

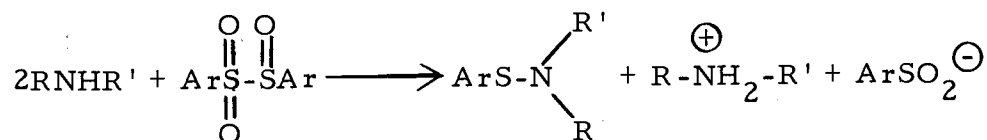
AN ABSTRACT OF THE THESIS OF

JOHN ROY YOUNG for the M. S.
 (Name of student) (Degree)
 in Organic Chemistry presented on April 24, 1969
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Title: THE REACTIONS OF AMINES AND GRIGNARD REAGENTS
WITH SULFINYL SULFONES

Abstract approved: Redacted for Privacy
John L. Kice

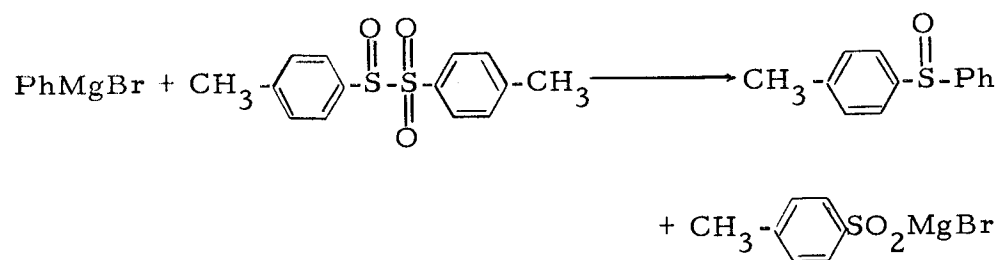
Pipiridine, morpholine, and n-propyl amine react readily with p-toluenesulfinyl p-tolyl sulfone in anhydrous dioxane at room temperature to form the corresponding sulfinamides in quite good yield. When a similar synthesis was carried out using the aromatic aniline only a poor yield of highly impure sulfinamide could be obtained. The reaction has the stoichiometry



It is felt that this reaction will be applicable to the synthesis of a wide variety of sulfinamides.

Reaction of an excess of phenyl magnesium bromide with p-toluenesulfinyl p-tolyl sulfone in anhydrous ether at room temperature gave phenyl p-tolyl sulfoxide in good yield. The reaction

has the stoichiometry



The reaction appears to be analogous to the reaction of other sulfinyl compounds, such as sulfinate esters, with Grignard reagents.

The Reactions of Amines and Grignard
Reagents with Sulfinyl Sulfones

by

John Roy Young

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Professor of Chemistry *✓*
in charge of major

Redacted for Privacy

Chairman of Department of Chemistry

Redacted for Privacy

Dean of Graduate School

Date thesis is presented

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Typed by Opal Grossnicklaus for

John Roy Young

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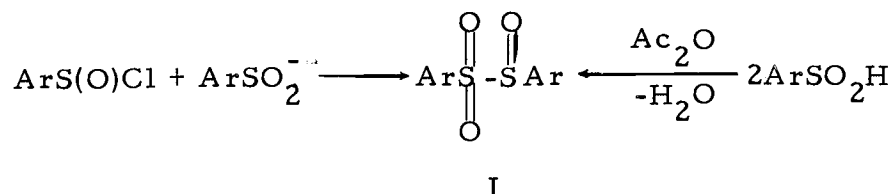
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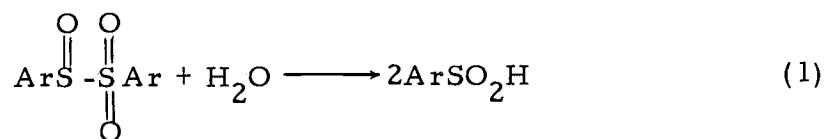
THE REACTIONS OF AMINES AND GRIGNARD REAGENTS WITH SULFINYL SULFONES

