SULFONIUM SALTS,

ALIPHATIC AND AROMATIC DIAZONIUM SALTS,

FORMATION AND ISOLATION

by

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Senior Thesis Submitted
in Partial Fulfillment
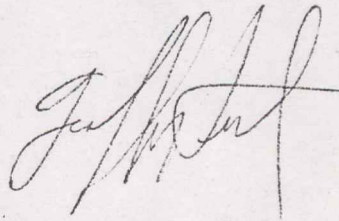of the Requirements for Graduation

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I wish to thank John R. Sowa, without whose
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could never have been conducted.

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ABSTRACT

An improved method for the preparation of diazonium salts was developed. Aliphatic diazonium salts were isolated for the first time. A method for their preparation was also worked out.

The use of sulfonium salts as a route to deuteration of organic compounds was looked into.

Deuterated organic compounds are expensive. It was thought that they could be made less expensively by certain exchange reactions. Deuterated compounds are used for spectroscopic and kinetic studies.

It is known that in the presence of base sulfonium salts undergo exchange reactions [1]. (Reaction 1)

$$1 \quad (RCH_2)_3S^+ + D_2O \rightleftharpoons (RCD_2)_3S^+ + HOD$$
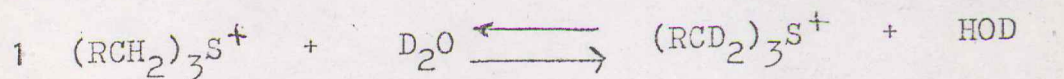
The purpose of this work then is to prepare a sulfonium salt that would have good solubility characteristics i.e., soluble in hot D_2O and insoluble in cold D_2O. The salt should also thermally decompose to give a high yield of haloalkane. (Reaction 2)

$$2 \quad (RCD_2)_3S^+ Br^- \longrightarrow (RCD_2)_2S + RCD_2Br$$
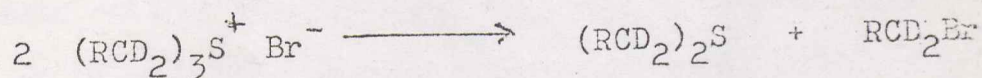
Previous experiments have shown that aliphatic sulfonium salts do not recrystalize from D_2O [2]. When the salts are decomposed in D_2O other undesirable products such as the alcohol are formed [3]. It was felt that the introduction of an aromatic group into the salts would improve on the solubility in addition to requiring less D_2O in the exchange reaction.

Sulfonium salts are characteristically made by the following reactions. (Reactions 3,4,5)

$$3 \quad ROC_6H_5 + SO_2 + AlCl_2 \longrightarrow ROC_6H_4SO_2AlCl_2 +$$

$$HCl$$

$$ROC_6H_4SO_2AlCl_2 \; + \; 2 \; ROC_6H_5 \; + \; HCl \longrightarrow$$

$$(ROC_6H_4)_3SCl \; + \; HOAlCl_2 \; + \; H_2O$$

4. $(ArS)_2Pt \; + \; 3 \; (CH_3)SO_4 \xrightarrow{\Delta} \; 2 \; ArS(CH_3)_2^+ \; +$

