Synthesis and Spectral Data on Some Benzo[*b*]thiophenesulfonic Acid Derivatives

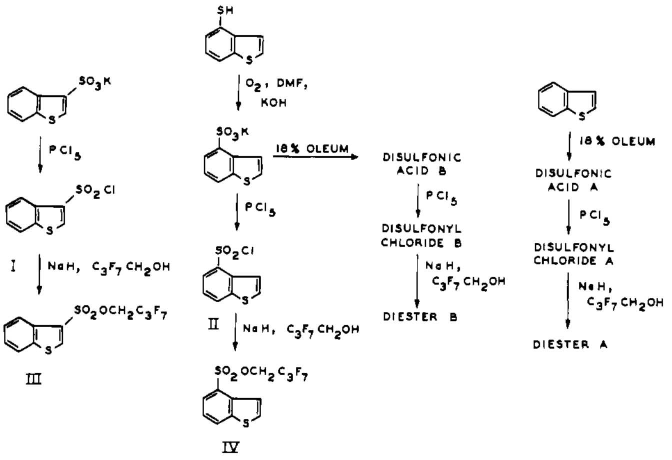
PHILLIP S. LANDIS
Mobil Oil Corp., Central Research Division, Princeton, N.J. 08540

JAMES A. BRENNAN and PAUL B. VENUTO[1]
Mobil Oil Corp., Applied Research and Development Division, Paulsboro, N. J. 08066

Benzo[*b*]thiophene-3- and 4-sulfonyl chlorides and their heptafluorobutyl esters are prepared and details of their NMR, infrared, ultraviolet, and mass spectra are recorded.

SULFONATION of benzo[*b*]thiophene has been demonstrated to yield predominantly the 3-sulfonate (*3*). Other positional isomers have not been reported and no spectral data are available on any benzo[*b*]thiophene sulfonate. The authors have prepared 3- and 4-benzo[*b*]thiophene sulfonyl chlorides I and II and 3- and 4-benzo[*b*]thiophene-(2,2,3,3,4,4,4-heptafluorobutyl)sulfonates III and IV and record here details of their infrared, ultraviolet, nuclear magnetic resonance, and mass spectra.

The preparative schemes are outlined below.



Ultraviolet data for I to IV are recorded in Table I. The sulfonyl chlorides show two strong bands at about 240 and 300 mμ, with substitution in the 4-position generally producing a band shift to longer wavelengths when compared with the analogous 3-substituted derivatives. The short wavelength bands have higher extinction coefficients than the longer wavelength bands.

Infrared data and assignments and mass spectrometer data for I to IV are given in Table I. Mass spectral patterns are consistent with facile cleavage of the R—SO_2R' bond (R′ = Cl, O—$CH_2C_3F_7$) and fragmental loss of SO_2 and Cl.

The nuclear magnetic resonance data in Table II provide convincing corroboration of structural assignments. In line with previous observations (*2,4,5*), long range couplings between the 2- and 6-protons (0.5 c.p.s.) and between the 3- and 7-protons (0.9 c.p.s.) are observed in the benzo[*b*]thiophene derivatives.

Polysulfonation of benzo[*b*]thiophene has never been reported but disulfonation can be effected by sulfonation of benzo[*b*]thiophene itself or of potassium benzo[*b*]thiophene-4-sulfonate. Purification and definitive characterization were extremely difficult, however.

EXPERIMENTAL

Spectra. Infrared spectra were run neat or as KBr disks using a Perkin-Elmer 421 instrument. Ultraviolet spectra were determined in ethanol solution using a Carey 14 spectrophotometer. NMR spectra were run on 10 weight % solutions in benzene-d_6 using a Varian A-60 spectrometer. Mass spectra were obtained at 70 e.v. on a Consolidated Electrodynamics Corp. Model 21-103 with an inlet temperature of 350° C. Gas chromatographic analyses were carried out with an F & M Model 720 dual-column chromatograph, using a 12-foot column containing 20% silicone gum rubber on Chromosorb.

