Grignard Reagents of Sulfones. VI. Alkylation and Related Reactions[1]

BY LAMAR FIELD, JOHN R. HOLSTEN AND R. DONALD CLARK[2]

An arylsulfonylmethylmagnesium bromide (I) underwent halogenolysis with iodine, coupling with cupric chloride and no apparent reaction with cobaltous chloride–ethyl bromide. The I was monoalkylated in modest yield by benzyl chloride and n-hexyl p-toluenesulfonate, in poor yield by benzhydryl chloride and apparently not at all by n-hexyl iodide and t-butyl chloride. Although compound I reacted negligibly with ethyl orthoacetate, ethyl orthoformate gave 1,3,5-tris-(p-tolylsulfonyl)-benzene, the structure of which was confirmed by oxidation and independent synthesis; the probability that an arylsulfonylacetal was an intermediate was shown by isolation of an acetal when substituents precluded cyclization and by cyclization of an independently prepared acetal. The I with methoxyamine gave, presumably, an α-aminosulfone which decomposed with water to a sulfinic acid and, in some instances, an aldehyde. With p-tolyl disulfide, the I gave tris-(p-tolyl)-trithioorthoformate, but the lithium analog gave a better yield. Tetrahydrofuran dissolved the characteristically insoluble I, but was unpromising as a solvent in an addition reaction. The reactions of I are explained by regarding it as a weakly nucleophilic Grignard reagent rather than as a carbanion salt.

Various addition reactions of such Grignard reagents of sulfones as are typified by structure

$$R_1SO_2CR_2R_3MgX$$
II

II have been considered previously.[3] They resembled those of typical Grignard reagents,[3b-d] except that if the product could be metalated by the II and if the attacking species were sufficiently susceptible to nucleophilic attack a second addition ensued.[3a]

Reagents like II could show yet another facet of behavior if the sulfone group so affected the C–Mg bond as to confer significant similarity to metal salts of resonance-stabilized carbanions (hereafter called simply carbanion salts). Indeed, with earlier studies as a basis, the statement was made that "(these) halomagnesium derivatives behave like enolates in their reactions."[4]

Theoretically, the sulfone group conceivably might exert such influence by induction, or in consequence of resonance contributions from structures like IIIa and IIIb. Similar canonical forms have
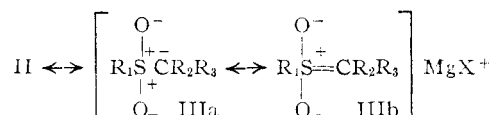
been invoked for a salt of tris-methylsulfonylmethane.[5] Methylene disulfones, but not monosulfones, apparently give analogous forms in alkaline solution.[6]

In our continuing study of Grignard reagents of sulfones, it seemed desirable at this point to attempt an approximation of their position on a scale for which typical Grignard reagents and typical carbanion salts provide two reference points.

Submission of reagents like II to alkylation and related reactions, characteristic of carbanion salts on the one hand or of Grignard reagents on the other, promised a means of making such an approximation and simultaneously of assessing the synthetic utility of the reactions. Previously, reactions related to alkylation apparently have been attempted with reagents like II only in the use of methoxymethylpiperidine,[7] chlorosilanes[8] and three other agents mentioned later.

Treatment of carbanion salts with halogens often results in coupling.[9] Reaction of phenylsulfonylmethylmagnesium bromide (IV) with iodine, however, gave iodomethyl phenyl sulfone (43%), a result quite like that given by bromine.[10] If the generally accepted mechanism of coupling[9] had applied, alkylation of IV by the iodomethyl sulfone initially formed would have been required. Accordingly, since halomethyl sulfones resist metathesis,[10] and since more iodine was used than is usual for coupling, the result need not be interpreted as indicating lack of resemblance of IV to a carbanion salt.

On the other hand, cupric chloride, which effects coupling of Grignard reagents,[11] also effected coupling of IV to 1,2-bis-(phenylsulfonyl)-ethane, although in only 5% yield. Attempted coupling of the IV with cobaltous chloride and ethyl bromide, which function by free-radical processes,[12] gave no coupling product. The latter result suggests that Grignard reagents of sulfones may resist homolytic processes and thus implies that coupling with cupric chloride involved a non-radical path, such as has been suggested for silver bromide.[13]

Alkylation with alkyl halides and tosylates next was examined. A bromomagnesium derivative of bis-(phenylsulfonyl)-methane has been alkylated with benzhydryl bromide,[14] and one of a β-keto-

(1) Presented in part at the Southeastern Regional Meeting of the American Chemical Society at Durham, N. C., Nov. 14–16, 1957. Abstracted mainly from the Ph.D. dissertations of J. R. H., March, 1957, and R. D. C., January, 1959. Paper V, L. Field and R. D. Clark, J. Org. Chem., 22, 1129 (1957).

(2) Eastman Kodak Fellow, 1957–1958.

(3) (a) L. Field, J. E. Lawson and J. W. McFarland, THIS JOURNAL, 78, 4389 (1956); (b) L. Field, ibid., 78, 92 (1956); (c) L. Field and J. W. McFarland, ibid., 75, 5582 (1953); (d) L. Field, ibid., 74, 3919 (1952). Research of previous investigators is cited in these papers.

(4) R. Connor in "Organic Chemistry," H. Gilman, Ed., Vol. I, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 881.

(5) H. J. Backer, Bull. soc. chim. France, 67 (1958).

(6) E. A. Fehnel and M. Carmack, THIS JOURNAL, 71, 231 (1949).

(7) H. Hellman and G. Opitz, Chem. Ber., 90, 15 (1957).

(8) H. Gilman, L. F. Cason and H. G. Brooks, Jr., THIS JOURNAL, 75, 3760 (1953).

