IS-T- 948

Application of selected chemical reactions to the organic chemistry of coal

by

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MS Thesis submitted to Iowa State University

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Date Transmitted: February 1981

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. W-7405-eng-82

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Springfield, VA 22161

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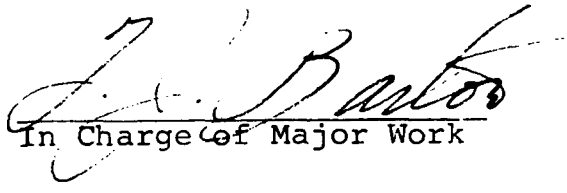
Robert Merle Metzler

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
MASTER OF SCIENCE

Department: Chemistry
Major: Organic Chemistry

Approved: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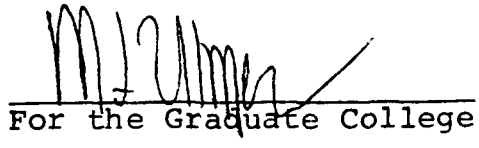
For the Graduate College

Iowa State University
Ames, Iowa

1980

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DEDICATION

This thesis is dedicated to my daughter,

Erica Lynn Metzler

INTRODUCTION

A study of the structure or chemistry of coal is a difficult task due to the complexity of coal. Neavel (1) defined coal as "a sedimentary rock accumulated as peat and composed principally of macerals, subordinately of minerals, and containing water and gases in submicroscopic pores. Macerals are organic substances derived from plant tissue and exudates that have been variably subjected to decay, incorporated into sedimentary strata, and then compacted, hardened, and chemically altered by natural geological processes."

Coal is not a uniform mixture of carbon, hydrogen, oxygen, sulfur, and the other elements present in minor proportions in coal; nor is it simply a uniform, polyaromatic, polymeric substance. Rather it is a heterogeneous aggregate of microscopically distinguishable, chemically different, and physically distinctive macerals and minerals. The heterogeneity of coal is a direct result of the diversity of its source materials.

The importance of organically bound oxygen in the structure and properties of coals has been recognized for many years (2-6). Angelova et al. (4) found coals containing higher amounts of oxygen had larger values for heat of wetting with methanol. In Part I of this thesis a method for analyzing hydroxyl content of coal has been investigated.

The viability of using organosulfur specific chemical reactions to delineate the organosulfur functional group distribution in coal has been investigated in Parts II and III of this thesis. Sulfur levels in coal range from 0.2 to 10 weight per cent, with most samples falling between 1.0 and 4.0 weight per cent (7). The type of sulfur of interest here is organic sulfur, in which the sulfur atoms are an integral part of the organic framework. This type of sulfur can account for between 20 and 70 per cent of the total sulfur in coal (8); usually, about one-third of the sulfur in coal is organic (8).

Though some progress has been made in determining the nature of the organosulfur components in coal, there is still very little information identifying these sulfur moieties (9). Specific organosulfur compounds such as substituted thiophenes 1, benzothiophenes 2, and dibenzothiophenes 3 have been

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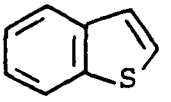

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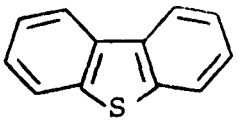

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detected by vacuum distillation of highly volatile bituminous coal at 150°C (10). However, these materials were identified as an incidental consequence of investigating other types of

compounds in coal. Efforts have also been made to determine the organosulfur functional group distribution through physical (11) and chemical properties (12). The physical and chemical bases for these studies were, at best, obscure and the results were, in most cases, inconclusive. The best of these methods (13) was developed in 1936, and is based on the following reactions of methyliodide with sulfides, and mercaptans.

$$R\text{-}S\text{-}R' + CH_3I \longrightarrow R\text{-}\overset{+}{\underset{\displaystyle CH_3}{S}}\text{-}R' + I^-$$

$$R\text{-}S\text{-}H + CH_3I \longrightarrow R\text{-}S\text{-}CH_3 + HI$$

Although it is not necessary to determine the organosulfur functional group distribution in order to evaluate the effectiveness of existing desulfurization processes, it could be extremely beneficial. Due to the heterogeneous and complex nature of coal it is difficult to determine what effect a process will have on a specific organosulfur functional group. The effectiveness of a given process is much easier to determine when applied to a series of model compounds. However, the validity of this approach is only as good as the choice of models. Elucidation of the organosulfur functionalities might also guide future researchers to develop new methods to

remove organic sulfur from coal. Two reactions will be investigated, in Parts II and III, as potential methods for analyzing the organosulfur functionalities in coals and coal derived liquids.

PART I. ATTEMPT TO QUALITATIVELY ANALYZE HYDROXYL GROUPS IN COAL

Introduction

A number of methods have been utilized for the determination of hydroxyl groups in coal. One of the initial techniques, developed by Yohe and Blodgett (14), was O-alkylation with dimethyl sulfate. In 1941 Tronov (15) proposed that atmospheric oxidation of coal was initiated by attack of the phenolic components by molecular oxygen. To test this theory Yohe and Blodget converted the phenolic groups to the corresponding methyl ethers. These workers found that mesitol and 1-naphthol could be oxidized at 100°C in a 5 per cent sodium hydroxide solution using an oxygen atmosphere while their methyl ethers could not. Eight coals, ranging from lignite to anthracite, were methylated by treating the coals with aqueous sodium hydroxide and then refluxing them with dimethyl sulfate. These coals and their methylated derivatives were subjected to the oxidation conditions described above. High-volatile bituminous and lower ranking coals were appreciably methylated; and this methylation reduced their susceptibility to oxidation. Medium and low-volatile bituminous coals and anthracite were not appreciably methylated and their oxygen uptake was essentially unaffected. Although other bases and alkylating agents have been used

(16-19), only recently has the procedure been substantially modified by Liotta (20) (see below).

The organic molecules which make up coal are held together not only by covalent bonds, but also by a substantial network of hydrogen bonds and other weak intermolecular forces which make up the secondary structure of coal. Researchers have tried to break up this secondary structure by swelling the coal matrix with solvents such as pyridine. Although pyridine is effective in disrupting the secondary structure of coal, prolonged heating and high vacuum are required to remove it.

Liotta (20) developed a method for disrupting the secondary structure under very mild conditions. He reported that tetrabutylammonium hydroxide caused considerable swelling of low-rank bituminous coals. This reagent is also an effective base for the O-alkylation of coal. The initial reaction is shown in Scheme 1. Liotta followed the reaction

Scheme 1

$$\text{(Coal)-OH} + (C_4H_9)_4N^+\ ^-OH \longrightarrow \text{(Coal)-O}^-\ ^+N(C_4H_9)_4 + H_2O$$

$$\text{(Coal)-COOH} + (C_4H_9)_4N^+\ ^-OH \longrightarrow \text{(Coal)-COO}^-\ ^+N(C_4H_9)_4 + H_2O$$

by monitoring the pH of the solution. Generally, a slight excess of base was added, followed by a two-fold excess of iodomethane. The O-alkylation step proceeded as shown in Scheme 2. The reaction was run in tetrahydrofuran. After

Scheme 2

$$(\text{Coal})\text{-}O^- \ ^+N(C_4H_9)_4 + CH_3I \longrightarrow (\text{Coal})\text{-}OCH_3 + (C_4H_9)_4N^+ \ ^-I$$

$$(\text{Coal})\text{-}COO^- \ ^+N(C_4H_9)_4 + CH_3I \longrightarrow (\text{Coal})\text{-}COOCH_3 + (C_4H_9)_4N^+ \ ^-I$$

completion of the alkylation, the volatile materials (solvent and iodomethane) were removed under vacuum (less than 70°C), and the ammonium salts were removed by aqueous washing.

A different method, using diazomethane, was employed by Fuchs and coworkers (18,21,22) to methylate coal. This method was subsequently used by other workers (23,24). Brooks et al. (23) noted two shifts in the infrared spectra following alkylation. The carbonyl band at 1700 cm^{-1} shifted to 1720 cm^{-1} with the conversion of the acids to methyl esters and the aromatic ring stretching band at 1615 cm^{-1} shifted to 1600 cm^{-1} with the conversion of phenols to ethers. This was confirmed by alkaline hydrolysis of the methylated coal which caused a reversal of the change in the 1700 cm^{-1} without altering the 1600 cm^{-1} absorption. Further-

more, demethylation of the saponified methylated coal with hyriodic acid reversed the change in the 1600 cm^{-1} region. These experiments provided a basis for distinguishing between hydroxyl and carboxyl groups in coal.

Hillis (25), using acetic anhydride and pyridine, was the first to acetylate coal and this method, with slight modifications, has been used by a number of workers (19,24, 26-32) to determine the hydroxyl content. In most of these investigations the acetyl uptake was determined by titration. However Abdel-Baset and coworkers (33) used a radiochemical method (34) to determine acetyl uptake.

Absorption of cations from basic solutions has been used by several workers (19,24,26) to measure the total acidity of coals. Syskov and Kukharenko (35) developed the method sometimes called baryta absorption. In this method, crushed coal is mixed with a barium hydroxide solution for four days; and then, after washing out the excess base, the coal mixture is back titrated with hydrochloric acid. This general procedure, treatment of the coal with excess base and back titration with acid, has been used more than any other method for quantitative determination of acid content in coals (21,36-44).

Brooks and Maher (45,46) were the first to directly titrate the acidic content of coal. The method was originally developed by Moss and his collaborators (47) and utilized

potentiometric titration with sodium aminoethoxide in ethylenediamine to determine weakly acidic functionalities, such as hydroxyl groups. Pringle (48) also used the potentiometric method with sodium methoxide in n-butylamine.

Several other methods have been developed, but have been used very infrequently. A deuterium exchange procedure was developed by Blom and collaborators (49). In this method coal was treated with deuterium oxide and pyridine, and the number of exchangeable protons were determined. The results of this method were generally in good agreement with those determined by acetylation.

Blom and coworkers (24) also evaluated a procedure developed by Nabar and Padmanabhan (50) to determine the acid content of oxidized cellulose samples. This method utilizes the reaction of iodate and iodide with acidic protons in the coal (Scheme 3). Thiosulfate, which is present in excess,

Scheme 3

$$6H^+ + 5I^- + IO_3^- \longrightarrow 5HI + HIO_3$$

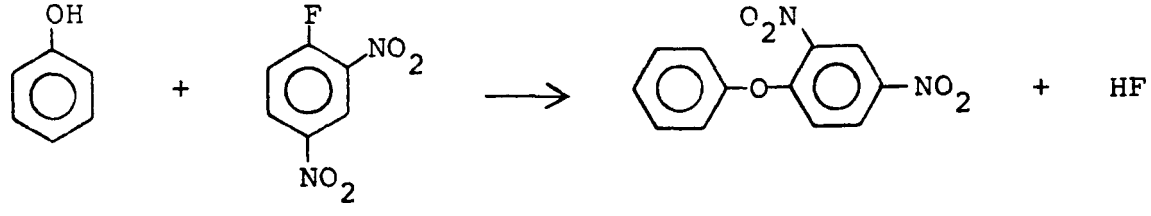
$$5HI + HIO_3 \longrightarrow 3H_2O + 3I_2$$

reduces the iodine formed back to iodide ions. At the end of the reaction, the excess thiosulfate is titrated with a stand-

ard iodine solution. This method, when applied to coal, afforded less reproducible results than did other methods; these results were generally slightly higher.

Another method for determining the hydroxyl content of coal investigated by Blom and coworkers (24) was the reaction of Sanger's Reagent, 2,4-dinitrofluorobenzene, with phenols (51,52) to quantitate the phenolic content of coal (Scheme 4).

Scheme 4



By measuring the increase in the nitrogen content of the coal, the phenolic hydroxyl concentration in the original coal sample was calculated, and these values were in satisfactory agreement with those obtained from acetylation experiments. The use of Grignard reagent to analyze for hydroxyl groups in coal has also been evaluated (22,31). The reagent was not specific, reacted readily with water, and was too weak to react quantitatively with all hydroxyl groups in coal. Consequently, the results from this method were generally unsatisfactory.

In a series of papers, Kini, Nandi, and coworkers (53-55) attempted to correlate the absorption of polar gases versus

nonpolar gases, the heats of wetting with polar solvents versus nonpolar solvents, and the hydroxyl content of the coal. In these studies, the values obtained for nonpolar molecules were assumed to be a measure of surface area whereas the values for polar molecules were assumed to be a measure of the concentration of polar groups in coal. Although there was a correlation, the authors did not even try to use this method to quantitatively analyze hydroxyl content in coal.

