An improved synthesis of β-hydroxysulfones via α-sulfonylcarbanions in liquid ammonia. The direct metalation of dialkyl and aryl alkyl sulfones

D. F. TAVARES AND P. F. VOGT
Department of Chemistry, University of Calgary, Calgary, Alberta

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Dimethyl sulfone, methyl *p*-tolyl sulfone, ethyl *p*-tolyl sulfone, benzyl *p*-tolyl sulfone, and tetrahydrothiophene 1,1-dioxide were rapidly and quantitatively metalated by lithium amide (or potassium amide) in liquid ammonia, and the resulting organometallic compounds were added to a variety of carbonyl compounds to form the corresponding β-hydroxysulfones in good to excellent yields. The advantages of this method are speed, convenience, and versatility. Possible reasons for the failure of 1-phenyl-1-(*p*-tolylsulfonyl)methyllithium (XVIII) to form β-hydroxysulfones are discussed.

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The preparation and reactions of Grignard[1] and lithium (2, 3) reagents of sulfones have been investigated extensively. Typical of these reagents is the normal addition reaction to carbonyl compounds to form the corresponding β-hydroxysulfones, as illustrated by dimethyl sulfone in eq. [1] (2, 4). The synthesis of II (33% yield, based on sulfone) from the Grignard reagent was reported (4) to be complicated by dimetalation of the dialkyl sulfone in benzene–ether. Though a superior yield (65%) of II was obtained in anisole (2), the Grignard derivatives of sulfones are characteristically insoluble in most of the common solvents for Grignard reagents (1*a*). The best yield of II (85%) was obtained by metalation with *n*-butyllithium (2).

In all of the reported procedures with either the Grignard or lithium reagents, the metalating agents are relatively expensive or require special conditions in their preparation, or both, and the addition reactions have required refluxing for extended periods of time (from 1 to 18 h) in relatively high boiling solvents. The present investigation concerns a method for the direct metalation of both dialkyl and aryl alkyl sulfones, without complications, and the subsequent addition of the resulting organometallic compounds to a variety of aldehydes and ketones, as illustrated by dimethyl sulfone in eq. [2]. The advantages of this method are shorter reaction times, convenience, superior or comparable yields, and greater generality. The time required for the complete synthesis of a representative β-hydroxysulfone is less than 30 min, with few exceptions (Table I); the metalating agent is very easily prepared from readily available and inexpensive materials; there are no high-boiling solvents to be removed, facilitating product isolation; and the yields are excellent, with a few notable exceptions. Our results are summarized in Table I.

The choice of lithium amide as the metalating agent was dictated, in part, by the experiences of others in aldol-like condensation of metallo esters with carbonyl compounds (6). Reversion of the adducts (e.g. III*a*) to starting materials is apparently a more serious problem when the metal is sodium or potassium (6*a*–6*c*). Metal–hydrogen exchange, in condensations with ketones having an α hydrogen, has been a complicating factor when the metal is sodium or potassium, but condensations have been effected, in a good yield, when the metal is lithium (6*a*, 6*d*). We have found that the lithium reagents I, VII, XII, XVI, and XVIII, as representative examples, are formed rapidly and quantitatively with lithium amide in liquid ammonia. In general, lithium amide gave better results than potassium amide (compare experiments 1 and 2). Since isopropyl phenyl sulfone was readily metalated with phenyl-

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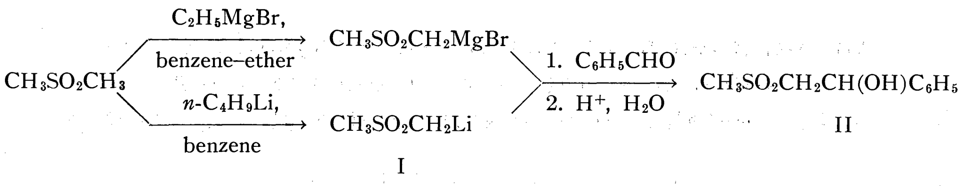
[1] For leadings references, see ref. 1.