(9) A. C. Cope, H. L. Holmes and H. O. House in "Organic Reactions," Vol. IX, John Wiley and Sons, Inc., New York, N. Y., 1957, p. 107.
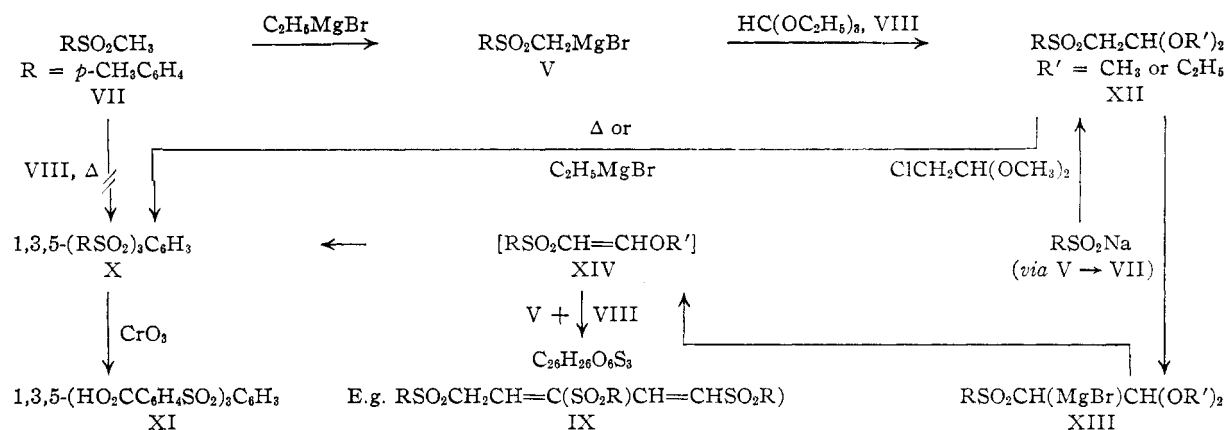
(10) W. M. Ziegler and R. Connor, THIS JOURNAL, 62, 2596 (1940).

(11) E. Sakellarios and T. Kyrimis, Ber., 57, 322 (1924).

(12) M. S. Kharasch and E. K. Fields, THIS JOURNAL, 63, 2316 (1941).

(13) E. A. Bickley with J. H. Gardner, J. Org. Chem., 5, 126 (1940).

(14) E. P. Kohler and M. Tishler, THIS JOURNAL, 57, 217 (1935).

$$RSO_2CH_3 \xrightarrow{C_2H_5MgBr} RSO_2CH_2MgBr \xrightarrow{HC(OC_2H_5)_3,\ VIII} RSO_2CH_2CH(OR')_2$$

$$R = p\text{-}CH_3C_6H_4 \qquad\qquad\qquad V \qquad\qquad\qquad\qquad\qquad\qquad R' = CH_3 \text{ or } C_2H_5$$

VII   XII

Δ or

VIII, Δ C_2H_5MgBr $ClCH_2CH(OCH_3)_2$

$$1,3,5\text{-}(RSO_2)_3C_6H_3 \longleftarrow [RSO_2CH{=}CHOR'] \qquad\qquad RSO_2Na$$

X   XIV $(via\ V \to VII)$

$$CrO_3 \qquad\qquad\qquad\qquad V + VIII$$

$$C_{26}H_{26}O_6S_3$$

$$1,3,5\text{-}(HO_2CC_6H_4SO_2)_3C_6H_3 \qquad E.g.\ RSO_2CH_2CH{=}C(SO_2R)CH{=}CHSO_2R) \qquad RSO_2CH(MgBr)CH(OR')_2$$

XI   IX   XIII

sulfone with methyl sulfate,[15] but reagents of type II seemingly have been alkylated only once.[3b]

Benzyl chloride alkylated IV to form phenyl 2-phenylethyl sulfone (29%) and benzhydryl chloride alkylated it to form phenyl 2,2-diphenylethyl sulfone (10%). Neither n-hexyl iodide nor t-butyl chloride[16] alkylated p-tolylsulfonylmethyl-magnesium bromide (V).

The V was alkylated by n-hexyl p-toluenesulfonate to n-heptyl p-tolyl sulfone in 34% yield (benzene–ether; 22% in anisole). Surprisingly, use of p-tolylsulfonylmethyllithium (VI) gave only an 11% yield. The recovery of methyl p-tolyl sulfone (VII) in these reactions suggests that the low yields may be a consequence of metalation of part of the monoalkyl product, followed by further alkylation. The quite low yield with VI then would be understandable, in terms of the greater susceptibility of the lithium compound to polyalkylation. It might be remarked that the reaction of α-(p-tolylsulfonyl)-isopropylmagnesium bromide with γ-chloro-n-propyl p-toluenesulfonate, in which dialkylation was impossible, gave alkylation only to the extent of 38%,[3b] but steric hindrance may have been culpable in this instance.

The profile of results with the halides and tosylates indicates that reagents like II more nearly resemble Grignard reagents than carbanion salts. Thus, if there were pronounced resemblance to a carbanion salt it seems that the reaction of V with n-hexyl iodide would have given results more like those obtained with n-hexyl p-toluenesulfonate.

The reaction of Grignard reagents with ortho-esters has been studied fairly extensively.[17,18] Ethyl orthoformate (VIII), most used, affords a valuable means for preparing acetals. Although VIII yields ethoxymethylene derivatives simply when heated with active-methylene compounds,[19] the fact that a strong base shows only slight promoting action[19] may mean that reaction with VIII is more a characteristic of a Grignard reagent than of a carbanion salt.

When conventional conditions were used for the reaction of V and VIII in ether, acidification gave only the original sulfone (VII, 90%), a clear indication that V is less nucleophilic than conventional Grignard reagents.[20] With a large excess of V, in benzene–ether, a material (IX) which could not be purified was obtained in low yield. The IX appeared to be a mixture of unsaturated sulfones, such as that shown in the chart. An increase in the relative amounts of benzene and of VIII resulted in material which subsequently proved to be 1,3,5-tris-(p-tolylsulfonyl)-benzene (X). With the assumption of the stoichiometry embodied in equation 2, given later, the yield of X was 16%. Forcing conditions being indicated, the ether–benzene in which V usually is prepared and used was distilled while the ester VIII was added to replace it; reaction then was effected at 125°.

During the reaction, distillate formed slowly and was removed. It had a bromine content consistent with a yield of 21% of ethyl bromide. The presumed ethyl bromide seemed likely to have been formed from bromomagnesium ethoxide (present in consequence of equation 2, given later). It could not have originated from the ethoxide alone, because strong heating of bromomagnesium n-propoxide (from n-propyl alcohol and ethylmagnesium bromide) was found to produce no n-propyl bromide. The formation of ethyl bromide is explained

$$VIII + BrMgOC_2H_5 \longrightarrow$$

$$Mg(OC_2H_5)_2 + HCO_2C_2H_5 + C_2H_5Br \quad (1)$$
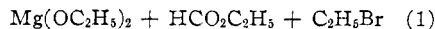
quite adequately by equation 1, however, which has a precedent in the formation of ethyl iodide and ethyl formate from iodine, magnesium and VIII.[21] Equation 1 was verified directly by heating bromomagnesium n-propoxide with the ester VIII (125°, 5 hr.); material which distilled apparently was the expected mixture of ethyl bromide and ethyl formate.[22]

(15) E. P. Kohler and H. A. Potter, THIS JOURNAL, **58**, 2166 (1936).

(16) t-Butyl chloride was used because it forms neopentane in 42–50% yield with methylmagnesium chloride; F. C. Whitmore and G. H. Fleming, ibid., **55**, 3803 (1933).

