REACTIONS OF ALKANESULPHONIC ACID DERIVATIVES WITH ORGANOALKALI METAL COMPOUNDS

FORMATION AND REACTIVITY OF α-SULPHONYLCARBANIONS

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Abstract—The effects of solvents, metals and structural variation of the substrates on the reactions between alkanesulphonic acid derivatives with organoalkali metal reagents have been examined and the formation and reactivity of α-sulphonylcarbanions are discussed. The formation of 4-membered cyclic sulphones from a sulphonyl fluoride and the Claisen ester condensation type reaction in a sulphonic ester, which have been observed for the first time, are described.

RECENTLY reactions of carbanions stabilized by sulphur containing functions have received much attention from both mechanistic and synthetic points of view. Methyl-

sulphinyl carbanion ($CH_3SO\overset{-}{C}H_2$) or ylides such as dimethylsulphonium methylide

($(CH_3)_2\overset{+}{S}—\overset{-}{C}H_2$), dimethyloxosulphonium methylide ($(CH_3)_2\overset{+}{\underset{\overset{\|}{O}}{S}}—\overset{-}{C}H_2$) have been

widely utilized as reactive and useful species in organic syntheses.[1,2] Ramberg–Bäcklund rearrangement reactions which proceed through α-sulphonyl-carbanions as transient intermediates have recently been studied in detail.[3a–d] Metalation reactions of many sulphone compounds to form stable carbanion intermediates in a solution are also well-known, and have been the subject of much interest with reference to the site of metalation.[4]
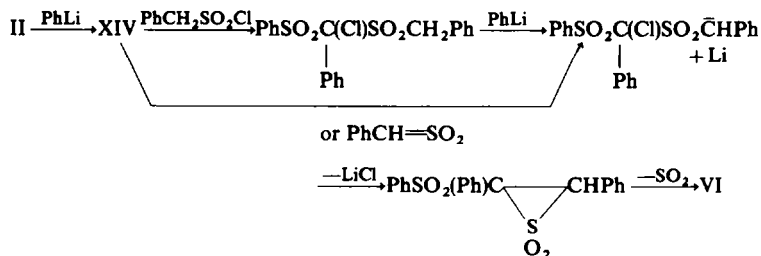
The formation and reactivity of α-sulfonylcarbanion intermediates in a new reaction system has led to the reactions of alkanesulfonic acid derivatives with organoalkali metal reagents, a study which does not appear to have been recorded in the literature.*

$$RCH_2SO_2X + C_6H_5M \rightarrow$$

$$X = Cl, F, OC_6H_5, N(CH_3)_2; M = Li, MgBr.$$
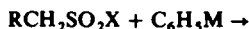
Since alkanesulfonic acid derivatives contain both acidic α-hydrogens activated by the sulphone group and functional groups reactive toward organoalkali metal reagents, it is anticipated that complex reactions through the intermediacy of α-sulfonylcarbanions occur between them.

The purpose of the investigation was to examine the above new reactions syste-

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* Reactions of some arylsulfonic acid derivatives with a Grignard reagent have been known for a long time.[5]

matically covering the effects of solvents, metals and structural variation of the substrates upon the reactions, and to gain possible information on the formation and reactivity of α-sulphonylcarbanions formed in the system. In an extension of our previously reported work on the reactions of benzylsulphonyl halide with phenyllithium,[6] this paper deals with the influence of solvents, metals and structural variation of the substrates and some probable mechanistic features of the reactions.*

RESULTS AND DISCUSSION

As reported[6] the reaction of benzylsulphonyl chloride with phenyllithium yielded α-benzylsulphonyl-α-benzenesulphonyl toluene (I), α-chlorobenzyl phenyl sulphone (II), chlorobenzene (III), *trans*-stilbene (IV), α,α-dichlorobenzyl phenyl sulphone (V), 1,2-diphenylvinyl phenyl sulphone (VI), benzyl phenyl sulphone (VII), α-benzyl-sulphonyl-α'-benzenesulphonyl dibenzyl sulphone (VIII) and lithium benzyl-sulphinate (IX, main product). A similar reaction of benzylsulphonyl fluoride with phenyllithium afforded I as a major product, together with IV, VII and VIII. It has been suggested that at the initial step, the competing lithium–halogen interconversion to give lithium benzylsulphinate (IX) and chlorobenzene (III), the metalation reaction at the α-position to the sulphone group to form α-lithiobenzylsulphonyl halide (X), and S_N2 type reaction on sulphur by phenyllithium leading to the formation of benzyl phenyl sulphone (VII), took place simultaneously and that the product or the intermediate thus formed underwent further reactions to give the above products. Such α-sulphonyl carbanions as shown below have been postulated to be involved as transient intermediates in the reactions.

$$\underset{\text{X}}{\underset{+\,\text{Li}}{\text{Ph}\bar{\text{C}}\text{HSO}_2\text{X,}}} \quad \underset{\text{XII}}{\underset{+\,\text{Li}}{\text{Ph}\bar{\text{C}}\text{HSO}_2\text{Ph,}}} \quad \underset{\text{XIII}}{\underset{+\,\text{Li}}{\underset{\text{Ph}}{\overset{|}{\text{Ph}\bar{\text{C}}\text{HSO}_2\text{CHSO}_2\text{Ph,}}}}} \quad \underset{\text{XIV}}{\underset{+\,\text{Li}}{\text{Ph}\bar{\text{C}}(\text{Cl})\text{SO}_2\text{Ph}}}$$

It has been suggested that products I and II are formed through the intermediate XII, and that products VI and VIII are formed through intermediates XIV and XIII respectively.†

When benzylsulphonyl fluoride was subjected to the action of phenylmagnesium bromide, only benzyl phenyl sulphone was produced and the products such as the

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* Two preliminary communications of a portion of the work have been published.[7a, b]