INTRODUCTION

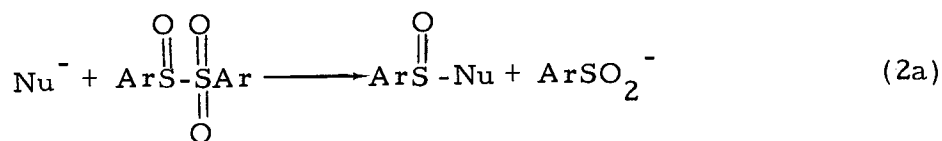
Aromatic sulfinyl sulfones, compounds arising from the treatment of an aromatic sulfinic acid with acetic anhydride, or, alternatively, from the reaction of the sodium salt of an aromatic sulfinic acid with the corresponding sulfinyl chloride, were known as early as 1908. At that time, however, they were formulated as sulfinic anhydrides. More recently, Bredereck et al. (5) have demonstrated that they possess the alternative sulfinyl sulfone structure I.



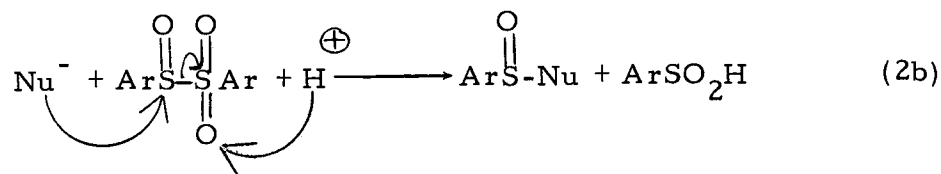
These compounds, like carboxylic anhydrides, may be readily hydrolyzed to the corresponding sulfinic acid (eq. 1).



A series of studies by Kice and Guaraldi (10, 11) have shown that sulfinyl sulfones can also react with a variety of other nucleophiles, such as halide ions, alkyl sulfides, thiourea, acetate ion, etc. Some of these reactions involve a direct displacement of ArSO_2^- by the attacking nucleophile (eq. 2a).



In others (eq. 2b) successful displacement of the ArSO_2 group by Nu^- requires that a proton be donated to the ArSO_2 group at the same time that Nu^- attacks the sulfinyl sulfur.



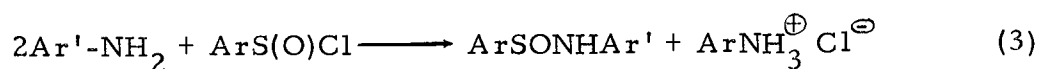
In general sulfinyl sulfones seem to exhibit quite high reactivity in nucleophilic substitution reactions involving attack at the sulfinyl sulfur. Although their reactivity in such reactions is not as great as that of the corresponding sulfinyl chlorides, it appears to be high enough to suggest that sulfinyl sulfones could be useful in a general way as sulfinylating agents.

Most sulfinyl chlorides are liquids at room temperature and tend both to decompose and to undergo hydrolysis so readily that they are difficult to keep for any length of time even in the refrigerator. The sulfinyl sulfones, on the other hand, are solids that if stored in a desiccator in the icebox can be kept for some time without significant decomposition or hydrolysis.

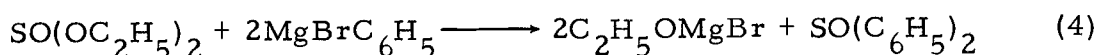
These facts suggested that use of sulfinyl sulfones as sulfinylating agents might have some advantages in practical work over the use of the hard-to-handle sulfinyl chlorides and prompted the present

investigation of their reactions with amines and Grignard reagents.

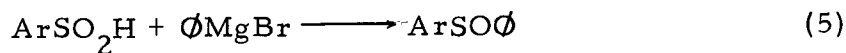
The usual example of nucleophilic substitution at sulfinyl sulfur by amines to be found in the literature is the synthesis of several benzene and p-toluenesulfinamides by means of reaction of the amine with appropriate sulfinyl chlorides (eq. 3). These reactions were first carried out in 1923 by Braun and Kaiser (4).



