilazane and Trimethylchlorosilane in Dimethylformamide

#### PREPARATION OF TRIMETHYLSILYL ETHER OF 2,4,6-TRI-*T*-BUTYLPHENOL (27)

A solution of 5 grams of 2,4,6-tri-*t*-butylphenol, 25 ml of hexamethyldisilazane, and 25 ml of trimethylchlorosilane in 30 ml of dimethylformamide was refluxed under nitrogen for 6 hours.<sup>8</sup> The reaction mixture separated into two layers after it cooled. The lower layer was extracted with (60°–68° C) petroleum ether. Evaporation of the solvent from the extract yielded 6 grams of crude product. Recrystallization from petroleum ether gave the 2,4,6-tri-*t*-butyl-trimethylsiloxybenzene, mp 85°–87.5° C.

Calculated for C<sub>21</sub>H<sub>38</sub>OSi: C 75.45, H 11.38, Si 8.38.

Found: C 75.56, H 11.54, Si 8.27.

The infrared spectrum of the product showed the absence of the hydroxyl absorption at 2.75 $\mu$  and the presence of the trimethylsilyl ether absorption bands at 7.9, 8.1, 9.75 (weak), 11.90, 13.20, and 14.60 (weak) $\mu$ . Ultraviolet (in cyclohexane)  $\lambda_{max}$ . 2791A ( $\epsilon$ 1010), 2726A ( $\epsilon$ 966). Low-ionizing voltage mass spectral analysis showed a peak at 334, with traces

(<1 percent) of higher and lower molecular weight homologues.

The trimethylsilyl ether formation proceeded satisfactorily in the absence of trimethylchlorosilane, but not in the absence of hexamethyldisilazane or of dimethylformamide. The use of a catalytic amount of dimethylformamide (0.1 ml) in the presence of pyridine, hexamethyldisilazane, and trimethylchlorosilane failed to bring about trimethylsilyl ether formation. No reaction was observed when piperidine was used as a solvent with both hexamethyldisilazane and trimethylchlorosilane. A published procedure (35), involving the use of a two-phase system consisting of the phenol, formamide, *n*-hexane, pyridine, and trimethylchlorosilane, failed to yield any trimethylsilyl ether.

#### PREPARATION OF TRIMETHYLSILYL ETHER OF 2,4,6-TRI-*T*-AMYLPHENOL (27)

2,4,6-tri-*t*-amyl-trimethylsiloxybenzene was prepared by a procedure similar to the preceding experiment. The product was initially a liquid. Crystallization from ethanol at –20° C yielded a solid, melting at 24.5°–25.5° C. The low-voltage mass spectrum of the solid showed a major peak at 376 mass units as well as small peaks at 362 and 390 mass units. The solid also showed characteristic infrared absorption at 7.9, 8.0, 9.47 (weak), 11.90, 13.20, and 14.5 (weak) $\mu$ . Hydroxyl absorption at 2.75 $\mu$  was absent. Ultraviolet  $\lambda_{max}$ . 2797A ( $\epsilon$ 981), 2740A ( $\epsilon$ 930).

Calculated for C<sub>24</sub>H<sub>44</sub>OSi: C 76.52, H 11.77, Si 7.46.

Found: C 76.46, H 11.75, Si 8.14.

#### PREPARATION OF THE TRIMETHYLSILYLETHER OF 2,6-DI-*T*-BUTYL-4-METHYLPHENOL (27)

A solution of 5 grams of 2,6-di-*t*-butyl-4-methylphenol (Eastman, recrystallized, mp 56° C) in 25 ml of hexamethyldisilazane and 35 ml of dimethylformamide was refluxed under nitrogen for 14 hours. The solvent and excess reagent were removed by distillation. The residue was chromatographed on alumina, and the main fraction recrystallized from petroleum ether (60°–68° C) to yield 4.5 grams of product, mp 122.8°–124° C, with the characteristic trimethylsilyl ether absorption at 8.0, 8.15, 9.75 (weak), 11.9, 13.15, and 14.45 (weak) $\mu$ ; hydroxyl absorption at 2.75 $\mu$  was completely absent. Low voltage mass spectrometry showed the expected peak at 292 mass units. Ultraviolet  $\lambda_{max}$ . 2823A ( $\epsilon$ 1127), 2754A ( $\epsilon$ 1054).

Calculated for C<sub>18</sub>H<sub>32</sub>OSi: C 73.90, H 11.03, Si 9.60.