$$SO_4CH_3^- \; + \; Pb(OSO_2OCH_3)_2$$

5. $Ar_2SO \; + \; C_6H_5OH \; + \; H_2SO_4 \longrightarrow ArSC_6H_4OH \; + \; SO_4H^- + H_2O$
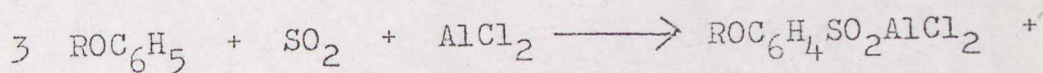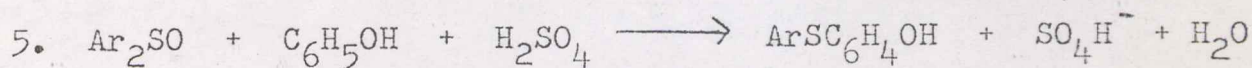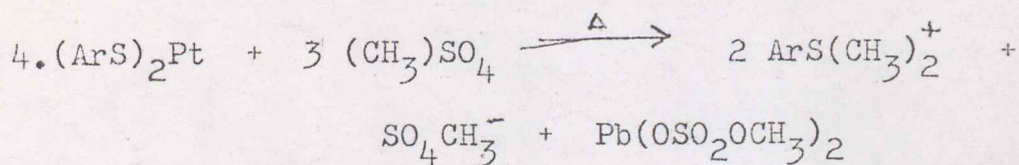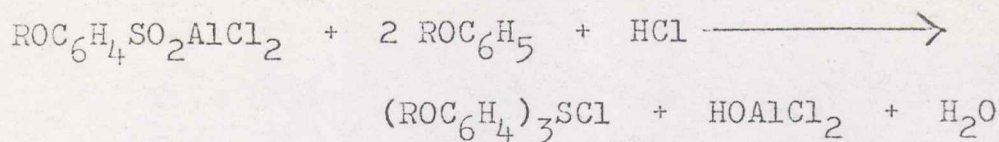
It was felt that perhaps aromatic sulfonium salts might
be more easily made from diazonium salts in a neat reaction
mixture. (Reaction 6)

6. $RN_2^+ \; Br^- \; + \; R'-S-R'' \longrightarrow RR'R''S^+ \; Br^- \; + \; N_2$

(where at least one R is aromatic)
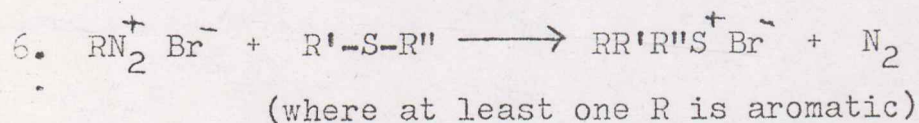
Diazonium salts are prepared by several different methods.
The most common and important method is the action of nitrous
acid on primary amines. Almost any aromatic amine can be
converted to a diazonium salt in the above way.

Although the stability of the aromatic diazonium salts
depends greatly on the anions present, their isolation is due
to the stability of the cation $Ph \; N_2^+$. This stability is
the result of the electron donating properties of the aromatic
nucleus in the resonating system [4].
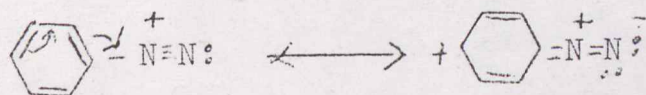
Aliphatic diazonium salts have never been isolated because the instability of the saturated aliphatic residue will not function as an appropriate electron donor. Although aliphatic diazonium ions are undoubtedly formed in solution they ionize immediately to the conjugate base; these bases have been detected in aqueous solutions [5] . (Reaction 7)

$$7. \quad RR'CH-N\equiv N^+ \; X^- \xrightarrow{\;-HX\;} RR'\overset{-}{C}-\overset{+}{N}\equiv N \longleftrightarrow RR'C=\overset{+}{N}=\overset{-}{N}$$
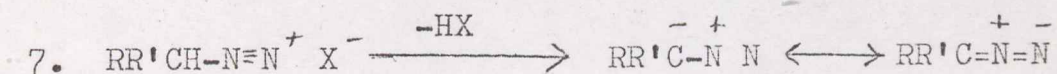
Nevertheless to extend the scope of this project the possible isolation of aliphatic diazonium salts was investigated.

Preparation of Benzene Diazonium Bromide

A.   To a 250-ml beaker sitting in a copper vessel and equip-
ped for magnetic stirring was added 20g of ice and 20 ml of
concentrated nitric acid. After the ice was permitted to melt
the temperature was lowered to -10° by addition of liquid ni-
trogen to the surrounding copper vessel. The mixture was
stirred vigorously and 5g (.054 mole) of aniline was slowly
added. The reaction mixture exothermed but was kept below -5°.
A suspension of white to tan solid formed. Sodium nitrite (3g)
was ground with a mortar and pestal to a fine powder and was
added very slowly to the reaction mixture using a small spat-
ula. To keep the temperature below -5° about 10 ml of liquid
nitrogen had to be added to the outer vessel after each addi-
tion. About 30 seconds was given between additions so that
allthe sodium nitrite had reacted. When the tan solid dis-
appeared the total addition was complete. This was confirmed
by the starch-iodine test.

