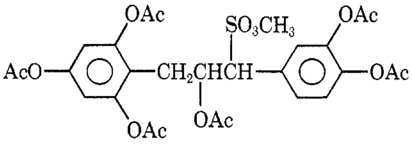
data for this material, purified by tlc, shows it to have structure III.



III

The nmr spectrum and acetyl analysis shows the presence of six acetyl groups. The two protons in the phloroglucinol ring appear as a singlet, as theory would predict, at τ 3.15. The hydrogen on the carbon bearing the sulfonate group is seen as a one-proton doublet at τ 5.23 with the methyl sulfonate absorption being observed as a singlet at τ 6.20. A small amount of the stereoisomeric epimer which differs in configuration about the carbon bearing the methyl sulfonate group is present; a small singlet (τ 6.35, $-SO_2OCH_3$) and doublet (τ 5.33, $-CHSO_2OCH_3$) for the epimer were observed in the nmr spectrum. The ir spectrum shows strong alkyl sulfonate absorption for III at 1370 and 1180 cm^{-1}. An elemental analysis corroborated the molecular formula as $C_{28}H_{30}O_{15}S$. An attempt to obtain a parent peak by mass spectrum failed; the highest mass observed was at *m/e* 596, corresponding to M − 42 (loss of ketene).

On the basis of these results, it is clear that catechin undergoes ready attack by the sulfonate group at C-2 in the pyran ring. Facile introduction of a sulfonic acid group at this position is reasonable, since it is a benzylic carbon involved in ether formation that is activated to attack by a *p*-hydroxyl group; the corresponding position in lignin molecules was also shown to be readily reactive to acidic sulfonation in recent model compound studies.[5-7] Sulfonation at this position is clearly inhibited by methylation of the *p*-hydroxyl group; reaction of a flavan bearing a 4′-methoxyl group with calcium bisulfite at pH 1.5 and 130° resulted in substitution of a sulfonic acid group at C-2 only after 48 hr.[8]

Experimental Section

Nmr spectra were obtained with a Varian T-60 spectrometer and the ir spectra on a Beckman IR-20 spectrophotometer. Analyses were performed by Alfred Bernhardt Microanalytical Laboratories, Elbach über Engelskirchen, West Germany. Decationizations were carried out with Ionac C-242 resin (H^+ form). Evaporations were *in vacuo* (25 mm).

Reaction of D-Catechin (II) with Aqueous Sodium Sulfite–Bisulfite.—D-Catechin (1.000 g), a mixture of sodium metabisulfite (0.130 g) and sodium sulfite (0.060 g), and water (8 ml) were placed in a small stainless steel vessel that was sealed and heated for 0.5 hr at 170°. After cooling, the solution was diluted with water (75 ml) and decationized.

Processing by the General Method of Gellerstedt and Gierer.[5]—The cation-free solution was adjusted to 50 ml by evaporation and neutralized with aqueous barium hydroxide to pH 8.0. After removal of a small amount of precipitate by centrifuging, the solution was decationized. . The solution was neutralized with triethylamine to pH 8.0 and evaporated to dryness. The solids were dissolved in pyridine–acetic anhydride (10 ml of each). After 24 hr, the solution was poured into ice water (150 ml) and stirred for 2 hr. This mixture was evaporated at 40-45°, and the residue was dissolved in water and decationized. The solution was neutralized to pH 8.5 with silver acetate and freeze dried, yield 1.30 g.

The sample was placed in a solution of acetonitrile (125 ml) and methyl iodide (25 ml). The mixture was gently refluxed, with stirring, for 20 hr, during which time more methyl iodide (2 × 10 ml) was added. Solids were removed by centrifuging and the filtrate was evaporated to give 0.90 g. Tlc analysis (silica gel G) using 200:47:15:1 (v/v) benzene:ethanol:water: acetic acid (upper layer) (solvent A) or 5:4:1 (v/v) toluene:ethyl acetate:formic acid (solvent B) with I_2 visualization showed a mixture of four to five components.