(17) H. W. Post, "The Chemistry of the Aliphatic Orthoesters," Reinhold Publishing Corp., New York, N. Y., 1943, p. 96.

(18) M. S. Kharasch and O. Reinmuth, 'Grignard Reactions of Nonmetallic Substances," Prentice–Hall, Inc., New York, N. Y., 1954, p. 586 f.

(19) R. G. Jones, THIS JOURNAL, **74**, 4889 (1952).

(20) An earlier conclusion that IV and phenylmagnesium bromide compete about equally well for benzaldehyde[30] is consistent with this view, if one assumes that benzaldehyde is so susceptible to nucleophilic attack as to be poorly discriminatory.

(21) M. T. Dangyan, Bull. Armenian Branch Acad. Sci. U.S.S.R., No. 2(7), 31 (1941); C. A., **40**, 3398 (1946).

(22) After redistillation, on series of fractions had b.p. 38–39°, $n^{25}D$ 1.4025–1.4033 (yield of ethyl bromide ca. 68%); another series had b.p. 47–56°, $n^{25}D$ 1.3644–1.3737 (yield of ethyl formate, ca. 67%). Separation of the bromide and formate was not clean-cut, but the matter was not pursued since the question at issue had been answered.

Under the forcing conditions, the presumed tris-sulfone X was obtained in 81% yield, based on equation 2. A recovery of 51% of the original VII was realized (77% of that predicted from equation 2). The essential role of the Grignard reagent in the formation of X was demonstrated by quantitative recovery of VII and VIII when they were heated alone.

The analysis and mol. wt. of the X were consistent with its formulation as 1,3,5-tris-(p-tolylsulfonyl)-benzene, and the infrared spectrum seemed reasonably so. This structure was confirmed by oxidation of the X to the tricarboxylic acid XI and by independent synthesis, as shown in the chart.

In this independent synthesis, the acetal XII was prepared from sodium p-toluenesulfinate and dimethyl chloroacetal. Prolonged heating of the XII effected its cyclization to X.

Other routes to X also were explored, either before the expedient of heating XII was adopted or by reason of general interest. Although results were unsatisfactory, these approaches warrant brief comment because of the information afforded on the nature of the various substances involved. Efforts to obtain and cyclize the aldehyde corresponding to XII by reflux of the XII during 72 hr. in water or 10% hydrochloric acid gave no more than a trace of X. Heating of the XII with two molar equivalents of sodium ethoxide in refluxing ethanol for 71 hr. also failed to effect cyclization. Since XII was cyclized by ethylmagnesium bromide (vide infra), the inability of sodium ethoxide to effect cyclization may result from too low a basicity to produce a sodium counterpart of the magnesium derivative XIII; for example, dibenzyl sulfone could not be alkylated using sodium ethoxide,[23] although potassium amide is effective.[24] Alternatively, the sodium counterpart of XIII may form but, failing to lose sodium ethoxide and form XIV, it may be unable to enter the sequence of reactions which will be proposed as a major pathway for magnesium compounds. Despite the failure of sodium ethoxide to cyclize the acetal XII, it was of interest to learn whether bases other than ethylmagnesium bromide would effect conversion of VII and VIII to the tris-sulfone X. Bromomagnesium ethoxide was heated with VII in VIII as a solvent in view of the possibility, unlikely though it seemed, that the VII might be sufficiently acidic so that distillation of ethanol (15 hr., 140°) would force the formation of V. No X was formed and the VII was recovered (78%). When the VII was heated (19 hr., 120°) in VIII with 3.6 molar equiv. of sodamide, gas evolution before heating indicated metalation, but a little VII was the only isolable product (the excess sodamide considered necessary may have cleaved any X formed).[25]

Reactions leading to the tris-sulfone X from the reagent V and ester VIII probably are numerous and complex. Nevertheless, enough can be said
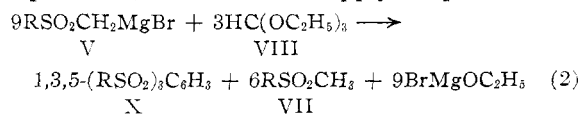
about them to clarify the over-all result.[26] At least four paths require consideration:

Path A.—The Grignard reagent V and ester VIII give the acetal XII. This reaction is plausible, because α-(p-tolylsulfonyl)-isopropylmagnesium bromide reacted with VIII to permit isolation of α-(p-tolylsulfonyl)-isobutyraldehyde as its 2,4-dinitrophenylhydrazone in 60% yield and of the acetal itself in about 29% yield; cyclization of course was precluded.

Action of V as a base then converts the acetal XII to XIII, as shown in the chart. Next, XIII loses bromomagnesium ethoxide, yielding XIV.[27] The isolation of a compound like IX mentioned above confirms the probable importance of XIV in the normal cyclization; the conversion of XIV to IX instead of to the tris-sulfone X can be attributed to eliminations adverse to cyclization. The Grignard reagent XIII or V then adds to the vinyl sulfone XIV in a reaction analogous to that of a typical Grignard reagent with an α,β-unsaturated sulfone.[29] Further reactions of metalation, elimination and addition, like those mentioned, then would eventuate in X.

If path A is correct, treatment of the acetal XII with ethylmagnesium bromide should effect formation of X. This prediction was realized, and path A thus supported. The yield of X was only 6%, however, probably because of competing reactions (e.g., addition of ethylmagnesium bromide to unsaturated intermediates).

The stoichiometry of path A is embodied in equation 2, and also would apply for paths B or C.

$$9RSO_2CH_2MgBr + 3HC(OC_2H_5)_3 \longrightarrow$$
$$\underset{V}{} \qquad \underset{VIII}{}$$

$$1,3,5\text{-}(RSO_2)_3C_6H_3 + 6RSO_2CH_3 + 9BrMgOC_2H_5 \quad (2)$$
$$\underset{X}{} \qquad \underset{VII}{}$$

Path B.—Direct alkylation involving three moles of XIII would give triethoxyhexahydro X which could become aromatized by metalation and elimination. Since acetals react poorly with Grignard reagents,[17] path B is less probable.

Path C.—The acetal XII forms slowly and cyclizes by elimination of ethanol. The synthesis of X from XII by heating shows that path C is possible but also suggests that it proceeds too slowly to be important.

Path D.—If the Grignard reagent V and ester VIII formed the acetal XII rapidly, so that metalation of XII was obviated, the alcohol evolved in subsequent cyclization of the XII would not decompose the V, as it does according to path C. Nine proportions of V would yield *three* of the tris-sulfone X and the sulfone VII would not be recoverable. Both the slow cyclization of XII and the considerable recovery of VII indicate the improbability of path D.

(23) R. L. Shriner, H. C. Struck and W. J. Jorison, THIS JOURNAL, **52**, 2060 (1930).

