[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

The Properties of Unsaturated Sulfur Compounds. I. Alpha Beta Unsaturated Sulfones

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In continuation of our investigations on the mode of addition to unsaturated compounds it was desirable to study unsaturated sulfones because the sulfonyl group cannot participate in the kind of conjugation that is characteristic of α,β-unsaturated ketones without expanding the valence shell of sulfur. We have therefore prepared and studied benzal methyl tolyl sulfone.

$$C_6H_5CH{=}CHSO_2C_6H_4CH_3\text{-}(p)$$

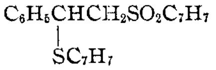
I

The sulfone, unlike benzalacetophenone and all other α,β-unsaturated monoketones which have hydrogen in the α-position, can be obtained in two stereoisomeric forms. In reactions which involve the addition of reagents for ethylenic compounds both forms behave like the corresponding unsaturated ketones; they combine with hydrogen, reduce permanganate, are oxidized by ozone and form a stable dibromide.

$C_6H_5CH_2CH_2SO_2C_7H_7$ II

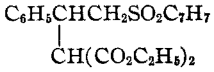
$C_6H_5CHBrCHBrSO_2C_7H_7$ III

Contrary to expectation, however, these unsaturated sulfones also add substances which, heretofore, have been regarded as typical reagents for the conjugated system $C{=}C{-}C{=}O$. In the presence of a small quantity of base, for example, they combine readily with thiocresol and with malonic esters, and the addition products are similar to those which are obtained from unsaturated ketones.



$$\begin{array}{l} C_6H_5CHCH_2SO_2C_7H_7 \\ \quad | \\ \quad SC_7H_7 \end{array}$$

IV



$$\begin{array}{l} C_6H_5CHCH_2SO_2C_7H_7 \\ \quad | \\ \quad CH(CO_2C_2H_5)_2 \end{array}$$

V

The unsaturated sulfones also add phenylmagnesium bromide. The reaction is slow, but the successive steps are surprisingly like those which have been observed with unsaturated ketones. When the sulfone is added to the Grignard reagent it immediately produces a yellow intermediate that gradually disappears if the reagent is in sufficient excess. The final product is a colorless magnesium compound which, on hydrolysis, yields a saturated sulfone.

$[(C_6H_5)_2CHCHSO_2C_7H_7]MgBr$ VI

$(C_6H_5)_2CHCH_2SO_2C_7H_7$ VII

The magnesium derivative behaves in all respects like the addition products that are obtained from α,β-unsaturated ketones; it combines with excess of unsaturated sulfone to form complex products, and it reacts with bromine to form an α-bromo sulfone, with acid chlorides to form ketosulfones and with carbon dioxide to form the corresponding carboxylic acid.

$$(C_6H_5)_2CHCHBrSO_2C_7H_7$$

VIII

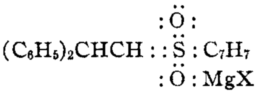
$$\begin{array}{l} (C_6H_5)_2CHCHSO_2C_7H_7 \\ \qquad\qquad | \\ \qquad\qquad COC_6H_5 \end{array}$$

IX

$$\begin{array}{l} (C_6H_5)_2CHCHSO_2C_7H_7 \\ \qquad\qquad | \\ \qquad\qquad COOH \end{array}$$

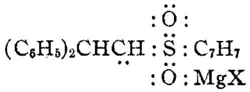
X

The bromosulfone and the ketosulfone have been synthesized by methods which establish their structure with certainty, but the structure of the magnesium derivative is open to discussion. For this substance the following formulas are possible



$$\begin{array}{c} :\ddot{O}: \\ (C_6H_5)_2CHCH::\ddot{S}:C_7H_7 \\ :\ddot{O}:MgX \end{array}$$

XI



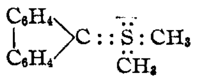
$$\begin{array}{c} :\ddot{O}: \\ (C_6H_5)_2CH\underset{\cdot\cdot}{C}H:\ddot{S}:C_7H_7 \\ :\ddot{O}:MgX \end{array}$$

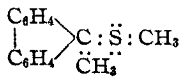
XII

$$\begin{array}{l} (C_6H_5)_2CHCHSO_2C_7H_7 \\ \qquad\qquad | \\ \qquad\qquad MgX \end{array}$$

XIII

The first two formulas, representing the possible 1,4-addition products, are unusual in type but they can be supported to a degree with analogies. Thus in sulfur hexafluoride the valence shell of sulfur is doubtless expanded beyond the normal octet as it is in formula XI, and it is not possible to represent the peculiar unsaturated sulfur compound reported by Ingold and Jessop[1] without assuming either a similar expansion of the outer shell of sulfur or negative carbon as shown in formula XII.