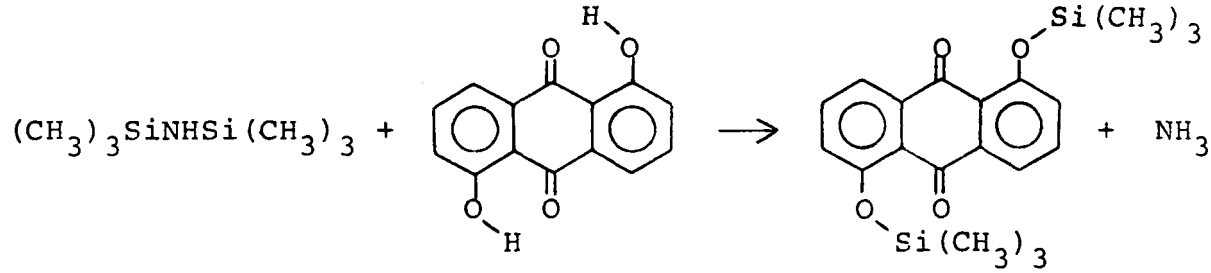
The most recently developed method of hydroxy determination in coal utilized silylation. Speier (56) showed that hexamethyldisilazane 4 reacted quantitatively with hydroxyl groups as shown in Scheme 5. Friedman and coworkers (57,58)

Scheme 5

$$2\ ROH + \underset{\underline{4}}{(CH_3)_3SiNHSi(CH_3)_3} \longrightarrow 2\ ROSi(CH_3)_3 + NH_3$$

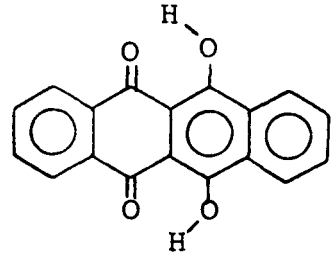
investigated the use of this reagent with hydrogen-bonded hydroxy-carbonyl compound such as 1,5-dihydroxyanthraquinone 5 (Scheme 6). These are the same types of hydrogen bonded quinone groupings that have been postulated to be present in coal (59). Compound 5 was reported to form the dimethyl ether only under severe reaction conditions (60): heating the dipotassium salt with dimethyl sulfate at 140°C. However,

Scheme 6



4 5 6

in the bis(trimethylsilyl) ether, 6, was readily formed by refluxing in hexamethyldisilazane; and the reaction was quantitative. Furthermore, these authors used hexamethyldisilazane on other compounds that had given unsatisfactory results with other etherification reagents. Two of these were 9,10-dihydroxynaphthacene-11,12-quinone 7 and purpurin, 1,2,4-trihydroxyanthraquinone 8. Quinone 7 has been reported



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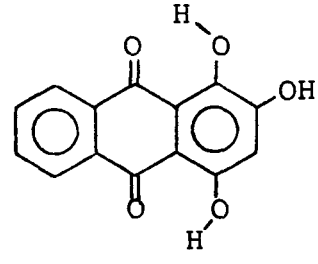

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to undergo acetylation in a yield of 90 per cent, and methylation to the extent of 5 per cent (24). The bis(trimethyl-

silyl)ether was formed quantitatively. Purpurin 8 formed only the diacetate when treated with acetic anhydride (30) under conditions normally used for acetylating coal (24), whereas compound 8 reacted with hexamethyldisilazane to form the tris(trimethylsilyl)ether in quantitative yield.

Further work has demonstrated that the highly hindered 2,6-di-t-butylphenol reacted quantitatively with hexamethyldisilazane in the presence of trimethylchlorosilane and pyridine (57,58). Attempts to form other ether derivatives of this phenol were unsuccessful. It was necessary to form the sodium salt before any reaction took place (61,62), and the compounds formed under these conditions were para substitution products and not true phenol derivatives. Thus, in the case of hindered phenols silylation represents the only convenient and quantitative method for derivatization. When Friedman and coworkers (57,58) used hexamethyldisilazane on coal the results were analyzed by two different methods. One was an analytical method based on the infrared absorption of the trimethylsilyl ethers and the other was the increase in silicon content as determined by elemental analysis. Now, analysis of the silylated products is accomplished by nuclear magnetic resonance (nmr) integration of the trimethylsilyl protons (63). Silylation is becoming a popular tool with which to study coal (63-67).

There are disadvantages to most of the methods which have been used to determine the hydroxyl content of coal. Methylation using dimethyl sulfate or diazomethane have both given low values, presumably due to incomplete reaction. The method of ion exchange, using barium hydroxide, may have produced hydrolysis products; and in high rank coals, some of the hydroxyl groups appeared to be inaccessible to the reagent. Potentiometric titration, when used to analyze acidic hydroxyl groups, is known to include groups such as quinones and acidic non-hydroxylic hydrogens in the analysis. Acetylation of hindered or hydrogen bonded hydroxyl groups is very difficult; and the results can be further complicated by acetylation of amines. However, in hexamethyldisilazane, the silicon is already attached to nitrogen and there is no driving force for the silicon to leave the nitrogen of the starting material to bond to a nitrogen in coal. Hexamethyldisilazane also reacts quantitatively with a broad range of hydroxyl groups and seems to be the reagent of choice for selectively derivatizing the hydroxyl groups in coal.

In 1978, Schweighardt et al. (65) used silylation to differentiate between various types of hydroxyl groups present in complex mixtures such as coal derived oils. A 250 MHz nmr spectrometer was used to examine the silyl methyl region of the proton nmr. A number of model compounds were examined and the effect of structural variation upon the

chemical shift of the trimethylsilyl protons was measured. Aliphatic and benzylic alcohols were the most shielded, falling between 0 and 45 Hz, phenolic trimethylsilyl derivatives ranged from 40 to 70 Hz, and carboxylic acid and oxime derivatives from 65 to more than 110 Hz downfield from internal tetramethylsilane.

The work of Schweighardt represents an enormous gain in sophistication, because it is the first attempt to analyze alcoholic and phenolic hydroxyl groups separately in coal. The results obtained were somewhat ambiguous due to the slight overlap of ranges in the proton nmr. The purpose of our project was to examine the use of ^{29}Si nmr as a possible method to overcome this shortcoming. In general, ^{29}Si nmr has a much wider range than proton nmr (over 200 parts per million as compared to approximately 11 parts per million for proton nmr), and would then hopefully show a larger difference in chemical shift between aliphatic and aromatic trimethylsilyl ethers. Examination of the ^{29}Si nmr instead of the silylmethyl protons also moves the probing nucleus two atoms closer to the etheral carbon, which could further enhance the difference between aliphatic and aromatic silyl ethers. This potential improvement in Schweighardt's method was investigated in this study; and its effectiveness as a tool to analyze the alcoholic and phenolic content of a complex mixture (e.g. a coal derived liquid) will be discussed.

Results and Discussions

The trimethylsilyl ethers of a series of model compounds were synthesized and their ^{29}Si nmr observed. The ^{29}Si nmr were run in a 10 per cent solution in benzene by Instrument Services, Department of Chemistry, Iowa State University. The results are shown in Table 1. These results show that

Table 1. ^{29}Si Chemical shifts[a] of trimethylsilyl ethers, R = $(CH_3)_3SiO-$

Structure	Chemical Shift parts per million (ppm)
R-phenyl	100.85
R-CH_2-CH=CH_2	100.60
R-n-butyl	98.75
R-sec-butyl	96.56
R-t-butyl	89.33
R-β-naphthyl	101.75

[a]Shifts are reported with respect to tetraethoxysilane and positive shifts are downfield.

the difference in chemical shifts between aliphatic and aromatic trimethylsilylethers is much larger when using ^{29}Si

nmr instead of proton nmr. The middle of the aliphatic ether range and the middle of the aromatic ether range are separated by approximately 6 ppm, whereas in Schweghardt's (65) work with the proton nmr of the silyl methyl protons, the entire range studied was less than 0.5 ppm. This procedure was then used on the benzene soluble, pentane insoluble portion of Lovilia coal. The proton nmr showed approximately 30 per cent of the protons present were silicon methyl protons, but the ^{29}Si nmr showed no signal. This was not a completely surprisingly result. Coal is only about 10 per cent oxygen by weight (33), and only about half of that is present as hydroxyl groups (33,65). Therefore, the silicon concentration in the coal will be low and ^{29}Si makes up only 4.7 per cent of the silicon atoms (68).

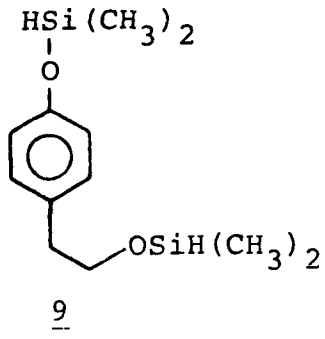
It was then suggested (69) and later proven (70) that enhancement of the ^{29}Si signal could be accomplished using cross-polarization between ^{1}H and ^{29}Si in silyl hydrides. A series of dimethylsilyl ethers were synthesized and their ^{29}Si nmr observed using the technique of cross-polarization. These nmr were run in a 10 per cent solution in benzene by Dr. B. C. Gerstein's group at Iowa State University. The results are shown in Table 2. These results show that the ^{29}Si nmr signals of aromatic and aliphatic ethers are much closer together in the case of dimethylsilyl ethers than they were in the case of trimethylsilyl ethers. To determine if

Table 2. ^{29}Si chemical shifts[a] of dimethylsilyl ethers, with cross-polarization between H^1 and Si^{29}, R = $(CH_3)_2HSiO-$

Structure	Chemical Shift, ppm
R-phenyl	-4.6
R-n-butyl	-3.6
R-sec-butyl	-0.5
R-n-pentyl	-3.3
$R-CH_2-CH_2-R$	-4.9
R-α-naphthyl	-5.8
R-β-naphthyl	-5.3

[a]Shifts are reported with respect to tetramethylsilane and negative shifts are downfield.

it was possible to get complete separation of ^{29}Si signals in aliphatic and aromatic dimethylsilyl ethers, the diether of p-hydroxyphenethyl alcohol 9 was synthesized and its ^{29}Si nmr is shown in Figure 1. In this case no internal standard was added, as we were mainly interested in the difference of chemical shift. This difference was only 0.57 ppm. Because of the complex nature of coal and the fact that the ^{29}Si signals could not be separated in pure compound 9 this project was discontinued.



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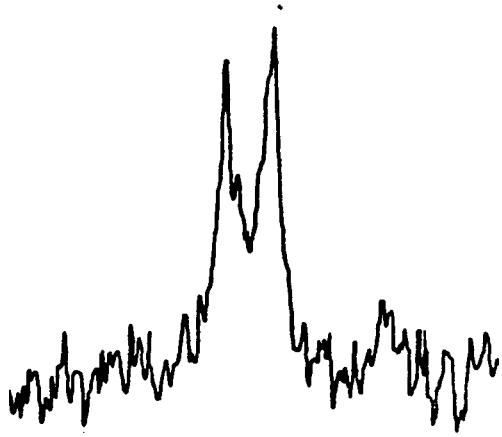


Figure 1. ^{29}Si nmr of $(CH_3)_2HSiOCH_2CH_2C_6H_4OSiH(CH_3)_2$ 9

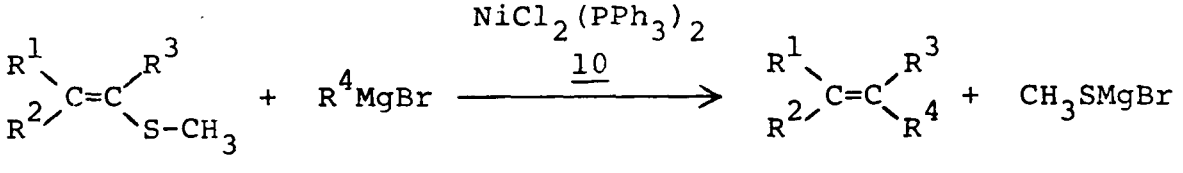
The ^{29}Si nmr did have a larger difference in chemical shift between alcoholic and phenolic derivatives than did the ^{1}H nmr, as we have expected. But in the case of trimethylsilyl derivatives of coal fractions the ^{29}Si concentration was too low to produce an observable signal. In an effort to increase the signal, dimethylsilyl ethers were used with the technique of cross-polarization between ^{1}H and ^{29}Si. This technique did enhance the signal of the model compounds examined by a factor of approximately five (70), but the ^{29}Si chemical shifts of aliphatic and aromatic dimethylsilyl derivatives were much closer than the trimethylsilyl derivatives. Thus, the two types of ethers could not be distinguished by ^{29}Si nmr. Therefore, these results represent no improvement over those reported by Schweighardt (65). The use of trimethylsilyl ethers might still succeed if a ^{29}Si enriched silylating agent were used, but the high cost of the ^{29}Si enriched reagent is inhibitive.