[1]



[2]

$$CH_3SO_2CH_3 \xrightarrow[\text{liquid } NH_3]{LiNH_2,} \underset{I}{CH_3SO_2CH_2Li} \xrightarrow[\text{2. } NH_4Cl]{\text{1. } (C_6H_5)_2CO} \underset{III\ (87\%)}{CH_3SO_2CH_2C(OH)(C_6H_5)_2}$$

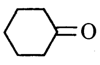
lithium (3), there is no reason to believe that the lithium derivative XIX could not be prepared by our method, though no examples of disubstitution at the α position were considered in the present investigation.

Much of the convenience of this new method is in the use of liquid ammonia as solvent. However, the yields of the β-hydroxysulfones derived from benzaldehyde are notably low (experiments 1, 7, and 11) when compared to the results with Grignard reagents (1, 4), and for this the liquid ammonia seems culpable, by virtue of its reaction with benzaldehyde to form hydrobenzamide and water (7), which destroys the organometallic reagent (eq. [3]). Such a reaction must also be suspect in condensations with other aldehydes. Replacement of the liquid ammonia by anhydrous ether before the addition of aldehyde might improve the yield of the condensation product, but at the sacrifice of convenience. By the use of a special mode of addition (see those sections marked with an asterisk in the Experimental), fair to good yields have been obtained.

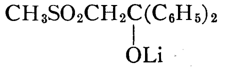
No general explanation can be offered in commenting on the variance in yields, since any kinetic or equilibrium considerations in these reactions would require a knowledge of many parameters at present unknown or

TABLE I

β-Hydroxysulfones from α-lithiosulfones with carbonyl compounds in liquid ammonia

Experiment	α-Lithio-sulfone	Carbonyl compound	Time* (min)	β-Hydroxysulfone (yield)†	Melting point‡	Reference (yield)§
1	I	C_6H_5CHO	8	II (37%)	103–104°	2 (85%)
2	I‖	C_6H_5CHO	8	II (20%)‖	103–104°	
3	I	$(C_6H_5)_2CO$	30	III (87%)	137–138°	2 (48%)
4	I	$C_6H_5COCH_3$	15	IV (36%)	b.p. 143–144° at 0.1 mm	¶
5	I	$(CH_3)_2CO$	5	V (45%)	43–45°	4**
6	I		60	VI (16%)	175.5–176.5°	¶
7	VII	C_6H_5CHO	12	VIII (24%)	71.5–72.5°	5**
8	VII	$(C_6H_5)_2CO$	10	IX (35%)	114.5–115.5°	5**
9	VII	$C_6H_5COCH_3$	30	X (85%)	103–104°	¶
10	VII	$(CH_3)_2CO$	10	XI (47%)	52–53°	¶
11	XII	C_6H_5CHO	20	XIII (50%)	99–100°	4 (22%)
12	XII	$C_6H_5COCH_3$	300**	XIV (13%)	124–125°	¶
13	XII	$(CH_3)_2CO$	60	XV (82%)	b.p. 142–146° at 0.15 mm	4 (92%)
14	XVI	$(C_6H_5)_2CO$	120	XVII (64%)	203.5–204.5°	¶

*Time necessary for condensation, after addition of the carbonyl compound.
†Yield by isolation.
‡Melting points given are for analytical samples and are corrected.
§Maximum yield, if reported.
‖Potassiosulfone, from KNH_2, was used.
¶New compound.
**See Experimental for the details.



$CH_3SO_2CH_2\underset{\displaystyle OLi}{\underset{|}{C}}(C_6H_5)_2$

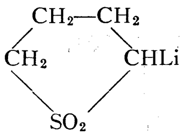
IIIa

$CH_3C_6H_4SO_2CH_2Li$

VII

$CH_3C_6H_4SO_2CH(CH_3)Li$

XII



XVI[2]

$CH_3C_6H_4SO_2CH(C_6H_5)Li$

XVIII

$CH_3C_6H_4SO_2C(CH_3)_2Li$

XIX

not well understood, such as how the relative solubilities of the adducts and how the different modes of hydrolysis of the adducts (e.g. III*a*) affect the equilibria, and how the structure and the medium affect the rates.[3]