† For the formation of VI, the following paths are also possible mechanisms in addition to the original proposal.[6]

$$\text{II} \xrightarrow{\text{PhLi}} \text{XIV} \xrightarrow{\text{PhCH}_2\text{SO}_2\text{Cl}} \underset{\text{Ph}}{\overset{|}{\text{PhSO}_2\text{C(Cl)SO}_2\text{CH}_2\text{Ph}}} \xrightarrow{\text{PhLi}} \underset{\text{Ph}}{\overset{|}{\text{PhSO}_2\text{C(Cl)SO}_2\bar{\text{C}}\text{HPh}}} \; +\text{Li}$$

or $\text{PhCH}{=}\text{SO}_2$

$$\xrightarrow{-\text{LiCl}} \text{PhSO}_2(\text{Ph})\text{C}\underset{\underset{\text{O}_2}{\overset{|}{\text{S}}}}{\diagdown \quad \diagup} \text{CHPh} \xrightarrow{-\text{SO}_2} \text{VI}$$

disulphone (I), the trisulphone (VIII) or *trans*-stilbene (IV) which formed on treatment with phenyllithium were not obtained. The results are listed in Table 1.
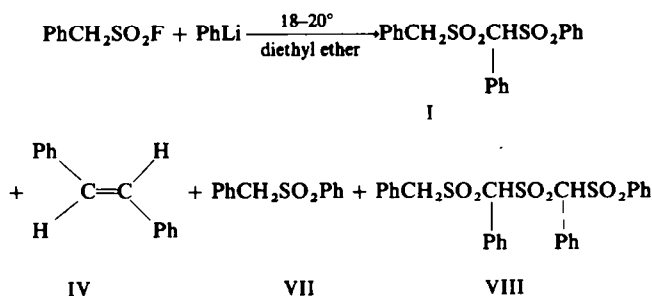
$$PhCH_2SO_2F + PhLi \xrightarrow[\text{diethyl ether}]{18-20°} PhCH_2SO_2CHSO_2Ph$$

$$|$$
$$Ph$$

I

$$+ \quad \underset{H}{\overset{Ph}{\diagdown}}C=C\underset{Ph}{\overset{H}{\diagup}} \quad + PhCH_2SO_2Ph + PhCH_2SO_2CHSO_2CHSO_2Ph$$

$$| \quad \quad |$$
$$Ph \quad Ph$$

IV   VII   VIII

TABLE 1. METAL EFFECT ON THE REACTION OF BENZYLSULPHONYL FLUORIDE WITH ORGANOALKALI METAL REAGENT

Reactions	Products (%)			
	I	IV	VII	VIII
PhCH$_2$SO$_2$F + PhLi	59·1	3·9	1·8	4·0
PhCH$_2$SO$_2$F + PhMgBr	0	0	88·0	0

It is interesting to note that the corresponding Grignard reagent presented a striking contrast to the organolithium reagent. Although sulphone compounds are capable of undergoing metalation by a Grignard reagent as exemplified by dimethyl sulphone,[4e,f] phenyl methyl sulphone[4c] or benzyl phenyl sulphone,[4g] the S_N2 type reaction to give VII predominated over the metalation reactions to form X or XII type intermediate in the interaction of benzylsulphonyl fluoride with phenyl-magnesium bromide (Scheme 1). The lower carbanion character of phenylmagnesium bromide as compared with phenyllithium may be responsible for this difference.

The striking solvent effect, was shown by using THF or diglyme where polysul-

TABLE 2. SOLVENT EFFECTS ON THE REACTION OF BENZYLSULPHONYL FLUORIDE WITH PHENYLLITHIUM AT 18-20°

Solvents	Products (%)			
	I	IV	VII	VIII
Diethyl ether	59·1	3·9	1·8	4·0
Benzene	30·1	2·7	9·6	2·8
Hexane[a]	28·6	1·9	14·6	—
THF[b]	17·1	1·2	Trace	Trace
Diglyme[c]	12·0	—	0·9	1·7

[a] Heterogeneous reaction.
[b] Polysulphones were formed in 5·0 per cent yield in addition to 2·2% yield of 1,2-diphenylvinyl benzyl sulphone.
[c] Polysulphones were formed in 5·2% yield.

phones[8] which appear to contain a unit of —C(C$_6$H$_5$)SO$_2$— with molecular weight

of 850–1000 were produced. It was found that the use of THF and particularly low temperature favored the formation of polysulphones.[8] The marked effect of THF was also observed in the reaction of methanesulphonyl fluoride with phenyllithium as described later in this paper.

It is evident from the data that the yield of the disulphone (I) decreases, while the yield of the monosulphone (VII) increases significantly, in the decreasing order of solvent polarity or basicity; diethyl ether > benzene > hexane, the only exceptions to this being in the cases of THF and diglyme where polysulphones were formed and total yields of the products were low. This indicates that metalation on benzyl-sulphonyl fluoride or on benzyl phenyl sulphone (VII) formed occurs less readily as solvent basicity decreases (Scheme 1). These data, together with the result of the reaction in the presence of ketene diethylacetal described later, help to suggest feasible mechanisms for the formation of the main product (I) in the interaction of benzylsulphonyl fluoride with phenyllithium, which are shown in Scheme 1.

SCHEME 1. FORMATION MECHANISMS OF THE DISULPHONE (I)*

$$PhCH_2SO_2F + PhLi$$

$$PhCH_2SO_2Ph \xrightarrow{PhLi} Ph\bar{C}HSO_2Ph \xrightarrow{PhCH_2SO_2F} I \quad (A)$$

$$S_N2 \qquad VII \qquad +Li \qquad XII$$

$$metalation$$

$$Ph\bar{C}HSO_2F \xrightarrow[-LiF]{} PhCH{=}SO_2 \xrightarrow{PhLi} Ph\bar{C}HSO_2Ph$$

$$+Li \qquad\qquad +Li$$

$$X \qquad\qquad XI \qquad XII$$

$$(or PhLi)$$

$$\xrightarrow{PhCH_2SO_2F} I \quad (B)$$
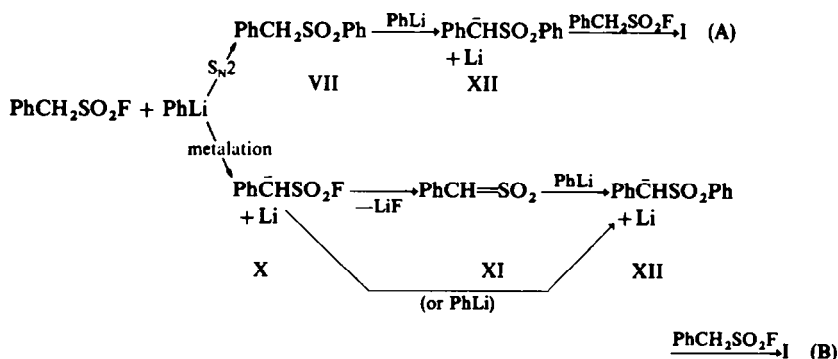
Although the ratio of competing S$_N$2 to metalation at the initial step is unknown and probably varies with solvents, both path A and B appear to be operative simultaneously for the formation of I. That the S$_N$2 type reaction by phenyllithium on sulphur actually occurs is evidenced by the isolation of VII which contains no deuterium when worked up with D$_2$O, excluding the possibility that VII may form from XII upon hydrolysis in path B. The transformation form VII to I was easily done.[6] The simultaneous participation of path B for the formation of I is deduced from the result of the reaction in the presence of ketene diethyacetal.