(24) C. R. Hauser and T. M. Harris, *ibid.*, **79**, 6342 (1957).

(25) W. Bradley, *J. Chem. Soc.*, 458 (1938).

(26) We are indebted for helpful discussion of this and related matters to Professors Erling Grovenstein of the Georgia Institute of Technology and Donald E. Pearson of Vanderbilt University.

(27) It is possible that XIII has no finite existence and that XII goes to XIV directly, simply by a base-induced elimination of ethoxide ion. β Haloethers, with magnesium, yield olefins along with a magnesium alkoxide and halide, apparently without intervention of an actual Grignard reagent.[28]

(28) Leading references are given by L. Crombie and S. H. Harper, *J. Chem. Soc.*, 1707, 1714 (1950).

(29) E. P. Kohler and H. Potter, THIS JOURNAL, **57**, 1316 (1935).

Although numerous variations of these paths are obvious, we feel that path A is a major one and path C perhaps a minor one.

The reaction of V with ethyl orthoacetate gave only a trace of monoalkylation product and no indication of an aromatic tris-sulfone (recovery of VII, 85%).

Analogy with typical Grignard reagents[30] suggested that treatment of methoxyamine with V should result in an α-aminosulfone. An α-aminosulfone, however, apparently decomposes in water to an aldehyde and the ammonium salt of a sulfinic acid.[31] This sequence thus had interesting possibilities as a potential degradation for alkyl sulfones.

$$RSO_2CHR'MgX + CH_3ONH_2 \longrightarrow$$

$$RSO_2CHR'NH_2 \xrightarrow{H_2O, H^+} RSO_2H + R'CHO + NH_4^+$$
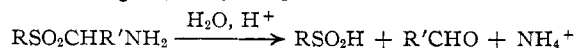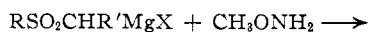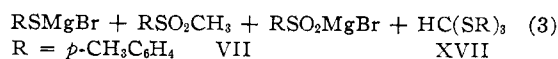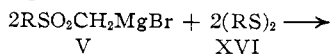
The reaction of methoxyamine with excess V resulted in p-toluenesulfinic acid (XV) in 52% yield, but in a formaldehyde derivative in the maximum yield of only 1%. The Grignard reagent of n-propyl sulfone resulted in 1-propanesulfinic acid (as a derivative) in only 6% yield and in no propionaldehyde.

α-(p-Tolylsulfonyl)-benzylmagnesium bromide gave benzaldehyde in 7% yield (as a derivative) and the acid XV in 53% yield. It was conceivable, however, that alkylation by methoxyamine actually was not involved in the formation of this aldehyde and acid; for example, benzhydryl phenyl sulfone is largely destroyed simply upon brief heating with ethylmagnesium bromide.[3c] To eliminate this possibility, the experiment was repeated, but without methoxyamine. No benzaldehyde was isolated, and the yield of the acid XV was reduced to 19%; it is noteworthy that benzyl p-tolyl sulfone was recovered in 56% yield, showing that its Grignard reagent is more stable than that of benzhydryl phenyl sulfone.

Although the yields of cleavage products were disappointingly low, perhaps because of side reactions of the products[31] or complications from disubstitution, they do signify the occurrence of alkylation in the reactions with methoxyamine.

Organic disulfides and Grignard reagents yield sulfides.[32] Surprisingly, p-tolyl disulfide (XVI) with V gave tris-(p-tolyl)-trithioorthoformate (XVII). Recovery of the sulfone VII (39%) suggests that disubstitution of the V first occurred, yielding p-tolylsulfonylformaldehyde di-p-tolyl mercaptal, and that nucleophilic displacement of p-toluenesulfinate ion then resulted in the XVII.

The reaction can be represented reasonably by equation 3. Based on this equation, the yields

$$2RSO_2CH_2MgBr + 2(RS)_2 \longrightarrow$$
$$\quad V \qquad\qquad XVI$$
$$RSMgBr + RSO_2CH_3 + RSO_2MgBr + HC(SR)_3 \quad (3)$$
$$R = p\text{-}CH_3C_6H_4 \quad VII \qquad\qquad XVII$$

were 15% of XVII and 78% of the sulfone VII. The necessary function of the Grignard reagent was demonstrated by the lack of reaction between VII and XVI alone.

(30) Reference 18, p. 1236.
(31) *Cf.* H. Böhme and D. Morf, *Chem. Ber.*, **90**, 446 (1957).
(32) Reference 18, p. 1301.

The analogous lithium compound VI gave XVII in 54% yield, strongly implying that the reaction is heterolytic. If so, the fact that the lithium derivative VI gave a higher yield of the XVII than did the magnesium compound V, but a lower yield of n-heptyl p-tolyl sulfone as mentioned above, can be attributed to its greater nucleophilicity and consequent greater ability to undergo disubstitution. Even so, the lithium compound VI evidently resembles the Grignard reagent V in being less nucleophilic than is usual for its class, because conditions comparable to those satisfactory for the reaction of phenyllithium with disulfides[33] gave XVII in only 5% yield (recovery of XVI, 80%).

A point of incidental but noteworthy interest developed during study of the reactions of V and XVI in various solvents. The Grignard reagent V was found to yield a clear solution when heated with tetrahydrofuran, although phenylsulfonylmethylmagnesium iodide had proved to be insoluble in common solvents for Grignard reagents.[3b] This observation suggested the desirability of testing tetrahydrofuran as a solvent for an addition reaction which might be improved by its use. Addition of methylsulfonylmethylmagnesium bromide to benzaldehyde gave 33% of adduct in benzene–ether,[3c] and 65% in anisole.[34] When the earlier procedure[3c] was repeated except for the use of tetrahydrofuran instead of benzene, however, the Grignard reagent did not dissolve. Addition of benzaldehyde resulted in solution, but only 16% of methyl β-phenyl-β-hydroxyethyl sulfone could be isolated. Presumably the greater basicity of tetrahydrofuran makes it a better solvent for Grignard reagents of sulfones but also inhibits their addition reactions.[35]

The question was raised at the outset as to whether reagents like II more nearly resemble typical carbanion salts or typical Grignard reagents. It now seems that none of the reactions which have been described above are better understood by regarding these reagents as carbanion salts.

The results can be explained quite adequately by analogy with typical Grignard reagents; the vigor of conditions, and failure of certain reactions even so, suggests however that reagents like II are less nucleophilic. Indeed, all reactions encountered thus far[3] seem consistent with the behavior of substances like II as weakly nucleophilic Grignard reagents.