All attempts to add lithium reagent XVIII or the potassium reagent XX to any of the carbonyl compounds used in this investigation failed. A steric argument is not very convincing in the case of acetone or benzaldehyde, and sodium diphenylmethide has been condensed with benzophenone (9*a*). The hypothesis suggested by Hauser (6*b*, 9) seems applicable here. That is, the formation of III from I is favored thermodynamically (eq. [2]) because III*a* is more stable in the basic medium that is I (the conjugate base of a weaker acid).[4] In this instance, however, XVIII (or XX) may well be the weaker base (stronger acid)[3] and so is thermodynamically favored over the *O*-lithio compound, like III*a*, which would be formed from it in the reaction illustrated in eq. [2]. In all the attempted condensation reactions of compounds XVIII and XX, benzyl *p*-tolyl sulfone was recovered in a quantitative yield. That the reagent was indeed formed in an essentially quantitative yield was established by the conversion of XX into compound XXI (eq. [4]) in a 91% yield, but this result is not incompatible with the possibility of reversion by thermodynamic control (6*c*). It has been reported that an attempt to make the Grignard reagent of benzhydryl *p*-tolyl sulfone failed, and that only 6% of the starting material could be recovered (4).

In contrast to the metalation of thiolane 1,1-dioxide[2] with ethylmagnesium bromide in anisole (2) to give only 4% of 1-phenyl-1-(1,1-dioxy-2-thiolanyl)methanol,[2] the metalation with lithium amide to form reagent XVI gave compound XVII in a 64% yield.

The structures of all the β-hydroxysulfones were confirmed by infrared absorption spectra and by nuclear magnetic resonance spectra.

EXPERIMENTAL

All melting points were determined on a Kofler hot stage and are corrected; infrared spectra were determined with a Perkin–Elmer model 337 spectrophotometer by the potassium bromide pellet method, unless otherwise indicated (see Table II); nuclear magnetic resonance spectra were measured at 60 Mc/s in deuteriochloroform (10–20%, by weight), with tetramethylsilane as an internal standard ($\tau = 10$); microanalyses, except for sulfur, were performed by S. J. Bagley, University of Calgary; sulfur analyses were performed by C. Daesslé, Montreal.

Reagents

Reagent-grade methyl sulfone from Matheson, Coleman, and Bell, m.p. 108–110°, and reagent-grade tetrahydrothiophene 1,1-dioxide (thiolane 1,1-dioxide)[2] from Matheson, Coleman, and Bell were used without further purification.[5] The benzaldehyde used was purified (11) and stored under nitrogen. Reagent-grade benzophenone from Fisher Scientific,

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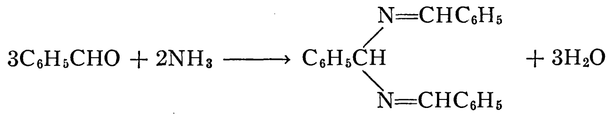
[2] The heterocyclic system $C_4H_8O_2S$ is best known by the trivial names (*i*) tetramethylene sulfone, (*ii*) sulfolane, and (*iii*) tetrahydrothiophene 1,1-dioxide. The naming of univalent radicals derived from these is, however, difficult and often awkward. The names used here (thiolane 1,1-dioxide for the parent compound and 2-thiolanyllithium 1,1-dioxide for compound XVI) are in accord with I.U.P.A.C. rules B-1 and B-5 for the "Organic Nomenclature of Fundamental Heterocyclic Systems" (see J. Am. Chem. Soc. 82, 5566 and 5572 (1960)). Also, see Experimental for the naming of compound XVII.

[3] For an excellent discussion of the problems involved, see ref. 8, chap. I; see also ref. 6*c*.

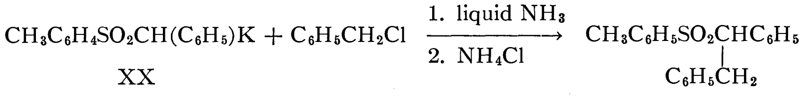
[4] For pertinent data and information, see ref. 8, pp. 1–20 and 138–143.