The reaction of benzylsulphonyl fluoride with phenyllithium in the presence of

* The following alternative mechanism for the formation of I appears unlikely, since the α-benzyl-sulfonylbenzylsulphonyl halide was never isolated in any condition examined. This is contrasted with the reaction of phenyl benzylsulphonate.

$$PhCH_2SO_2F \xrightarrow{PhLi} X \xrightarrow{PhCH_2SO_2F} PhCH \begin{array}{c} SO_2F \\ \\ SO_2CH_2Ph \end{array} \xrightarrow{PhLi} I$$
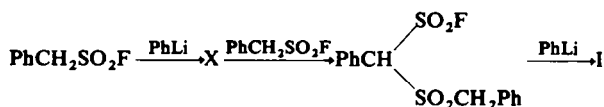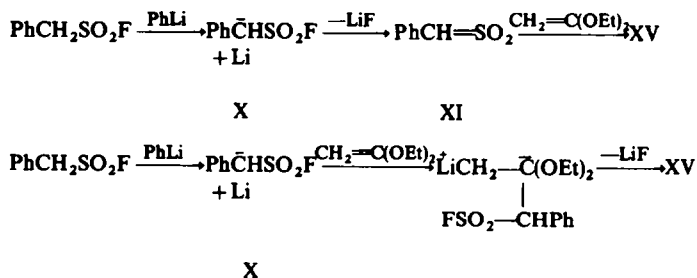
ketene diethylacetal was tried as a phenylsulphene intermediate (XI) which forms from X through β-elimination of lithium halide may be involved in the reaction. It has now been observed for the first time that 4-membered cyclic sulphones are formed in this reaction system.* The reaction yielded disulphone (I), 2-phenyl-3,3-diethoxythietane 1,1-dioxide (XV) and 2-phenyl-3-ethoxythiete 1,1-dioxide (XVI) in 30·0, 9·3 and 7·4% yields respectively.

$$CH_2—C(OEt)_2 \qquad CH_2—C—OEt$$
$$| \qquad | \qquad\qquad | \qquad ||$$
$$SO_2—CHPh, \qquad SO_2—C—Ph$$

$$XV \qquad\qquad\qquad XVI$$
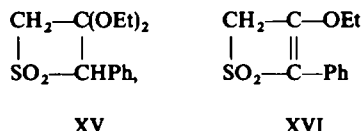
The thietane sulphone derivative (XV) was identified by comparison of the IR spectrum with that of an authentic sample[9b] and the mixed m.p. The IR and NMR spectra of XVI proved to be identical with those previously reported.[10] The formation of the thiete sulphone derivative (XVI) results from the action of phenyllithium on XV which is converted to XVI on treatment with sodium ethoxide in ethanol.[10] Since no appreciable reaction takes place between benzylsulphonyl fluoride and ketene diethylacetal under the present conditions, the initial step for the formation of XV seems to be the formation of X and the two mechanisms given in Scheme 2 are probable.

SCHEME 2. FORMATION MECHANISMS OF 2-PHENYL-3,3-DIETHOXYTHIETANE 1,1-DIOXIDE (XV)

$$PhCH_2SO_2F \xrightarrow{PhLi} PhC\bar{H}SO_2F \xrightarrow{-LiF} PhCH{=}SO_2 \xrightarrow{CH_2{=}C(OEt)_2} XV$$
$$+Li$$

$$X \qquad\qquad\qquad XI$$

$$PhCH_2SO_2F \xrightarrow{PhLi} PhC\bar{H}SO_2F \xrightarrow{CH_2{=}C(OEt)_2} LiCH_2—\bar{C}(OEt)_2 \xrightarrow{-LiF} XV$$
$$+Li \qquad\qquad\qquad\qquad\qquad\qquad |$$
$$FSO_2—CHPh$$

$$X$$

One is a cycloaddition of phenylsulphene (XI) and the other involves a nucleophilic attack of X on ketene diethylacetal, followed by an intramolecular displacement by the resulting carbanion on the S atom. Phenylsulphene intermediate (XI) can also account for the formation of a small amount of *trans*-stilbene (IV) in the absence of ketene diethylacetal.[9a] Although it is too early to establish the existence of XI from these data alone, the present result, does allow the following mechanistic deduction to be made concerning the formation of I. In the original proposal[6] only path A in the Scheme 1 was postulated, however, the present result that the yield of I is decreased by over 20% in the presence of ketene diethylacetal and instead cyclic sulphones are formed in about 17% yield, suggests that path B involving the intermediacy of X is operative at the same time in the formation of I in the reaction between benzylsulphonyl fluoride and phenyllithium.

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* Benzylsulphonyl fluoride, unlike benzylsulphonyl chloride, does not react with triethylamine under comparable reaction conditions.