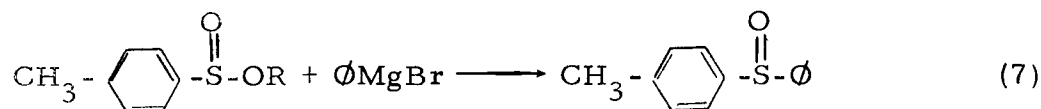
The first synthesis of a sulfoxide arising from the reaction of a Grignard reagent with a sulfinyl compound was performed in 1910 by Strecker (16). Di-phenyl sulfoxide was prepared by means of reaction of di-ethyl sulfite with phenyl magnesium bromide (eq. 4).



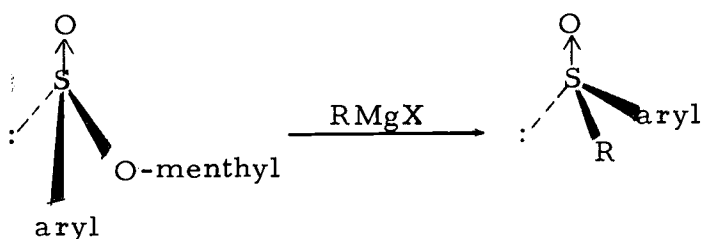
The reactions of phenyl magnesium bromide with p-toluenesulfinic acid (eq. 5) and with p-toluenesulfinyl chloride (eq. 6) were studied by Burton and Davy (6).



Gilman and coworkers (8) synthesized p-tolyl phenyl sulfoxides via reactions of phenyl magnesium bromide with various p-toluenesulfinates (eq. 7).



These reactions were later employed by Andersen et al. (1, 2, 3) to establish the absolute configuration of (-)-menthyl (-) aryl sulfinates and to demonstrate that reaction of the Grignard with the sulfinate leads to inversion of configuration at the sulfinyl sulfur.



These examples of the successful reaction of these nucleophiles at sulfinyl sulfur suggested that similar reactions with aryl sulfinyl sulfones could also prove to be useful synthetic procedures.

Furthermore, successful synthesis of sulfinamides and sulfoxides from sulfinyl sulfones would lay the groundwork for a variety of future investigations aimed at ascertaining the intimate details of the mechanism of nucleophilic substitution at sulfinyl sulfur.

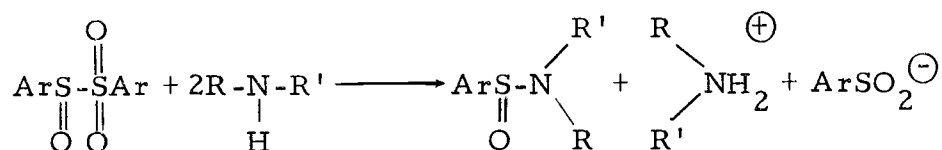
It was for these various reasons that the present work was undertaken.

RESULTS

Reactions of Amines with *p*-Toluenesulfinyl *p*-Tolyl Sulfone

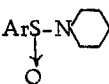
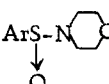
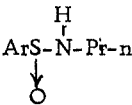
Previous reactions (11) of various nucleophiles with *p*-toluenesulfinyl *p*-tolyl sulfone have been carried out in aqueous dioxane as solvent. In order to keep hydrolysis of the sulfinyl sulfone from being a problem the current reactions of amines with the sulfinyl sulfone were run in anhydrous dioxane at room temperature.

The reactions were carried out by initially distilling a volume of anhydrous dioxane directly onto a quantity of sulfinyl sulfone contained in an air-tight vessel. The mixture was stirred rapidly to dissolve the sulfinyl sulfone, and a measured amount of amine (2 mmole/mmole sulfinyl sulfone) was slowly added. After enough time had elapsed for the reaction to go to completion, the reaction mixture was poured into a large volume of water. The resulting dioxane-water solution was subsequently extracted with ether and the ether extract was dried. Evaporation of the ether left a product which was purified by appropriate techniques. In each instance this product could be identified as being the appropriate sulfinamide resulting from the reaction



The results of the various experiments are summarized in Table 1.

