which are hydrogen-bond acceptors, but poor (or nonexistent) hydrogen-bond donors. A change in solvent structure may account for part of the observed rate increase. The hydrogen-bond acceptor should break up the pseudo-polymeric structure of methyl alcohol into smaller aggregates. The solvent mixture then may be able to accommodate the electrostrictive effects associated with charge formation or charge dispersal more easily than the rigid, highly associated methyl alcohol.[44]

A change in solvent structure may account for the rate increase observed upon addition of the tetraethylammonium salt, and the rate decrease observed with the lithium salt. In aqueous systems ammonium salts have been classified as "order destroying" while lithium salts were termed "order producing."[45] Once again the breakup of the highly ordered solvent structure may show up in enhanced reaction rates.

**Acknowledgment.**—Mr. Martin Berwick is thanked for help in checking certain kinetic data. The American Chemical Society Petroleum Research Fund is thanked for a type G grant making this research possible. Part of this data was obtained during a postdoctoral fellowship at Harvard University. Professor P. D. Bartlett is thanked for encouragement and the use of laboratory facilities.

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[44] J. H. Hildebrand and R. L. Scott, "The Solubility of Non-Electrolytes," Reinhold Publishing Corp., New York, N. Y., 1950, p. 172.

[45] See ref. 33, p. 190.

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# The Reaction of Phenyllithium with Some Dialkyl and 1,2-Alkylene Sulfates

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The reactions of phenyllithium with methyl sulfate, isopropyl sulfate, *n*-butyl sulfate, *cis*-1,2-cyclohexylene sulfate, *trans*-1,2-cyclohexylene sulfate, and *cis*-1,2-cyclopentylene sulfate have been carried out. Reaction schemes in which the phenyllithium acts as a nucleophile on carbon or sulfur in substitution reactions or as a base in elimination reactions are postulated to account for the various products. Methyl sulfate gave toluene; isopropyl sulfate gave cumene, propene, and isopropyl bromide; *n*-butyl sulfate gave *n*-butyl benzene; *cis*-1,2-cyclohexylene sulfate gave 1-phenylcyclohexanol; *trans*-1,2-cyclohexylene sulfate gave *trans*-1,2-cyclohexanediol, phenyl sulfone, benzenesulfonic acid, and *cis*- and *trans*-2-phenylcyclohexanol; and *cis*-1,2-cyclopentylene sulfate gave 1-phenylcyclopentene.

The alkylation of Grignard reagents by alkyl sulfates and the closely related alkyl esters of sulfonic acids is an old reaction which has seen extensive use.[2] Besides alkylation (eq. 1), several side reactions take place (eq.

$$\mathrm{RM + R'OSO_2OR' \longrightarrow R{-}R' + MOSO_2OR'} \quad (1)$$

2, 3, and 4). In these equations, M stands for the

$$\mathrm{RM + R'OSO_2OR' \longrightarrow RH + R'({-}H) + MOSO_2OR'} \quad (2)$$

$$\mathrm{(X^-) + R'OSO_2OR' \longrightarrow R'X + ROSO_3^-} \quad (3)$$

$$\mathrm{RM + R'OSO_2OR' \longrightarrow R'OM + RSO_2OR'} \quad (4)$$

magnesium and its attached groups and ($X^-$) for the halide ion present in the Grignard solution. These equations were written with the assumption that the products arise *via* SN2-like and E2-like processes.[3] That is, the Grignard reagent acts both as a carbon nucleophile on carbon (eq. 1) or on sulfur (eq. 4) in substitution reactions, and as a base (eq. 2), abstracting a $\beta$-hydrogen, in an elimination reaction. The halide ion acts as a nucleophile on carbon (eq. 3). The sulfur-containing products in eq. 1 to 4 may react further in similar fashion. The extent to which any of these various reactions takes place is determined by the nature of RM, R′, and $X^-$.

In order to compare the reaction of phenyllithium on alkyl sulfates with the reaction of phenylmagnesium bromide on alkyl sulfates, three alkyl sulfates were treated with excess phenyllithium. The results are tabulated in Table I. The yields show that both alkyl groups of the alkyl sulfates are replaceable by phenyllithium. The higher yields of alkylation products obtained using phenyllithium compared with phenylmagnesium bromide suggest that organolithium compounds may be superior to organomagnesium halides in synthetic applications of this type of reaction. Using a 1:1 molar ratio of phenyllithium to alkyl sulfate should increase the per cent of the phenyllithium which is alkylated above the yields reported in Table I.