[5] For a very interesting discussion on the purification of thiolane 1,1-dioxide, see ref. 10.

[3]



[4]



$$CH_3C_6H_4SO_2CH(C_6H_5)K + C_6H_5CH_2Cl \xrightarrow[\text{2. }NH_4Cl]{\text{1. liquid }NH_3} CH_3C_6H_5SO_2\underset{C_6H_5CH_2}{\underset{|}{C}}HC_6H_5$$

XX XXI

m.p. 47.8–48.8°, reagent-grade acetophenone from British Drug Houses, m.p. 18–20°, spectro-grade acetone from Matheson, Coleman, and Bell, and cyclohexanone from Eastman were used without further purification. The benzyl chloride was freshly distilled, b.p. 77° at 22 mm, before use.

General Procedure

Lithium amide was prepared by a procedure based on that of Hauser (12). In a 500 ml, three-necked flask equipped with a stirrer, an addition funnel, and a Dry Ice condenser (carbon dioxide – acetone coolant) with a drying tube (KOH) was placed 200 ml of commercial anhydrous liquid ammonia. To the blue-colored solution, produced immediately upon the addition of a small portion of lithium,[6] was added a few crystals of ferric nitrate to form lithium amide (gray suspension). Additional small portions of lithium were added to a total of 0.76 g (0.11 mole), and the final suspension was light gray to white. To this suspension were added the sulfone (0.1 mole) and 200 ml of anhydrous ether[7] to give (usually) a dark-green solution. The aldehyde or ketone (0.1 mole), dissolved in anhydrous ether (100 ml), was added and the mixture stirred for the indicated length of time (Table I). Solid ammonium chloride (10 g) was added and, after the mixture was stirred for 5 min, it was poured into a beaker, the solvent was evaporated by heating on a steam bath, and the residue was agitated with dilute hydrochloric acid. The solids were separated by filtration and washed with water, and the liquids were extracted with ether. Purification of the crude products by recrystallization or distillation at a reduced pressure gave analytical samples. Satisfactory elemental analyses were obtained for all new compounds.

Reactions of Methylsulfonylmethyllithium (I)

The solution was dark green in color.

With Benzaldehyde. 2-Methylsulfonyl-1-phenylethanol (II)*

Purified (11) benzaldehyde (10.6 g, 0.1 mole), dissolved in 50 ml of anhydrous ether, was injected directly into the solution of I with a hypodermic syringe to form a homogeneous black solution. The product was isolated by the usual procedure. Recrystallization of II from ether gave 7.4 g (37%), m.p. 103–104° (lit. m.p. 106–106.5° (2) and 102–104° (4)). If the benzaldehyde was added with a separatory funnel rather than directly into the solution with a syringe, the best yield of II obtainable was 20%. The nuclear magnetic resonance spectrum showed three methyl protons at 7.02 τ, two methylene protons (doublet) at 6.7 τ with J_{AB} 5.0 c.p.s., one hydroxyl proton at 6.60 τ, one methinyl proton (triplet) at 4.70 τ with J_{AB} 5.0 c.p.s., and five aromatic protons at 2.59 τ.

Methylsulfonylmethylpotassium with Benzaldehyde to form II

Potassium amide (13) was used to prepare methylsulfonylmethylpotassium; the latter reacted with purified (11) benzaldehyde to give 4.0 g (20%) of II, identical in every respect with the II obtained with the lithium reagent.

With Benzophenone. 2-Methylsulfonyl-1,1-diphenylethanol (III)

Crude III was crystallized from ethanol and then from *n*-hexane. The nuclear magnetic resonance spectrum showed 3 methyl protons at 7.65 τ, 2 methylene protons at 6.03 τ, 1 hydroxyl proton at 5.01 τ, and 10 aromatic protons at 2.65 τ.

With Acetophenone. 1-Methylsulfonyl-2-phenylpropan-2-ol (IV)

Compound IV was obtained as a light-yellow, viscous liquid. The nuclear magnetic resonance spectrum showed three methyl protons at 8.33 τ (CH_3C—), three methyl protons at 7.53 τ (CH_3SO_2—), two methylene protons at 6.55 τ, one hydroxyl proton at 5.71 τ, and five aromatic protons at 2.67 τ.