Such behavior can be rationalized reasonably well. The C–Mg bond of compounds like II must be more nearly like the covalent bond of Grignard reagents than the electrovalent bond of carbanion salts, even though its ionic character may exceed that of typical Grignard reagents. Hence, the electrons should be less readily available for nucleophilic action than those of corresponding alkali salts. In alkylation and related reactions, therefore, a magnesium derivative like II should lack the desirable nucleophilic character of the corresponding carbanion salt. In addition reactions where its

(33) A. Schönberg, A. Stephenson, H. Kaltschmitt, E. Petersen and H. Schulten, *Ber.*, **66**, 237 (1933).
(34) W. E. Truce and K. R. Buser, THIS JOURNAL, **76**, 3577 (1954).
(35) *Cf.* R. N. Lewis and J. R. Wright, *ibid.*, **74**, 1253 (1952).

weak nucleophilicity suffices, on the other hand, the magnesium derivative reasonably can be expected to serve better, at least than the sodium salt, because of the probable ability of magnesium to reduce reversion of adducts through its coordinating power.[36]

As Grignard reagents, compounds like I reasonably could be expected to be less nucleophilic than is usual for the class if the inductive effect of the sulfonyl group dominated and resonance effects were minor. In such a situation, the electrons of the C–Mg bond should be quite localized and of a low order of polarizability. The relative nucleophilic characters of II and typical Grignard reagents thus would resemble those of chloride and iodide ions. The aura of negative charge on the oxygens of the sulfonyl group, and perhaps the size itself of the sulfonyl group, also may reduce the nucleophilic capability of substances like II.[37]

In summary, the properties of Grignard reagents of sulfones reported here and previously[3] seem best understood by regarding these reagents as conventional Grignard reagents which are atypical chiefly in that: (1) The inductive effect of the sulfonyl group effects significantly lower availability of the electrons of the C–Mg bond. (2) Metalation of initial products may result in further reactions, if species are at hand which are sufficiently susceptible to nucleophilic attack by the metalated product.

Acknowledgment.—We are indebted to the Office of Ordnance Research, U. S. Army, for support of this research.

Experimental[38]

Reaction of Phenylsulfonylmethylmagnesium. Bromide (IV) and Iodine.—In a procedure resembling one used with bromine,[10] iodine (7.61 g.) in warm benzene (30 ml.) was added in 0.3 hr. at 2–10° to the IV[2d] from 5.00 g. of methyl phenyl sulfone (XVIII). The mixture was stirred (3 hr., 25°) and poured into aqueous sodium bisulfite. The washed benzene layer gave 7.33 g. of sirup; 4.09 g. in 7.2 ml. of ethanol was treated with carbon and adjusted at 25° to incipient turbidity with water (0.72 ml.). The solution was seeded, cooled slowly, and then chilled overnight. Recrystallization from 2-propanol (8 ml.) gave 2.01 g. (43%) of iodomethyl phenyl sulfone of constant m.p. and mixture[3b] m.p. 58–59.5°.

Reaction of IV with Cupric and Cobaltous Chloride.—The IV was prepared as usual[3d] from 5.00 g. of XVIII but no benzene was added prior to reflux. Ether (30 ml.) was added, then 5.54 g. of anhydrous cupric chloride at 2°. The mixture was stirred at 25° (2 hr.), then under reflux (2.5 hr.); it then was acidified. Benzene extraction gave 3.7 g. of semi-solid which was rubbed with 2-propanol and thrice recrystallized; yield of 1,2-bis-(phenylsulfonyl)-ethane, 0.23 g. (5%), m.p. and mixture[3b] m.p. 182.5–184.5°. A reflux period of 17 hr. gave the same result.

Essentially the same experiment with 0.52 g. of anhydrous cobaltous chloride and 4.40 g. of ethyl bromide instead of cupric chloride (4.5 hr. of reflux) resulted in recovery of 87% of the XVIII and no indication of 1,2-bis-(phenylsulfonyl)-ethane.

Reactions of Alkyl Halides.[39] (a) **Benzyl Chloride.[40]**—Benzyl chloride (12.7 g.) in benzene (20 ml.) was added to

(36) C. R. Hauser and W. H. Puterbaugh, THIS JOURNAL, **75**, 4756 (1953).

(37) The relations of factors like those discussed to nucleophilic reactivity are considered by C. G. Swain and C. B. Scott, *ibid.*, **75**, 141 (1953).

(38) General procedures are summarized in footnote 19 of ref. 3a.

(39) Redistilled before use.

(40) We are indebted to Mr. E. A. Blair and D. J. W. McFarland for this experiment.

the IV[3d] from 7.00 g. of XVIII and 47 mmoles of ethylmagnesium bromide. The mixture then was stirred at 75° for 28 hr. Acidification and extraction gave oil which upon distillation yielded material (5 g.) of b.p. 140–182° (1 mm.). Seeding with phenyl 2-phenylethyl sulfone (XIX) and trituration with cold ethanol gave 3.50 g. (32%) of XIX, m.p. 47–55°. Recrystallization from aqueous ethanol left 3.16 g. (29%), m.p. and mixture[3d] m.p. 53–57.5°. Further recrystallization improved the purity only slowly, but an identical reaction (except for presence of 0.3 g. of magnesium) gave XIX with m.p. and mixture m.p. 56–57.5° (27%).

(b) **Benzhydryl Chloride.**—Benzhydryl chloride (36 g.) was heated under reflux with the IV[3d] from 13.80 g. of XVIII and 98.7 mmoles of ethylmagnesium bromide for 72 hr. Acidification (aqueous ammonium chloride) and extraction gave 50.7 g. of oily solid which, shaken with hexane (100 ml.), left a solid. Recrystallization (acetic acid) gave 2.95 g. (10%) of phenyl 2,2-diphenylethyl sulfone, m.p. 177–179°, 6%, m.p. 180.5–181.5°. Similar material, sublimed (*ca.* 150–190°, 2 mm.) and recrystallized, had a constant m.p. of 180.5–181.5°.

Anal. Calcd. for $C_{20}H_{18}O_2S$: C, 74.50; H, 5.63; S, 9.94. Found: C, 74.57; H, 5.61; S, 10.08.

A reflux time of 28 hr. resulted in recovery of 81% of the benzhydryl chloride and 60% of the XVIII and in 4% of phenyl 2,2-diphenylethyl sulfone (m.p. 180.5–181.5°); there was no indication of other water-insoluble sulfur-containing substances.

(c) **n-Hexyl Iodide.**—The same molar proportions of reactants and solvents were used as in (a). The V[3a] from 23.8 g. of methyl p-tolyl sulfone (VII) was heated with the iodide at 78° for 60 hr. Acidification and extraction gave solid (24.4 g.) which was crystallized and distilled repeatedly in an effort to isolate n-heptyl p-tolyl sulfone (XX). A total of 18.97 g. (80%) of VII was recovered. The only other material isolated was 1.1 g. of oil from which no XX could be obtained.