For various reasons the formula with negative carbon does not appeal to us. In our opinion the choice lies between formulas XI and XIII, and we prefer XI for the following reasons. Many sul-

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[1] Ingold and Jessop, *J. Chem. Soc.*, 713 (1930).

fones—saturated as well as unsaturated—behave toward organic magnesium compounds very much like ketones. The experiments of Hepworth and Clapham,[2] which have led to the impression that sulfones are not attacked by Grignard reagents, show only that these reagents neither combine with nor readily reduce the sulfonyl group. In reality they react quite readily with Grignard reagents. Thus the magnesium derivative VI can be obtained without difficulty by the action of ethylmagnesium bromide on the corresponding saturated sulfone, and the same reagent converts methyl tolyl sulfone into a similar magnesium halide derivative. Sulfones, therefore, behave toward Grignard reagents like ketones in which the hindrance to addition is prohibitive.

The magnesium derivatives of sulfones, in turn, behave precisely like those of similarly constituted ketones. Thus, as has already been shown, the derivative obtained by adding phenylmagnesium bromide to the unsaturated sulfone reacts like the one obtained by adding it to benzalacetophenone. And similarly the magnesium derivative of methyl tolyl sulfone reacts like that of acetomesitylene.[3]

$$2[\mathrm{CH_2SO_2C_7H_7}]\mathrm{MgBr} + 2\mathrm{C_6H_5COCl} \longrightarrow \underset{\mathrm{XIV}}{(\mathrm{C_6H_5CO})_2\mathrm{CHSO_2C_7H_7}} + \mathrm{CH_3SO_2C_7H_7}$$

Evidently the magnesium derivatives of ketones and of sulfones are similar both in their origin and in their activity. In the case of some of the magnesium derivatives of ketones it has been possible to prove definitely that the magnesium halide residue is attached to oxygen. We therefore prefer a similar formula for the magnesium halide derivatives of sulfones.

Experimental Part

At the time our work was begun but one α,β-unsaturated sulfone was known, namely, divinyl sulfone which had been obtained by Kretov[4] by oxidizing β,β-dichlorodiethyl sulfide and eliminating hydrogen chloride from the resulting sulfone. This method could not be adapted to our needs. While the work was in progress Rothstein[5] reported the preparation of $\mathrm{C_6H_5CH_2SO_2CH{=}CHCH_3}$, but the method by which this substance was obtained is likewise limited in scope.

In search of a more general method we first studied the condensation of benzaldehyde with methyl tolyl sulfone. This condensation can be effected but the yield of unsaturated sulfone is small and the difficulties involved in separating it from a variety of other products are great. We therefore examined the addition of thiocresol to phenylacetylene. These substances combine with great rapidity to form two stereoisomeric α,β-unsaturated sulfides. These sulfides, in turn, can be oxidized in steps to the corresponding sulfoxides and sulfones. As all these reactions are nearly quantitative, they serve well for preparing a variety of α,β-unsaturated sulfides, sulfoxides and sulfones.

Benzal Methyltolyl Sulfide, $\mathrm{C_6H_5CH{=}CHSC_6H_4CH_3}$-(*p*).—To 20.4 g. of phenylacetylene was added, slowly and with sufficient cooling to prevent the temperature from rising above 100°, 24.8 g. of thiocresol. The mixture was allowed to cool, then diluted with low-boiling petroleum ether. It gradually deposited the higher melting sulfide which, after recrystallization from the same solvent, or from methyl alcohol, melted at 65°.

The filtrates were combined, freed from solvent and distilled under diminished pressure. In this manner the second isomer was obtained as a solid melting at 44°. The relative amounts of the two isomers depend on the temperature during the reaction and the completeness of the separation before distillation. At temperatures but little above the melting point the two isomers are formed in nearly equal proportions. Higher temperatures favor the formation of the lower melting compound and the higher melting compound is slowly isomerized by distillation. The total yield is almost 100%.