PART II. ACTION OF GRIGNARD REAGENT ON MODEL ORGANOSULFUR COMPOUNDS WITH VARIOUS ORGANOMETALLIC CATALYSTS

Introduction

Nickel complexes have proven to be an exceedingly valuable tool to the synthetic organic chemist. The utility of this class of compound has been reviewed several times (71-78). Recently a new reaction was developed by Okamura, Muira, and Takei (79) using a nickel complex as a catalyst. These workers reported selective carbon-carbon bond formation by cross-coupling of Grignard reagents with olefinic and aromatic sulfides. In a typical reaction 1.25 to 1.50 equivalents of Grignard reagent was added to a solution of vinyl sulfide and 0.03 equivalents of bis(triphenylphosphine)dichloronickel 10 in tetrahydrofuran. The Grignard reagent displaced the sulfur atom from the vinylic carbon. The reaction is shown in Scheme 6. These authors ran this reaction

Scheme 6



with a variety of vinyl sulfides using both n-butylmagnesium bromide and phenylmagnesium bromide; with one exception the yield of cross-coupled product ranged from 60 to 97 per cent.

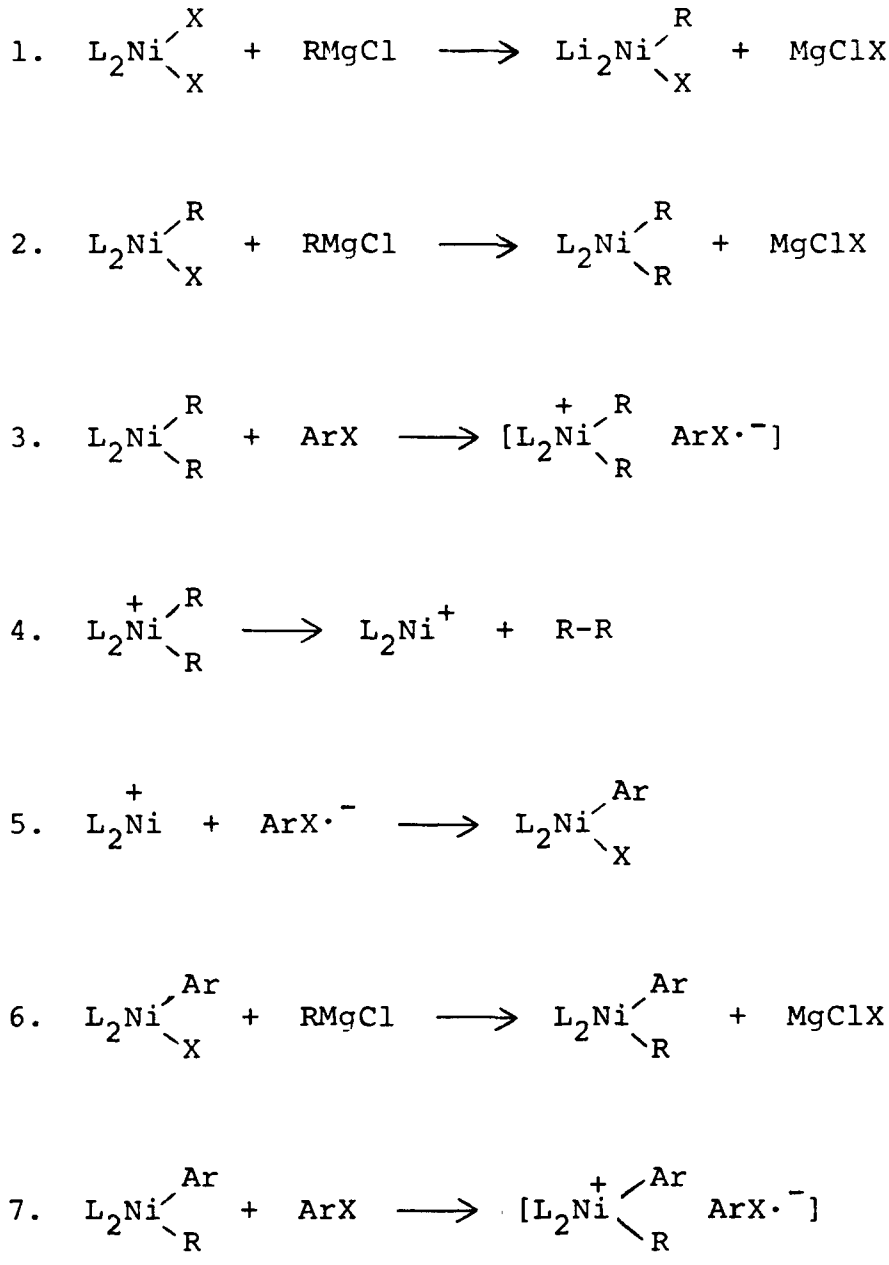
With each substrate, phenylmagnesium bromide gave the higher yield, but the use of this reagent on aryl sulfides presented a problem. The nickel complex was found to effectively catalyze the coupling of Grignard reagents, and therefore in the case of phenyl sulfides the cross-coupled product, biphenyl, would also be formed by the coupling of phenylmagnesium bromide with itself, making yield determination only possible by measuring the disappearance of the starting sulfide. Thioanisole was the only aryl sulfide studied in this work and with n-butylmagnesium bromide the yield of n-butylbenzene was 29 per cent.

Other nickel catalyzed cross-coupling reactions of Grignard reagents with vinyl and aryl derivatives have been investigated. For example Julia has reported the reaction of Grignard reagents with vinyl sulfones (80). Corriu and Masse (81) and Tamao et al. (82,83) have independently reported the coupling of aryl and vinyl halides with Grignard reagents; and Wenkert, Michelotti, and Swindell (84) described the coupling of Grignard reagents with enol ethers and aryl ethers. In each of these cases, whether the atom being displaced is sulfur, halogen or oxygen, the displacement must be from an sp^2 hybridized carbon.

On this basis, one might assume that a similar mechanism is operating in each reaction. Tamao et al. (83) offered a mechanism based upon known reactions of organonickel com-

pounds. Morrell and Kochi (85), on the basis of kinetic experiments and isotopic labeling experiments proposed the following modification of Tamao's mechanism (Scheme 2). In

Scheme 7



8. $L_2\overset{+}{N}i\begin{matrix}\diagup Ar \\ \diagdown R\end{matrix} \longrightarrow L_2Ni^+ + Ar\text{-}R$

9. $L_2Ni^+ + ArX\cdot^- \longrightarrow L_2Ni\begin{matrix}\diagup Ar \\ \diagdown X\end{matrix}$

steps 4 and 7 an electron transfer takes place leaving nickel in the +3 oxidation state from which reductive elimination is more facile.

Because Grignard reagent, under these conditions, attacked only aryl and vinyl sulfides, incorporation of Grignard reagent would be a measure of these types of organosulfur compounds, with the remainder being aliphatic sulfur compounds. This is an important characteristic because it has been suggested that aliphatic organosulfur compounds are much easier to reduce during hydrodesulfurization than aryl and thiophenic sulfides (86,87). The implication of these results was that coal that contained a substantial fraction of organic sulfur could be desulfurized under relatively mild conditions if most of the organic sulfur was in aliphatic structures. Attar suggested using the distribution of the organic sulfur groups to screen coals with a large fraction of organic sulfur into "easily desulfurizable" coals and stubborn coals (86,87).

This reaction appeared to afford the type of organosulfur specificity that is needed to elucidate the sulfur functionalities in coal. If the yield for aryl sulfides could be improved over that reported by Okamura et al. (79) and the Grignard reagent made distinguishable from compounds present in coal, it would be possible to use this reaction to study the organosulfur segment of coal. In this section, the effectiveness of this reaction on model aryl sulfides will be studied.

Results and Discussion

The purpose of this study was to determine the effectiveness of the bis(triphenylphosphine)dichloronickel as a catalyst in the coupling of Grignard reagents with aryl sulfides. The results of Okamura and coworkers (79) showed that in tetrahydrofuran phenylmagnesium bromide gave a higher yield of cross-coupled produce than did n-butylmagnesium bromide for each of the sulfides studied. For this reason, we wanted to use an aryl Grignard reagent. Because the nickel reagent also catalyzed the coupling of Grignard reagent with itself (79), the Grignard reagent would have to be selected so that the phenyl ring from the sulfide would be distinguishable from the phenyl ring from the Grignard reagent. For this reason, when one or both of the aryl groups on the sulfide was a simple phenyl ring, p-tolylmagnesium bromide 11 was the Grignard

reagent used. The model compounds used to study this reaction and the results are shown in Table 3.

Thioanisole and phenylsulfide reacted in a much higher yield (54 per cent and 77 per cent respectively) than the 29 per cent reported by Okamura et al. (79) for thioanisole reacting with n-butylmagnesium bromide. Part of this was undoubtedly due to the increase in reaction time from 14 hours to 24 hours.

In the reactions of substituted thiophenes some unexpected products were found. In the case of thianaphthene a trace of the substitution product 2-phenylthianapthene was found. Its structure was determined by comparison of the C^{13} nmr with an authentic sample (88). Stilbene was also an unexpected product. A possible route to this product is shown in Scheme 8. Compound 12 is formed by initial attack of phenylmagnesium bromide on the thiophenic double bond. Then a nickel(0) species, which has been proposed in similar reactions (85), could undergo oxidative addition, as they are known to do with aryl halides (85). Acidic work-up would then cleave the nickel complex 13. Dibenzothiophene (DBT) yielded only 10 per cent of the desired o,o'-quaterphenyl and 7 per cent of o-terphenyl. A pathway similar to Scheme 8 can be used to rationalize the formation of o-terphenyl.

Table 3. Results of reactions of Grignard reagents with aryl sulfides in tetrahydrofuran in the presence of bis(triphenylphosphine)dichloronickel

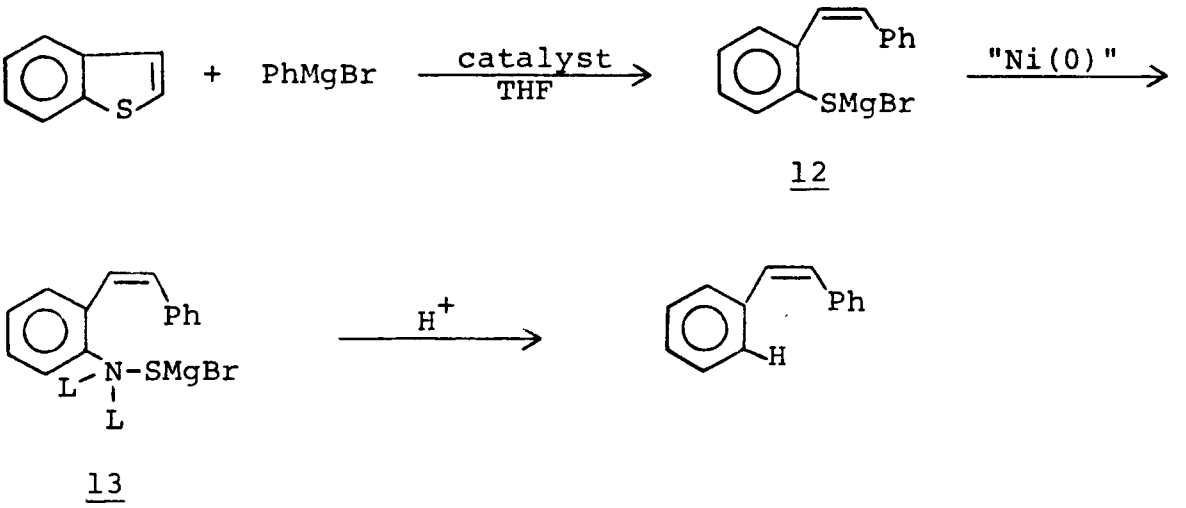
Starting sulfide	Product	Per cent yield
Thioanisole[a]	4-Phenyltoluene	77
Phenylsulfide[a]	4-Phenyltoluene	76
Thianaphthene[b]	o-Phenylstilbene (~3:1)[c]	53
	Stilbene (~3:1)[c]	<5
	2-Phenylthianaphthene	trace
Dibenzothiophene[b]	o,o'-Quaterphenyl	9
	o-Terphenyl	7
Benzylphenylsulfide[a]	4-Phenyltoluene	73
	Phenyl-p-tolylmethane	19
	Diphenylmethane	8
Benzylsulfide[b]	1,2-Diphenylethane	54
	Diphenylmethane	45

[a]p-Tolymagnesium bromide was the Grignard reagent used.

[b]Phenylmagnesium bromide was the Grignard reagent used.