B.   To 100 ml of water saturated with sodium bromide was added
about 3 ml of bromine. This was cooled to -5° and added to
the above solution of diazonium salt. Although yellow orange
crystals formed immediately the solution was stirred for 15
minutes to insure a complete reaction. The mixture was filtered
through Whatman 40 filter paper in a Buchner funnel which had
been cooled to 0°. Five grams of wet solid (about .015 mole)

were obtained which decomposed at about 78° and was benzene

diazonium tribromide. They were added to about 100 ml of

acetone. Bromoacetone, a lacrymator, and 1.5g (.008 mole)

of benzene diazonium bromide were obtained; dec 105°; yield 18.5%

Preparation of Benzene Diazonium Chloride

To the solution of product of IA was added 100 ml of water saturated with sodium chloride and about 3 ml of bromine. This was cooled to -5° before addition. Although yellow green crystals formed immediately the solution was stirred for 15 minutes to insure a more complete reaction. The mixture was filtered through Whatman 40 filter paper in a Buchner funnel cooled to 0° before filtration. Less than .1g of wet solid was obtained. This solid decomposed at 107° and was benzene diazonium chloride.

Attempted Preparation of Benzene Diazonium Iodide

Into a 250-ml beaker sitting in a copper vessel and equipped for magnetic stirring was added 20 grams of ice and 20 ml of concentrated nitric acid. After the ice was permitted to melt the temperature was lowered to -20° by addition of liquid nitrogen to the surrounding copper vessel. The mixture was stirred vigorously and 5 g (0.054 moles) of aniline was slowly added. the reaction mixture exothermed but was kept blow -10°. A suspension of white to tan solid formed. Sodium nitrite (3.0 grams) was ground with a mortar and pestal to a fine powder and was very slowly added to the reaction mixture using a small spatula. To keep the temperature below -10° about 10 ml of liquid nitrogen had to be added to the outer vessel after each addition. Sufficient time was given between additions, about 30 seconds, so that all the sodium nitrite had reacted. When the tan solid disappeared the total addition was complete. This was confirmed by starch iodide test.

To 100 ml of water saturated with potassium iodide was added about 4 ml of bromine. This was cooled to -5° and added to the above solution of diazonium ion.

Reddish brown crystals formed immediately and then decomposed upon formation at -10°. The product of decomposition had a bp of 188° and was iodobenzene. The product was not soluble in water.

Reaction between Benzene Diazonium Bromide and Diethyl Sulfide

Into a 50-ml round-bottom flask equipped with a condenser, magnetic stirring bar and an oil bath was added 1.5 g (.008 mole) of benzene diazonium bromide and 5ml (.056 mole) of diethyl sulfide. The mixture was heated overnight while stirring. Nitrogen was evolved and the mixture turned brown. The unreacted diethyl sulfide was evaporated on a Rotovap. The residue weighed .5 g and melted at 120-130°. It was soluble in ethanol and acetone but insoluble in water. It was purified by precipitation from ethanol by the addition of water. One tenth gram (.0004 mole) of white crystalline diethyl phenyl sulfonium bromide was isolated, mp 118-120°; yield 5 percent.

Decomposition of Diethylphenyl Sulfonium Bromide in Triglyme

Into a 50-ml round-bottom flask equipped with a conden-
ser and heating mantle was added 20 ml triglyme, 2g (.002
mole) sodium bromide and 1.5g (.007 mole) diethylphenyl
sulfonium bromide. A 25-ml round-bottom flask attached
with a copper wire was submerged in liquid nitrogen and used
as the collecting vessel. The mixture was heated to 200°
for 1 hour. The collecting flask had two substances in it.
One was liquid and one solid at -196°. The liquid boiled
away at -180°, the boiling point of qxygen and the solid
melted at -169° and boiled at -105°; the melting and boiling
points of ethylene. The residue distilled (using the same
set up) at 204° giving .5g (.004 mole) ethylphenyl sulfide
(50 % yield).