The action of phenyllithium on methanesulphonyl fluoride yielded methyl phenyl sulphone (XVII), methanesulphonyl benzenesulphonyl methane (XVIII) and bis-(methanesulphonyl) benzenesulphonyl methane (XIX) on 7·9, 19·6 and 3·7% yields respectively. In addition a very small amount of what appears to be a linear tri-sulphone, α-methanesulphonyl-α'-benzenesulphonyl dimethyl sulphone was also formed. When the reaction was carried out in THF, XIX was mainly formed together with a small amount of XVII. No volatile material has been analysed in these reactions. The results are shown in Table 3.

$$\text{MeSO}_2\text{F} + \text{PhLi} \xrightarrow[\text{diethyl ether}]{18-20^\circ} \text{MeSO}_2\text{Ph} + \text{CH}_2 \underset{\text{SO}_2\text{Me}}{\overset{\text{SO}_2\text{Ph}}{\diagdown}} + \text{CH} \underset{\text{SO}_2\text{Me}}{\overset{\text{SO}_2\text{Ph}}{\diagup}} \text{SO}_2\text{Me}$$
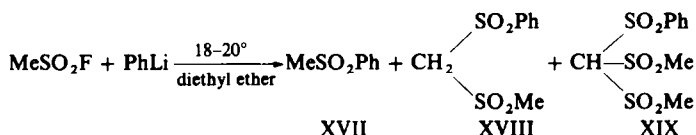
<center>XVII   XVIII   XIX</center>

TABLE 3. REACTIONS OF METHANESULPHONYL FLUORIDE WITH
PHENYLLITHIUM AT 18–20°

Solvents	Products (%)		
	XVII	XVIII	XIX
Diethyl ether	7·9	19·6	3·7
THF	0·5	0	28·1

The identification of XVIII, m.p. 146–147° (lit.[11] m.p. 146°) and XIX, m.p. 242–243°, was based on the IR and NMR spectra and elementary analyses. The features of the NMR spectrum (in CF_3COOH) of XIX were: (1) a singlet at $\tau = 6\cdot4$ (6H, Me protons) (2) a singlet at $\tau = 3\cdot65$ (1H, methine proton) (3) a broad multiplet covering the range of $\tau = 1\cdot9-2\cdot5$ (5H, Ph protons). As expected from the result of benzylsulphonyl fluoride, monosulphone (XVII), disulphone (XVIII) and trisulphone (XIX) were likewise formed in the case of methanesulphonyl fluoride. The solvent effect on the products formed between diethyl ether and THF may be ascribed to a stronger cation solvating ability of THF, in which metalation and displacement reactions are fascilitated. The trisulphone obtained from benzylsulphonyl fluoride is only a linear trisulphone (VIII) instead of a trisulphonyl methane derivative, while the trisulphone derived from methanesulphonyl fluoride is principally a trisulphonyl methane (XIX), the formation of which seems plausible since the methylene hydrogens are more acidic than the methyl hydrogens in the disulphone (XVIII), hence preferential metalation occurs on the methylene, leading to the formation of XIX (Scheme 3). In the case of benzylsulphonyl halide the S_N2 type reaction by a resulting carbanion (XX) on the starting sulphonyl halide to form a trisulphonyl methane derivative may perhaps be sterically unattractive.

In the next place, reactions of an alkanesulphonic ester with organoalkali metal reagents have been studied.* The compound chosen was phenyl benzylsulphonate. A comparison between the reactions of the sulphonic ester with those of the sulphonyl halide should show the effect of a functional group on the reactivity of α-sulphonyl-

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* The reaction of phenyl ethanesulphonate with a Grignard reagent to give phenyl ethyl sulphone has been reported.[12]

SCHEME 3

$MeSO_2F \xrightarrow{PhLi} MeSO_2Ph$ XVII

$MeSO_2F \xrightarrow[\text{2. MeSO}_2\text{F}]{\text{1. 2PhLi}} CH_2 \Big\langle \begin{array}{l} SO_2Ph \\ SO_2Me \end{array}$ XVIII

$CH_2 \Big\langle \begin{array}{l} SO_2Ph \\ SO_2Me \end{array} \xrightarrow{PhLi} \overset{-}{C}H \Big\langle \begin{array}{l} SO_2Ph \\ +Li \quad SO_2Me \end{array} \xrightarrow{MeSO_2F} CH \Big\langle \begin{array}{l} SO_2Ph \\ -SO_2Me \\ SO_2Me \end{array}$ XIX

$Ph\overset{-}{C} \Big\langle \begin{array}{l} SO_2Ph \\ +Li \quad SO_2CH_2Ph \end{array}$ XX
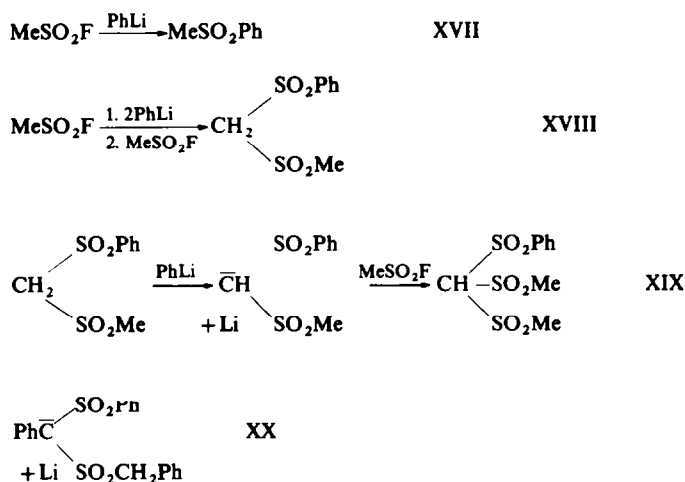
carbanions. When phenyl benzylsulphonate was treated with phenyllithium, in addition to phenol, I, VIII and phenyl [α-benzylsulphonyl]-benzylsulphonate (XXI) formed in 17·1, 3·5 and 13·7% yields respectively. When the reaction was conducted in THF–ether (1:1) at 18–20°, 9·7% of I and 24·7% of XXI were obtained together with phenol. The striking increase of the yield of XXI was observed when the reaction was carried out at −60 ~ −70° in THF–ether. In cyclohexane solvent XXI was not obtained. In sharp contrast, however, with the reaction of the organolithium reagent, the reaction of phenylmagnesium bromide under a comparable reaction condition gave only benzyl phenyl sulphone (VII) in a high yield together with a corresponding yield of phenol. These results are presented in Table 4.

$$PhCH_2SO_2CHSO_2OPh$$
$$\mid$$
$$Ph$$

XXI
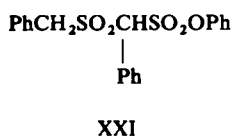
TABLE 4. REACTIONS OF PHENYL BENZYLSULPHONATE WITH ORGANOALKALI METAL REAGENT

Reactions	Conditions		Products (%)		
	Solvent	Temp. (°C)	I	VII	XXI
PhCH₂SO₂OPh + PhLi	Ether[a]	18–20	17·1	0	13·7
PhCH₂SO₂OPh + PhLi	THF–Ether	18–20	9·7	0	24·7
PhCH₂SO₂OPh + PhLi	Cyclohexane	18–20	32·8	0	0
PhCH₂SO₂OPh + PhMgBr	Ether	18–20	0	84·0	0
PhCH₂SO₂OPh + PhMgBr	THF	18–20	0	69·0	0
PhCH₂SO₂OPh + PhLi	THF–Ether	60–70	0	0	84·5

[a] In addition a small amount of VIII was formed.