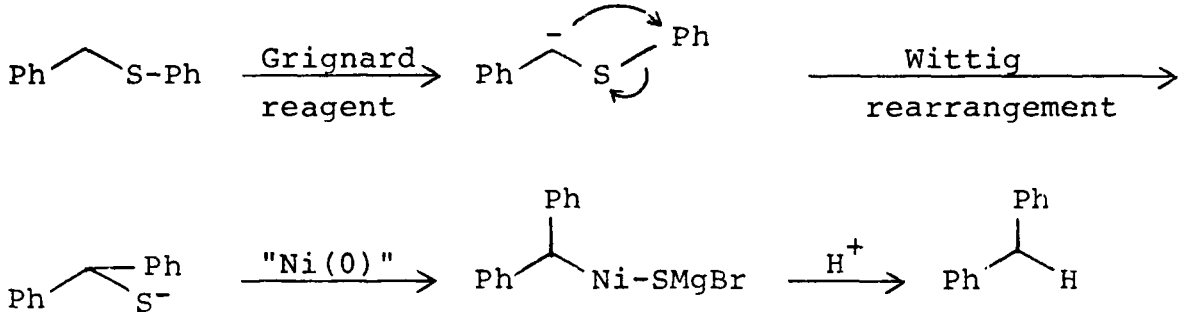
[c]Cis:trans ratio.

Scheme 8



The effect of Grignard reagent on benzylic sulfides was then studied. First the competitive reaction of benzyl group versus phenyl group was examined in the case of benzylphenyl-sulfide. The sulfide was completely consumed while forming three products. The phenyl group was displaced in 73 per cent yield, very close to the 77 per cent displacement of phenyl group from phenyl sulfide. The benzylic groups was attacked, forming phenyl-p-tolylmethane in 19 per cent yield. The third product was diphenyl methane. Our proposed route to this product is shown in Scheme 4. Initially the Grignard reagent abstracted a proton and the anion then underwent a Wittig rearrangement. The Wittig rearrangement of organosulfur compounds is known (89). Anion 14 in the form of its magnesium salt is analogous to compound 12 in Scheme 8 and can

Scheme 9



follow the same path to reduce off the sulfur and form diphenylmethane. In the case of benzyl sulfide approximately half (54 per cent) of the sulfide underwent the Wittig rearrangement followed by reduction, and in the other half (45 per cent) the benzyl group was simply displaced by the phenylmagnesium bromide. The reactions, except in the case of DBT, went in a high enough yield to be useful in the analysis of coal derived liquids. After this work was completed, Wenkert and coworkers (90) published results of the same reactions in benzene. The only yield that was substantially different from our results was that of DBT, which went in 52 per cent. The difference in this case might be due to a limited solubility of DBT in tetrahydrofuran.

The catalytic effect of other organometallic reagents was examined. Wilkinson's catalyst and the palladium analog of catalyst 10, bis(triphenylphosphine)dichloropalladium, were ineffective. The zerovalent nickel complex developed by

Kende et al. (91) catalyzed the reaction just as effectively as catalyst 10. Phenylsulfide was converted by p-tolylmagnesium bromide to 4-phenyltoluene in the presence of zerovalent nickel in 79 per cent yield as compared to 77 per cent for the nickel(II) catalyst 10. Because of the instability of the zerovalent nickel complex, it must be prepared from 10 and since the results of the two catalysts were well within experimental error, bis(triphenylphosphine)dichloronickel remains the catalyst of choice.

Before this method could be used to analyze coal derived liquids, the Grignard reagent must be altered in such a way that it would be distinguishable from compounds present in coal. The use of fluorine was examined because the fluorine can be analyzed in two ways; by elemental analysis and by ^{19}F nmr. Phenylsulfide was reacted with p-fluorophenylmagnesium bromide in the presence of compound 10 and 4-fluorobiphenyl was produced in 71 per cent yield. Therefore having fluorine present did not inhibit the reaction or cause an undesirable side reaction, and the use of p-flurophenylmagnesium bromide as a tool to analyze organosulfur compounds is possible.

Some complications can be foreseen in the use of this method on coal derived liquids. First, in whole coal, or even the pyridine extract of coal, there would be many functional groups susceptible to attack by Grignard reagent. Dark and McGough (92) recently developed a separation scheme using

preparative liquid chromatography on asphalts, in which nine different fractions are collected. Two of these were designated saturates and aromatics. If this technique were to be used on a coal derived sample, the saturates and aromatics should be freed of other functional groups that would react with Grignard reagent. Use of Dark and McGough's (92) separation scheme on the pyridine extract of Lovilia coal resulted in approximately 0.6 per cent of the pyridine extract being in the saturates and 2.3 per cent in the aromatics (93). The method of loading these samples on the column required starting with only 1-2 grams of pyridine extract. Because of the small yield of saturates and aromatics, this method was not satisfactory to generate enough coal fractions to study this reaction. Therefore, methods to solubilize coal will have to be used prior to separation into saturates and aromatics.

In conclusion, it was found that Grignard reagent, in the presence of a catalytic amount of bis(triphenylphosphine)-dichloronickel, could displace aryl groups in greater than 70 per cent yield. Tetrakis(triphenylphosphine) was found to be equally effective as a catalyst, while Wilkinson's catalyst and bis(triphenylphosphine)dichloropalladium were found to be ineffective. p-Fluorophenylmagnesium bromide was shown to react with phenylsulfide to the same extent as p-tolylmagnesium bromide. In our future investigations, the fluorinated

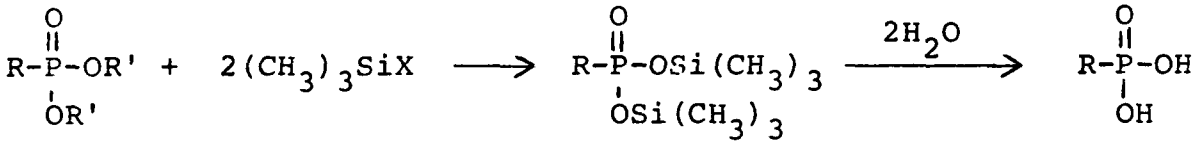
Grignard reagent will be used; since it provides a means of measuring the extent of reaction of the Grignard reagent with a complex substance such as coal. Elemental analysis or ^{19}F nmr analysis of the reaction products can be used as a semi-quantitative measure of the aryl and vinyl sulfur content. Our future studies will include evaluation of the methods to solubilize or depolymerize coal (66,94-99), the development of a liquid chromatographic method to separate the solubilized coal, the treatment of fractions of the solubilized coal with p-fluorophenylmagnesium bromide, and the analysis of the fluorine content of the resulting reaction mixture.

PART III. REACTION OF TRIMETHYLIODOSILANE WITH MODEL ORGANOSULFUR COMPOUNDS

Introduction

Trimethylhalosilanes have been used quite successfully for the effective cleavage of a variety of types of carbon-oxygen bonds. Trialkylphosphates and dialkylphosphonates react with halosilanes to form the silyl esters of phosphoric and phosphonic acids (100-108), which are easily cleaved under extremely mild conditions, leading to the free phosphorous acids (Scheme 10) (102-106,109). Of the various tri-

Scheme 10



methylhalosilanes, the iodosilane was found to be the most reactive (100,102,103,106). For example Zygmunt et al. (106) found that phosphonic esters could be silylated with trimethyliodosilane within minutes at 0°C, while trimethylbromosilane required about one hour at room temperature (103).

Several workers (110-113) have reported the cleavage of carbon-oxygen bonds in silylethers (Scheme 11). Jung and Ornstein (114) have recently reported the use of the same

Scheme 11

$$(CH_3)_3SiOR + (CH_3)_3SiI \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + RI$$

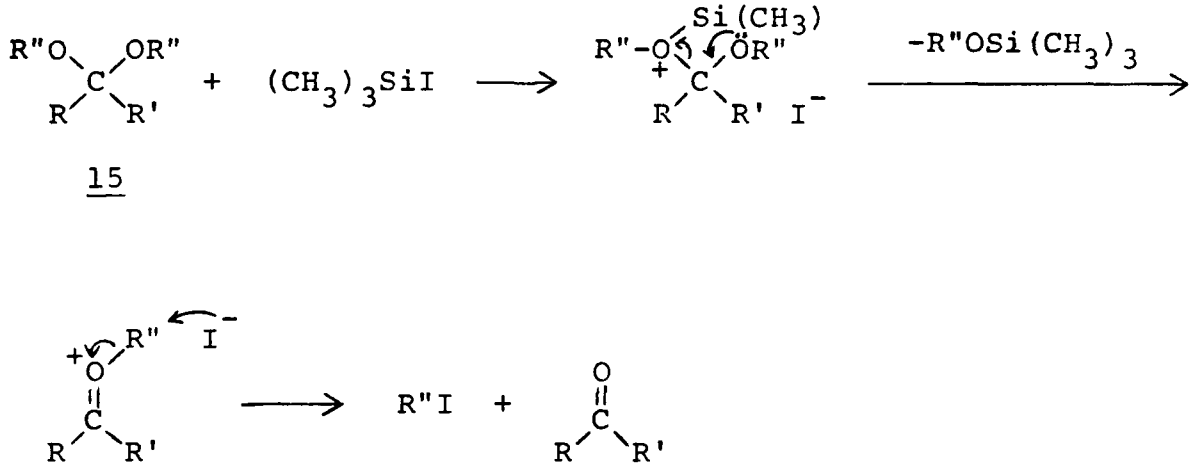
reaction to convert alcohols to iodides by first converting the alcohols to trimethylsilylethers.

Esters and lactones have been cleaved with trimethyliodosilane (115-121); and alkyl ethers are also succeptible to attack by this reagent (116,122-124). Alkyl ethers, such as tetrahydropyranyl ethers, have found extensive use in organic chemistry as protecting groups for alcohols (125-127). However, simple methyl ethers had been used sparingly to protect aliphatic alcohols because it was difficult to remove the methyl group. Recently trimethyliodosilane has been found to effect the selective cleavage of methyl ethers (123,124).

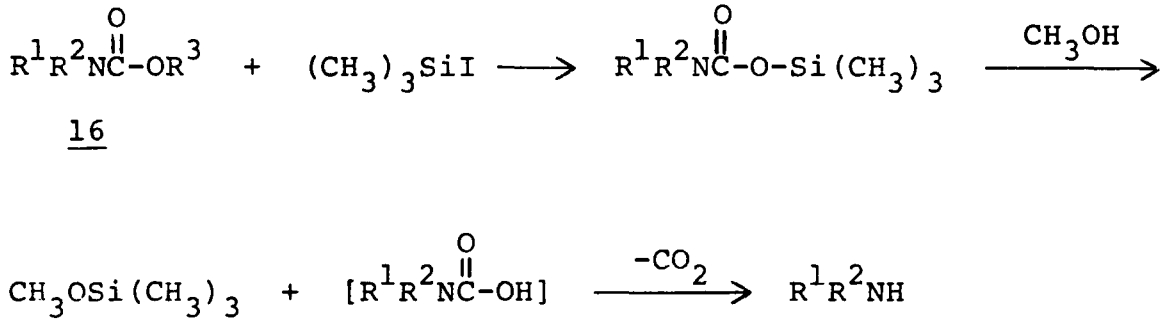
Jung and coworkers have used the reagent to convert ketals 15 to ketones (Scheme 12) (128) and carbamates 16 to amines (Scheme 13) (129).

In some cases, it has been found advantageous to generate the trimethyliodosilane in situ. Two methods have been used for this purpose. The first, by Ho and Olah (130), was originally developed by Pray and coworkers (131). In this

Scheme 12



Scheme 13



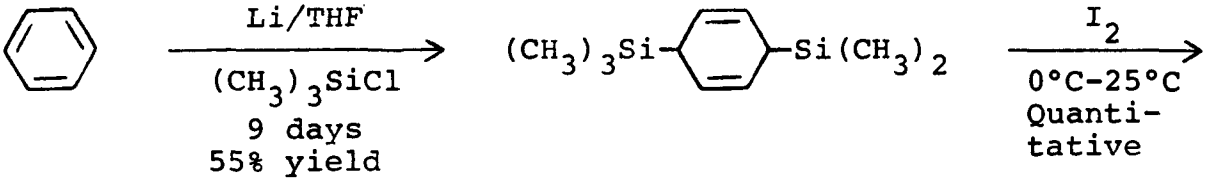
method, phenyltrimethylsilane is heated in the presence of iodine as shown in Scheme 14. The second method, developed by Jung and Blumenkopf (132), involved initial Birch reduction

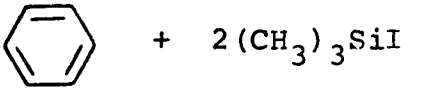
Scheme 14

$$Ph\text{-}Si(CH_3)_3 + I_2 \xrightarrow[2\text{-}6\ hrs]{110°C} PhI + (CH_3)_3SiI$$

of benzene followed by addition of trimethylchlorosilane to give 3,6-bis(trimethylsilyl)-1,4-cyclohexadiene, which quantitatively gave trimethyliodosilane upon treatment with iodine (Scheme 15).