Anal. Calcd. for $\mathrm{C_{15}H_{14}S}$: C, 79.6; H, 6.2. Found: (65°) C, 79.8; H, 6.2. (44°) C, 79.3; H, 6.3.

Oxidation: Benzal Methyltolyl Sulfoxide.—To a solution of 22.6 g. of the sulfide (44°) in 200 cc. of glacial acetic acid, which was kept near the freezing point, was added an equivalent quantity of about 30% aqueous hydrogen peroxide. The mixture was kept near the freezing point for several hours, then allowed to warm up gradually and left at the ordinary temperature overnight. The resulting solution deposited an oil when it was poured into cracked ice. Oil and water were therefore extracted with ether and the extract was freed from acid, dried and evaporated under diminished pressure. The residue solidified completely. After recrystallization from petroleum ether, from which it separated in needles, the sulfoxide melted at 64°.

The higher melting sulfide, oxidized in the same manner, yielded an oil which solidified to a crystalline mass but which could neither be crystallized satisfactorily nor distilled without decomposition under diminished pressure. Its melting point was nearly the same as that of the isomer.

Anal. Calcd. for $\mathrm{C_{15}H_{14}OS}$: C, 74.4; H, 5.8. Found: (64°) C, 74.5; H, 5.9; (60°) C, 75.0; H, 5.9.

Oxidation: Benzal Methyltolyl Sulfone, I.—The two isomeric sulfones were obtained both from the sulfides and

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(2) Hepworth and Clapham, *J. Chem. Soc.*, **119**, 1188 (1921).

(3) Kohler and Baltzly, THIS JOURNAL, **54**, 4015 (1932).

(4) Kretov, *J. Russ. Phys.-Chem. Soc.*, **62**, 1 (1930).

(5) Rothstein, *J. Chem. Soc.*, 684 (1934).

from the sulfoxides. They were prepared in quantity by oxidizing the sulfides because these crystallize better than the sulfoxides The procedure was the same as that employed for making the sulfoxides, except that the peroxide was used in slight excess and that there was no need of controlling the temperature. The sulfones were precipitated as solids when the acetic acid solutions of the oxidation products were poured on cracked ice, the lower melting sulfide being oxidized to the higher melting sulfone. The solids were washed with water and recrystallized from methyl alcohol. They crystallized in needles melting at 77 and 121°. The higher melting isomer was also obtained, in a maximum yield of 15%, by condensing benzaldehyde with methyl tolyl sulfone in the presence of potassium hydroxide.

Anal. Calcd. for $C_{15}H_{14}O_2$: C, 69.8; H, 5.4; mol. wt., 258. Found: (77°) C, 70.0; H, 5.5; (121°) C, 69.4; H, 5.3; mol. wt., 235.

Isomerization.—A solution of 1.75 g. of the sulfone melting at 77° in chloroform containing a trace of iodine was exposed to sunlight for several days in a quartz vessel and then evaporated. The residue contained at least 0.75 g. of the form melting at 121°. In a parallel experiment with the higher melting form the residue still melted at 121°.

Degradation.—Both sulfones reduce permanganate rapidly in acetone. They also react with ozone but do not form insoluble ozonides. An ozonized solution was shaken with potassium hydroxide, then acidified and extracted with ether. The extract contained only benzoic acid. The aqueous layer was evaporated to dryness and the residue was extracted with alcohol. The alcoholic extract, on evaporation, left a residue which when treated, first with phosphorus pentachloride and then with aniline, formed para-toluenesulfone anilide.

Hydrogenation: β-Phenyl Ethyltolyl Sulfone, II.—The unsaturated sulfones are not reduced as easily as α,β-unsaturated ketones. Thus a solution of 0.516 g. of the higher melting sulfone in glacial acetic acid was heated on a steam-bath for twenty-four hours with excess of zinc dust, then poured on cracked ice. It deposited 0.45 g. of unchanged sulfone. Under the same conditions most α,β-unsaturated ketones are reduced within an hour.