Preparation and Isolation of 1-Methylsulfonate-(3,4-diacetoxyphenyl)-2-acetoxy-3-(1,3,5-triacetoxyphenyl)propane (III).—The product (0.90 g) of the preceding sequence was placed in benzene (200 ml). Sodium acetate (1.5 g) and acetic anhydride (2 ml) were added. The suspension was refluxed overnight with stirring; the condenser was fitted with a drying tube. After cooling, the mixture was poured into water (v/v) and stirred for 0.5 hr. The benzene layer was removed using a separatory funnel. Two additional extractions were carried but with benzene. Drying ($MgSO_4$) and evaporation gave 0.254 g of III. Tlc showed only one major spot upon development with solvents A and B and I_2 visualization. Purification by preparative tlc using solvents A and B gave purified III as an amorphous, white solid. The material was stored under N_2 to prevent decomposition: nmr ($CDCl_3$) τ 2.72 (m, 3), 3.15 (s, 2), 4.42 (m, 1), 5.23 (d, 1, J = 7 Hz), 6.20 (s, 3), 7.12 (m, 2), 7.73 (m, 15), 8.08 (m, 3) (nmr spectra were also obtained in CD_3CN and CD_3COCD_3); ir ($CHCl_3$) 1770 (s), 1370 (s), and 1189 cm^{-1} (s). An attempt to crystallize purified III (CH_2Cl_2 and C_6H_{14}) gave an amorphous white solid that melted at 68°. *Anal.* Calcd for $C_{28}H_{30}O_{15}S$: C, 52.66; H, 4.74; S, 5.02. Found: C, 52.55; H, 4.87; S, 4.89. Calculated acetyl analysis for six acetyl groups: 40.4%. Found: 37.7%.

Registry No.—II, 154-23-4; III, 35639-04-4.

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[6] G. Gellerstedt and J. Gierer, *Acta Chem. Scand.*, **22**, 2029 (1968).

[7] G. Gellerstedt and J. Gierer, *ibid.*, **22**, 2510 (1968).

[8] H. Richtzenhain and B. Alfredsson, *Ber.*, **89**, 378 (1956).

α,β-Ethylenic Sulfones from Sulfonomethylphosphonate Carbanions and Aldehydes and Ketones

GARY H. POSNER* AND DANIEL J. BRUNELLE[1]

Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218

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For our current investigation into the reactions of organocopper reagents with α,β-unsaturated sulfur compounds, we required an efficient method for converting aldehydes and ketones to vinylic sulfones. α,β-Ethylenic sulfones have been prepared in various ways.[2] Oxidation of ethylenic sulfides to sulfones can be accomplished with hydrogen peroxide in acetic acid, but the yields of unsaturated sulfone are generally low.[3] The most direct procedure is reaction of a carbonyl substrate with the anion of a sulfonomethylphosphonate ester (**1a**, **1b**). This Horner–Wittig reaction using sodium hydride or sodium methoxide at room temperature to generate the phosphonate anion

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[1] NSF Trainee, 1970–present.

[2] I. C. Popoff, J. L. Dever, and G. R. Leader, *J. Org. Chem.*, **34**, 1128 (1969), and references cited therein.

[3] (a) V. Baliah and S. Shanmuganathan, *J. Indian Chem. Soc.*, **35**, 31 (1958). (b) G. Wittig and M. Schlosser, *Chem. Ber.*, **94**, 1373 (1961). (c) In our hands, hydrogen peroxide–acetic acid oxidation of methyl cyclohexylidenemethyl sulfide (prepared from cyclohexanone) and *trans*-methyl styryl sulfide (prepared from benzaldehyde) to the corresponding vinylic sulfones proceeded in 33 and 40% overall yields (from cyclohexanone and benzaldehyde, respectively).