TABLE I

YIELDS OF ALKYLATION PRODUCTS

| $R_2SO_4$ | % $C_6H_5R$ | |
|---|---|---|
| | Using $C_6H_5MgBr$[a] | Using $C_6H_5Li$ |
| $(CH_3)_2SO_4$ | 31[b] | 61[c] |
| $(i\text{-}C_3H_7)_2SO_4$ | 10[d] | 32[e] |
| $(n\text{-}C_4H_9)_2SO_4$ | 16[f] | 80[e] |

[a] The reactant molar ratio is 1. [b] A. Werner and F. Zilkens, *Ber.*, **36,** 2116 (1903). [c] Two moles of $C_6H_5Br$ to 1.0 mole $R_2SO_4$; propene and isopropyl bromide also formed as in eq. 2 and 3. [d] L. Bert, *Compt. rend.*, **176,** 840 (1923). [e] Two and one-half moles of $C_6H_5Br$ to 1.0 mole of $R_2SO_4$; yields for *c* and *e* based on alkyl sulfate and calculated assuming both R groups replaceable. [f] C. M. Suter and H. L. Gerhart, *J. Am. Chem. Soc.*, **57,** 107 (1935).

The main part of this investigation was concerned with the reaction of three cyclic sulfates, *trans*-1,2-cyclohexylene sulfate (**1**), *cis*-1,2-cyclohexylene sulfate (**2**), and *cis*-1,2-cyclopentylene sulfate (**3**), with phenyllithium in ethyl ether. The cyclic sulfates **1** and **2** had

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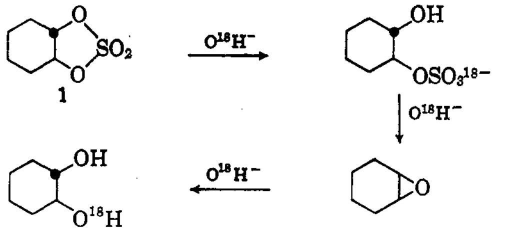
[1] Based in part on the Ph.D. Thesis of K. K. Andersen submitted to the Graduate School of the University of Minnesota, May, 1959; National Science Foundation Predoctoral Fellow, 1955–1959; Department of Chemistry, University of New Hampshire, Durham, N. H.

[2] For a review see M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Nonmetallic Substances," Prentice-Hall Co., Inc., New York, N. Y., 1954, pp. 1277–1285.

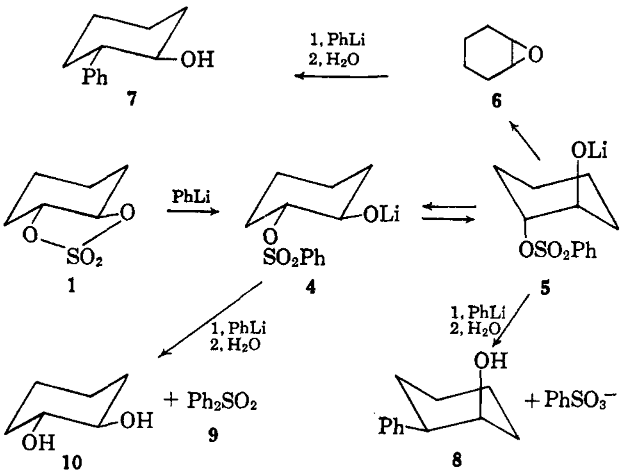
[3] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Henry Holt and Co., Inc., New York, N. Y., 1959, Chapter 8, 12.

been hydrolyzed in alkaline aqueous solution by others.[4] We were interested in comparing these results with the case in which phenyllithium was the nucleophile. We were also interested in the possibility of synthesizing *cis*- and *trans*-1,2-dialkyl- or -diarylcycloalkanes by treating *cis*- or *trans*-1,2-cycloalkylene sulfates with organolithium reagents.