A solution of 1.32 g. of the same sulfone in glacial acetic acid was shaken with hydrogen in the presence of a platinum catalyst. At first the rate of absorption was fairly rapid but it soon diminished and it dropped to almost nothing before a third of the calculated quantity had disappeared. The addition of fresh catalyst had a similar result—indicating that hydrogenation occurred and that the catalyst was poisoned. The product was a mixture of saturated and unsaturated sulfones which was separated by crystallization from methyl alcohol. The saturated sulfone crystallizes in needles and it melts at 75°. It is easily prepared by the method which Posner[6] evolved for the preparation of β phenyl ethylphenyl sulfone.

Anal. Calcd. for $C_{15}H_{16}O_2S$: C, 69.2; H, 6.2. Found: C, 69.2; H, 6.1.

Addition of Bromine: α,β-Dibromo-β-phenyl Ethyltolyl Sulfone, III.—The unsaturated sulfones do not combine with bromine in the dark, but in direct sunlight the addition is fairly rapid. Under these conditions both isomers form the same dibromide—a substance which crystallizes from methyl alcohol in thin needles and melts at 132°.

Anal. Calcd. for $C_{15}H_{14}O_2Br_2S$: C, 43.1; H, 3.4. Found: C, 42.8; H, 3.5.

Addition of Thiocresol, IV.—The unsaturated sulfones do not, like unsaturated hydrocarbons, combine with free thiocresol. As in the case of unsaturated ketones so here addition occurs only in the presence of bases. The addition product—best obtained by converting the thiocresol into its sodium compound with metallic sodium in ether, adding an equivalent quantity of the unsaturated sulfone in benzene and keeping the mixture at the ordinary temperature for several days—is sparingly soluble in methyl alcohol, readily soluble in acetone. From acetone–methyl alcohol it crystallizes well in needles melting at 175–176°.

Anal. Calcd. for $C_{22}H_{22}O_2S_2$: C, 69.1; H, 5.8. Found: C, 69.1; H, 5.9.

The structure of the thiocresol addition product was established by oxidizing it to the corresponding disulfone and comparing this substance with an α,α-disulfonyl derivative which was prepared by benzylating di-(tolylsulfonyl)-methane. As the two substances were found to be isomeric the thiocresyl group must be in the β-position.

Oxidation: $C_6H_5CH(SO_2C_7H_7)CH_2SO_2C_7H_7$.—The thiocresol addition product was oxidized in the usual manner, with 30% hydrogen peroxide in glacial acetic acid. The product was only sparingly soluble in acetone, in chloroform and in dioxane, and even less soluble in alcohol. It crystallized in very fine needles melting with decomposition above 225°.

Anal. Calcd. for $C_{22}H_{22}O_4S_2$: C, 63.8; H, 5.3. Found: C, 63.9; H, 5.6.

Benzyl Di-(*p*-tolylsulfonyl)-methane, $C_6H_5CH_2CH(SO_2C_7H_7)_2$.—The 1,1-ditolyl sulfone was obtained by benzylating di-(tolylsulfonyl)-methane by means of the procedure developed by Shriner.[7] It is readily soluble in hot methyl alcohol from which it crystallizes in fluffy needles melting at 103°.

Anal. Calcd. for $C_{22}H_{22}O_4S_2$: C, 63.8; H, 5.3. Found: C, 63.5; H, 5.4.

Addition of Malonic Ester, V.—One and six-tenths grams of diethyl malonate was converted into the sodium compound with metallic sodium in 50 cc. of benzene. To this suspension 2.6 g. of benzal methyltolyl sulfone was added and the mixture was shaken until all the solid had disappeared—about twenty-four hours. The benzene solution was then washed with water and evaporated. It left a crystalline solid. The solid was recrystallized from methyl alcohol, from which it separated in fluffy needles melting at 78°. The yield was nearly quantitative.

Anal. Calcd. for $C_{22}H_{26}O_6S$: C, 63.2; H, 6.2. Found: C, 63.1; H, 6.2.

Reaction with Phenylmagnesium Bromide: β,β-Diphenyl Ethyltolyl Sulfone, VII.—It is much more difficult

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[6] Posner, *Ber.*, **38**, 651 (1905).