Scheme 15

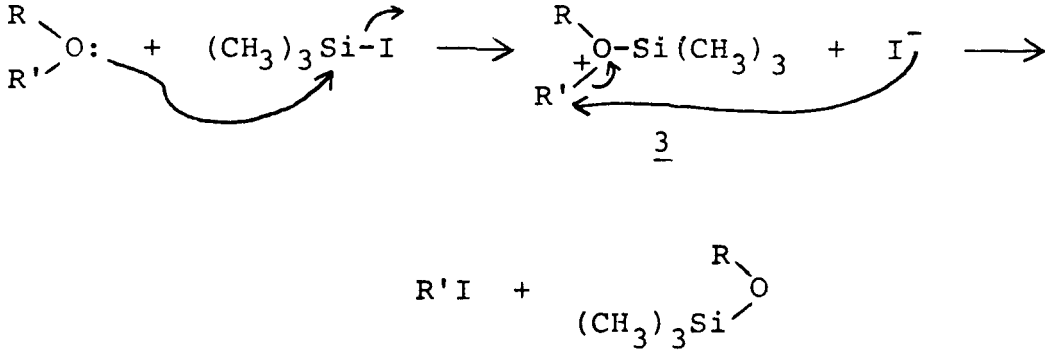




In the cleavage reactions with trimethyliodosilane the initial step is envisioned as a nucleophilic displacement of iodide ion from trimethyliodosilane by a lone pair of electrons of an oxygen atom forming an oxonium ion 17. The

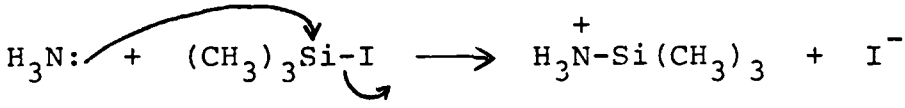
iodide ion then attacks one of the groups attached to the oxygen displacing the neutral oxygen (Scheme 16).

Scheme 16



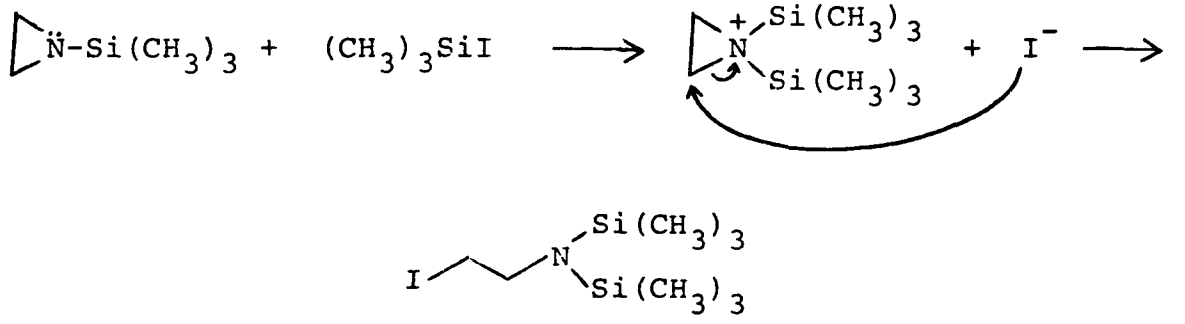
There are at least two instances where the lone pair of electrons from a nitrogen displaced iodide from the iodosilane. The synthesis of hexamethyldisilazane from ammonia and trimethyliodosilane involves a series of displacement reactions, the first of which is shown in Scheme 17. Another

Scheme 17



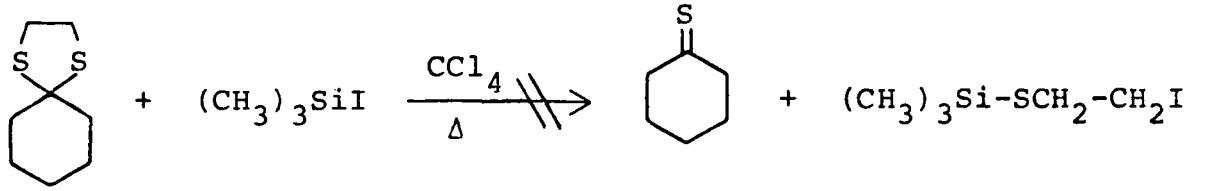
example is the opening of aziridine rings with trimethylhalosilanes (Scheme 18) reported by Piper and Ruhlmann (133).

Scheme 18



The literature shows no record of sulfur displacement of iodide from silicon. Jung and coworkers (128) examined this possibility in their work on conversion of ketals to ketones, attempting to react trimethyliodosilane with the ethylene thioketal of cyclohexanone 18 in refluxing carbon tetrachloride, (Scheme 19), but 18 was recovered unchanged.

Scheme 19



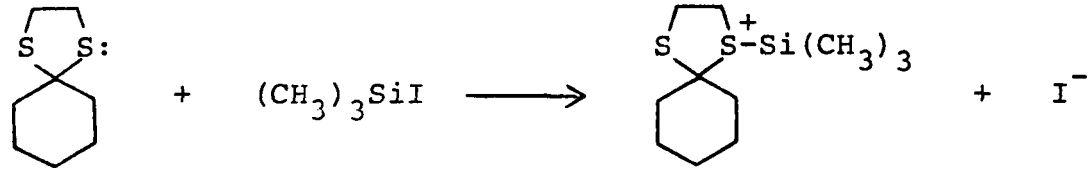
18

The oxygen analogue of 18 reacted sluggishly and afforded only 20 per cent cyclohexanone; while other ketals, including the

diethyl ketal of cyclohexanone, afforded the ketone in greater than 95 per cent yield. The stability of the ethylene ketal and thioketal must be attributed to the 5-membered ketal ring.

The silicon-sulfur bond is known to be much weaker than the silicon-oxygen bond (134) and thus there should be much less thermodynamic driving force for the displacement of iodide ion by sulfur. Jung et al. (128), by using the one sulfur compound whose oxygen analog reacted in very poor yield, did not select a sulfide suitable to displace iodide ion. The use of carbon tetrachloride as solvent was a poor choice for the generation of the sulfonium ion 19 (Scheme 20).

Scheme 20



19

For these reasons the nucleophilic displacement of iodide ion by sulfur was re-examined and constitutes Part III of this thesis.

Results and Discussion

Initially, in the study of the reaction of trimethyliodosilane with organic sulfides, thioanisole was the organosulfur reagent used. The desired reaction is shown in Scheme 21. Thioanisole was used because it gave the

Scheme 21

$$R\text{-}S\text{-}R' + (CH_3)_3SiI \longrightarrow \underset{\underset{20}{}}{R\text{-}\overset{+}{S}(Si(CH_3)_3)\text{-}R'} + I^- \longrightarrow R'I + R\text{-}S\text{-}Si(CH_3)_3$$

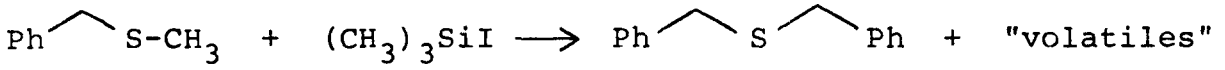
$$R'I + R\text{-}S\text{-}Si(CH_3)_3 \xrightarrow{(CH_3)_3SiI} R'I + RI + (CH_3)_3Si\text{-}S\text{-}Si(CH_3)_3$$

iodosilane reagent the option to displace either an alkyl group or an aryl group first. The reaction was attempted in a variety of solvents at reflux, but no reaction could be detected.

In their work on the hydrolysis of alkyl ethers, Jung and Lyster (123) reported that trityl, benzyl, and t-butyl ethers were cleaved at a much higher rate than other alkyl ethers and that aryl alkyl ethers (such as anisole) reacted at a much slower rate. Therefore, we turned our attention to benzylmethylsulfide. This sulfide was found to react with

trimethyliodosilane at 140°C in about 70 per cent yield, but the product was benzylsulfide (Scheme 22). There were also

Scheme 22



several volatile products, but the only ones identified were methyl iodide and hexamethyldisiloxane. The polarity of the solution was increased by the addition of hexamethylphosphoramide (HMPA), in hopes that a more polar solvent system would stabilize the sulfonium ion 20. Benzylsulfide was again the product formed, but in a slightly lower yield (64 per cent). Silyl iodides form complexes with HMPA (135), and might possibly slow the reaction for that reason. An even stronger silylating reagent, trimethylsilyl perchlorate, was then used in an attempt to accomplish the desired cleavage of the benzyl-sulfur bond. It had no effect on benzylmethylsulfide and the attempted cleavage of organic sulfides with silyating agents was discontinued.

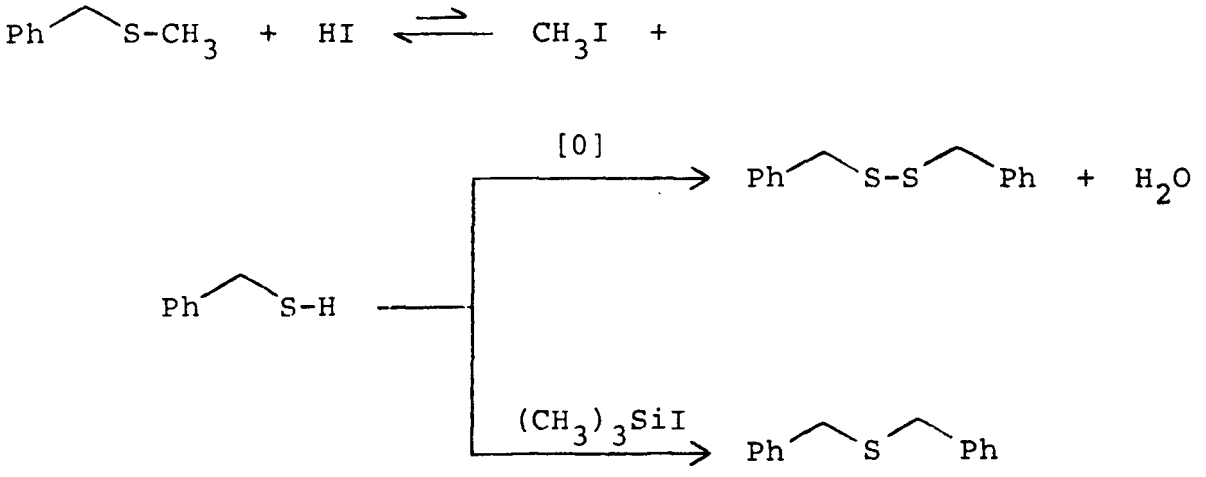
Benzylsulfide, while not the desired product, was an interesting product, and a study of the mechanism of this reaction was undertaken. When more care was taken to exclude water, benzylmethylsulfide was found to be stable to the

reaction conditions. After 5 days of refluxing in chlorobenzene no reaction had taken place and approximately 0.03 equivalents of water was added. Twelve hours later all the benzylmethylsulfide had reacted, giving an 86 per cent yield of benzylsulfide and the same volatile products reported in the previous case. Evidently the water generated a reactive intermediate which attacked the starting sulfide. The action of this intermediate must be catalytic in nature for the reaction to be driven to completion with just 0.03 equivalents of water.