The alkaline hydrolysis of *trans*-1,2-cyclohexylene sulfate (**1**) yields *trans*-1,2-cyclohexanediol. The following mechanism based on $O^{18}$ tracer studies has been proposed.[4]

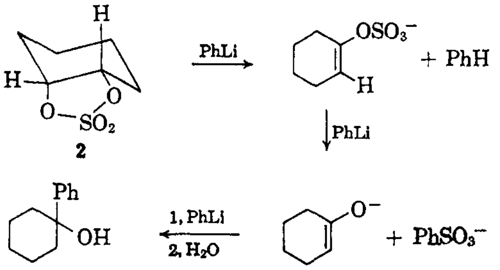


A mixture of products was obtained when *trans*-1,2-cyclohexylene sulfate (**1**) was treated with phenyllithium. The products and a mechanistic scheme accounting for their formation are given below. Consideration of molecular models indicate that the *trans* C–O bonds in **1** cannot adopt a diaxial conformation, but must exist in the diequatorial form. This diequatorial conformation makes substitution on carbon unlikely and accounts for the initial attack on sulfur to give intermediate **4**. This intermediate then leads to cyclohexene oxide (**6**) in a manner analogous to the saponification reaction. Cyclohexene oxide is known to react with phenyllithium to give *trans*-2-phenylcyclohexanol (**7**).[5] Since *cis*-2-phenylcyclohexanol (**8**) is formed as well, it seems that **5** must also react with phenyllithium besides forming **6**. The formation of phenyl sulfone (**9**) and *trans*-1,2-cyclohexanediol (**10**) is explained by two substitution reactions on sulfur.



The alkaline hydrolysis[4] of *cis*-1,2-cyclohexylene sulfate (**2**) proceeds with S–O bond cleavage to the diol monosulfate which then hydrolyzes slowly with C–O bond cleavage to *trans*-1,2-cyclohexanediol.

The reaction of *cis*-1,2-cyclohexylene sulfate (**2**) follows a different path as shown below. This reaction scheme is analogous in part to the reaction of *cis*-1-acetoxy-2-*p*-toluenesulfonoxycyclohexane with aqueous sodium hydroxide or with methanolic sodium methoxide; in both cases, cyclohexanone was the major product.[6]



*cis*-1,2-Cyclopentylene sulfate (**3**) leads to 1-phenylcyclopentanol when treated with phenyllithium. The 1-phenylcyclopentanol was not isolated as such since it dehydrated upon distillation during the reaction work-up to give water and 1-phenylcyclopentene. This dehydration upon distillation has been reported.[7] A reaction sequence similar to the one above for **2** and phenyllithium is also applicable to the reaction of **3** and phenyllithium.

The addition of phenyllithium to the cyclopentanone and cyclohexanone enolate anions seems somewhat unusual. However, a referee has pointed out the similarity of this reaction to that of the addition of phenyllithium to lithium carboxylates which results in ketone formation.[8]

## Experimental

***cis*-1,2-Cyclopentylene Sulfate (3).**—*cis*-1,2-Cyclopentylene sulfite was prepared from *cis*-1,2-cyclopentanediol (38.8 g., 0.38 mole) and freshly distilled thionyl chloride (48 g., 0.43 mole) in a 74% yield (42.1 g., 0.284 mole, b.p. 98–101° at 40 mm.) using the method of Kyrides.[9] Glacial acetic acid (200 ml.) was placed in an ice–salt bath until freezing began; then, *cis*-1,2-cyclopentylene sulfite (40 g., 0.27 mole) was added with mechanical stirring. A solution of sodium permanganate trihydrate (41 g., 0.21 mole) in 50 ml. of water was added dropwise over a 15-min. period.[10] The temperature was kept between 0 and −5° by adding crushed ice. Next, the precipitated manganese dioxide was reduced by passing sulfur dioxide into the stirred reaction mixture. Sufficient concentrated ammonium hydroxide was added to neutralize the acidic solution. The temperature was kept between 10 and 20° by adding crushed ice. The aqueous solution was extracted with three 300-ml. portions of ether. The combined organic layers were dried over magnesium sulfate, filtered, and concentrated at reduced pressure to give an oil with a freezing point just below room temperature. This oil was recrystallized three times from anhydrous ether by cooling the solution to −80°. A 44% yield of *cis*-1,2-cyclopentylene sulfate (19 g., 0.12 mole), m.p. 22–23°, was obtained.

*Anal.* Calcd. for $C_5H_8O_4S$: C, 36.58; H, 4.91. Found: C, 36.37; H, 4.72.