[7] Shriner, Struck and Jorison, This Journal, **52**, 2060 (1930).

to get a satisfactory yield of addition product with the unsaturated sulfone than with the corresponding unsaturated ketone. The difference seems to lie mainly in the relative speeds of the primary and secondary reactions. In the case of unsaturated ketones the primary reaction is relatively fast, hence by adding the ketone to a sufficiently large excess of reagent it is possible to exclude the secondary reaction almost completely. In the case of unsaturated sulfones the difference in the speeds of the primary and secondary reactions appears to be much less. Even under the most favorable conditions the yield of primary product seldom exceeds 50%. The following procedure gave as good results as any of the many that were tried.

To a solution of 0.1 mole of phenylmagnesium bromide in boiling benzene was added, gradually and with constant stirring, 0.02 mole of the unsaturated sulfone. The mixture was boiled for three hours then acidified in the usual manner. The benzene solution was washed, dried and freed from solvent, leaving an oily residue which was dissolved in methyl alcohol because the addition product does not crystallize well from benzene. The methyl alcoholic solution gradually deposited 3 g. of the addition product and a small additional quantity was obtained after the unchanged sulfone had been removed by oxidation with permanganate. The remainder was a viscous oil of unknown complexity.

Anal. Calcd. for $C_{21}H_{20}O_2S$: C, 75.0; H, 5.9; S, 9.5. Found: C, 74.6; H, 5.9; S, 9.5.

The addition product crystallizes in needles and it melts at 149°. In order to prove its structure it was synthesized by adding thiocresol to unsymmetrical diphenylethylene and oxidizing the resulting sulfide with excess of hydrogen peroxide. The yield was excellent.

$$(C_6H_5)_2C{=}CH_2 + HSC_7H_7 \longrightarrow$$
$$(C_6H_5)_2CH{-}CH_2SC_7H_7 \longrightarrow (C_6H_5)_2CH{-}CH_2SO_2C_7H_7$$

α-Bromo-β,β-diphenyl Ethyltolyl Sulfone, VIII.—The sulfone itself does not react with bromine but the α-bromo compound was obtained without difficulty by adding a slight excess of bromine to a solution of the magnesium derivative. It crystallizes in needles and melts at 155°.

Anal. Calcd. for $C_{21}H_{19}O_2BrS$: C, 60.7; H, 4.6. Found: C, 60.4; H, 4.7.

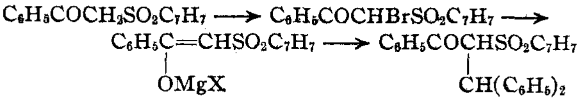
α-Iodo-β,β-diphenyl Ethyltolyl Sulfone.—The iodo compound was obtained accidentally when bromine was added to an ethereal solution of the magnesium compound which had been made by treating the sulfone with methylmagnesium iodide. It crystallizes in prisms and melts at 186°.

Anal. Calcd. for $C_{21}H_{19}O_2IS$: C, 54.5; H, 4.1. Found: C, 55.3; H, 4.2.

α-Benzoyl-β,β-diphenyl Ethyltolyl Sulfone, IX.—The keto sulfone was obtained by adding benzoyl chloride to a solution of the magnesium derivative. As it crystallizes readily and is sparingly soluble it serves admirably for estimating the quantity of magnesium derivative in a solution. It crystallizes from acetone or benzene in minute needles that melt at 253°.

Anal. Calcd. for $C_{28}H_{24}O_3S$: C, 76.4; H, 5.5. Found: C, 76.6; H, 5.3.

The structure of the benzoyl derivative was established by a synthesis which can be represented as follows:



$$C_6H_5COCH_2SO_2C_7H_7 \longrightarrow C_6H_5COCHBrSO_2C_7H_7 \longrightarrow \underset{\displaystyle OMgX}{C_6H_5\overset{}{C}}{=}CHSO_2C_7H_7 \longrightarrow C_6H_5CO\underset{\displaystyle CH(C_6H_5)_2}{CH}SO_2C_7H_7$$

Contrary to the opinion of Arndt and Martius[8] the first step in this series can be accomplished without difficulty by adding the ketosulfone to a solution of an equivalent solution of bromine in chloroform. Bromination is not instantaneous but, once started, the reaction proceeds to completion quite rapidly. The bromo compound crystallizes in plates and melts at 164°.

Anal. Calcd. for $C_{15}H_{13}O_3BrS$: C, 59.9; H, 3.7. Found: C, 59.7; H, 3.8.