Trimethyliodosilane, like most halosilanes, is extremely sensitive to water, forming hydrogen iodide 21 and hexamethyldisiloxane 22 upon hydrolysis. Due to the inert behavior of compound 22, hydrogen iodide 21 was assumed to be the reactive intermediate formed. Under more severe conditions hydrogen iodide had been reported to cleave sulfides in low yields (136). When benzylmethylsulfide was treated with excess hydrogen iodide under the reaction conditions, only starting sulfide was observed by GC, but when trimethyliodosilane was added to this solution benzylsulfide was produced in high yield. When benzylmethylsulfide was treated with hydrogen iodide in an air atmosphere, it was converted quantitatively to benzyldisulfide and methyl iodide. Knowing that mercaptans are easily air oxidized to the disulfide (137), this suggested that hydrogen iodide indeed cleaved

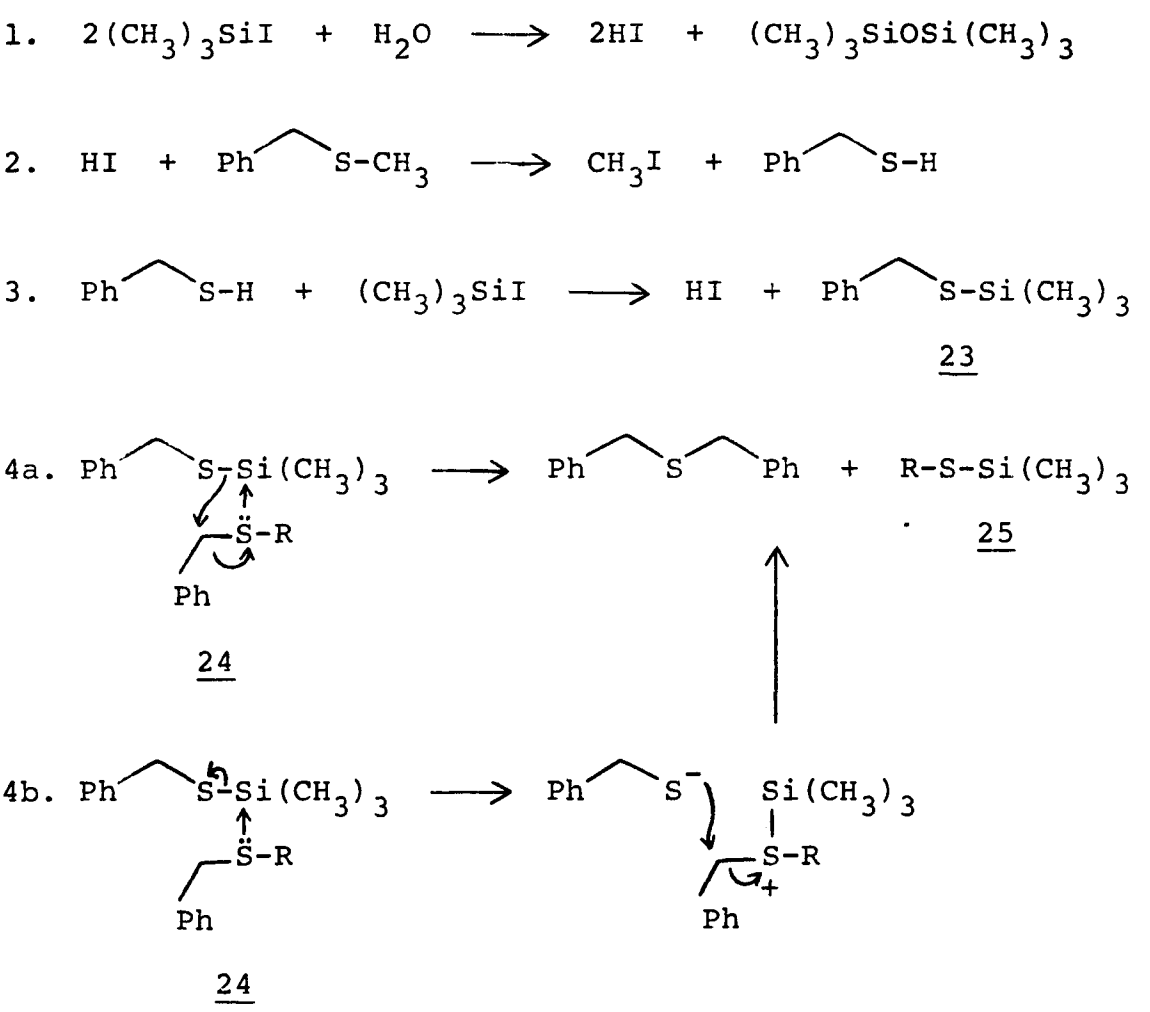
the starting sulfide, but it was an equilibrium reaction favoring the starting sulfide (Scheme 23). Mercaptans are

Scheme 23



known to react with halosilanes to produce the silylsulfide and hydrogen halide (138). The regeneration of hydrogen iodide would make it a catalyst for the reaction. The results, to this point, suggested the mechanism shown in Scheme 24, where in step 4 sulfur from compound 24, either the mercaptan formed in step 2, the silyl sulfide 23 formed in step 3, or the starting sulfide, displaces the sulfur in compound 23. This sulfur, in either a one-step (4a) or a two-step (4b) process migrates to the benzylic group of compound 24, forming benzylsulfide and a volatile silyl sulfide 25.

Scheme 24



5. R = CH_3, H, or $Si(CH_3)_3$

To test this mechanism, benzyl(trimethylsilyl)sulfide 24 was added to both benzylmethylsulfide and benzyl mercaptan at the original reaction conditions. In both cases no benzylsulfide was formed. A small yield of benzyldisulfide was

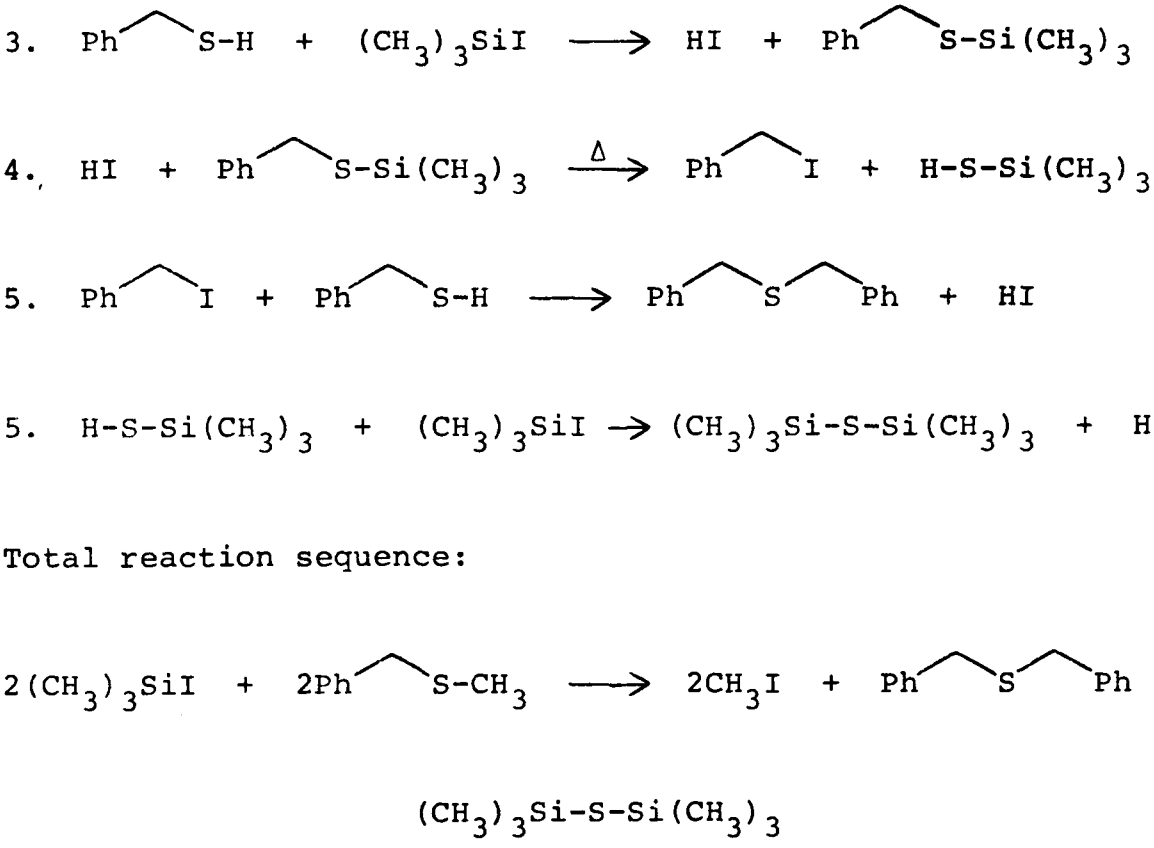
formed in each case probably due to a homolytic cleavage followed by radical recombination.

In this section, the reaction of sulfides with trimethyl iodosilane has been reported. Benzylmethyl sulfide reacts with trimethyliodosilane to give benzylsulfide, but only in the presence of a small amount of added water. Trapping experiments with oxygen, in which benzyldisulfide is formed, suggested the intermediacy of benzyl mercaptan, which is believed to arise from the hydrogen iodide induced cleavage of benzylmethylsulfide. Based on the relatively facile reaction of mercaptans with halosilanes, benzyl(trimethylsilyl)sulfide is also a likely intermediate. On the basis of these results, we propose the mechanism shown in Scheme 25. The first three steps are the same as in Scheme 24 and were discussed there. The cleavage of sulfides by hydrogen iodide was discussed earlier, but the use of the reagent on trimethylsilylsulfides as in Step 4 has not been reported. The alkylation of mercaptans with alkyl halides (Step 5) is an established reaction (139).

Scheme 25

1. $2(CH_3)_3SiI + H_2O \longrightarrow (CH_3)_3SiOSi(CH_3)_3 + 2HI$

2. $HI + Ph\overset{\frown}{S}\text{-}CH_3 \longrightarrow CH_3I + Ph\overset{\frown}{S}\text{-}H$



Total reaction sequence:

EXPERIMENTAL

General Information

Infrared spectra (ir) were recorded on a Beckman IR-4250 or Beckman 18A spectrophotometer. Routine proton magnetic resonance spectra (nmr, 60 MHz) were determined on a Varian Model A-60, Varian EM-360, or Hitachi R20-B spectrometer, and chemical shifts were reported as parts per million downfield from tetramethylsilane (TMS) (δ scale). Fourier transform silicon (^{29}Si) magnetic resonance spectra were recorded on a Bruker HX-90 (90 MHz) using tetraethoxysilane as an internal standard, or on an instrument constructed at Iowa State University and previously described (140,141), using TMS as an internal standard. Fourier transform carbon (^{13}C) magnetic resonance spectra were obtained on a Joel FX 90Q (90 MHz) using acetone-d_6 as an internal standard. Routine and high resolution mass spectra were determined on a MS902. Gas chromatography/mass spectral (GCMS) analysis were performed on a Finnigan 4023 spectrometer with INCOS data system. Routine analytical gas chromatography (GC) was done on a Varian Model 3700 or Tracor 550 gas chromatograph.

All yields were obtained by gas chromatographic analysis unless otherwise stated. A known amount of an internal standard was added to a given amount of sample. Response factors for each component relative to the internal standard were experimentally determined.

Part I

Trimethylsilylation of alcohols

The trimethylsilyl ethers were prepared from the corresponding alcohols. The liquid alcohols were used neat and the solid alcohols were dissolved in a minimal amount of anyydrous benzene. The alcohol (0.40 mol) was heated under reflux and the system was purged with nitrogen. Hexamethyldisilazane 4 (0.20 mol) and 1-2 drops of trimethylchlorosilane were then added and the solution heated under reflux with stirring for 8-12 hours. The crude trimethylsilyl ethers were separated from the reaction mixture by distillation through a short-path microdistillation apparatus. The ethers were further purified by preparative gas chromatography on 5 per cent OV-101 or 10 per cent Carbowax 20 M.

Phenoxytrimethylsilane 26

b.p. 182-183°C [lit. 181.9-182.4°C/742 torr (142)]

nmr (neat) 0.25(9H, s), 6.95(5H, m)

ir (thin film) 3025(w), 2960(w), 1595(s), 1490(s), 1265(w), 1250(s), 915(s), 840(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 166(27)(P), 151(100)($P-CH_3$), 121(37)

exact mass (P-15) 151.05805 (meas.), 151.05792 (calc. for $C_8H_{11}OSi$)

Allyloxytrimethylsilane 27

b.p. 101-102 [lit. 32-33°C/23 torr (143)]

nmr (neat) 0.09(9H, s), 4.10(2H, m), 5.15(2H, m), 5.85(1H, m)

ir (thin film) 2945(m), 1245(s), 1130(m), 1080(s), 1025(w), 910(m), 862(s), 830(s) cm^{-1}

exact mass (P-CH_3) 115.05721 (meas.), 115.05729 (calc. for $C_5H_{11}OSi$)

n-Butoxytrimethylsilane 28

b.p. 124-125°C [lit. 123.7-125°C/740 torr (142)]

nmr ($CDCl_3$) 0.05(9H, s), 0.88(3H, t, J=2.0 Hz), 1.40(4H, m), 3.55(2H, t, J=6.5 Hz)

mass spectrum (70 eV) m/e (rel. intensity) 131(95) (P-CH_3), 75(100), 73(48) ($SiMe_3$ or O-n-butyl), 45(26)

exact mass (P-CH_3) 131.08901 (meas.), 131.08922 (calc. for $C_6H_{15}OSi$)

sec-Butoxytrimethylsilane 29

b.p. 113-114°C [lit. 112.3°C (142)]

nmr ($CDCl_3$) 0.05(9H, s), 0.65-1.67(8H, m), 3.65(1H, sextet), J=5.9 Hz)

mass spectrum (70 eV) m/e (rel. intensity) 131(31)(P-CH_3), 117(81)(P-C_2H_5), 75(80), 73(100)($SiMe_3$ or O-sec-butyl), 45(28)

exact mass (P-CH_3) 131.08941 (meas.), 131.08922 (calc. for $C_6H_{15}OSi$)

t-Butoxytrimethylsilane 30

b.p. 101-103°C [lit. 101°C/754 torr (142)]

nmr (neat) 0.06(9H, s), 1.20(9H, s)

mass spectrum (70 eV) m/e (rel. intensity) 131(65)(P-CH_3), 75(100), 73(66)($SiMe_3$ or O-t-butyl)

exact mass (P-CH_3) 131.08920 (meas.), 131.08922 (calc. for $C_6H_{15}OSi$)