Preparation of Aliphatic Diazonium Salts in Aqueous Solutions

Into a 100-ml beaker sitting in a copper vessel and equipped for magnetic stirring was added 10 ml of water and 10 ml concentrated nitric acid. The temperature was lowered to -25° by addition of liquid nitrigen to the surrounding copper vessel. The mixture was stirred vigorously and 2-ml of butyl amine was slowly added. The temperature rose to -20°. Sodium nitrite was ground with a mortar and pestal to a fine powder and added very slowly. The mixture was kept at -20° by addition of about 10 ml of liquid nitrogen to the outer vessel after each addition. White crystals formed and the solution turned pale blue from the presence of N_2O_3. The solid was not separated but the temperature was allowed to rise and decomposition took place with the evolution of nitrogen at -18°. The crystals appeared to be butyl diazonium nitrate.

Preparation of Aliphatic Diazonium Chlorides

Into a 100-ml Erlenmeyer flask was added 20 ml dry ether
and 2 ml RNH_2, R being methyl, ethyl, butyl, pentyl, or hexyl.
The contents were cooled to $-50°$ by lowering the flask into
liquid nitrogen. Into another 100-ml Erlenmeyer flask was
added 20 ml of dry ether and about 4g (.093 mole) nitrosyl
chloride. This solution was slowly added to the first with
vigorous stirring. It was kept below $-40°$ by lowering the
flask into liquid nitrogen. Crystals formed immediately and
the addition was complete when an aliquot was added. The ether
was then poured away from the salt.

Decomposition temperatures:

Methyl diazonium chloride; $-30°$ $-32°$
Ethyl diazonium chloride; $-24°$ $-23°$
Propyl diazonium chloride; $-20°$ $-18°$
Butyl diazonium chloride; $-15°$ $-16°$
Pentyl diazonium chloride, $-10°$ $-8°$
Hexyl diazonium chloride; $-5°$ $-0°$

The yields of all salts are greater than 75%. The
butyl was as high as 95%.

Preparation of Aliphatic Oxonium Chlorides

Methyl, ethyl, propyl, butyl, pentyl and hexyl diazonium chlorides prepared by the preceding method were allowed to slowly warm to room temperature in dry ether. The warming process took about 30 minutes. During this time nitrogen was evolved and a solid with a new crystal structure was formed. At room temperature the solid settled to the bottom of the test tube. Some solid was taken out with a spatula and allowed to react with moist air. The solids decomposed to a clear liquid that had an alcoholic odor.

Formation and Observation of Oxonium Ions

Oxonium salts were produced by letting aliphatic diazonium chlorides decompose in dry ether. In all cases (methyl, ethyl, propyl, butyl, pentyl, and hexyl iiazonium ions) a white solid formed which settled to the bottom of the ether. If anhydrous rather than practical grade ether were used, more solid was formed. These reactions were executed at the decomposition temperature of each ion.

(Reaction 8)

$$R_2\overset{+}{-}O\text{-}R + HOH \longrightarrow ROH + R_2O$$
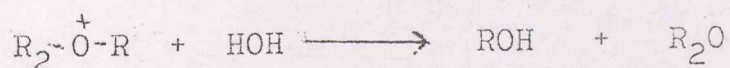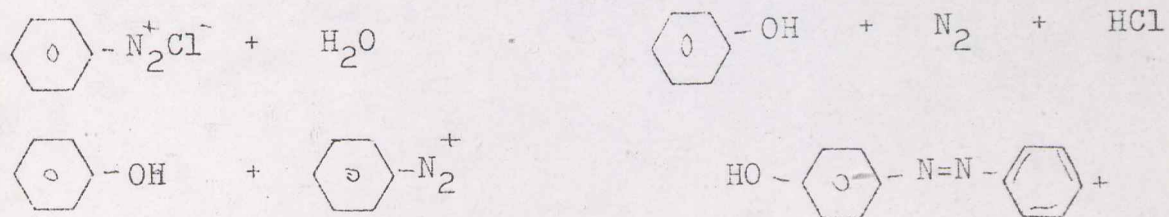
It was observed that when the oxonium salts were removed with a spatula and allowed to react with moist air they decomposed into a liquid without the evolution of N_2. In all cases the liquid had an alchoholic odor. In the case of the products from methyl and ethyl diazonium ions the two distinct alcholic odors could be discerned.

Effect of Water on Reactions

If there is an excess of water in the reaction mixture coupling reactions will occur.   (Reaction 9)

$\langle O \rangle - N_2^+ Cl^-$ + H_2O $\langle O \rangle - OH$ + N_2 + HCl

$\langle O \rangle - OH$ + $\langle O \rangle - N_2^+$ $HO - \langle O \rangle - N=N - \langle O \rangle$ +

These reactions are noted by the appearance of a deep blood red color along with the lack of an appropriate amount of nitrogen.