TABLE I

CONVERSION OF CARBONYL SUBSTRATES TO α,β-ETHYLENIC SULFONES USING SULFONOMETHYLPHOSPHONATE CARBANIONS (EQ 1)

Product	R_1	R_2	R_3	Mp or bp, °C (mm)	Yield, %	Nmr	
						C=CHSO$_2$	R_2
I	C_6H_5	H	CH_3	78–79[a]	87[b]	7.01 (d, 16)	7.75[c] (d,[d] 16[e])
II	$CH_3(CH_2)_5$	H	CH_3	105–106 (0.15)	97[b]	6.40 (d, 15)	6.90 (d of t, 15, 6)
III	$CH_3(CH_2)_4$	CH_3	CH_3	80–81 (0.05)	86[b]	See Experimental Section	
IV	Cyclohexanone		CH_3	94–95 (0.1)	97[b]	6.13 (s)	
V	C_6H_5	H	p-ClC$_6$H$_4$	78–78.5	90[f]	6.95 (d, 16)	
VI	$CH_3(CH_2)_5$	H	p-ClC$_6$H$_4$	158–160 (0.05)	80[g]	6.50 (d, 15)	7.13 (d of t, 15, 6.5)
VII	Cyclohexanone		p-ClC$_6$H$_4$	71–72.5	72[h]	6.20 (s)	

[a] Lit.[4] mp 80°. [b] Yield of crude product. [c] Chemical shift (δ) relative to TMS. [d] Multiplicity: s (singlet), d (doublet), t (triplet). [e] Coupling constant in cps. [f] Yield after recrystallization (ethanol). [g] Yield after distillation. [h] Yield after column chromatography (Florisil/benzene).

has thus far been limited to preparation of arylidene sulfones.[2,4] We report here a modification of this procedure; when *n*-butyllithium is used to generate the phosphonate anion in tetrahydrofuran at −78°, this anion reacts not only with aryl aldehydes to form arylidene sulfones but also with aliphatic aldehydes *and ketones* to give alkylidene sulfones in high yield (eq 1).[4a]

$$(EtO)_2POCH_2SO_2R_3 \xrightarrow[2.\ R_1R_2C=O]{1.\ n\text{-BuLi/THF/}-78^\circ} R_1R_2C{=}CHSO_2R_3 \quad (1)$$

1a, $R_3 = CH_3$
b, $R_3 = p$-ClC$_6$H$_4$

The results are summarized in Table I.[5]

In agreement with previous reports,[2,4] the *trans*-vinyl sulfone is the exclusive product in reactions with aldehydes, as indicated by the high nmr coupling constants of the vinyl protons (see Table I); in the reaction with 2-heptanone, two products are formed in 2:1 ratio, but no stereochemical assignment could be made (see Experimental Section for nmr of sulfone III).

Experimental Section

Nmr spectra were recorded on a Varian A-60 nmr spectrometer in CCl$_4$ (liquid products) or CDCl$_3$ (solid products), with chemical shifts reported in parts per million (δ), relative to internal TMS. Infrared spectra were recorded on a Perkin-Elmer 337 spectrophotometer as neat films or in CHCl$_3$ solution (solid products). Melting points are uncorrected.

Starting Materials.—Diethyl methylthiomethylphosphonate, prepared by the method of Green,[6] was oxidized with KMnO$_4$ in neutral solution, as described by Shahak and Almog,[4] to yield diethyl methylsulfonomethylphosphonate (**1a**), which was recrystallized from benzene (71% yield, mp 96°).

Chloromethyl *p*-chlorophenyl sulfide, which was prepared according to Fancher,[7] was refluxed with triethyl phosphite (1:1.7 molar ratio) for 6 hr and distilled [bp 144–147° (0.05 mm), 82% yield]. Oxidation with KMnO$_4$ in acidic solution[4] followed by recrystallization from benzene–octane (1:1) gave diethyl (*p*-chlorophenylsulfono)methylphosphonate (80% yield, mp 68–70°).

The ketones and aldehydes were freshly distilled. Tetrahydrofuran was dried by distillation over LiAlH$_4$. *n*-Butyllithium (1.32 *M* in pentane, Foote Mineral Co.) was used without purification.

General Procedure for the Formation of Vinyl Sulfones.—To a stirred solution of 2.415 g (10.0 mmol) of diethyl methylsulfonomethylphosphonate (**1a**) or 3.267 g (10.0 mmol) of diethyl (*p*-chlorophenylsulfono)methylphosphonate (**1b**) in 50 ml of dry THF under N$_2$ and at −78° was added 7.5 ml (10.0 mmol) of 1.32 *M* *n*-butyllithium in pentane. The resulting solution was stirred at −78° for 15 min to 3 hr, at which time 10.0 mmol of the aldehyde or ketone was added in 10 ml of THF. The clear, colorless solution was stirred at −78° for 1 hr, then allowed to warm to 25°, and stirring was continued at that temperature overnight, or at 35–50° for 3–4 hr.