The remaining operations in the series were carried out in accordance with the procedure employed by Kohler and Tishler[9] in an analogous case. The yields were good.

α-Aceto-β,β-diphenyl Ethyltolyl Sulfone.—The acetyl derivative was obtained by adding excess of acetyl chloride to a solution of the magnesium derivative. It crystallizes in needles and melts at 205°.

Anal. Calcd. for $C_{23}H_{22}O_3S$: C, 73.0; H, 5.8. Found: C, 72.6; H, 5.9.

Benzohydryl Tolylsulfoneacetic Acid, X.—A stream of carbon dioxide was passed for three hours through a solution of the magnesium derivative in benzene. The solution changed color but did not deposit a solid magnesium derivative. Acidification with dilute hydrochloric acid, however, caused the precipitation of an acid in very minute plates that melted, with effervescence, at 195–197°. The yield was 87%.

Anal. Calcd. for $C_{22}H_{20}SO_4 \cdot H_2O$: C, 66.4; H, 5.53. Found: C, 66.9; H, 5.5.

II. The Action of Grignard Reagents on Saturated Sulfones

Hepworth and Clapham heated di-isoamyl sulfone and benzyl phenyl sulfone for eighteen hours with benzene solutions of methylmagnesium iodide and on acidification recovered nearly all of the material with which they started. Their experiments were not properly designed to show the activity of sulfones. We examined β-phenyl ethyltolyl sulfone (II), β,β-diphenyl ethyltolyl sulfone (VII) and methyltolyl sulfone in our modified Zerewitinoff apparatus and found that all three behave toward methylmagnesium iodide like ketones which are not enolic, but which can form metallic derivatives of enolic modifications. With the first two sulfones there is no appreciable reaction at the ordinary temperature but evolution of gas commences at 50–75° and continues until one mole of substance has liberated at least one mole of methane. Methyltolyl sulfone lib-

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[8] Arndt and Martius, *Ann.*, **499**, 244 (1932).

[9] Kohler and Tishler, THIS JOURNAL, **57**, 217 (1935).

erates methane slowly at the ordinary temperature.

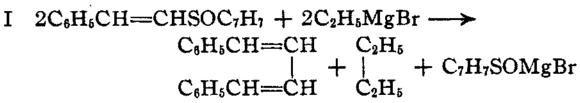
The magnesium derivative that is formed by heating diphenylethyl tolyl sulfone for an hour with ethylmagnesium bromide is the same that is formed by adding phenylmagnesium bromide to the unsaturated sulfone; it forms the same products when it is treated with the same reagents and all the reactions are nearly quantitative. When unsaturated sulfone is added to a solution of the magnesium derivative it reacts with it to form a product that is similar in physical properties to the intractable by-product of the Grignard reaction.

Dibenzoylmethyl Tolyl Sulfone, XIV.—A benzene solution of 3.5 g. of methyl tolyl sulfone was added to an ethereal solution of ethylmagnesium bromide which contained 1.2 g. of magnesium. A white precipitate formed as the two solutions came in contact but it redissolved rapidly and gas was evolved at the ordinary temperature. The solution was heated for fifteen minutes, then treated with 7.0 g. of benzoyl chloride. The product was isolated in the usual manner and purified by recrystallization from methyl alcohol. It separated in needles and melted at 164°.

Anal. Calcd. for $C_{22}H_{18}O_4S$: C, 72.2; H, 4.6. Found: C, 72.1; H, 4.6.

III. Reactions of the Sulfoxide

The action of Grignard reagents on the unsaturated sulfoxide is completely different from their action on the sulfone. The principal products are diphenylbutadiene, an organic sulfide and an inorganic magnesium compound. The reaction therefore involves both cleavage and reduction, and, since direct experiments showed that the unsaturated sulfide does not react with organic magnesium compounds, cleavage must precede reduction. The most probable sequence of events may therefore be represented as



$$\text{I}\quad 2C_6H_5CH{=}CHSOC_7H_7 + 2C_2H_5MgBr \longrightarrow \begin{matrix} C_6H_5CH{=}CH \\ | \\ C_6H_5CH{=}CH \end{matrix} + \begin{matrix} C_2H_5 \\ | \\ C_2H_5 \end{matrix} + C_7H_7SOMgBr$$

$$\text{II}\quad C_7H_7SOMgBr + C_2H_5MgBr \longrightarrow C_7H_7SC_2H_5$$

In the case of phenylmagnesium bromide the product contained small variable quantities of an oily substance which could be oxidized to a crystalline sulfone. The composition of this sulfone showed that it must contain three phenyl groups—indicating as the most probable formulas