Table I. Reaction of Amines with p-toluenesulfinyl p-tolyl Sulfone in Anhydrous Dioxane

Amine	Reaction Conditions	Product	Yield	Melting Point	Anal.			
					Calc'd C	Calc'd H	Found C	Found H
Piperidine	(Room temp. 16 hours)		65%	61-62°	64.60%	7.60%	64.50%	7.45%
Morpholine	"		69%	119-120	58.7%	6.67%	58.4%	6.45%
n-propylamine	"		76%	liquid b. p. 89-90° (0.12mm)	61.0%	7.62%	61.1%	7.62%

As can be seen from the table the yields of purified sulfinamides were generally of the order of 70% with the three aliphatic amines investigated. When a similar synthesis was carried out using the aromatic amine aniline only a rather poor yield of a still very impure sulfinamide could be obtained, in contrast to the behavior of the aliphatic amines.

Reaction of Phenylmagnesium Bromide with p-Toluenesulfinyl p-Tolyl Sulfone

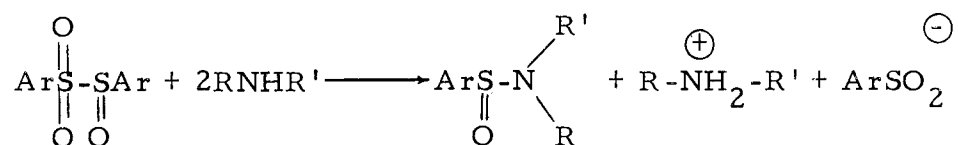
Previous reactions (4, 6, 8, 16) of Grignard Reagents with other sulfinyl compounds such as sulfinate esters (1, 2, 3) have been generally carried out in anhydrous ether as solvent.

In the present work, a quantity of sulfinyl sulfone was placed in a dry flask containing a volume of anhydrous ether at room temperature. Phenyl magnesium bromide prepared earlier by reaction of bromobenzene and magnesium was slowly added to the sulfinyl sulfone-ether mixture over a 1.5-hour period while the reaction mixture was vigorously stirred. After the addition was complete the mixture was allowed to stand at room temperature for 16 hours and was then worked up by adding ammonium chloride to the mixture. The ether layer was then decanted, the inorganic residue extracted with ether, and the combined ether solutions dried. Evaporation of the ether yielded a product which was purified by appropriate techniques and identified as phenyl p-tolyl sulfoxide by comparison with the properties of a known sample. The yield of purified sulfoxide was 51%.

DISCUSSION

The Sulfinyl-Sulfone-Amine Reaction

Three different alkyl amines, piperidine, morpholine, and *n*-propyl amine, have been found to react with *p*-toluenesulfinyl *p*-tolyl sulfone in anhydrous dioxane to give the expected *p*-toluene-sulfinamide in good yield.



Because of the basicity of the amines and the acidity of sulfinic acids one must use two moles of amine per mole of sulfinyl sulfone, the second mole of amine being converted to the salt $\text{RNH}_2^+\text{R}' \text{ ArSO}_2^-$.

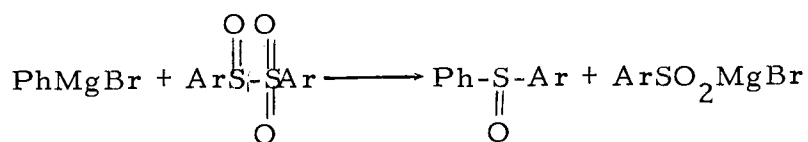
The reaction proceeds in a straightforward manner and would seem to be one that could be used conveniently in practical work to prepare a wide variety of sulfinamides. As already noted, sulfinyl sulfones are much easier to keep for some period of time than sulfinyl chlorides, and so the use of sulfinyl sulfones to prepare sulfinamides may have some considerable practical utility. One point that should be investigated in future work is whether or not the reactions with the alkyl amines proceed enough more rapidly than the hydrolysis of the sulfinyl sulfone so that the synthesis of the sulfinamides could be carried out in at least a partially aqueous medium. If this were the

case, it could further increase the utility of the reaction.