(d) **t-Butyl Chloride.**—The V[3a] from 30.00 g. of VII was heated with 32.6 g. of t-butyl chloride under reflux for 71 hr. Acidification (aqueous ammonium chloride) and extraction yielded 29.90 g. (100%) of VII, m.p. 85–87°. Chromatography then gave 91% of VII (m.p. and mixture m.p. 85–87.5°), 2% of VII (m.p. and mixture m.p. 79–86°) and only 0.1 g. of unidentified oil.

Reactions of n-Hexyl p-Toluenesulfonate (XXI).—The V[3a] from 17.02 g. of VII was alkylated essentially as previously described[3b] with 67.3 g. of XXI (washed with aqueous sodium bicarbonate and distilled from potassium carbonate). The residue (45 g.) from the benzene extract was heated with 66 g. of sodium iodide in acetone for 23 hr. to destroy excess XXI. Removal of acetone and addition of water was followed by extraction with benzene. The extract was washed with aqueous sodium bisulfite to remove iodine. It gave 22 g. of semi-solid which upon distillation yielded material of b.p. 25–115° (0.03 mm.) and of 115–133° (0.07 mm.). Treatment of both fractions with pentane left insoluble VII amounting after recrystallization to 3.70 g. (22%), m.p. and mixture m.p. 87–88°. The combined pentane solutions upon evaporation gave n-heptyl p-tolyl sulfone (XX) which, thrice recrystallized from iso-octane, amounted to 8.55 g. (34%), m.p. 47.5–50°. Further recrystallization gave XX with constant m.p. 49–50°.

Anal. Calcd. for $C_{14}H_{22}O_2S$: C, 66.10; H, 8.72. Found: C, 65.82; H, 8.76.

Alkylation of V in anisole (from 8.51 g. of VII and 62.5 mmoles of ethereal ethylmagnesium bromide as described later) with XXI (33.4 g.) resulted in XX in 22% yield, m.p. and mixture m.p. 48–49.5°, and VII in 32% recovery. This result suggests that dialkylation occurred to a greater extent than in benzene–ether.

p-Tolylsulfonylmethyllithium (VI), prepared in benzene by metalating 17.02 g. of VII with 125 mmoles of n-butyllithium, upon alkylation as before with 35 g. of XXI gave crude XX (m.p. and mixture m.p. 44–49°) in 11% yield and VII in 50% recovery.

Reactions of Ethyl Orthoformate (VIII).[39] (a) **With V under Conventional Conditions.**—Essentially according to Smith and Nichols,[41] 29.64 g. of VIII was added to the V prepared[3a] in ether as the sole solvent from 30.00 g. of VII

(41) L. I. Smith and J. Nichols, *J. Org. Chem.*, **6**, 489 (1941).

and 190 mmoles of ethylmagnesium bromide. The mixture was heated under reflux for 5 hr. Removal of ether gave no indication of the usually vigorous reaction.[41] Acidification (aqueous ammonium chloride), extraction, concentration and chromatography returned 90% of the VII, m.p. and mixture m.p. 81–84°; the only other material isolated was amorphous.

As a control experiment, the reaction was repeated without the sulfone VII and with phenylmagnesium bromide instead of ethylmagnesium bromide. Distillation gave 17.80 g. (52%) of benzaldehyde diethyl acetal, b.p. 72–77° (4 mm.), n^{25}D 1.4755–1.4761.

(b) **With V in Benzene-Ether.**—The V[3a] from 14.00 g. of VII was heated under reflux with 2.7 g. of VIII in a mixture of 125 ml. of benzene and 50 ml. of ether (25 hr.). Acidification and extraction gave solid (14.1 g.) which was washed with ether. The insoluble portion (IX, 0.97 g.) resisted purification. After several recrystallizations, the m.p. remained 155–174°.

Anal. Calcd. for $C_{26}H_{26}O_6S_3$: C, 58.84; H, 4.94; S, 18.12. Found: C, 58.75; H, 4.95; S, 18.12.

The IX decolorized potassium permanganate in acetone and slowly absorbed two molar equiv. of hydrogen (but no crystalline reduction product could be isolated).

The ether wash gave 8.07 g. (58%) of VII, m.p. and mixture m.p. 86.5–87.5°, and brown glass (3.8 g.) which formed no sulfur-containing 2,4-dinitrophenylhydrazone.

Reaction of V (58 mmoles) and VIII (100 mmoles) in refluxing 1:5 ether–benzene (8 hr.) gave 16% of X, m.p. 256–260° (uncor.).

(c) **With V under Forcing Conditions. Preparation of X.**—The V (prepared[3a] from 30.00 g. of VII and 197 mmoles of ethylmagnesium bromide using 200 ml. of benzene) was heated. As ether–benzene distilled, it was replaced by adding 200 ml. of VIII. The distillate obtained during heating from 95–125° evolved gas with sodium (ethyl bromide, ethyl formate?). The temperature of the liquid rose to about 125° during *ca.* 1.5 hr. and then was kept at 125–130° for 18 hr. Meanwhile, distillate was removed under anhydrous conditions; redistillation gave 20.7 g. of liquid, b.p. 40–75°, which contained 16.4% bromine (21% of that in the Grignard reagent) presumably as ethyl bromide; another fraction, b.p. 75–89° (9.1 g.), evolved gas strongly with ethylmagnesium bromide (presence of ethanol?).

After the 18-hr. period, the mixture was taken to dryness under reduced pressure and acidified with hydrochloric acid (acidification with aqueous ammonium chloride or ethanol instead gave similar results). Insoluble material was separated and washed with hot ethanol. There remained 8.53 g. (81%) of 1,3,5-tris-(p-tolylsulfonyl)-benzene (X), m.p. 256–260°, which after recrystallization (chloroform) left 4.88 g. (46%; 61% in a similar experiment), m.p. 263.5–264°. Similarly prepared material in acetone, which had been recrystallized to a constant m.p. of 263–264°, did not decolorize one drop of 2% aqueous permanganate in 30 minutes.

Anal. Calcd. for $C_{27}H_{24}O_6S_3$: C, 59.98; H, 4.48; S, 17.79; mol. wt., 541. Found: C, 59.89; H, 4.52; S, 17.75; mol. wt. (Rast), 506.

The ethanol wash gave white solid which was placed atop a one-inch column of alumina in a Soxhlet thimble. Extraction with hexane slowly removed 15.31 g. (51%) of VII, m.p. and mixture m.p. 86–87°.

When only the VII (15 g.) and VIII (100 ml.) were heated at 110–120° for 19 hr., they were recovered in yields of 100 and 96%, respectively.