The structure of the new compound XXI was confirmed on the basis of the IR and NMR spectroscopy and elemental analysis. The IR spectrum shows strong sulphone bands at 1330 and 1135 cm^{-1}. The NMR spectrum shows peaks centred at $\tau = 2{\cdot}75$ (15H, mu, Ph protons), at $\tau = 4{\cdot}62$ (1H, si, methine proton) and at $\tau = 5{\cdot}35$ (2H, qu, methylene protons, $J_{AB} = 13{\cdot}8$ c/s, $\delta_{AB} = 0{\cdot}455$ ppm). The formation of XXI probably involves phenyl α-lithiobenzylsulphonate (XXII) as shown below.

$$PhCH_2SO_2OPh \xrightarrow[+Li]{PhLi} Ph\bar{C}HSO_2OPh \xrightarrow{PhCH_2SO_2OPh} XXI$$

XXII
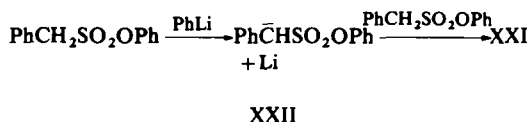
The route to yield phenyl [α-benzylsulphonyl]-benzylsulphonate (XXI) corresponds to a Claisen condensation of carboxylic esters and the present observation appears to be the first example of a sulphonic ester. It is evident that this Claisen type reaction of a sulphonic ester is favoured by the use of a low temperature in THF. It is of interest that the corresponding XXI was not obtained in the reaction of benzyl-sulphonyl halide. Under the condition favouring the formation of XXI, the reaction of benzylsulphonyl halide yielded polysulphones.[8]

$$PhCH_2SO_2OPh \rightarrow PhCH\begin{matrix} \diagup SO_2OPh \\ \diagdown SO_2CH_2Ph \end{matrix} \qquad XXI$$

$$PhCH_2SO_2X \not\rightarrow PhCH\begin{matrix} \diagup SO_2X \\ \diagdown SO_2CH_2Ph \end{matrix} \qquad or \quad (\not\rightarrow PhCHSO_2CH_2Ph) \atop -SO_2 \;\; | \atop X$$

$$(X = F, Cl)$$
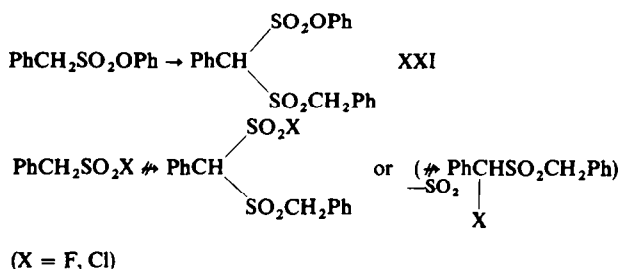
The formation of the disulphone (I) in the sulphonic ester reaction also results through the α-sulphonylcarbanion intermediate, XII or XXII, but no details are available. The reaction of phenyl benzylsulphonate with the organolithium reagent proceeded through α-sulphonylcarbanion intermediates, but nucleophilic displacement on sulphur only occurred in the reaction with the Grignard reagent both in diethyl ether and in THF. This is in agreement with the case of the sulphonyl fluoride.

The action of phenyllithium on benzylsulphone N,N-dimethylamide under reflux for 15 hr in diethyl ether afforded about 38% yield of α-benzyl-α-hydroxybenzyl-sulphone N,N-dimethylamide (XXIII), but no details are available.
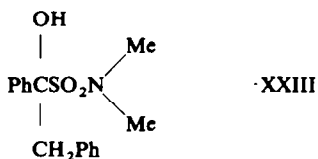
$$PhCSO_2N\begin{matrix} OH \\ | \\ \;\; \diagup Me \\ \diagdown Me \\ | \\ CH_2Ph \end{matrix} \qquad \cdot XXIII$$

prior to a reaction. Benzene and hexane were dried and purified by a conventional method. PhLi was prepared immediately before use from Li and bromobenzene[13] and titrated with acid.[14] Benzylsulponyl fluoride, m.p. 92–93° (lit.[15] m.p. 91–92°) and methanesulphonyl fluoride, b.p. 125–126° (lit.15 b.p. 126°), were prepared from the corresponding chlorides and NaF in DMF.[16] Ketene diethylacetal was prepared from bromoacetaldehyde diethylacetal.[17] Phenyl benzylsulphonate was prepared from benzylsulphonyl chloride, phenol and excess pyridine.[18] Phenol (14 g; 0·15 mole) and benzylsulphonyl chloride[19] (28·7 g; 0·15 mole) were dissolved in about 400 ml anhyd ether and pyridine (24 g; 0·3 mole) was added dropwise over a period of 30 min at a temp of 0–5°. After completion the mixture was warmed to 10° and a white ppt of pyridine hydrochloride began to form. After stirring for 1 hr it was allowed to stand overnight at 10°. The salt was filtered off and the filtrate was evaporated to give crude phenyl benzylsulphonate (25 g). It was washed with water and recrystallized from ether, m.p. 87·5–88° (lit.[20] 87–88°). Benzylsulphone N,N-dimethylamide was prepared by dissolving benzylsulphonyl chloride in a large excess of 40% aqueous dimethylamine by heating. It was recrystallized first from dil MeOH and then from CHCl$_3$–ligroin, m.p. 101–101·5° (lit.[21] 101°).

Apparatus. IR spectra were taken on a EPI- S2 type Hitachi infrared spectrometer. NMR spectra were obtained with a JNM3H-60 spectrometer. Mol. wts were determined with a Mechrolab vapour pressure osmometer.