The traditional method for the preparation of diazonium salts has been by the action of nitrous acid on the primary amines.[6] The mechanism is[7] (Reaction 10)

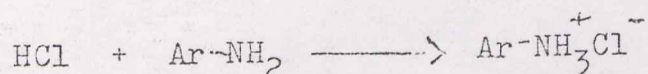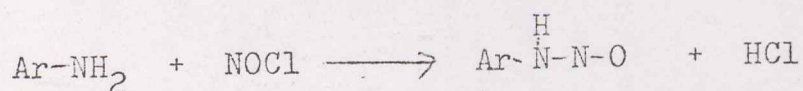$$2HONO \xrightarrow{slow} N_2O_3 + H_2O$$

$$ArNH_2 + N_2O_3 \longrightarrow Ar-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-N=O + NO_2^-$$

$$Ar-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{N}}-N=O \xrightarrow{-H} Ar-\overset{}{\underset{\underset{H}{|}}{N}}-N=O$$

$$Ar-\overset{}{\underset{\underset{H}{|}}{N}}-N=O \longrightarrow Ar-N=N-O-H$$

$$Ar-N=N-O-H \xrightarrow{H^+} Ar\overset{+}{N}\equiv N + H_2O$$
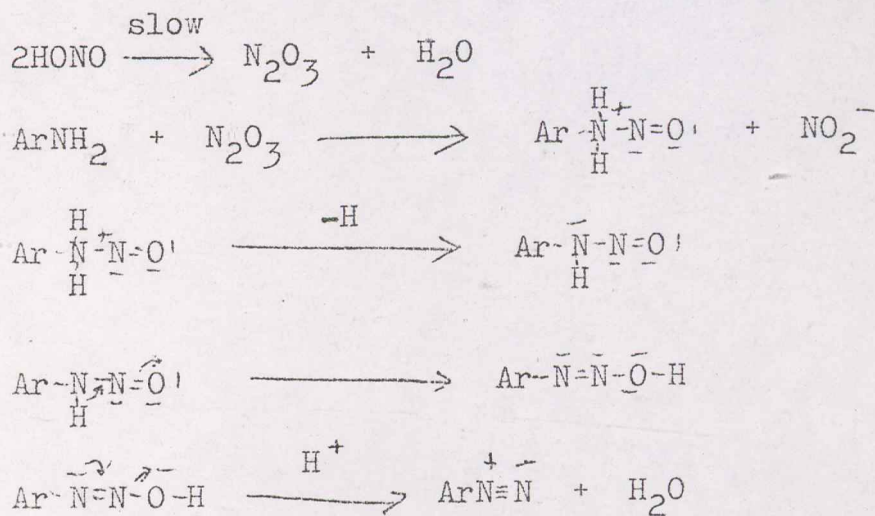
Diazonium salts have probably not been extensively researched for they are thought to be too unstable and unpredictable for the average research student to explore. It was found that this is not the case. Rather, some of the traditional methods of preparation should be modified or changed completely. Griess[8] prepared the aromatic diazonium salts by using one mole of the mineral acid while the use of two moles is much better. This cuts down on the yield slightly[9] but the decomposition follows first order kinetics rather than that of the corresponding products of isomerisation with increasing pH.[10]

Aliphatic diazonium salts have not been produced until now for their decomposition points in aqueous media are usually below the freezing points of the solutions. In the scope of this work aliphatic diazonium salts have been produced in an aqueous mixture but extreme care must be taken to keep the temperature very low, usually at the melting point of the mixture, around -20c. The salts when produced this way are hard to isolate and therefore this preparative method is not desirable.[11] To expand the scope of this work nitrosyl compounds and the primary amine were tried to produce the desired diazonium salt.[12] Dry ether and nitrosyl chloride were used. When the temperature of the mixture was lowered below 0° the aromatic diazonium salts were not produced but rather the nitroso amines and hydrochlorides of the aromatic amine. (Reaction 11)

$$Ar\text{-}NH_2 \ + \ NOCl \ \longrightarrow \ Ar\text{-}\overset{H}{N}\text{-}N\text{-}O \ + \ HCl$$

$$HCl \ + \ Ar\text{-}NH_2 \ \longrightarrow \ Ar\text{-}NH_3^+Cl^-$$

The compounds must stay in solution long enough to change to the diazonium salts. At $20\text{-}40^o C$ the aromatic amines in ether do form insoluble diazonium salts. The elevated temperature apparently allows the reaction between the nitroso compound and the hydrochloric acid to occur before precipitation; see

reaction 10 . The decomposition point of aromatic diazonium salts produced in this manner is over a very narrow range and violent, indicating their high purity.