When the same reaction was carried out with aniline, a typical aromatic amine, the sulfinyl sulfone was thought to react, but there were severe problems encountered in getting any pure sulfinamide by the simple work-up procedure used for the reactions with the alkyl amines. The exact reason for this is not known for sure, but one possibility is that the failure of the aniline-sulfinyl sulfone reaction to yield pure product is due to the low basicity of aniline as compared to alkyl amines, which causes the formation of $\text{O}^{\oplus}\text{NH}_3\text{ArSO}_2^{\ominus}$ to be incomplete and leaves one with considerable aniline in the crude product. In view of the rather large acidity ($\text{pK}_a \approx 1.5$) of aromatic sulfinic acids this doesn't seem very likely, however, and the difficulty may simply be that the aromatic amine reacts only very slowly with the sulfinyl sulfone, because of its nucleophilicity being much less than that of the alkyl amines. Further work, especially kinetic studies of the amine-sulfinyl sulfone reaction are necessary to answer the question.

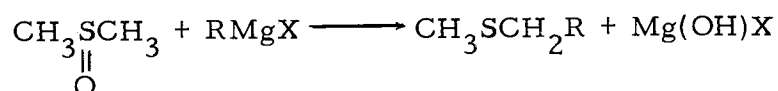
The Grignard Reagent-Sulfinyl Sulfone Reaction

In anhydrous ether phenyl magnesium bromide reacts with p-toluenesulfinyl p-tolyl sulfone to give phenyl p-tolyl sulfoxide in fairly good yield.



In the reaction of the sulfinyl sulfone with the Grignard an excess of the Grignard reagent was employed, since Andersen (3) in his work on the reaction of esters of aromatic sulfinic acids with Grignard reagents found that the use of such an excess appeared to lead to higher yields of the sulfoxide than when only stoichiometric amounts of the Grignard were employed.

Since Hepworth et al. (9) have shown that aryl Grignard reagents do not react with diaryl sulfoxides at room temperature, such an excess can be employed without any problem. However, the same would probably not be true for a reaction which led to an alkyl aryl sulfoxide. Reactions of alkyl sulfoxides with alkyl and aryl Grignard reagents have been demonstrated by Potter (15) and by Oda and Yamamoto (13) to form a sulfide in which an alkyl or aryl group has replaced a hydrogen on the carbon alpha to the sulfur atom. Such a reaction may be illustrated by the reaction of DMSO with a Grignard.



In the preparation of p-tolyl alkyl sulfoxides via the sulfinyl sulfone reaction it would probably therefore be advisable to avoid an excess of Grignard reagent above the necessary stoichiometric

amount, in order to minimize side reactions leading to the formation of sulfides.

Further studies of the sulfinyl sulfone-Grignard reagent reaction using alkyl sulfinyl sulfones and/or alkyl Grignard reagents could elucidate this point further.

EXPERIMENTAL

Materials

Dioxane

Reagent grade dioxane (Mallinckrodt) was purified by the method suggested by Wiberg (18, p. 245) and stored over the sodium ketyl of benzophenone which keeps it anhydrous and free of peroxides. The dioxane was distilled from the deep blue sodium ketyl as it was needed, b. p. 101° .

Ethyl Ether

Anhydrous ethyl ether (Allied Chemical Company) was used without further purification.

Aniline

Reagent grade aniline (Matheson, Coleman and Bell) was distilled immediately before use.

Pipiridine, Morpholine, and n-Propylamine

Reagent grade pipiridine, morpholine and n-propylamine were distilled from barium oxide prior to use.

Phenyl Magnesium Bromide

Phenyl magnesium bromide was prepared from bromobenzene and magnesium by the method suggested by Vogel (17, p. 276). Reagent grade bromobenzene was used without further purification.

Sodium p-Toluenesulfinate

Sodium p-toluenesulfinate was prepared by the procedure found in Organic Synthesis, Collected Volume I (7), and was recrystallized once from water and stored in this form.

p-Toluenesulfinyl p-Tolyl Sulfone

p-Toluenesulfinyl p-tolyl sulfone was prepared and purified as described by Brederick and coworkers (5) with the modifications suggested by Pawlowski (14). Melting point of the sulfone was 87° (literature value (5), m. p. 87°). The extinction coefficient in anhydrous dioxane showed it to be better than 90% pure. The sulfinyl sulfone was stored in a desiccator at -20°.