The infrared spectrum had very strong bands at 1390 and 1210 cm.$^{-1}$ and none in the 3500-cm.$^{-1}$ region consistent with the presence of a covalent sulfate and the absence of an alcohol.[11]

**Reaction of *n*-Butyl Sulfate with Phenyllithium.**—A solution of phenyllithium was prepared from bromobenzene (39 g., 0.25

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[4] J. S. Brimacombe, A. B. Foster, E. B. Hancock, W. G. Overend, and M. Stacey, *J. Chem. Soc.*, 201 (1960).

[5] J. W. Cook, C. L. Hewett, and C. A. Lawrence, *ibid.*, 71 (1936).

[6] M. F. Clarke and L. N. Owen, *ibid.*, 315 (1949).

[7] Y. Amiel, A. Loffler, and D. Ginsburg, *J. Am. Chem. Soc.*, **76**, 3625 (1954).

[8] G. G. Lyle, R. A. Covey, and R. E. Lyle, *ibid.*, **76**, 2713 (1954).

[9] L. Kyrides, *ibid.*, **66**, 1006 (1944).

[10] H. K. Garner and H. J. Lucas, *ibid.*, **72**, 5497 (1950).

[11] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, p. 364.

mole) and lithium (4.3 g., 0.62 g.-atom).[12] The solution was siphoned in a dry nitrogen atmosphere into a 1-l., three-necked flask equipped with a dropping funnel fitted with a nitrogen inlet tube, ball-joint stirrer, and condenser fitted with a drying tube. The solution was diluted to 500 ml. with ether. *n*-Butyl sulfate[13] (21 g., 0.10 mole) in ether (100 ml.) was added dropwise with stirring over a 1-hr. period. After standing overnight, the solution was hydrolyzed. The two layers were separated and the ether layer was dried over magnesium sulfate, filtered, and concentrated on the steam bath to give a light brown oil (22.7 g.). A portion (9.1 g.) of the oil was distilled through a 15 × 1 cm., spiral-wire column at atmospheric pressure to give a liquid, b.p. 180°. The infrared spectrum of the distillate was virtually identical with that obtained from an authentic sample of *n*-butylbenzene. A vapor phase chromatograph of the undistilled reaction material using a 2-m. silicone grease column gave one predominate peak occupying 99% of the total peak area. The yield of *n*-butylbenzene (22 g., 0.16 mole) was 80%.

**Reaction of Methyl Sulfate with Phenyllithium.**—Methyl sulfate (25 g., 0.20 mole) in ether (200 ml.) was added dropwise to a phenyllithium solution prepared from bromobenzene (63 g., 0.40 mole) and lithium (6.2 g., 0.90 g.-atom). The procedure outlined above was followed.

The ether was removed from the dried organic layer by distillation through a 20 × 2 cm. Vigreux column. A portion (17.8 g.) of the remaining residue (31.0 g.) was fractionated at atmospheric pressure through a 15 × 1 cm., spiral-wire column to give four fractions, b.p. 108–112°. The two center fractions (8.7 g.) were pure toluene with refractive indices and infrared spectra identical with those obtained from reagent grade toluene. A vapor phase chromatogram of the lower and higher boiling fractions through a 2-m., silicone grease column gave a main peak occupying 83% of the total peak area and with a retention time equal to that obtained from reagent grade toluene. The total yield of toluene from the reaction was calculated to be 61% (22.4 g., 0.244 mole).

**Reaction of Isopropyl Sulfate with Phenyllithium.**—Isopropyl sulfate (19.5 g., 0.107 mole) in ether (50 ml.) was added dropwise over a 30-min. period with stirring to a solution of phenyllithium prepared from bromobenzene (42 g., 0.27 mole) and lithium (4.2 g., 0.60 g.-atom).[14] The procedure described above was followed.

A gas was evolved from the reaction mixture in large quantities. It decolorized a dilute sodium permanganate solution. The gas was evolved only when isopropyl sulfate was added to the phenyllithium solution and at a rate which increased as the rate of addition was increased.

The ether was removed from the dried organic layer by distillation through a 30 × 2 cm. Vigreux column leaving a liquid (28.5 g.) in the distillation pot. A vapor phase chromatogram of the ether (159 g.), distilled from the organic layer, using a 2-m. column packed with polyethylene glycol gave three peaks whose retention times were equal to those for ether, benzene, and isopropyl bromide. The relative peak areas were for ether, 256; benzene, 1; and isopropyl bromide, 8. The amount of isopropyl bromide calculated from the peak areas is 5.0 g.