Reaction of benzylsulphonyl chloride or benzylsulphonyl fluoride with phenyllithium in ether. These reactions and the identification of the products, I–IX, are described in detail in the previous paper.[6]

Reaction of benzylsulphonyl fluoride with a Grignard reagent. Benzylsulphonyl fluoride, 8·7 g (0·05 mole), was dissolved in 110 ml dry ether in a 500 ml 4-necked flask with a thermometer. PhMgBr prepared from Mg turnings (1·8 g; 0·074 atom) and bromobenzene (11·6 g; 0·074 mole) in ether (70 ml) was slowly added at 18–20° over a period of 25 min under an argon atm. Simultaneously with the addition, the reaction became cloudy. After stirring for additional 4 hr at 20° the reaction was worked up with dil HCl. A large amount of an insoluble white solid (6·5 g) was separated by filtration, washed with and recrystallized from EtOH. m.p. 146°. It was identified as benzyl phenyl sulphone by comparison of its IR spectrum with that of an authentic sample and the mixed m.p. The solvent was evaporated to give 3·5 g benzyl phenyl sulphone and a reddish yellow liquid, which gave 0·3 g additional benzyl phenyl sulphone after column chromatography on alumina. No other products were obtained. The total yield of benzyl phenyl sulphone was 10·3 g (88·0%).

General procedure for the reaction of benzylsulphonyl fluoride with phenyllithium in various solvents. PhLi was prepared in ether and then the ether was replaced by benzene or hexane. When THF or diglyme was employed as a solvent ethereal PhLi was used. To a stirred soln of benzylsulphonyl fluoride (8·7 g; 0·05 mole) dissolved in a given solvent was slowly added PhLi prepared from 1·1 g Li and 11·6 g (0·074 mole) bromobenzene at 18–20° over a period of 15 min. After stirring for 4 hr the reaction was worked up with dil HCl aq. All the treatment was conducted under an argon atm. The disulphone (I) separated as an insoluble product and was collected by filtration. The solvents were evaporated to separate products and the residues were chromatographed over alumina. In benzene 2·9 g (30·0%) of I, 0·12 g (2·7%) of IV, 1·2 g (9·6%) of VII and 0·25 g (2·8%) of VIII, and in n-hexane 2·6 g (28·6%) of I, 0·08 g (1·9%) of IV and 1·6 g (14·6%) of VII. 0·5 g of recovered benzylsulphonyl fluoride were obtained. In THF 1·65 g (17·1%) of I, 0·05 g (1·2%) of IV. a trace of VIII and 0·35 g of polysulphones were obtained. In this case 0·12 g (2·2%) of 1,2-diphenylvinyl benzyl sulphone was formed in addition. In diglyme 1·1 g (12%) of I, 0·15 g (1·7%) of VIII, 0·1 g (0·9%) of VII and 0·4 g (5·2%) of polysulphones were isolated. Polysulphones were obtained by concentration of organic layer after removal of I, followed by addition of MeOH. When hexane was used as a solvent the reaction was worked up with D$_2$O. The IR (KBr) and NMR spectra of isolated benzyl phenyl sulphone were identical in all respects with a natural sample, indicating no incorporation of deuterium in isolated benzyl phenyl sulphone. 1,2-Diphenylvinyl benzyl sulphone was recrystallized from EtOH as white needles, m.p. 139–140°; IR: $\nu_{C=C}^{KBr}$ cm^{-1} 1630, ν^{KBr} cm^{-1} 830, $\nu_{SO_2}^{KBr}$ cm^{-1} 1300, 1140, 1120; NMR:

$$\underset{R}{\overset{R}{>}}C=C\overset{R}{\underset{H}{<}}$$
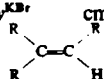
(CDCl$_3$) τ = 2·2 (si, 1H, vinyl proton). τ = 2·6–3·1 (mμ. 15H. Ph protons). τ = 5·94 (si, 2H. methylene protons); UV: λ_{max}^{EtOH} mμ 271 (ε = 13,900). (Found: C, 75·52; H, 5·33; S, 9·41. C$_{21}$H$_{18}$O$_2$S requires: C, 75·43; H, 5·43; S, 9·57%).

Reaction of benzylsulphonyl fluoride with phenyllithium in the presence of ketene diethylacetal. Benzylsulphonyl fluoride, 8·7 g (0·05 mole), was dissolved in 120 ml anhyd ether and 7 g (0·06 mole) freshly distilled

ketene diethylacetal was added. To this stirred soln was immediately added PhLi prepared from 1·1 g
Li and 11·6 g bromobenzene in 70 ml ether over a period of 15 min at 18–20° under an argon atm. Simul-
taneously with the addition of PhLi a yellow color developed. After stirring for 4 hr the reaction was worked
up with H_2O. An insoluble solid, 2·55 g, was collected and identified as I. The organic layer was concen-
trated to give 0·3 g of additional I. The filtrate was evaporated. The residue was dissolved in benzene and
submitted to a column chromatography over alumina (Sumitomo activated alumina KCG 1225). Elution
with benzene gave a yellow oil, which solidified upon standing. It was washed with MeOH and recrystallized
from EtOH, m.p. 93·5–94° (lit.[9b] m.p. 89–90°), the yield being 1·25 g. The identification as XV was made by
comparison of its IR and NMR spectra with those of an authentic sample and the mixed m.p. 93–94°.
Subsequent elution with benzene–ether yielded a yellow semi-solid, which was recrystallized from n-hexane–
EtOH as white needles (0·82 g), m.p. 133–134° (lit.[10] m.p. 132–134°). It was identified as XVI based on the
IR, NMR spectroscopy and elemental analysis. The IR and NMR spectra were identical with those re-
ported.[10] It decolorized a 1% $KMnO_4$ aq; IR: $\nu_{C=C}^{Nujol}$ cm^{-1} 1640, $\nu_{SO_2}^{Nujol}$ cm^{-1} 1345, 1185; NMR: (CDCl$_3$)
$\tau = 8·59$ (tr, 3H, Me protons), $\tau = 5·85$ (qu, 2H, methylene protons in the EtO group), $\tau = 5·42$ (si, 2H,
ring methylene protons) and $\tau = 2·6$ (5H, Ph protons). (Found: C, 58·89; H, 5·58. Calc. for $C_{11}H_{12}O_{13}S$:
C, 58·92; H, 5·35%).