(d) **With α-(p-Tolylsulfonyl)-isopropylmagnesium Bromide.**—The benzene–ether containing the α-(p-tolylsulfonyl)-isopropylmagnesium bromide[3c] from 17.50 g. of isopropyl p-tolyl sulfone was distilled while 100 ml. of VIII was added. The mixture was heated at 100–110° for 19 hr. and then was acidified with saturated aqueous ammonium chloride (200 ml.). Benzene extraction gave 23.46 g. of yellow oil (XXII).

The XXII (4.00 g.) was heated with 2.64 g. of 2,4-dinitrophenylhydrazine in 55 ml. each of 12 N hydrochloric acid and ethanol for 20 hr. under reflux. Insoluble material then was washed well with hot 3 N hydrochloric acid; yield of α-(p-tolylsulfonyl)-isobutyraldehyde 2,4-dinitrophenylhydrazone, 3.68 g. (60% from the isopropyl sulfone), m.p. 200.5–201.5° unchanged by recrystallization (ethanol, nitromethane and ethyl acetate).

Anal. Calcd. for $C_{17}H_{18}O_6N_4S$: C, 50.24; H, 4.46; N, 13.79. Found: C, 50.21; H, 4.52; N, 14.21.

Distillation of 13.22 g. of the XXII gave 7.96 g. (53%) of crude α-(p-tolylsulfonyl)-isobutyraldehyde diethyl acetal (XXIII), b.p. 130–155° (1–2 mm.), n^{25}D 1.5105–1.5151. Material of b.p. 120–130° (1–2 mm.), recrystallized from hexane, proved to be recovered isopropyl p-tolyl sulfone (1.40 g., 14%). The crude XXIII, redistilled through a 25-cm. Vigreux column having a total-condensation variable take-off head, gave 4.40 g. (29%) of XXIII, b.p. 152–160° (1 mm.), n^{25}D 1.5098–1.5137 (the m.p. of fractions lay in the range of 47–56°). Although seeding of the XXII gave solid which after recrystallization (heptane) had m.p. 57–58°, recrystallization was difficult (low yield, extreme sensitivity to hydrolysis), and a distillation fraction therefore was analyzed directly (n^{25}D 1.5100, m.p. 50–56°).

Anal. Calcd. for $C_{15}H_{24}O_4S$: C, 59.97; H, 8.05. Found: C, 59.92; H, 7.68.

Oxidation of X.—Chromium trioxide (4.27 g.) was added during 1 hr. to a mixture of 2.80 g. of X, 24 ml. each of glacial acetic acid and acetic anhydride, and 4 ml. of concentrated sulfuric acid. Stirring was continued at 30° for 21 hr. and the mixture then poured onto ice. Solid was washed and dissolved in hot 10% aqueous sodium carbonate. Filtration and acidification gave 2.00 g. (61%) of tris-(p-carboxyphenylsulfonyl)-benzene (XI), m.p. 401–402° (dec., uncor.). The XI, sparingly soluble, could not be recrystallized well and hence was reprecipitated from 1% aqueous sodium carbonate; m.p. 397–398° (dec., cor. with potassium dichromate as a m.p. standard; sample immersed at 380° and heated at 1–2°/min.).

Anal. Calcd. for $C_{27}H_{18}O_{12}S_3$: C, 51.42; H, 2.88; S, 15.26; neut. equiv., 210. Found: C, 51.03; H, 3.22; S, 14.91; neut. equiv., 214.

Dimethyl p-Tolylsulfonylacetal (XII).—A mixture of 40.6 g. of sodium p-toluenesulfinate, 5.0 g. of anhydrous sodium carbonate, 42.0 g. of dimethyl chloroacetal[42] and 100 ml. of dimethylformamide was heated at 125° for 16 hr. and then was poured into 600 ml. of water. Benzene extraction gave 22.3 g. (40%) of XII, m.p. 42.5–46°. Recrystallization gave XII in 30% yield, m.p. 50–51°. Further recrystallization (hexane, cyclohexane) gave XII with the constant m.p. 49.5–50°; strong absorption at 1075, 1090 cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{16}O_4S$: C, 54.08; H, 6.60; S, 13.13. Found: C, 54.53; H, 6.67; S, 13.17.

Use of methanol for the reaction resulted in no XII (24-hr. reflux period).

Conversion of Acetal XII to Tris-sulfone X. (a) By Heating.—The XII (1.00 g.) was heated under nitrogen at 110–120° for 73 hr.; solid appeared after 2 days and then increased rather rapidly in amount. Digestion of the mixture with hot ethanol (25 ml.) left 0.19 g. (26%) of insoluble X, m.p. 255–262°. Recrystallization gave 0.11 g. (15%) of X, m.p. and mixture m.p. 263–264°.

(b) **With Ethylmagnesium Bromide.**—Ethereal ethylmagnesium bromide (86 mmoles) was added to 10.00 g. of XII in 50 ml. of p-xylene. p-Xylene (50 ml.) then was added and distillate removed until the temperature of the liquid rose to 120°. The mixture was stirred and heated at 120–130° for 19 hr.; solvent then was removed under reduced pressure. Acidification gave oil which, taken up in ethanol, deposited 0.42 g. (6%) of X, m.p. and mixture m.p. 259–262°.

Reaction of Ethyl Orthoacetate with V.—The V[3a] from 15.00 g. of VII was heated with ethyl orthoacetate (100 ml.) as in (c) of the reactions involving the orthoformate VIII. Evaporation, followed by digestion with hot ethanol left only an acid-soluble residue which presumably contained no material resembling X. The alcohol-soluble material was treated with acid and then extracted with benzene. The benzene, washed with aqueous alkali, contained 12.7 g. (85%) of VII (purified, m.p. and mixture m.p. 86–87°). The alkaline wash, acidified, gave oil which could be converted to only 0.20 g. (1%) of the 2,4-dinitrophenylhydrazone of p-tolylsulfonylacetone. This hydrazone, recrystallized, had constant m.p. and mixture[43] m.p. 201.5–203.5°.

(42) Kindly provided by General Aniline and Film Corporation, 247 Park Ave., New York 17, N. Y.

(43) Authentic sample prepared from known p-tolylsulfonylacetone.[9]

Anal. Calcd. for $C_{16}H_{16}N_4O_6S$: C, 48.97; H, 4.11. Found: C, 49.11; H, 4.11.

Reactions of Methoxyamine (XXIV).—Potassium hydroxylamine disulfonate[44] was converted to methoxyamine hydrochloride[45] and thence to XXIV[46] (b.p. 47–48°).