A portion of the liquid from which the ether had been distilled was fractionated through a 15 × 1 cm., spiral-wire column. The low-boiling fractions, 34–80°, were analyzed as above by vapor phase chromatography. They consisted of ether, 7.3 g.; benzene, 5.2 g.; and isopropyl bromide, 0.35 g. A higher boiling fraction, 149°, was also obtained. It gave a one-peak vapor phase chromatogram with a retention time equal to that for an authentic sample of cumene. The infrared spectrum of this material was identical with that for an authentic sample of cumene. The over-all yield of isopropyl bromide (5.4 g., 0.043 mole) was 20% and of cumene (8.2 g., 0.068 mole), 32%.

The sulfate content of the aqueous layer, determined gravimetrically as barium sulfate, was 94% of the original sulfate radical present in the isopropyl sulfate.[15]

**Reaction of *trans*-1,2-Cyclohexylene Sulfate (1) with Phenyllithium.**—A solution of 1[4] (43.6 g., 0.245 mole) in ether (300 ml.) was added dropwise over a 30-min. period with stirring and cooling with an ice bath to a solution of phenyllithium in ether (500 ml.) prepared from bromobenzene (96 g., 0.61 mole) and lithium (9.3 g., 1.3 g.-atoms). The apparatus and technique described above were used.

After standing overnight, the mixture was hydrolyzed using a dilute hydrochloric acid–ice mixture. The organic layer gave a light brown oil (42 g.) upon concentration. Phenyl sulfone (4.7 g.) crystallized from the oil. After recrystallization from methanol, it did not depress the melting point of an authentic sample.

Some of the oil was chromatographed on alumina to give biphenyl, phenyl sulfone, 2-phenylcyclohexanol, *trans*-1,2-cyclohexanediol, and some unidentified oils. The biphenyl did not depress the melting point of an authentic sample. The phenyl sulfone after recrystallization did not depress the melting point of an authentic sample. Its infrared spectrum was identical with that obtained from an authentic sample. A 12% yield of phenyl sulfone (6.6 g., 0.030 mole) was obtained for the over-all reaction.

The crude 2-phenylcyclohexanol from the chromatograph was distilled, b.p. 75° (1 mm.). A phenyl urethan derivative was made from the distillate. After five recrystallizations from petroleum ether, the melting point of the derivative rose from less than 100 to about 134°. None of the melting points were sharp.

*Anal.* Calcd. for $C_{19}H_{21}NO_2$: C, 77.26; H, 7.17. Found: C, 77.14; H, 7.14.

The literature melting points of the phenyl urethans are for *cis*-2-phenylcyclohexanol, 127.5–128°; *trans*-2-phenylcyclohexanol, 136–137°; m.m.p. 110–125°.[16] An attempt to separate the *cis* and *trans* isomers using both a mixture of the authentic compounds and the mixture isolated from the reaction by gas chromatography was unsuccessful. The over-all yield of the isomeric 2-phenylcyclohexanols (5.4 g., 0.031 mole) was 13%.

The *trans*-1,2-cyclohexanediol from the chromatograph was recrystallized from an ethyl acetate–petroleum ether mixture to give a white solid, m.p. 103–104°, which did not depress the melting point of an authentic sample. Continuous ether extraction of the aqueous layer from the hydrolysis of the reaction mixture gave some more *trans*-1,2-cyclohexanediol (3.4 g.). The over-all yield of *trans*-1,2-cyclohexanediol (16.0 g., 0.138 mole) was 56%.

The extracted aqueous hydrolysis solution was evaporated to dryness and fused with potassium hydroxide.[17] The melt was dissolved in water, acidified with hydrochloric acid, and bromine water was added dropwise. A grayish precipitate of 2,4,6-tribromophenol formed.

**Reaction of *cis*-1,2-Cyclohexylene Sulfate (2) with Phenyllithium.**—A solution of 2[4] (40.0 g., 0.225 mole) in ether (400 ml.) was added dropwise with stirring and with cooling in an ice bath to a solution of phenyllithium in ether (700 ml.) prepared from bromobenzene (139 g., 0.900 mole) and lithium (13 g., 1.9 g.-atoms). The apparatus and technique described above were used. After the addition was complete, the solution was allowed to stand overnight, after which it was hydrolyzed using an ice-dilute hydrochloric acid mixture. The organic layer was dried and concentrated to give an oil (58 g.).