The resulting pale yellow solution was poured into 50 ml of saturated aqueous NH$_4$Cl and extracted with three 25-ml portions of ether. The combined extract was successively washed with 50-ml portions of H$_2$O, saturated NaHCO$_3$, and brine, and each aqueous phase was back-extracted with a 10-ml portion of ether. The combined ether extracts were dried over MgSO$_4$, and the solvents were removed on a rotary evaporator, yielding the crude product, which was generally pure by nmr.

Following are three examples of this general procedure, *i.e.*, the preparation of vinyl sulfones III, IV, and VII.

Methyl 2-Methyl-1-heptenyl Sulfone (III).—The solution of diethyl methylsulfonomethylphosphonate anion was stirred at −78° for 1 hr before addition of 2-heptanone. Work-up involved stirring at 40° for 3 hr. The crude product III (1.628 g, 86% from 2-heptanone) was analyzed by vpc on a 5-ft 3% SE-30 column (Varaport 30), with temperature programming from 110 to 150°, which indicated 2% 2-heptanone and two product peaks in a ratio of 1.75:1. Preparative gas chromatography on a 20-ft 20% SE-30 (Chromosorb W) column at 245° allowed separation of the isomers. The major product had nmr δ 0.90 [distorted t, 3 H, $\mathbf{CH_3}(CH_2)_3$], 1.3–1.4 (multiplet, 6 H, CH$_2$ protons), 1.92 (d, 3 H, J = 1 Hz, allylic CH$_3$), 2.2–2.4 (multiplet, 2 H, allylic CH$_2$), 2.90 (s, 3 H, SO$_2$CH$_3$), 5.23 (broad s, 1 H, vinyl proton); ir 1130 and 1160 (SO)$_2$ and strong bands at 1320, 965, and 915 cm^{-1}. The minor product had nmr δ 0.90 [distorted t, 3 H, $\mathbf{CH_3}(CH_2)_3$], 1.35 (broad multiplet, 6 H, CH$_2$ protons), 2.15 (d superimposed on multiplet, 5 H, J = 1.3 Hz, allylic CH$_3$ on allylic CH$_2$), 2.87 (s, 3 H, SO$_2$CH$_3$), 6.17 (broad s, 1 H, vinyl proton). The ir was identical with that of the major product, but lacked absorption at 915 cm^{-1}. The analytical sample was prepared by distillation of the crude product and thus contained both isomers.

Anal. Calcd for $C_9H_{18}SO_2$: C, 56.80; H, 9.53; S, 16.85. Found: C, 56.57; H, 9.70; S, 16.87.

Methyl Cyclohexylidenemethyl Sulfone (IV).—The solution of diethyl methylsulfonomethylphosphonate anion was stirred at −78° for 30 min before addition of cyclohexanone. Work-up involved stirring overnight at 25°. The crude product IV (1.638 g, 97%) was analyzed by vpc on a 5-ft 3% SE-30 column (Varaport 30) at 150°, which showed about 0.5% impurity: nmr δ 1.67 (broad s, 6 H, cyclohexyl protons β and γ to double bond), 2.2 (broad multiplet, 2 H, cyclohexyl protons α to double bond), 2.7–2.8 (broad multiplet, 2 H, cyclohexyl protons α to double bond), 2.90 (s, 3 H, SO$_2$CH$_3$), and 6.13 (s, 1 H, vinyl proton); ir 1030 and 1190 cm^{-1} (SO$_2$). The product was distilled [bp 94–95° (0.1 mm)] for microanalysis.

Anal. Calcd for $C_8H_{14}SO_2$: C, 55.14; H, 8.10; S, 18.36. Found: C, 55.00; H, 7.97; S, 18.34.

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(4) I. Shahak and J. Almog, *Synthesis*, 170 (1969); 145 (1970).