Product Study of the p-Toluenesulfinyl p-Tolyl Sulfone-Amine Reaction

General Procedure

The general procedure was as follows. Into a three neck flask

equipped with a 10 ml. dropping funnel and a calcium chloride drying tube was placed approximately ten millimoles of p-toluenesulfinyl p-tolyl sulfone and a magnetic stirring bar. About 150 ml. of anhydrous dioxane was then introduced into the reaction vessel by direct distillation. At this time 2.0 mmole of amine per mmole of the sulfinyl sulfone was introduced from the dropping funnel and the reaction solution was allowed to stir for 16 hours. At the end of this time period, the reaction solution was poured into three times its volume of ice-cold water. This solution was then extracted with three 200-250 ml. portions of ether, and the ether solution was washed with several portions of ice-cold water. The ether solution was then dried over anhydrous sodium sulfate and the ether evaporated. The product was then purified by either recrystallization or distillation, depending upon whether it was a liquid or solid.

Piperidyl p-Toluenesulfinamide

From the reaction of piperidine (2.92 g., 0.0343 moles) with p-toluenesulfinyl p-tolyl sulfone (5.05 g., 0.019 moles) there was obtained 2.49 g. (65%) of a product, subsequently identified as piperidyl p-toluenesulfinamide. After two recrystallizations from benzene-hexane the product had a melting point of 61-62°. The infrared spectrum of the product in carbon tetrachloride had absorption peaks at 3650, 3590, 2950, 2850, 1600, 1490, 1460, 1450, 1440, 1200, 1175,

1155, 1090, 1070, 1030, and 910 cm^{-1} . In anhydrous dioxane, the ultraviolet spectrum showed an absorption maximum at $246\text{ m}\mu$ ($\log \epsilon = 3.72$).

The nuclear magnetic resonance spectrum of the compound in deuteriochloroform containing 1% TMS showed a quintet centered at 7.5 δ attributed to the benzene ring protons; a sharp singlet at 2.5 δ , attributed to the toluene methyl group; a medium broad peak at 1.65 δ , attributed to the six methylene protons not attached to the piperidine nitrogen, and a broad distorted peak at 3.05 δ attributed to the methylene protons adjacent to the nitrogen. These have relative areas of 4:3:6:4 respectively.

Anal. Calculated for $\text{C}_{12}\text{H}_{18}\text{SON}$: C, 64.60% H, 7.60%.

Found: C, 64.50% H, 7.45%.

Morpholine p-Toluenesulfinamide

From the reaction of morpholine (1.84 g., 0.021 moles) with p-toluenesulfinyl p-tolyl sulfone (3.12 g., 0.0106 moles) there was obtained 1.65 g. (69%) of a product which was subsequently identified as morpholine p-toluenesulfinamide. The product was "salted out" of the dioxane-water solution with a saturated solution of sodium sulfate prior to extraction with ether. After three recrystallizations from benzene-hexane, the compound had a melting point of $119-120^\circ$. The infra-red spectrum of the compound in carbon tetrachloride had

absorption peaks at 3610, 3550, 2980, 2850, 2700, 1620, 1440, 1250, 1190, 1140, 1110, 1090, 1060, and 910 cm^{-1} . In anhydrous dioxane, the ultraviolet spectrum showed an absorption maximum at $246\text{ m}\mu$ ($\log \epsilon = 3.79$).

The nuclear magnetic resonance spectrum of the compound in deuterio-chloroform containing 1% TMS showed a quintet centered at 7.5δ , a sharp singlet at 2.4δ , a triplet centered at 3.1δ attributed to the methylene protons adjacent to the nitrogen, and a triplet centered at 3.7δ attributed to the methylene protons adjacent to the oxygen of the morpholine ring. These had relative ratios of 4:3:4:4 respectively.

Anal. Calculated for $\text{C}_{11}\text{H}_{15}\text{SO}_2\text{N}$: C, 58.7% H, 6.67%.