Reaction of methanesulphonyl fluoride with phenyllithium. Methanesulphonyl fluoride, 11·8 g (0·12 mole),
was dissolved in 120 ml dry ether. Ethereal PhLi (120 ml; 0·13 mole) prepared from 2·6 g Li and 27·6 g
bromobenzene was slowly added over 17 min at 18–20° (bath temp 7°). Simultaneously with the addition
the reaction became cloudy. After completion of the addition the reaction was stirred for 3·5 hr at 18–20
and worked up with dil HClaq. Insoluble yellow coloured gummy products were separated and removed.
From the yellow gum 0·21 g of XIX and 0·2 g of XVIII were obtained by dissolving the gum in dil NaOHaq,
followed by reprecipitation with cold dil HClaq. The organic layer was again washed with water. From
this aqueous layer 0·25 g of XIX crystallized as white needles. The organic layer was dried and condensed
to about 30 ml to give 2·3 g of XVIII. The ethereal layer was evaporated to give 0·05 g of XVII and 5·0 g
of a residue. The residue was dissolved in benzene and chromatographed over alumina. Elution with
benzene and subsequently with ether yielded 1·43 g of XVII. Elution with 1:1 ether–MeOH gave 0·25 g
of XVIII. Finally, on elution with MeOH gave what appear to be α-methanesulphonyl-α′-benzenesulphonyl
dimethyl sulfone, 0·075 g. The total yields of XIX, XVIII and XVII were 0·46 g (3·7%), 2·75 g (19·6%),
1·48 g (7·9%), respectively. Sulphone XVII, m.p. 87–88°, was identified by comparison of the IR spectrum
with that of the authentic sample[22] and the mixed m.p. The IR, NMR spectra and elementary analyses of
XVIII, m.p. 146–147° (lit.[11] m.p. 146°), are in good agreement with the structure; IR: $\nu_{SO_2}^{Nujol}$ cm^{-1} 1310,
1150; NMR (CDCl$_3$) $\tau = 6·7$ (si, 3H, Me protons), $\tau = 5·35$ (si, 2H, methylene protons), $\tau = 1·9$–2·8 (mu,
5H, Ph protons). (Found: C, 40·96; H, 4·29. Calc. for $C_8H_{10}O_4S_2$: C, 41·02; H, 4·27%). The structure of
XIX was confirmed on the basis of the IR, NMR spectra and elemental analysis; IR: $\nu_{SO_2}^{Nujol}$ cm^{-1} 1340,
1315, 1165, 1140. (Found: C, 34·73; H, 3·79; S, 30·54. $C_9H_{12}O_6S_3$ requires: C, 34·60; H, 3·87; S, 30·79%).
α-Methanesulphonyl-α′-benzenesulphonyl dimethyl sulphone, m.p. 145–147°; IR: $\nu_{SO_2}^{Nujol}$ cm^{-1} 1320, 1150,
1130; NMR(CF$_3$COOH) $\tau = 1·9$–2·3 (5H, Ph protons), $\tau = 4·6$ (4H, methylene protons), $\tau = 6·55$ (3H,
Me protons). (Found: C, 34·25; H, 4·00; $C_9H_{12}O_6S_3$ requires: C, 34·60; H, 3·87%).

Reaction of methanesulphonyl fluoride with phenyllithium in THF–ether. Methanesulphonyl fluoride,
8·8 g (0·09 mole), was dissolved in dry THF (100 ml) and to this soln was slowly added ethereal PhLi
prepared from 1·35 g Li and 20·7 g bromobenzene over 15 min at 18–20° (bath temp 10°). The same pro-
cedure described before was followed hereafter and 2·18 g of XIX was obtained upon concentration of
the organic layer, followed by evaporation. From aqueous layer 0·45 g of additional XIX was obtained.
The residue was chromatographed over alumina to give 0·07 g of XVII.

General reaction of phenyl benzylsulphonate with an organoalkali metal reagents. To a stirred soln of
phenyl benzylsulphonate dissolved in a given solvent was slowly added 5–10% excess of PhLi or PhMgBr
over 10–20 min under an argon atm. The reaction mixture was stirred for additional 3 to 5 hr and then
hydrolysed with dil HClaq. After removal of the insoluble products, the organic layer was again shaken
with dil NaOHaq. The aqueous layer thus obtained was again acidified and extracted with ether. Evapora-
tion of ether gave phenol, which was identified by comparison of its IR spectrum with that of an authentic
sample. The organic layer was evaporated to give products. In some cases chromatographic separation
was made. Detailed procedures are given for the reaction of phenyl benzylsulphonate with PhLi in THF–
ether at 18–20° and the reaction of phenyl benzylsulphonate with PhMgBr in ether at 15–20°.

Reaction of phenyl benzylsulphonate with phenyllithium in THF–ether at 18–20°. Phenyl benzylsulphonate,
6·2 g (0·0245 mole), was dissolved in 50 ml dry THF and to this soln was added 50 ml ethereal PhLi pre-

pared from 0·6 g Li and 5·8 g bromobenzene. The reaction mixture was stirred for 5 hr and hydrolysed. The disulphone I, 0·45 g (9·6%), was obtained and after evaporation of solvents 0·9 g of XXI was isolated. By column chromatography 0·3 g of XXI and 0·19 g of recovered phenyl benzylsulphonate were obtained. The reaction in THF–ether at −70° was carried out by stirring the reaction mixture for 5 hr at −70°, allowing to stand overnight at that temp and then warming to 20°, followed by hydrolysis. From 12·4 g (0·05 mole) phenyl benzylsulphonate 8·5 g of XXI was obtained. In ether at 18–20°, 1·2 g of I, 1·0 g of XXI, 0·23 g of VIII and 1·4 g of recovered phenyl benzylsulphonate were obtained from 10·4 g (0·04 mole) phenyl benzulsulphonate. In cyclohexane solvent 1·2 g of I was obtained from 7·5 g (0·03 mole) phenyl benzylsulphonate, together with 3·0 g recovered starting material. Compound XXI, m.p. 174–175°; (Found: C, 59·48; H, 4·33; S, 15·87. $C_{20}H_{18}O_5S_2$ requires: C, 59·68; H, 4·51; S, 15·93%).