A portion (30.2 g.) of the oil was chromatographed through a 25 × 3 in. alumina-packed column to give crude phenylcyclohexanol (19.6 g.) and crude biphenyl (4 g.). The crude phenylcyclohexanol-1 was recrystallized from an ethyl acetate–petroleum ether mixture to give the pure product (14.5 g.), m.p. 62.5–63.5°, which did not depress the melting point of an authentic sample. The infrared spectra of the synthetic sample and of an authentic sample were identical. The over-all yield of crude 1-phenylcyclohexanol was 95% (38 g., 0.21 mole) and of recrystallized 1-phenylcyclohexanol, 70% (28 g., 0.16 mole).

*Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.15. Found: C, 81.88; H, 9.22.

Continuous ether extraction of a portion of the aqueous hydrolysis layer gave only a trace of organic material.

The presence of benzenesulfonic acid was confirmed by converting it to 2,4,6-tribromophenol, m.p. 93–95°, which did not depress the melting point of an authentic sample.

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[12] H. Gilman, E. A. Zoellner, and W. M. Selby, *J. Am. Chem. Soc.*, **55**, 1252 (1933).

[13] C. M. Suter and H. L. Gerhart, "Organic Syntheses," Coll. Vol. I. John Wiley and Sons, Inc., New York, N. Y., p. 111.

[14] M. Katuno, *J. Soc. Chem. Ind. Japan*, **43**, 5 (1940); see K. Beilstein, "Handbuch der Organischen Chemie," Vol. 1, 4th Ed., Supplement 3, Part 2, Springer-Verlag, Berlin, 1958, p. 1463.

[15] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., Macmillan and Co., Ltd., New York, N. Y., 1952, p. 322.

[16] C. C. Price and J. V. Karabinos, *J. Am. Chem. Soc.*, **62**, 1159 (1940).

[17] P. Degener, *J. prakt. Chem.*, [2] **17**, 394 (1878).

An aqueous solution of barium chloride caused some turbidity when it was added to a portion of the unextracted aqueous layer. Not enough sulfate anion was present in the aqueous layer for a gravimetric determination as barium sulfate.

**Reaction of *cis*-1,2-Cyclopentylene Sulfate (3) with Phenyllithium.**—A solution of **3** (16 g., 0.10 mole) in ether (50 ml.) was added dropwise over a 30-min. period with stirring and cooling in an ice bath to a solution of phenyllithium in ether (400 ml.) prepared from bromobenzene (48 g., 0.31 mole) and lithium (4.8 g., 0.70 g.-atom). The apparatus and technique described above were used. The reaction mixture was stirred for 10 hr. and then hydrolyzed with an aqueous ammonium chloride solution. The ether layer was separated, dried over magnesium sulfate, filtered, and concentrated on the steam bath using a 30 × 2 cm. Vigreux column to give a brown oil (26.5 g.). The ether which distilled gave only one peak in a vapor phase chromatogram using a 2-m. column packed with polyethylene glycol.

A portion (16.4 g.) of the reaction oil (26.5 g.) was distilled through a 15 × 1 cm., spiral-wire column to give 1-phenylcyclopentene (6.6 g., b.p. 130–132° at 30–32 mm., lit. b.p. 107–108° at 12 mm).[18] Water codistilled with this material. A portion of the reaction oil (26.5 g.) was redried over calcium sulfate. 1-Phenylcyclopentene and water codistilled from this mixture as above. A vapor phase chromatogram of the 1-phenylcyclopentene using a 2-m. column packed with Apiezon L grease gave two peaks. The large peak occupied 99% of the peak area, while the small peak occupied 1%. The retention time for the small peak was equal to that for biphenyl. The infrared spectra of the synthetic 1-phenylcyclopentene and of an authentic sample were identical. The freezing point of the synthetic sample was 19.4° and for an authentic sample 23.6°; the mixture freezing point was 21.4°; lit.[17] m.p. 22–23°. The total yield of 1-phenylcyclopentene (12.8 g., 0.0889 mole) was 89%.

The aqueous hydrolysis layer was continuously extracted with ether. No *cis*-1,2-cyclopentanediol was isolated but only a trace of unidentified oil.

The presence of benzenesulfonic acid in the aqueous layer was confirmed as above.

A 1.3% recovery of the sulfate anion from the aqueous hydrolysis layer was made gravimetrically as barium sulfate.

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[18] G. Baddeley, J. Chadwick, and H. T. Taylor, *J. Chem. Soc.*, 448 (1956).