With Acetone. 1-Methylsulfonyl-2-methylpropan-2-ol (V)

Crude V was obtained as a liquid which, after distillation (b.p. 112–114° at 0.4 mm), became solid. Two recrystallizations from dimethyl ether gave a white crystalline solid. The nuclear magnetic resonance spectrum showed six methyl protons at 8.57 τ (CH_3C—), three methyl protons at 6.98 τ (CH_3SO_2—), two methylene protons at 6.77 τ, and one hydroxyl proton at 6.60 τ.

Compound V was reported by Field and McFarland (4) as a liquid (their compound XXIII, b.p.

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[6] Foote Mineral Company, Exton, Pennsylvania; lithium ribbon, in small pieces, was added under a stream of argon.

[7] Most of the sulfones are not readily soluble in ether and were most conveniently added as a powder and washed in with the ether. The more soluble sulfones were added as a solution in ether (200 ml). "Anhydrous ether" indicates commercial anhydrous ether freshly distilled from lithium aluminium hydride.

120° at 3 mm, n_D^{25} 1.4670), but was considered by them to be impure. The analysis reported (4) was poor and the compound was not characterized further.

With Cyclohexanone. 1-(Methylsulfonylmethyl)-cyclohexanol (VI)

Crude VI was recrystallized twice from ethanol. The nuclear magnetic resonance spectrum (in pyridine) showed three methyl protons at 6.99 τ (CH_3SO_2—) and two methylene protons at 5.22 τ.

Reactions of p-Tolylsulfonylmethyllithium (VII)

Methyl *p*-tolyl sulfone was prepared from dimethyl sulfate and sodium-*p*-toluenesulfinate in a 75% yield, m.p. 86.5–87.5° (lit. m.p. 83–87.5° (14)), and was converted into VII with lithium amide. The solution was dark green in color.

With Benzaldehyde. 1-Phenyl-2-(p-tolylsulfonyl)-ethanol (VIII)*

Compound VIII was obtained as a colorless, viscous liquid, b.p. 205–210° at 0.3 mm, the nuclear magnetic resonance and infrared spectra (film between NaCl plates) of which were in agreement with the proposed structure. When left for 1 day, this material solidified to give 6.2 g (24%) of white crystals which were recrystallized from methyl cyclohexane. Compound VIII has been made by Potter (5) as an intermediate in the synthesis of the corresponding unsaturated sulfone, but its characterization was not reported. The nuclear magnetic resonance spectrum showed three methyl protons at 7.65 τ (CH_3Ar), two methylene protons (doublet) at 6.67 τ with J_{AB} 4.0 c.p.s., one hydroxyl proton at 5.92 τ, one methinyl proton (triplet) at 4.80 τ with J_{AB} 4.0 c.p.s., five phenyl protons at 2.75 τ, and four phenyl protons at 2.20 and 2.70 τ with J_{AB} 8.5. c.p.s.

With Benzophenone. 1,1-Diphenyl-2-(p-tolylsulfonyl)ethanol (IX)

This compound was recrystallized from *n*-hexane. Compound IX has been made by Potter (5) as an intermediate in the synthesis of the corresponding unsaturated sulfone, but its characterization was not reported. The nuclear magnetic resonance spectrum showed 3 methyl protons at 7.67 τ, 2 methylene protons at 5.87 τ, 1 hydroxyl proton at 4.68 τ, and 14 aromatic protons at 2.5–3.0 τ.

With Acetophenone. 2-Phenyl-1-(p-tolylsulfonyl)-2-propanol (X)

This compound was recrystallized from *n*-hexane. The nuclear magnetic resonance spectrum showed three methyl protons at 8.35 τ (CH_3C—), three methyl protons at 7.70 τ (CH_3Ar), two methylene protons at 6.39 τ, one hydroxyl proton at 5.45 τ, and nine aromatic protons at 2.5–3.0 τ.