(4a) NOTE ADDED IN PROOF.—The diethyl (*p*-chlorophenylsulfono)methylphosphonate anion does not react well with *n*-alkyl ketones.

(5) All new compounds gave satisfactory microanalyses.

(6) M. Green, *J. Chem. Soc.*, 1324 (1963).

(7) German Patent 1,112,735 (1958); L. W. Fancher (Stauffer Chemical Co.); *Chem. Abstr.*, **56**, 11499 (1962).

p-**Chlorophenyl Cyclohexylidenemethyl Sulfone (VII).**—The solution of diethyl (*p*-chlorophenylsulfono)methylphosphonate anion was stirred at −78° for 2 hr before addition of cyclohexanone. Work-up involved stirring at 50° for 4 hr. The crude product (2.865 g of yellow oil) was purified by column chromatography over 100 g of Florisil with benzene eluent, to give 1.953 g (72% of VII, mp 70–71.5°) upon evaporation. Recrystallization from ethanol gave 1.782 g of white needles: mp 71–72.5°; nmr δ 1.6 (broad s, 6 H, cyclohexyl protons β and γ to double bond), 2.2 (broad s, 2 H, cyclohexyl protons α to double bond), 2.79 (broad s, 2 H, cyclohexyl protons α to double bond), 6.20 (s, 1 H, vinyl proton), 7.55 (d, 2 H, J = 9 Hz, aromatic protons), and 7.92 (d, 2 H, J = 9 Hz, aromatic protons); ir 2925, 2845 (CH), 1620, 1580 (C=C), 1140, 1083 cm^{-1} (SO$_2$).

Anal. Calcd for $C_{13}H_{15}SO_2Cl$: C, 57.66; H, 5.58; S, 11.84; Cl, 13.09. Found: C, 57.79; H, 5.67; S, 11.98; Cl, 12.92.

Registry No.—II, 35324-47-1; III, 35378-30-4; IV, 35378-31-5; V, 7854-83-7; VI, 35324-49-3; VII, 35324-50-6.

Synthesis of Sulfonyl Fluorides by Use of a Fluoride Ion Exchange Resin

C. L. BORDERS, JR.,* D. L. MACDONELL,[1a] AND
J. L. CHAMBERS, JR.[1b]

*Department of Chemistry, College of Wooster,
Wooster, Ohio 44691*

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We wish to report an extremely rapid and efficient method for the synthesis of small quantities of sulfonyl fluorides from the corresponding sulfonyl chlorides by ion exchange chromatography. The technique is characterized by high yields (82–94%, starting with 1 g of aromatic sulfonyl chloride) and pure products which are easily isolated by evaporation of the solvent and need no recrystallization.

Experimental Section

General.—Melting points were determined on a Mel-Temp apparatus and are uncorrected. Infrared spectra were measured on a Perkin-Elmer Model 700 spectrophotometer. Solvents were evaporated on a Buchler flash evaporator. Elemental analyses were determined by Galbraith Laboratories, Knoxville, Tenn.

Starting Materials.—2,4-Dinitrobenzenesulfonyl chloride, *p*-chlorobenzenesulfonyl chloride, *p*-bromobenzenesulfonyl chloride, and *p*-fluorosulfonylbenzenesulfonyl chloride were purchased from Aldrich Chemical Co. *p*-Nitrobenzenesulfonyl chloride and *m*-nitrobenzenesulfonyl chloride were purchased from Matheson Coleman and Bell. *p*-Toluenesulfonyl chloride was obtained from Eastman Organic Chemicals, and methanesulfonyl chloride was a product of the J. T. Baker Co. For the purposes of comparison, authentic samples of *p*-nitrobenzenesulfonyl fluoride, *m*-nitrobenzenesulfonyl fluoride, *p*-chlorobenzenesulfonyl fluoride, and *p*-bromobenzenesulfonyl fluoride were synthesized by the method of Davies and Dick.[2]

Preparation of the Fluoride Anion Exchange Resin.—The strongly basic quaternary amine anion exchange resin, AG1-X10 (200–400 mesh), was purchased from Bio-Rad Laboratories in the chloride form. Oven-dried resin (80 ml, 40 g) was suspended in water and transferred to a burette. The resin was eluted with 5.0 *M* aqueous potassium fluoride, at a rate of 150 ml per hour, until a spot test of the eluate with aqueous AgNO$_3$ indicated the absence of chloride. Approximately 3 l. of 5.0 *M* KF solution was needed to elute the chloride from the resin.[3] The fluoride form resin was washed with three 100-ml portions of distilled water, dried in an oven at 115° for 2 hr, and stored in a desiccator. This preparation yielded 38.7 g of dried resin.