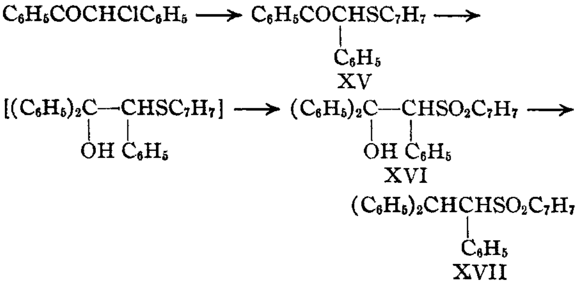
$$\underset{C_6H_5}{(C_6H_5)_2CHCHSO_2C_7H_7}$$

XVII

$$(C_6H_5)_3CCH_2SO_2C_7H_7$$

XVIII

We synthesized the sulfone represented by formula XVII but found it different from the substance under consideration. The successive steps in the synthesis can be represented as follows



$$C_6H_5COCHClC_6H_5 \longrightarrow \underset{\text{XV}}{C_6H_5CO\underset{C_6H_5}{CH}SC_7H_7} \longrightarrow$$

$$[(C_6H_5)_2\underset{OH}{C}{-}\underset{C_6H_5}{CH}SC_7H_7] \longrightarrow \underset{\text{XVI}}{(C_6H_5)_2\underset{OH}{C}{-}\underset{C_6H_5}{CH}SO_2C_7H_7} \longrightarrow$$

$$\underset{\text{XVII}}{(C_6H_5)_2CH\underset{C_6H_5}{CH}SO_2C_7H_7}$$

All attempts to synthesize the substance represented by XVIII were unsuccessful but we finally succeeded in proving that this formula is correct by cleaving the sulfone with phosphorus pentachloride and identifying the cleavage products.

$$(C_6H_5)_3CCH_2SO_2C_7H_7 \longrightarrow (C_6H_5)_3CCH_2Cl + [C_7H_7SO_2Cl] \longrightarrow [ClC_6H_4CCl_3] \longrightarrow ClC_6H_4CO_2H$$

The validity of this proof was established by similar treatment of a phenylated sulfone of known structure

$$(C_6H_5)_2CHCH_2SO_2C_7H_7 \longrightarrow (C_6H_5)_2C{=}CCl_2 + ClC_6H_4COOH$$

It is impossible, at present, to account for the formation of this highly phenylated compound but experiments now under way with unsaturated sulfones and sulfoxides which have two phenyl groups in the β-position may throw some light on the subject.

Reaction with Ethylmagnesium Bromide.—When benzal methyltolyl sulfoxide is added to a solution of one equivalent of ethylmagnesium bromide, it immediately produces a yellow precipitate that is insoluble in ether and in benzene. This precipitate evidently is one of the colored complexes which are formed at the outset of most reactions between Grignard reagents and unsaturated compounds because it is hydrolyzed to ethane and unchanged sulfoxide. It dissolves slowly, and with evolution of gas, in excess of the reagent.

A solution obtained by adding the sulfoxide to a large excess of the reagent was left to itself for a day, then decomposed with ammonia and ammonium chloride. The ethereal layer was freed from solvent under diminished pressure and the residue was distilled with steam. The distillate contained ethyl tolyl sulfide—identified by its boiling point under diminished pressure, its composition and oxidation to ethyl tolyl sulfone. The solid residue after the distillation with steam was crystallized from methyl alcohol. It was identified as 1,4-diphenylbutadiene by comparison with a reliable sample. The yield was 80%.

Reaction with Phenylmagnesium Bromide.—The procedure was the same as with ethylmagnesium bromide.

The steam distillate contained only diphenyl. The methyl alcoholic solution of the residue slowly deposited diphenylbutadiene. The oil that was left after this had been removed as far as possible was oxidized with excess of hydrogen peroxide and thus converted into two solid sulfones which were readily separated by crystallization from methyl alcohol. The more soluble component was identified as phenyl tolyl sulfone. The less soluble component was very sparingly soluble in methyl alcohol. After recrystallization from acetone it melted at 229–230°.