Found: C, 58.4% H, 6.45%.

N-Propyl p-Toluenesulfinamide

From the reaction of n-propyl amine (1.62 g., 0.027 moles) with p-toluenesulfinyl p-tolyl sulfone (4.01 g., 0.0136 moles) the initial product obtained was a brown liquid. Vacuum distillation yielded 2.03 g. (76%) of a light yellow liquid (b.p. $89-90^\circ/0.12\text{ mm}$). The infra-red spectrum of this material in carbon tetrachloride had absorption peaks at 3610, 3550, 3200, 2990, 2940, 2860, 1630, 1590, 1490, 1450, 1200, 1150, 1090, 1050, 1010 and 980 cm^{-1} . In anhydrous dioxane, the ultraviolet spectrum showed an absorption

maximum at 246 $m\mu$ ($\log \epsilon = 3.73$). The product had a refractive index of 1.5501.

The nuclear magnetic resonance spectrum of the compound in carbon tetrachloride containing 1% TMS showed a quartet centered at 7.4 δ , a low broad peak centered at 5.2 δ , attributed to the hydrogen bonded to nitrogen, a sextet centered at 2.7 δ attributed to the methylene group bonded to nitrogen, a singlet at 2.5 δ , a quintet centered at 1.4 δ attributed to the other methylene of the propyl group, and a triplet centered at 0.85 δ attributed to methyl protons. These have relative ratios of 4:2:3:2:3 respectively.

Anal. Calculated for $C_{10}H_{15}SON$; C, 61.0% H, 7.62%.

Found: C, 61.1% H, 7.50%.

N-Phenyl Toluenesulfinamide

From the reaction of aniline (2.54 g., .027 mole) with p-toluenesulfinyl p-tolyl sulfone (4.11 g., .014 mole) there was obtained a reddish-brown solid product. This compound was freed from its reddish-brown impurity by successive triturations with an ice-cold benzene-hexane solution to yield 1.24 g. of a slightly brown solid. Repeated recrystallizations from benzene hexane yielded a white solid, m.p. 129-134°. The melting point could not be raised above this value.

The infra-red spectrum of the product in carbon tetrachloride

when compared with that of a known sample of N-phenyltoluenesulfonamide indicated that the compound was highly impure. (Literature value for N-phenyltoluenesulfonamide (12) m.p. 137-138°).

Product Study of the p-Toluenesulfinyl
p-Tolyl Sulfone-Grignard Reaction

General Procedure

The general procedure followed was one suggested by Andersen et al. (3). A 500 ml. three-neck flask was equipped with a motor driven stirrer, a 250 ml. dropping funnel, and a glass condenser protected by a calcium chloride drying tube. A mixture of the sulfinyl sulfone in anhydrous ether was placed in the flask. An ether solution of two millimoles of phenyl magnesium bromide/millimole sulfinyl sulfone was prepared by the method suggested by Vogel (17, p. 756) and introduced into the 250 ml. dropping funnel under a nitrogen atmosphere. The Grignard reagent was added dropwise over a 1.5 hour period to the sulfinyl sulfone which was stirred continuously. The reaction was allowed to proceed for 16 hours at room temperature after which a saturated solution of aqueous ammonium chloride was added until the inorganic salts precipitated, leaving a clear ether solution. The ether was decanted, and the inorganic residue was extracted by shaking with ether in a separatory funnel. The combined ether solutions were dried over magnesium sulfate. The

ether solution was then filtered and evaporated. The product was then obtained by appropriate purification of the residue from the evaporation of the ether solution.

Phenyl p-Tolyl Sulfoxide

From the reaction of phenyl magnesium bromide (6.16 g., 0.034 moles) with p-toluenesulfinyl p-tolyl sulfone (5.00 g., 0.017 moles) the crude product was an oil, which upon addition of a seed crystal followed by recrystallization from hexane-ether yielded 1.87 g. (51%) of phenyl p-tolyl sulfoxide, m.p. 68-69° (literature value (6), 69-70°). Both the infra-red and nuclear magnetic resonance spectra were consistent for that expected from phenyl p-tolyl sulfoxide.

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