Found: C 74.07, H 11.19, Si 10.0.

<sup>8</sup> When oxygen was not excluded, considerable oxidation took place

## Hydrolysis of the Trimethylsilyl Ethers of Phenols

### HYDROLYSIS OF TRIMETHYLSILYL ETHER OF 2,6-DI-*T*-BUTYLPHENOL (27)

A solution of 0.6 gram of the trimethylsilyl ether of 2,6-di-*t*-butylphenol in 15 ml of ethanol containing 1 ml of concentrated hydrochloric acid was refluxed for 1 hour. The solvent and excess reagent were stripped off. Infrared analysis of the residue showed complete hydrolysis of the ether to the parent phenol.

Refluxing the ether in a solution of 10 ml of pyridine, 5 ml of ethanol, and 1 ml of water failed to give any detectable hydrolysis.

### HYDROLYSIS OF TRIMETHYLSILYL ETHER OF 2,4,6-TRI-*T*-BUTYLPHENOL (27)

One gram of 2,4,6-tri-butyl-trimethylsilyloxybenzene was dissolved in a solution of 6 ml of concentrated hydrochloric acid in 25 ml of methanol, and the solution was refluxed for 4 hours under nitrogen. The reaction mixture was extracted with petroleum ether (60°-68° C), and the solvent evaporated off. Infrared analysis showed the product to consist entirely of 2,4,6-tri-*t*-butylphenol.

Attempts to hydrolyze the trimethylsilyl

ether in a pyridine-ethanol-water mixture and in dimethylformamide were unsuccessful.

### Treatment of Samples for Mass Spectrometry

#### TRIMETHYLSILYL ETHERS OF SUBSTITUTED INDANOLS

7-methyl-4-hydroxyindane, 7-methyl-5-hydroxyindane, and 6-methyl-4-hydroxyindane were treated separately with hexamethyldisilazane (and trimethylchlorosilane as catalyst) in order to prepare reference samples, mainly for the low-ionizing voltage technique of analyzing phenols by mass spectrometry (68).

#### TRIMETHYLSILYL ETHERS OF MIXED TAR ACIDS BY A TWO-STAGE PROCEDURE

A solution of 5 grams of coal tar acids in 20 ml of hexamethyldisilazane was refluxed for 5 hours under nitrogen. Six ml of trimethylchlorosilane and 10 ml of pyridine were then added and refluxing was continued for 14 more hours (overnight). The solvent and excess reagents were stripped off under vacuum, and the residue was submitted for mass spectrometric analysis. All phenols were found to have been converted to their respective trimethylsilyl ethers.

## PHYSICAL PROPERTIES OF TRIMETHYLSILYL ARYL ETHERS

The physical properties of three trimethylsilyl aryl ethers are given in table 8. The effect of the trimethylsilyl group on the change of boiling point of the parent alcohol has been discussed earlier (48, 86). The reported physical properties of the known low-boiling phenols have been collected and published by the Bureau of Mines (41).

Trimethylsilyl ethers of the simple phenols especially the hindered phenols, are stable. The trimethylsilyl ethers of some of the hydroxy-anthraquinones, however, seemed to be quite sensitive to moisture and/or air; they changed color on standing overnight in capped vials. On the other hand, when sealed in dry ampoules they appeared to be unchanged after several months.

TABLE 8.—*Physical properties of some trimethylsilyl aryl ethers (48)*

Trimethylsilyl derivative	Formula	Boiling point, ° C (mm)	$n_D^{20}$	$d_4^{20}$	$d_4^{25}$	$MR_D$ Calculated <sup>1</sup>	Found
Trimethylsilyloxybenzene	$C_9H_{14}OSi$	<sup>2</sup> 181.9–182.4 (742)	1. 4782	0. 9256	0. 9209	50. 80	50. 87
1,3-Bis(trimethylsilyloxy)-benzene.	$C_{12}H_{22}O_2Si_2$	237–240 (740)	1. 4748	. 950	. 946	75. 1	75. 4
1-Trimethylsilyloxynaphthalene.	$C_{13}H_{16}OSi$	271–272 (742)	1. 5590	1. 000	-----	68. 4	69. 8

<sup>1</sup> Molar refractivity calculated from the bond refraction data (79).

<sup>2</sup> Speier (70) reported bp 182.5° (736)  $n_D^{25}$  1.4753, and  $d_4^{25}$  0.920.

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