Aliphatic diazonium salts have never been isolated before. In this work aliphatic diazonium salts were produced in a non-aqueous environment. The physical and chemical behavior of the salts produced tend to support the assumption that they were truely aliphatic diazonium salts. The salts were colorless and when allowed to decompse in moist air turned into clear liquid with alcoholic odor. In the cases of methyl and ethyl diazonium salts the corresponding alcohol has the appropriate odor of methanol and ethanol. (Reaction 12)

$$R'-R''-N \equiv N^+ Cl^- + HOH \qquad R'-R''-OH + HCl + N_2 \uparrow$$
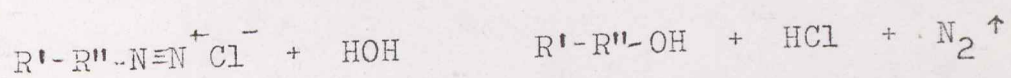
The salts were also allowed to decompose in ether. This produced a change in crystaline structure with the evolution of nitrogen. The new products did not decompose when at temperatures of 25°C. The salts produced this way are believed to be oxonium salts. (Reaction 13)

$$R'-R''-N \equiv N^+ Cl^- + R-O-R \longrightarrow R'-R''-\overset{+}{\underset{R}{O}}-R \ Cl^- + N_2 \uparrow$$
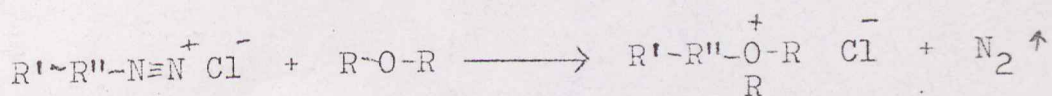
These oxonium salts were allowed to decompose in moist
air. There was a change to a liquid without the evolution
of nitrogen. Again an alcoholic odor was detected. (Reaction 14)

$$R'-R''-\overset{+}{\underset{R}{O}}-R \quad \overset{-}{Cl} \; + \; H-OH \longrightarrow R'-R''-OH \; + \; R-O-R \; + \; HCl$$
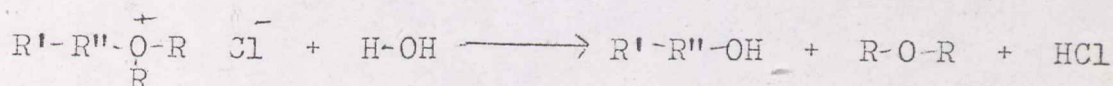
The temperatures of the reaction mixtures during the formation of the aliphatic diazonium salts could be lowered to
$-50^{\circ}C$ due to use of ether and nitrosyl chloride.

The lack of an aqueous solution also meant there would
be little or no OH^- to replace the good leaving group of $N\equiv N^+$:
(see reaction 9) From the low decomposition points of these
compounds and the evolution of nitrogen during decomposition
along with their chemical behavior it can be deduced that the
salts produced are aliphatic diazonium salts.

The Next Step

Since the synthesis of diazonium chlorides, both aliphatic and aromatic, have been dealt with further work should be carried out to determine synthesis and characteristics of other anions. It should be relatively easy to use nitrosyl compounds such as the floride and bromide to obtain respective diazonium salts, both aliphatic and aromatic.

The reaction between diazonium salts and sulfides should also be carried out using different reactor solvents, i.e. tetrahydrofuran, dioxane so as to find a sulfonium salt that would be infinitely soluble in hot D_2O and insoluble in cold D_2O. The synthesis of diethylphenyl sulfonium chloride would de a logical next step using benzene diazonium chloride and ethyl sulfide in THF.

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