β-Naphthoxytrimethylsilane 31

nmr (neat) 0.21(9H, s), 7.35(7H, m)

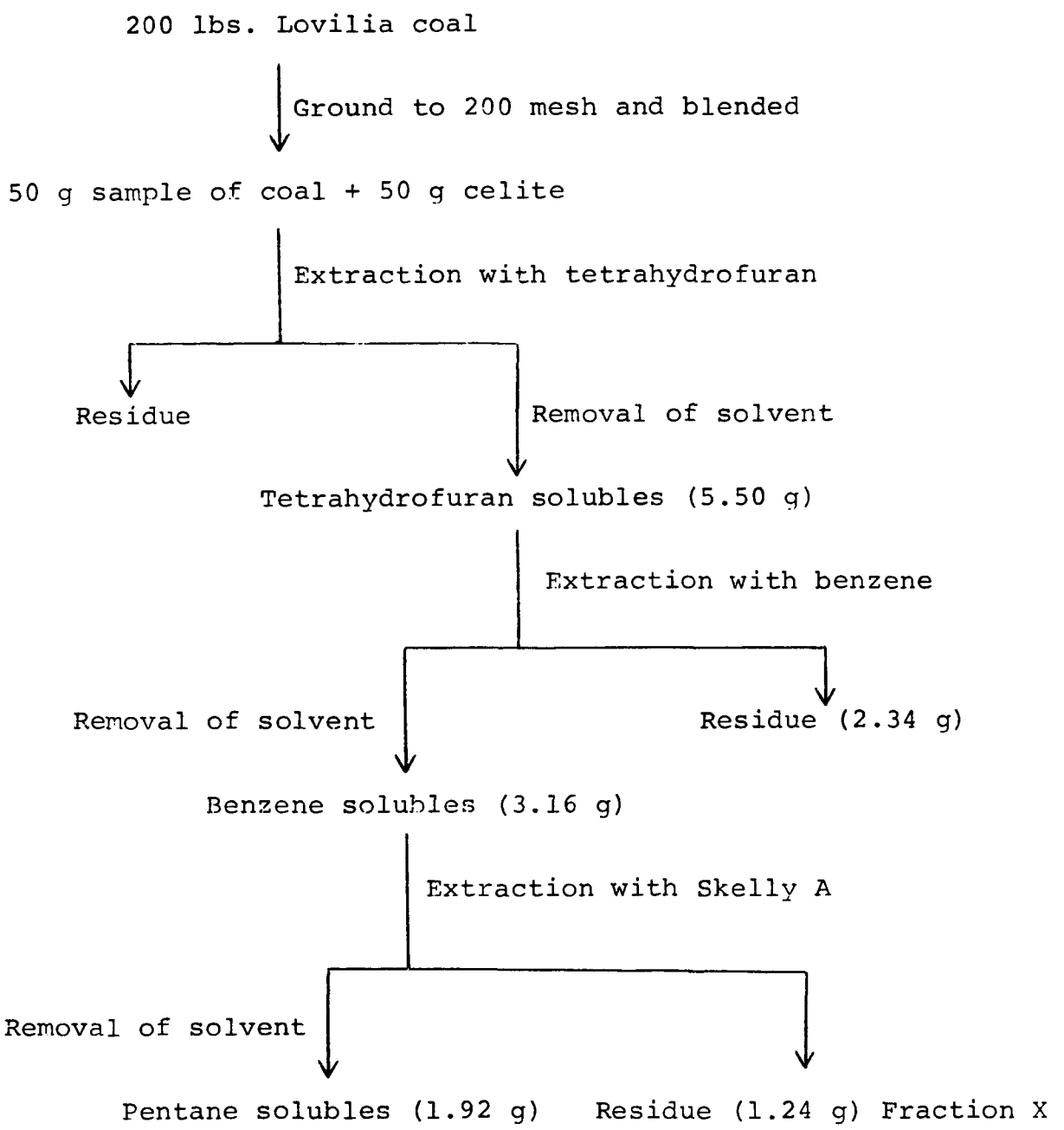
mass spectrum (70 eV) m/e (rel. intensity) 216(80)(P), 201(100)(P-CH_3), 73(45)($SiMe_3$)

exact mass (P) 216.09724 (meas.), 216.09705 (calc. for $C_{13}H_{16}OSi$)

Trimethylsilylation of coal derived liquid

A mixture of 50 grams of dry Lovilia coal that had been ground to 200 mesh and 50 grams of celite was extracted with a Soxhlet extractor for ten days with anhydrous tetrahydrofuran. The solvent was then removed at reduced pressure from the extracted residue. This was then extracted with anhydrous benzene for four days and the solvent was again removed at reduced pressure from the extracted material. This was then extracted with dry Skelly A (a mixture of pentanes) and the insoluble fraction was used (fraction X in Scheme 26). The silylation procedure was identical to that used with the pure alcohols. Fraction X (0.46 g) was treated with an excess of

Scheme 26


200 lbs. Lovilia coal
Ground to 200 mesh and blended
50 g sample of coal + 50 g celite
Extraction with tetrahydrofuran
Residue
Removal of solvent
Tetrahydrofuran solubles (5.50 g)
Extraction with benzene
Removal of solvent
Residue (2.34 g)
Benzene solubles (3.16 g)
Extraction with Skelly A
Removal of solvent
Pentane solubles (1.92 g)
Residue (1.24 g) Fraction X

hexamethyldisilazane 4 (10 ml) and two drops of trimethylchlorosilane for two days. The volatiles were then removed at reduced pressure. The nmr (in $CDCl_3$) showed that approximately 30 per cent of the protons were trimethylsilyl protons, but ^{29}Si nmr showed no peaks after 3 days accumulation of signal.

Dimethylsilylation of alcohols

The experimental procedure for dimethylsilylation of alcohols was the same as the procedure for trimethylsilylation, except that tetramethyldisilazane was used in place of hexamethyldisilazane 4, and dimethylchlorosilane was used instead of trimethylchlorosilane.

Phenoxydimethylsilane 32

nmr ($CDCl_3$) 0.28(6H, d, J=2.5 Hz), 5.90(1H, septet, J=2.5 Hz), 7.00(5H, m)

ir (thin film) 3060(w), 3040(w), 2962(m), 2120(s), 1493(s), 1260(s), 1168(m), 1070(m), 1023(m), 1000(m), 920(s), 890(w), 835(m), 779(w), 754(s), 690(m) cm^{-1}.

mass spectrum (70 eV) m/e (rel. intensity) 152(71)(P), 151(52)(P-H), 137(100)(P-CH_3), 77(48)(C_6H_5), 59(27)($SiHMe_2$), 51(35)

exact mass (P) 152.06528 (meas.), 152.06575 (calc. for $C_8H_{12}OSi$); (P-CH_3) 137.0419 (meas.), 137.04227 (calc. for C_7H_9OSi)

n-Butoxydimethylsilane 33

nmr ($CDCl_3$) 0.11(6H, d, J=2.6 Hz), 0.70-1.60(7H, m) 3.61 (2H, t, J=6.0 Hz), 4.56(1H, septet, J=2.6 Hz)

ir (thin film) 2965(s), 2940(m), 2883(m), 2120(s), 1258(s), 1099(s), 910(s)

mass spectrum (70 eV) m/e (rel. intensity) 131(29)(P-H), 117(27)(P-CH_3), 89(100)($CH_2OSiHMe_2$), 75(57)($OSiHMe_2$) 61(84), 59(78)($SiHMe_2$)

n-Pentoxydimethylsilane 34

nmr ($CDCl_3$) 0.11(6H, d, J=2.6 Hz), 0.70-1.70(9H, m), 3.51 (2H, t, J=6.0 Hz), 4.51(1H, septet, J=2.6 Hz)

mass spectrum (70 eV) m/e (rel. intensity) 145(33)(P-H) 131(35)(P-CH_3), 89(100)($CH_2OSiHMe_2$), 75(67)($OSiHMe_2$) 69(42), 61(81), 59(73)($SiHMe_2$), 45(32)

exact mass (P-CH_3) 131.08908 (meas.), 131.08922 (calc. for $C_6H_{15}OSi$)

sec-Butoxydimethylsilane 35

nmr ($CDCl_3$) 0.10(6H, d, J=3.0 Hz), 0.75-1.60(8H, m), 3.68 (1H, sextet, J=6.0 Hz), 4.63(1H, septet, J=3.0 Hz)

ir (thin film) 2960(s), 2920(w), 2864(w), 2100(s), 1370(m), 1248(s), 1080(m), 1049(s), 944(m), 898(s) cm^{-1}

mass spectrum (70 eV) m/e (rel. intensity) 117(23)(P-CH_3), 103(100)(P-C_2H_5), 75(83)($OSiHMe_2$), 61(48), 59(62) ($SiHMe_2$)

exact mass (P-H) 131.08947 (meas.), 131.08922 (calc. for $C_6H_{15}OSi$); (P-CH_3) 117.07337 (meas.), 117.07358 (calc. for $C_5H_{13}OSi$)

1,2-bis(dimethylsiloxy)ethane 36

nmr ($CDCl_3$) 0.11(6H, d, J=2.0 Hz), 3.65(2H, s), 4.60(1H, septet, J=2.0 Hz)

ir (thin film) 2967(w), 2939(w), 2878(w), 2120(s), 1258(s), 1149(m), 1100(s), 895(s)

mass spectrum (70 eV) m/e (rel. intensity) 163(16)(P-CH_3), 135(58), 133(72)(163-CH_2O), 119(94)(P-$SiHMe_2$), 89(95)($CH_2OSiHMe_2$), 73(29), 59(100)($SiHMe_2$)

exact mass (P-CH_3) 163.0609 (meas.), 163.0611 (calc. for $C_5H_{15}O_2Si_2$)

α-Naphthoxydimethylsilane 37

nmr ($CDCl_3$) 0.40(6H, d, J-3.0 Hz), 5.10(1H, septet, 3.0 Hz) 6.80-8.25(7H, m)

ir (thin film) 3058(m), 2962(m), 2140(s), 1593(s), 1578(s), 1510(s), 1465(s), 1402(s), 1273(s), 1259(m), 1243(m), 1095(s), 919(s), 890(s), 793(m), 770(s)

mass spectrum (70 eV) m/e (rel. intensity) 202(94)(P), 201(77)(P-H), 187(23)(P-CH_3), 185(53), 128(100)($C_{10}H_8$), 127(45)($C_{10}H_7$), 115(42), 59(37)($SiHMe_2$)

exact mass (P-H) 201.07299 (meas.), 201.07357 (calc. for $C_{12}H_{13}OSi$); (P-CH_3) 187.05717 (meas.), 187.05792 (calc. for $C_{11}H_{11}OSi$)

β-Naphthoxydimethylsilane 38

nmr ($CDCl_3$) 0.35(6H, d, J=2.3 Hz), 5.00(1H, septet, J=2.3 Hz), 6.90-7.75(7H, m)

ir (thin film) 3030(m), 2470(m), 2140(s), 1635(s), 1604(s), 1512(s), 1471(s), 1272(m), 1261(s), 1224(s), 1175(m), 1124(m), 932(s), 922(s), 894(s)

mass spectrum (70 eV) m/e (rel. intensity) 202(100)(P), 187 (48)(P-CH_3), 159(32), 128(92)($C_{10}H_8$), 127(55)($C_{10}H_7$), 115(28)

Bis(dimethylsilyl)ether of p-hydroxyphenethyl alcohol 9

nmr ($CDCl_3$) 0.08(6H, d, J=2.8 Hz), 0.27(6H, d, J=3.0 Hz), 2.72(2H, t, J=7.0 Hz), 3.73(2H, t, J=7.0 Hz), 4.52(1H, septet, J=2.8 Hz), 4.85(1H, septet, J=3.0 Hz)

ir (thin film) 3020(s), 2945(m), 2856(m), 2112(s), 1618(m), 1508(s), 1248(s), 1082(s), 900(s), 824(m), 760(m)

mass spectrum (70 eV) m/e (rel. intensity) 254(22)(P), 166 (30)($CH_3C_6H_4OSiHMe_2$), 165(100)(166-H), 135(30), 91(67) (C_7H_7), 89(36)

exact mass (P) 254.11584 (meas.), 254.11577 (calc. for $C_{12}H_{22}O_2Si_2$)

Part II

Bis(triphenylphosphine)dichloronickel 10

Bis(triphenylphosphine)dichloronickel 10 was prepared by a variation of Venanzi's method (144), developed by F. A.