Reaction of phenyl benzylsulphonate with phenylmagnesium bromide in ether. To a stirred soln of 7·5 g (0·03 mole) phenyl benzylsulphonate in 180 ml anhyd ether was added dropwise an ethereal soln of PhMgBr prepared from 1·1 g Mg and 7·1 g bromobenzene over 10 min at 13–18° under argon atm. After completion of the addition the reaction was stirred for 2·5 hr at 20°. When the reaction was hydrolysed a large amount of insoluble white solids was precipitated and identified as benzyl phenyl sulphone (VII), the yield being 4·2 g. The organic layer was evaporated to afford 1·7 g of VII. The yield of phenol was 2·3 g. When the reaction was conducted in THF, PhMgBr was prepared in THF. From 3·8 g (0·015 mole) of the sulphonate 1·7 g of VII and 1·2 g of the recovered starting material was isolated.

Reaction of benzylsulphone N,N-*dimethylamide with phenyllithium.* Benzylsulphone N,N-dimethylamide, 5·0 g (0·025 mole), was dissolved in about 350 ml anhyd ether at 32°. To this stirred soln ethereal PhLi prepared from 0·6 g Li and 5·8 g bromobenzene in 40 ml ether was added dropwise over a period of 15 min under reflux. The soln progressively developed a yellow colour. It was refluxed for 15 hr and hydrolysed with water. The aqueous layer had a strong odour of amine. The ether layer was evaporated and the residue was dissolved in benzene, followed by column chromatography over alumina. The recovered starting material, 0·7 g, was eluted with benzene. α-Benzyl-α-hydroxybenzylsulphone N,N-dimethylamide, 1·44 g (37·6%), was eluted with $CHCl_3$. It was recrystallized from ether–hexane as a white needle, m.p. 106·5–107°.

α-Benzyl-α-hydroxybenzulsulphone N,N-dimethylamide; IR; v_{OH}^{Nujol} cm^{-1} 3500, $v_{SO_2}^{Nujol}$ cm^{-1} 1325, 1140; NMR: $\tau = 7·45$ (si, 6H, Me protons), $\tau = 5·85$ (OH proton, 1H), centred at $\tau = 5·05$ (qu, 2H, methylene proton $J_{AB} = 10·2$ c/s), $\tau = 2·9$ (10H, Ph protons). (Found: C, 62·77; H, 6·26; N, 4·81; Mol. wt. 300. $C_{16}H_{19}O_3NS$ requires: C, 62·89; H, 6·27; N, 4·59%; Mol. wt. 305).

REFERENCES

[1] E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.* **87**, 1353 (1965). E. J. Corey and M. Chaykovsky, *Ibid.* **84**, 867 (1962).

[2] For a review of Ylide Chemistry, see A. W. Johnson *Ylid Chemistry* Academic Press, New York and London (1966).

[3] [a] F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.* **73**, 5187 (1951);
[b] N. P. Neureiter, *Ibid.* **88**, 558 (1966);
[c] L. A. Paquett and L. S. Wittenbrook, *Ibid.* **89**, 4483, 4487 (1967);
[d] F. G. Bordwell and J. M. Williams, Jr., *Ibid.* **90**, 435 (1968).

[4] [a] W. M. Ziegler and R. Conner, *Ibid.* **62**, 2596 (1940);
[b] H. Gilman and F. W. Webb, *Ibid.* **71**, 4062 (1949);
[c] L. Field, *Ibid.* **74**, 3919 (1952);
[d] W. E. Truce and M. F. Amos, *Ibid.* **73**, 3013 (1951);
[e] L. Field and J. W. McFarland, *Ibid.* **75**, 5582 (1953);
[f] W. E. Truce and K. R. Buser, *Ibid.* **76**, 3577 (1954);
[g] E. A. Lehto and D. A. Schirley, *J. Org. Chem.* **22**, 989 (1957);
[h] E. M. Kaiser and C. R. Hauser, *Tetrahedron Letters* 3341 (1967).

[5] [a] H. Gilman and R. E. Fothergiel, *J. Am. Chem. Soc.* **51**, 3501 (1929);
[b] H. Burton and W. A. Davy, *J. Chem. Soc.* 528 (1948);
[c] D. T. Gibson, *J. Prakt. Chem.* **142**, 218 (1935);
[d] H. Gilman, N. J. Beaber and C. H. Myers, *J. Am. Chem. Soc.* **47**, 2047 (1925).

[6] Y. Shirota, T. Nagai and N. Tokura, *Tetrahedron* **23**, 639 (1967).

[7] [a] Y. Shirota, T. Nagai and N. Tokura, *Tetrahedron Letters* 3299 (1967);
[b] *Ibid.* 2343 (1968).

[8]   N. Tokura, T. Nagai and Y. Shirota, *J. Polymer Sci.* C. to be published.
[9]   *a* J. F. King and T. Durst, *Tetrahedron Letters* 585 (1963);
      b W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.* **85**, 3231 (1963).
[10] W. E. Truce and J. R. Norell, *Ibid.* **85**, 3236 (1963).
[11] H. Bohme and P. Heller, *Chem. Ber.* **86**, 785 (1953).
[12] H. Gilman and J. D. Robinson, *Bull. Soc. Chim. Fr.* **45**, 636 (1929).
[13] H. Gilman, *Org. Reactions* (Edited by R. Adams) Vol. **6**, p 353 (1951).
[14] J. C. W. Evans and D. F. H. Allen, *Org. Syntheses* (Edited by A. H. Blatt) Coll. Vol **11** p 519 (1948).
[15] *a* D. E. Fahrney and A. M. Gold, *J. Am. Chem. Soc.* **85**, 987 (1963);
      b W. Davis and J. H. Dick, *J. Chem. Soc.* 483 (1912).
[16] C. W. Tullock and D. D. Coffman, *J. Org. Chem.* **25**, 2016 (1960).
[17] S. M. McElvain and D. Kundiger, *Org. Syntheses* Coll. Vol III, p 506 (1955).
[18] T. Kametani, O. Umezawa, K. Sekine, T. Oda, M. Ishiguro and D. Mizuno, *Yakugaku Zasshi* **84**, 237 (1964).
[19] E. Cherbuliez and O. Schnauder, *Helv. Chim. Acta* **6**, 256 (1923).
[20] O. R. Zaborsky and E. T. Kaiser, *J. Am. Chem. Soc.* **88**, 3084 (1966).
[21] C. K. Ingold, E. H. Ingold and F. R. Shaw, *J. Chem. Soc.* 813 (1927).
[22] *Beilstein's "Handbuch"*, VI, 297 (1923).