Synthesis of Sulfonyl Fluorides.—The oven-dried fluoride form resin (5 ml) was transferred to a 10-ml B-D disposable syringe and washed with 20 ml of acetonitrile. The appropriate sulfonyl chloride (1.000 g) was dissolved in 10 ml of acetonitrile and passed through the resin at a rate of approximately 1 ml/min.[4] The resin was then washed with two 5-ml portions of acetonitrile, and the combined eluent and washings were evaporated to near dryness on a rotary evaporator. On cooling in an ice bath for several minutes, the solid products crystallized. For the synthesis of methanesulfonyl fluoride (**8**), the quantities were increased by a factor of 3, and the final product was purified by microdistillation.

Results and Discussion

The results of the synthesis of eight different sulfonyl fluorides from the corresponding sulfonyl chlorides by the ion exchange method are indicated in Table I.

TABLE I
SYNTHESIS OF SULFONYL FLUORIDES BY USE OF A FLUORIDE ION EXCHANGE RESIN[a]

Compd	No.	Mp (bp), °C	Lit. mp (bp), °C	Yield, %
4-Bromobenzenesulfonyl fluoride	1	64–65	65–66[b]	92
4-Chlorobenzenesulfonyl fluoride	2	47–48	47–48[c]	82
p-Toluenesulfonyl fluoride	3	39–41	41–42[c]	86
3-Nitrobenzenesulfonyl fluoride	4	45–46	46–47[b]	86
4-Nitrobenzenesulfonyl fluoride	5	76–77	75–78[b]	89
2,4-Dinitrobenzenesulfonyl fluoride	6	97.5–98.5	*d*	91
1,4-Benzenedisulfonyl fluoride	7	155–156	*e*	94
Methanesulfonyl fluoride	8	(120–122)	(124)[f]	71

[a] Acetonitrile used as solvent. [b] See M. E. Aberlin and C. A. Bunton, *J. Org. Chem.*, **35**, 1825 (1970). [c] See ref 2. [d] Not reported in literature. Recrystallized from absolute ethanol. *Anal.* Calcd for $C_6H_3FN_2O_6S$: C, 28.45; H, 1.44. Found: C, 28.56; H, 1.50. [e] Not reported in literature. Recrystallized from ethanol–water. *Anal.* Calcd for $C_6H_4F_2O_4S_2$: C, 29.75; H, 1.66. Found: C, 29.55; H, 1.54. [f] See W. Davies and J. H. Dick, *J. Chem. Soc.*, 483 (1932).

These results were obtained using acetonitrile as solvent. They indicate high purity, as determined by the comparison of melting points to literature values for reported compounds, and by comparison of infrared spectra to those of the authentic materials for compounds **1**–**4**.

Infrared spectra were a useful tool in determining the extent of conversion of the sulfonyl chlorides to sulfonyl fluorides. The strong asymmetric and symmetric sulfur–oxygen stretching frequencies of aromatic sulfonyl chlorides occur at 1385–1340 and 1185–1160 cm^{-1}, respectively.[5] On conversion to the sulfonyl

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[1] (a) Taken in part from the Senior Independent Study Thesis of D. L. MacDonell, The College of Wooster, 1972. (b) NSF undergraduate research participant, summer, 1971.

[2] W. Davies and J. H. Dick, *J. Chem. Soc.*, 2104 (1931).

[3] Subsequent regeneration steps required approximately 2 l. of 5.0 *M* aqueous KF.

[4] When the sulfonyl chloride was dissolved in 50 ml of acetonitrile and passed through the resin, a low yield of impure product was obtained.

[5] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Boston, Mass., 1966, p 181.