Cotton, et al. (145), in which a solution of 23.8 g (0.100 mol) of nickel dichloride hexahydrate in 20 ml of water is added to a solution of 52.5 g (0.200 mol) of triphenylphosphine in 750 ml of glacial acetic acid. The dark green microcrystalline precipitate was kept in contact with its mother liquor for 24 hours, filtered off, washed with glacial acetic acid, and dried in a vacuum desiccator. 50.5 g (66%) of the product was collected.

m.p. 245-249° decomposed.

Phenylmagnesium bromide 39

A solution of 15.70 g (0.100 mol) of bromobenzene in 100 ml of anhydrous diethylether was added dropwise with stirring to 2.44 g (0.100 mol) of magnesium turnings in 100 ml of anhydrous diethylether (under nitrogen). After the addition was completed, the solution was stirred for an additional two hours at room temperature. An aliquot of the solution was acidified with a solution of hydrochloric acid and back titrated with a sodium hydroxide solution to a phenolphthalein endpoint.

Reaction of phenylmagnesium bromide 39 with thioanisole

To a mixture of 1.24 g (0.010 mol) of thioanisole and 0.20 g (3.0×10^{-4} mol) of bis(triphenylphosphine)dichloronickel 10 in 25 ml of anhydrous tetrahydrofuran under reflux, was added 0.015 mol of phenylmagnesium bromide 39 dropwise. After refluxing approximately 24 hours, the solvent was

removed under reduced pressure and the excess Grignard reagent reagent destroyed with 25 ml of 1N hydrochloric acid. The solution was then extracted with ether and the combined ether layers washed with saturated sodium bicarbonate followed by saturated sodium chloride. The reaction mixture in ether was analyzed by GCMS. The thioanisole had reacted in 60 per cent yield and the only product was biphenyl.

p-Tolylmagnesium bromide 11

The procedure for the synthesis of p-tolylmagnesium bromide 11, was the same as that used for the synthesis of phenylmagnesium bromide 39 except p-bromotoluene was used in place of bromobenzene.

Reaction of p-tolylmagnesium bromide 17 with various aryl sulfides

To a solution of 0.010 mol of aryl sulfide in 25 ml of anhydrous tetrahydrofuran was added 0.20 g (3.0×10^{-4} mol) of bis(triphenylphosphine)dichloronickel 10. The system was then purged with nitrogen and the solution heated to reflux and 0.015 mol of p-tolylmagnesium bromide 11 (0.025 mol in the cases where the sulfur is bonded to two replaceable aryl groups) was added dropwise. The reaction immediately turned darker in color eventually becoming black. The reaction was held at reflux for 20-50 hours after which the solvent was removed and the excess Grignard reagent destroyed by treatment with 25 ml of 1N hydrochloric acid. After the solution was

extracted with ether, and the combined ether layers washed with saturated sodium bicarbonate and saturated sodium chloride, the products were identified by GCMS and GC retention times and yields were obtained by GC. The reaction was run with thioanisole, phenylsulfide, and benzylphenyl-sulfide and the results are in Table 3 in the Results and Discussion section.

Reaction of phenylmagnesium bromide 39 with various aryl sulfides

When neither of the aryl groups on the sulfur were simple phenyl groups, phenylmagnesium bromide 39 was the Grignard reagent used. This made the products simpler and easier to identify. The procedure used was identical to that used with p-tolylmagnesium bromide 11. The aryl sulfides used in this reaction were thianaphthene, dibenzothiophene, and benzylsulfide and the results are in Table 3 in the Results and Discussion section.

p-Fluorophenylmagnesium bromide 40

To a flame dried 1 liter three-necked flask equipped with a mechanical stirrer and a reflux condensor was added 2.44 g (0.100 mol) of magnesium turnings in 100 ml of anhydrous diethylether (under nitrogen). To this mixture was added dropwise a solution of 17.60 g (0.100 mol) of p-fluorobromobenzene in 100 mls of diethyl ether. An ice bath was used to control the rate of reflux. After three

hours of additional stirring, the solution was titrated and stored under nitrogen.

Reaction of p-fluorophenylmagnesium bromide 40 with phenylsulfide in the presence of bis(triphenylphosphine)dichloronickel 10

The procedure followed was identical to that used in the reaction of p-tolylmagnesium bromide 11 with various aryl sulfides. The Grignard reagent was changed and phenylsulfide was the only aryl sulfide used. The only product formed was 4-fluoro-1,1'-biphenyl. It was identified by GCMS and its yield was 71 per cent with 16 per cent of the phenylsulfide recovered.

Reaction of p-tolylmagnesium bromide 11 with phenylsulfide in the presence of Wilkinson's catalyst

The reaction of p-tolylmagnesium bromide 11 with various aryl sulfides was repeated with 0.03 equivalents of Wilkinson's catalyst, tris(triphenylphosphine)chlororhodium, used as the catalyst in place of bis(triphenylphosphine)dichloronickel 10. Phenylsulfide was the aryl sulfide used and 4-phenyltoluene was produced in 8 per cent yield.

Reaction of p-tolylmagnesium bromide 11 with phenylsulfide in the presence of bis(triphenylphosphine)dichloropalladium

The above reaction was repeated with 0.03 equivalents of bis(triphenylphosphine)dichloropalladium used in place of

Wilkinson's catalyst. The yield of 4-phenyltoluene was 9 per cent.

Reaction of p-tolylmagnesium bromide 11 with phenylsulfide in the presence of tetrakis(triphenylphosphine)nickel 41

The method of Kende, Liebeskind, and Braitsch (91) was used to prepare tetrakis(triphenylphosphine)nickel 41. Bis(triphenylphosphine)dichloronickel 10 (0.2282 g, 3.49×10^{-4} mol), triphenylphosphine (0.1964 g, 7.49×10^{-4} mol) and 20 mesh zinc (0.0312 g, 4.77×10^{-4} mol) were added to a flame dried three-necked flask equipped with a reflux consensor and magnetic stirrer. Under nitrogen, 5 ml of anhydrous dimethylformamide was added and the reaction was stirred at 50°C. After 90 minutes 20 ml of anhydrous tetrahydryfuran and 2.1009 g (1.13×10^{-2} mol) of phenylsulfide was added to the reaction mixture. The solution immediately turned black upon addition of the sulfide. The reaction mixture was then heated to reflux and p-tolylmagnesium bromide (2.86×10^{-2} mol) in ether was added dropwise. Upon work-up a yield of 79 per cent of 4-phenyltoluene was found.

Part III

Reaction of trimethyliodosilane with thioanisole

Thioanisole was mixed with 2 equivalents of trimethyliodosilane in a number of solvents. No reaction was observed in refluxing carbon tetrachloride, chloroform, toluene or

chlorobenzene with greater than 90 per cent recovery of starting material in each case.

Reaction of benzylmethylsulfide with trimethyliodosilane

The reaction vessel consisted of a 50 ml three-necked flask equipped with a reflux condensor, and magnetic stirrer. The pieces of the apparatus were dried in an oven at 110°C, assembled, and positive nitrogen pressure was established. To the system was added 1.6155 g (0.0117 mol) of benzylmethylsulfide, 8.436 g (0.0422 mol) of trimethyliodosilane, and 20 ml of chlorobenzene. After 60 hours at 140°C, 70 per cent of the benzylmethylsulfide had been consumed and a 68 per cent yield of benzylsulfide was found. There were peaks for several volatile compounds on the GC that were not completely separable and therefore not quantitatively determined. Methyliodide and hexamethyldisiloxane were qualitatively identified among them.

Reaction of benzylmethylsulfide with trimethyliodosilane in the presence of hexamethylphosphoramide (HMPA)

The previous reaction was repeated with 0.02 equivalent of HMPA added. When trimethyliodosilane was added to the solution of benzylmethylsulfide and HMPA in chlorobenzene a pale yellow precipitate formed. The reaction was carried out as before and a yield of 64 per cent of benzylsulfide was determined.

Reaction of benzylmethylsulfide with trimethyliodosilane under anhydrous conditions

The initial reaction of benzylmethylsulfide with trimethyl iodosilane was repeated with the apparatus being flame dried under nitrogen flow prior to addition of reagents. Benzylmethylsulfide was found to be stable under these conditions with only a trace of benzylsulfide being fo formed after 5 days. Then 0.050 ml of water (2.78×10^{-3} mol) was added. After 12 hours all the benzylmethylsulfide had reacted completely, giving an 86% yield of benzylsulfide.

Reaction of benzylmethylsulfide with trimethylsilylperchlorate

This complete procedure was carried out under nitrogen with careful exclusion of water. After flame drying the flask, 2.0 ml of acetonitrile, 0.2296 g (1.11×10^{-3} mol) of silver perchlorate, and 0.2812 g (1.40×10^{-3} mol) of trimethyliodosilane were added with stirring. Immediately the solution became thick with a light yellow precipitate of silver iodide. After one hour the solid was filtered off in a Schlenk tube and 0.265 g (1.91×10^{-3} mol) of benzylmethylsulfide was added. After 2 days at 60°C the solution was quenched with water and the benzylmethylsulfide was recovered in 95 per cent yield.

Reaction of benzylmethylsulfide with hydrogen iodide 21

Hydrogeniodide 21 was generated in a 25 ml round bottom flask by addition of an excess (10 ml) of concentrated sulfuric acid to 1.523 g (1.08×10^{-2} mol) of sodium iodide. The hydrogen iodide 21 was carried by a slow nitrogen flow through a sulfuric acid drying tower and through a gas dispersion tube into a solution of 1.191 g (8.63×10^{-3} mol) of benzylmethylsulfide in 50 ml of chlorobenzene at 140°C. After four days no reaction was observed by GC, but addition of three equivalents of trimethyliodosilane and another 12 hours at 140°C caused complete conversion of benzylmethylsulfide to benzylsulfide (89 per cent yield).

Reaction of benzylmethylsulfide with hydrogen iodide 21 in the presence of air

The previous reaction was repeated with air being used as the carrier gas instead of nitrogen. After one day greater than 95 per cent of the benzylmethylsulfide was consumed with benzyldisulfide (91% yield) and methyl iodide (undetermined yield) being formed.

Benzyl(trimethylsilyl)sulfide 42

Into a flame dried 100 ml three-necked flask was added 25 ml of anhydrous benzene, 1.571 g (1.99×10^{-2} mol) of pyridine, 1.602 g (1.29×10^{-2} mol) of benzyl mercaptan, and 4.220 g (2.11×10^{-2} mol) of trimethyliodosilane. After the mixture was stirred for two hours at room temperature, the

pyridinium hydroiodide was filtered off under nitrogen, and the product was purified by preparative gas chromatography with an OV101 column.

b.p. 173-175°C [lit. 171-172.5°C (146)]

nmr (CCl_4) 0.26(9H, s), 3.68(2H, s), 7.25(5H, m)

Reaction of benzyl(trimethylsilyl)sulfide 42 with benzylmethylsulfide

Into a flame dried 25 ml three-necked flask, equipped with a magnetic stirrer and reflux condensor, was added 0.107 g (7.75×10^{-4} mol) of benzylmethylsulfide, 0.152 g (7.75×10^{-4} mol) of benzyl(trimethylsilyl)sulfide, 42 and 5.0 ml of chlorobenzene. The reaction mixture was placed in an oil bath at 140°C for three days. The only identified product was benzyldisulfide (~10 per cent) with 85 per cent recovery of benzyl(trimethylsilylsulfide and 95 per cent recovery of benzyl methyl sulfide.

Reaction of benzyl(trimethylsilyl)sulfide 42 with benzylmercaptan

The preceding reaction was repeated using 0.0961 g (7.75×10^{-4} mol) of benzylmercaptan in place of benzylmethylsulfide. The only identified product was again benzyldisulfide (12 per cent yield) with 81 per cent recovery of benzyl(trimethylsilyl)sulfide and 91 per cent recovery of benzylmercaptan.

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ACKNOWLEDGEMENTS

Several people were instrumental in the successful completion of this thesis. Dr. Thomas J. Barton and Dr. Thomas G. Squires co-directed this research. Their leadership, friendship, and compassion was indispensable and greatly appreciated throughout my research endeavors at Iowa State University. Second, I would like to express my gratitude to Dr. Cliff Venier for his valuable comments and suggestions. I would also like to thank Dr. B. C. Gerstein and his group for running the cross-polarized ^{29}Si nmr spectra. The moral support I received from my entire family and my ex-wife's family was also an invaluable asset. Finally, I would like to thank the fellow members of my research group for their friendship and their helpful suggestions.