With Acetone. 2-Methyl-1-(p-tolylsulfonyl)-propan-2-ol (XI)

This compound was recrystallized from *n*-hexane. The nuclear magnetic resonance spectrum showed six methyl protons at 8.57 τ ($(CH_3)_2C$—), three methyl protons at 7.55 τ (CH_3Ar), two methylene protons at 6.67 τ, one hydroxyl proton at 6.25 τ, and four aromatic protons at 2.13 and 2.60 τ with J_{AB} 8.0 c.p.s.

Reactions of 1-(p-Tolylsulfonyl)ethyllithium (XII)

Ethyl *p*-tolyl sulfone was prepared from diethyl sulfate and sodium *p*-toluenesulfinate by the method used for the synthesis of methyl *p*-tolyl sulfone (14), yield 47%, m.p. 54.5–55.5° (lit. m.p. 54–55° (4)); it was converted into XII with lithium amide. The solution was dark green in color.

With Benzaldehyde. 1-Phenyl-2-(p-tolylsulfonyl)-propanol (XIII)*

This compound was recrystallized from *n*-hexane. The nuclear magnetic resonance spectrum showed three methyl protons (doublet) at 8.83 τ (CH_3C—) with J_{AB} 7.5 c.p.s., one methinyl proton (doublet) at 8.50 τ (—CH(OH)—) with J_{AB} 7.5 c.p.s., one hydroxyl proton at 7.90 τ, three methyl protons at 7.59 τ (CH_3Ar), one methinyl proton (quintet) at 6.84 τ (—$CHSO_2$—) with J_{AB} 7.5 c.p.s., and nine aromatic protons at 2.0–3.0 τ.

With Acetophenone. 2-Phenyl-3-(p-tolylsulfonyl)-butan-2-ol (XIV)

This compound had m.p. 124–125° after two recrystallizations from aqueous ethanol and was obtained in only a 13% yield even after stirring for 5 h (Table I); 70% of the starting material was recovered unchanged. Shorter reaction times gave lower yields (e.g. 8% after 60 min) and a higher recovery of unchanged sulfone. The nuclear magnetic resonance spectrum showed three methyl protons at 8.70 τ (CH_3CH—), three methyl protons at 8.41 τ (CH_3C—), one hydroxyl proton at 7.87 τ, three methyl protons at 7.56 τ (CH_3Ar), one methinyl proton (quartet) at 6.97 τ (—$CHSO_2$—) with J_{AB} 7.5. c.p.s., five aromatic protons at 2.70 τ, and four aromatic protons at 2.31 and 2.85 τ (both doublets) with J_{AB} 8.0 c.p.s.

With Acetone. 2-Methyl-3-(p-tolylsulfonyl)-butan-2-ol (XV)

Compound XV was obtained as a colorless liquid, b.p. 142–146° at 0.15 mm (lit. b.p. 205–215° at 0.3–0.4 mm (4)), n_D^{23} 1.5352 (lit. n_D^{25} 1.5307 (4)). The nuclear magnetic resonance spectrum showed three methyl protons (doublet) at 8.80 τ (CH_3C—) with J_{AB} 7.0 c.p.s., six methyl protons at 8.70 and 8.42 τ ($(CH_3)_2C$—), one hydroxyl proton at 8.19 τ, three methyl protons at 7.58 τ (CH_3Ar), one methinyl proton (quartet) at 6.73 τ with J_{AB} 7.0 c.p.s., and four aromatic protons at 2.61 and 2.18 τ (both doublets) with J_{AB} 8.5 c.p.s.

Reactions of Thiolanyllithium 1,1-Dioxide (XVI)[2]

Tetrahydrothiophene 1,1-dioxide[2] (6.0 g, 0.05 mole) was converted into XVI with 10% excess lithium amide. The solution was dark gray in color and homogeneous.