(a) **With V.**—The V was prepared in anisole by a procedure similar to one used with methyl sulfone.[34] Ethereal ethylmagnesium bromide (125 mmoles) was added to 17.02 g. of VII in 65 ml. of anisole and ether was removed while heating for 23 minutes at 80° (the apparent desirability of this period is understandable if insoluble polymeric aggregates[3b] of the V are slowly being solvated and disrupted by anisole); amorphous solid then had become emulsified and the mixture gave a strong Tyndall effect.

The XXIV (1.55 g.) in anisole (3 ml.) was added. The mixture was stirred (3 hr., 25°, and 2 hr., 40°) and then acidified. A benzene extract was washed with aqueous alkali. The alkaline wash, acidified, gave 2.69 g. (52%) of *p*-toluenesulfinic acid (XV), m.p. and mixture m.p. 75–82°; the XV from another experiment was identified as *p*-tolyl 2,4-dinitrophenyl sulfone (XXV); 26% over-all, m.p. 188–189.5°. The benzene extract yielded VII (recovery, recrystallized, 8.01 g., 47%, m.p. and mixture m.p. 84–87°).

The aqueous layer, adjusted to *p*H 4, gave[47] only 0.02 g. of the dimedon derivative of formaldehyde, m.p. and mixture m.p. 185–191°.

No improvement was effected by variations in time or temperature, use of ether or benzene as solvents, or reduction in the proportion of ethylmagnesium bromide. The maximum yield of dimedon derivative was 1%. A typical reaction mixture acidified in the presence of 2,4-dinitrophenylhydrazine gave no formaldehyde derivative.

(b) **With α-(*p*-Tolylsulfonyl)-benzylmagnesium Bromide (XXVI).**—An anisole dispersion of XXVI was prepared from 37.0 g. of benzyl *p*-tolyl sulfone (XXVII, m.p. 146.5–147°) (as in (a), but with only 4 minutes of heating at 25–70°) and was treated with XXIV (1.55 g.) essentially according to (a). Solvent then was distilled at 30° and the mixture acidified and stirred. Neutralization and steam distillation gave benzaldehyde which as the recrystallized 2,4-dinitrophenylhydrazone (3:2 ethyl acetate–ethanol) amounted to 0.69 g. (7%), m.p. and mixture m.p. 240–241°.

Filtration of the undistilled residue gave XXVII (recrystallized, 46% recovery, m.p. and mixture m.p. 138–146°). The filtrate gave XV in 53% yield, m.p. and mixture m.p. 76–78°, part of which was converted to XXV, m.p. and mixture m.p. 185–188°.

Preparation of the XXVI by heating to 80° during 15 minutes and at 80° for 3 minutes, followed by reaction with XXIV as before, resulted in XV in 71% yield, the benzaldehyde derivative in 10% yield and the recovery of XXVII

in 47% yield. Repetition of this experiment without XXIV gave a 60% recovery of XXVII and no benzaldehyde.

(c) **With α-(*n*-Propylsulfonyl)-*n*-propylmagnesium Bromide.**—This Grignard reagent was prepared from 30.1 g. of freshly distilled *n*-propyl sulfone as described for V under (a). Addition of 3.15 g. of XXIV and stirring (16 hr., 25°; 2.5 hr., 80°) was followed by attempted isolation of products as described under (a). Steam distillation gave presumed *n*-propyl sulfone (56%) and no aldehyde. The residue contained the sulfinic acid, isolated as *n*-propyl 2,4-dinitrophenyl sulfone in 6% yield, m.p. 126–128°.

Reactions of *p*-Tolyl Disulfide (XVI). (a) **With VI.**—The sulfone VII (4.25 g.) was metalated[34] in 97 ml. of benzene with 25 mmoles of *n*-butyllithium (0.4 *N*, in benzene). After addition of 5.54 g. of the XVI in 35 ml. of benzene, the mixture was stirred at 80° for 20 hr. and then acidified. A benzene extract was washed with aqueous alkali and then with water. The alkaline wash after extraction with ether and acidification gave 1.94 g. of base-soluble material, which contained *p*-thiocresol (identified as 0.61 g. of XVI by melting point and mixture m.p. 43–46°). The benzene extract was evaporated and the residue triturated with cold hexane. Undissolved material then was digested with boiling ethanol which, after decantation and cooling, deposited tris-(*p*-tolyl)-trithioörthoformate (XVII); after further recrystallization, the XVII amounted to 1.32 g., m.p. 105.5–108°. With 0.99 g. more of XVII (m.p. *ca.* 100–107°) obtained by digesting further with 2-propanol, the yield of XVII was 54%. Evaporation of the ethanol left 1.70 g. (40% recovery) of VII, m.p. and mixture m.p. 84.5–87°.

An identical sample of XVII, prepared from XVI and V in anisole and recrystallized, had a constant m.p. of 109.5–110.5°.

Anal. Calcd. for $C_{22}H_{22}S_3$: C, 69.06; H, 5.80; S, 25.14; mol. wt., 383. Found: C, 69.02; H, 5.93; S, 25.14; mol. wt. (cryoscopic in benzene), 333. After analysis suggested the identity of the XVII, an authentic sample was prepared,[48] m.p. 109.5–110°, which was identical in mixture m.p. and infrared spectrum.

An identical reaction, but effected at 35° during 2 hr. (*cf.* ref. 33) gave XVII in only 5% yield (recoveries of XVI and VII, 80 and 86%, respectively).

(b) **With V.**—When XVI (9.98 g.) was heated at 85–90° for 20 hr. in an anisole suspension of V (obtained by adding 4.25 g. of VII to ethylmagnesium bromide prepared[35] directly in anisole), the XVII resulted in 15% yield (m.p. 105–109°) and the VII in 39% recovery.

The yields of XVII obtained in other solvents with XVI and V (V prepared as usual[3a] but with the solvent in question substituted for benzene), after distilling ether, replacing with the particular solvent, and heating for *ca.* 20 hr. under reflux, were: tetrahydrofuran, 12%; toluene, 11%; benzene, 1%. The recoveries of VII were 37–47%. Repetition of the reaction in toluene, but with omission of ethylmagnesium bromide, resulted in no XVII and in recoveries of the VII and XVI amounting to 77 and 96%, respectively.

NASHVILLE 5, TENN.

(44) G. K. Rollefson and C. F. Oldershaw, THIS JOURNAL, **54**, 977 (1932).

(45) C. H. Andrewes, H. King and J. Walker, *Proc. Roy. Soc. (London)*, **B133**, 43 (1946).

(46) W. Traube, H. Ohlendorf and H. Zander, *Ber.*, **53**, 1485 (1920).

(47) J. H. Yoe and L. C. Reid, *Ind. Eng. Chem., Anal. Ed.*, **13**, 238 (1941).

(48) F. Arndt, *Ann.*, **384**, 338 (1911).