Anal. Calcd. for $C_{27}H_{24}O_2S$: mol. wt., 412; C, 78.6; H, 5.8. Found: mol. wt., 417; C, 78.2; H, 5.0.

Benzoyl Phenyl Methyltolyl Sulfide, XV.—Equivalent quantities of desyl chloride and the sodium derivative of thiocresol were dissolved in alcohol. The reaction was rapid and the yield was quantitative. The product crystallized from ether–petroleum ether in needles and melted at 63–64°.

Anal. Calcd. for $C_{21}H_{18}OS$: C, 72.0; H, 5.1. Found: C, 71.8; H, 5.2.

α-Phenyl-β,β-diphenyl-β-hydroxy Ethyltolyl Sulfone, XVI.—When the sulfide XV was added to excess of phenylmagnesium bromide it appeared to react normally but the product showed no tendency to crystallize. It was therefore oxidized to the sulfone in the usual manner. The sulfone crystallized in inconspicuous needles, sintered at about 180° and finally melted at 275°. The yield was practically quantitative.

Anal. Calcd. for $C_{27}H_{24}O_3S$: C, 75.7; H, 5.7. Found: C, 74.9; H, 5.7.

α-Phenyl-β,β-diphenyl Ethyltolyl Sulfone, XVII.—The carbinol was reduced in the usual manner with phosphorus and iodine. The product crystallized well from methyl alcohol in lustrous plates. It melted at 187°. The yield was practically quantitative.

Anal. Calcd. for $C_{27}H_{24}O_2S$: C, 78.6; H, 5.8. Found: C, 78.2; H, 5.9.

β,β,β-Triphenyl Ethyltolyl Sulfone, XVIII.—One gram of the sulfone was heated in a sealed tube with 2 g. of phosphorus pentachloride for two hours at 200°. The resulting mixture was extracted with benzene, the benzene solution was washed with water, freed from solvent and distilled with steam. The residue was a mixture. By crystallization from ether it was separated into unchanged sulfone and a substance which was identified as α,α,α-triphenyl-β-chloroethane by comparison with an authentic sample. The distillate contained *p*-chlorobenzoic acid, a chlorinated toluene which was oxidized to *p*-chlorobenzoic acid by permanganate, and some more triphenylchloroethane. The yield of the chloroethane was 65% and that of *p*-chlorobenzoic acid 60%.

α,α-Dichloro-β,β-diphenyl Ethyltolyl Sulfone: $(C_6H_5)_2CHCCl_2SO_2C_7H_7$.—A mixture of 2 g. of the diphenyl sulfone and 4 g. of phosphorus pentachloride was heated for two hours at 200°. The product, manipulated as described in the preceding experiment, was found to contain *p*-chlorobenzoic acid, dichlorodiphenylethylene melting at 78.5°, and the dichloro sulfone which, after recrystallization from alcohol, melted at 157°.

Anal. Calcd. for $C_{21}H_{18}O_2Cl_2S$: C, 62.2; H, 4.4. Found: C, 62.9; H, 4.5.

β,β,β-[Trinitrophenyl] Ethyltolyl Sulfone: $(NO_2C_6H_4)_3CCH_2SO_2C_7H_7$.—An attempt was made to degrade the sulfone by oxidation with nitric acid but the result was nitration. The trinitro compound is also formed when the sulfone is treated with fuming nitric acid at −10°—the procedure employed for making the trinitro derivative of triphenylethane. It crystallizes in pale yellow needles and it melts with decomposition at about 265°.

Anal. Calcd. for $C_{27}H_{21}O_8N_3S$: C, 59.2; H, 3.8. Found: C, 59.3; H, 4.1.

Summary

α,β-Unsaturated sulfones add metallic derivatives, including Grignard reagents, precisely like α,β-unsaturated ketones. Saturated sulfones behave toward Grignard reagents like saturated ketones in which the hindrance to addition is prohibitive; they form magnesium halide derivatives by means of which they can be brominated, acylated and carbonated. α,β-Unsaturated sulfoxides are cleaved by Grignard reagents.

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