With Benzophenone. 1,1-Diphenyl-(1,1-dioxy-2-thiolanyl)methanol (XVII)

This compound was recrystallized from ethanol. The nuclear magnetic resonance spectrum showed 4 methylene protons (multiplet) at 7.9 τ, 3 protons

TABLE II

Summary of data for β-hydroxysulfones

β-Hydroxy-sulfone*	Molecular formula	Calculated (%)			Found (%)			Infrared frequencies (cm^{-1})		
		C	H	S	C	H	S	ν(OH)	ν_{as}(SO$_2$)	ν_s(SO$_2$)
II	$C_9H_{12}O_3S$	Reference 2						3 430	1 308	1 121
III	$C_{15}H_{16}O_3S$	Reference 2						3 440	1 301	1 117
IV	$C_{10}H_{14}O_3S$	56.05	6.59	14.96	56.26	6.46	14.83	3 475	1 302	1 128†
V	$C_5H_{11}O_3S$	39.45	7.95	21.07	39.41	7.83	20.96	3 500	1 302	1 137
VI	$C_8H_{16}O_3S$	49.97	8.39	16.68	50.02	8.43	16.62	3 520	1 281	1 118
VIII	$C_{15}H_{16}O_3S$	65.19	5.84	11.60	65.03	5.89	11.75	3 490	1 300	1 147
IX	$C_{21}H_{20}O_3S$	71.65	5.72	9.10	71.42	5.88	9.15	3 475	1 292	1 135
X	$C_{16}H_{18}O_3S$	66.19	6.25	11.03	66.09	6.50	11.28	3 495	1 300	1 155
XI	$C_{11}H_{16}O_3S$	57.87	7.06	14.04	58.01	7.12	14.28	3 505	1 297	1 138
XIII	$C_{16}H_{18}O_3S$	Reference 4						3 490	1 298	1 144
XIV	$C_{17}H_{20}O_3S$	67.16	6.63	10.55	67.18	6.65	10.59	3 480	1 302	1 143
XV	$C_{12}H_{18}O_3S$	Reference 4						3 505	1 298	1 143†
XVII	$C_{17}H_{18}O_3S$	67.52	6.00	10.60	67.23	6.13	10.60	3 500	1 300	1 122

*Refer to Table I.
†Thin film between NaCl plates.

(multiplet) at 6.9 τ, 1 hydroxyl proton at 5.65 τ, and 10 phenyl protons at 2.5–3.0 τ.

1-Phenyl-1-(p-tolylsulfonyl)methyllithium (XVIII) and 1-Phenyl-1-(p-tolylsulfonyl)methylpotassium (XX)

Benzyl *p*-tolyl sulfone was prepared from sodium *p*-tolylsulfinate (14) and benzyl chloride in an 80% yield (15), m.p. 149–150° (lit. m.p. 146–146.5° (15)). Conversion into XVIII with lithium amide gave a green suspension, whereas conversion into XX with potassium amide gave a dark-green, sometimes more reddish, solution.

1,2-Diphenyl-1-(p-tolylsulfonyl)ethane (XXI)

To a solution of XX (0.05 mole) in a mixture of anhydrous ammonia (200 ml) and anhydrous ether (125 ml) was added dropwise, over 2 min, with good stirring, 6.3 g (0.05 mole) of freshly distilled benzyl chloride in ether (50 ml), and the mixture was stirred for 30 min, during which the solution turned to a yellow and later almost colorless suspension. Solid NH_4Cl (10 g) was added and, after the mixture was stirred for 5 min, it was poured into a beaker and the solvents were evaporated in the usual way (see General Procedure). The residue was agitated with dilute HCl (1 l) and the crude XXI was separated by filtration. Crystallization from ethanol gave white needles, m.p. 180–181°, yield 15.3 g (91%). The infrared spectrum showed sulfonyl absorption at 1 305 (ν_{as}) and 1 142 cm^{-1} (ν_s). The nuclear magnetic resonance spectrum showed 3 methyl protons at 7.65 τ (CH_3Ar), 2 methylene protons (doublet) at 6.35 τ with J_{AB} 11.5 c.p.s., 1 methinyl proton (triplet) at 5.84 τ with J_{AB} 11.5 c.p.s., and 14 aromatic protons at 2.5–3.0 τ.

Anal. Calcd. for $C_{21}H_{20}O_2S$: C, 74.96; H, 5.99; S, 9.53. Found: C, 75.13; H, 6.28; S, 9.57.

ACKNOWLEDGMENT

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