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# Grignard Reagents of Sulfones. VIII. Reactions of Alkylene Disulfones with Ethylmagnesium Bromide[1]

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*Received May 26, 1964*

Reactions were studied between ethylmagnesium bromide and alkylene disulfones of the structure $\mathrm{ArSO_2(CH_2)}_n\mathrm{SO_2Ar}$. With $n = 2$, no stable metalated product could be demonstrated by addition to benzaldehyde, but the presence of such a product could not be altogether discounted; vigorous conditions resulted in difficultly reproducible elimination and reduction reactions which gave mixtures of products. With $n = 5$, formation of bis-Grignard reagents was demonstrated by reaction with ketones and bromine. Grignard reagents apparently were formed also with $n = 3$ and 4. Appropriate conditions for formation of Grignard reagents of alkylene disulfones are suggested. No indications were found of discrete monometalation of alkylene disulfones. Certain Grignard reagents of sulfones were found to be soluble in solutions of ethylmagnesium bromide, although such reagents usually are virtually insoluble in organic solvents; reasons for this solubility are considered.

Products obtained by metalating sulfones with Grignard reagents are most simply regarded as Grignard reagents themselves and are most conveniently formulated as shown by structure **1**. Previous work from our

$$\underset{\mathbf{1}}{\mathrm{R_1SO_2CR_2R_3MgX}}$$

laboratories has dealt with the preparation, properties, and reactions of such substances obtained by metalating monosulfones. This paper extends these studies to $\alpha,\omega$-alkylene disulfones.

Reaction of ethylmagnesium bromide (**2**) with 1,2-bis(phenylsulfonyl)ethane (**3**) gave no clear-cut evidence of formation of a stable Grignard reagent (**4**), which might occur according to the following equation. It should be mentioned that a major obstacle to smooth reactions of **3** lay in its sparing solubility in solvents commonly used for Grignard reactions, *e.g.*, benzene, ether, anisole, and tetrahydrofuran; more soluble substituted derivatives should be more amenable to study.

$$\underset{\mathbf{2}}{2\mathrm{EtMgBr}} + \underset{\substack{\mathbf{3},\ n = 2\\ \mathbf{5},\ n = 5\\ \mathbf{7},\ n = 3\\ \mathbf{9},\ n = 4}}{\mathrm{ArSO_2(CH_2)}_n\mathrm{SO_2Ar}} \longrightarrow$$

$$\underset{\substack{\mathbf{4},\ n = 2\\ \mathbf{6},\ n = 5\\ \mathbf{8},\ n = 3\\ \mathbf{10},\ n = 4}}{\mathrm{ArSO_2CH(MgBr)(CH_2)}_{n-2}\mathrm{CH(MgBr)SO_2Ar}} + 2\mathrm{C_2H_6}$$

Reaction of **3** with about 2 molar proportions of ethylmagnesium bromide (**2**) resulted in about twice the amount of gas which had been found in metalation of methyl phenyl sulfone,[2] suggesting that the reagent **4** might have been formed. Furthermore, recovery after acidification of the sulfone **3** (59%) suggested that **4** might have survived reasonably well. Nevertheless, attempted demonstration of the presence of **4** by trapping it with benzaldehyde[3] failed, nearly all of the benzaldehyde and 53% of sulfone **3** being recovered. Since a reagent of structure **1** gave poorer results upon heating,[3] there seemed little point in trying to force addition to benzaldehyde in this way.

The formation of **4** conceivably might be demonstrated using other trapping agents, but the failure with an aldehyde, representing the most active common functional group to which Grignard reagents add,[4] shows at least that synthetically useful addition reactions of **4** are unlikely.

Since elimination reactions seemed probable in reaction of the sulfone **3** with **2**, vigorous conditions and ex-

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[1] (a) Paper VII: L. Field and E. T. Boyd, *J. Org. Chem.*, **26**, 1787 (1961). (b) Results are abstracted from a portion of the Ph.D. Dissertation of E. T. B., Vanderbilt University, Jan., 1961. This investigation was supported in part by the U. S. Army Research Office, Durham, N. C.

[2] L. Field, *J. Am. Chem. Soc.*, **78**, 92 (1956).

[3] L. Field, *ibid.*, **74**, 3919 (1952).

[4] C. E. Entemann, Jr., and J. R. Johnson, *ibid.*, **55**, 2900 (1933).