Benzo[*b*]thiophene-3-sulfonyl Chloride I. This was prepared from potassium benzo[*b*]thiophene-3-sulfonate and PCl_5 by the method of Pailer and Romberger (*3*), yield 79%, m.p. 87.5–89.0° C. (lit. m.p. 88–90° C.).

Potassium Benzo[*b*]thiophene-4-sulfonate. A mixture of 10.5 grams (0.063 moles) of 4-mercaptobenzo[*b*]thiophene (Mobil Chemical Co., Metuchen, N.J.), 188 ml. of dimethylformamide, and 15.0 grams of pulverized potassium hydroxide was placed in a 500-ml. iodine flask fitted with a condenser and an oxygen inlet tube. The mixture was stirred magnetically, while oxygen was passed over the surface for 24 hours. The mixture was filtered and evaporated to dryness (vacuum) yielding 14.1 grams of residue. The residue was boiled with an equal volume of water and treated with an equal volume of saturated KCl solution. The precipitated salt was separated by filtration, dried overnight at 100° C., and extracted in a Soxhlet with 300 ml. of absolute ethanol. The cooled alcohol solution yield was 8.55 grams of platelets. Concentration of the mother liquor gave an additional 1.43 grams or a total yield of 63%.

Benzo[*b*]thiophene-4-sulfonyl Chloride II. This was prepared from potassium benzo[*b*]thiophene-4-sulfonate and PCl_5 by the method of Pailer and Romberger (*3*). Compound II was isolated as pale yellow needles, yield 84%, m.p. 85.0–86.5° C. after recrystallization from *n*-hexane.

Anal. Calcd. for $C_8H_5S_2O_3Cl$: C. 41.25; H, 2.16. Found: C. 41.05; H. 2.17.

Benzo[*b*]thiophene-3-(2,2,3,3,4,4,4-heptafluorobutyl) sulfonate III. Compound III was prepared from benzo[*b*]thiophene-3-sulfonyl chloride (I) (4.0 grams, 0.017 mole) and 2,2,3,3,4,4,4-heptafluorobutanol [9.66 grams, 0.0482 mole (Columbia Organic Chemicals, Columbia, S.C.), GLC

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[1] Present address: General Electric Co., Life Sciences Branch, General Chemistry Section. P.O. Box 8, Schenectady, N.Y. 12301

Table I. Spectral Data for Monosubstituted Derivatives

	Ultraviolet Data		Infrared Data		Mass Spectrometer Data		
Compound	Mμ	ϵ_{max}	Cm.$^{-1}$	Assignment	*m/e*	%	Assignment
I	274	11,460	1495, 1470, 1435	Aromatic C=C	89	100.0	Base peak^a
	299	9,440	1385, 1175	—SO_2Cl	133	77.3	Loss of SO_2Cl
			749, 606, 557, 535, 477	. . .	168	39.0	Loss of SO_2
					197	71.3	Loss of Cl
					232	56.2	M^-, $C_8H_5ClO_2S_2$
					234	23.7	M^-, isotopes
					236	2.0	M^-, isotopes
II	240	21,000	1560, 1460, 1430	Aromatic C=C	89	43.7	. . .
	305.5	6,600	1380,1335, 1171, 1157	—SO_2—	133	100.0	Loss of SO_2Cl
			792, 757, 604, 573, 542		168	18.5	Loss of SO_2
			528, 493	. . .	197	29.2	Loss of Cl
					232	32.3	M^-, $C_8H_5ClO_2S_2$
					234	13.5	M^-, isotope
					236	2.2	M^-, isotope
III	231	10,100	1490, 1460, 1430	Aromatic C=C	69	30.4	CF_3
	240	7,290	1380, 1183	—SO_2O—	133	72.8	Loss of $SO_2OCH_2C_3F_7$
	263	6,020	1230, 1130	—C_3F_7	197	42.2	Loss of $OCH_2C_3F_7$
	269	5,980	1047, 1013, 978, 915		396	100.0	M^-, $C_{12}H_7F_7O_3S_2$
	290	4,320	810, 760, 600	. . .			
	298	4,000					
IV	235.5	35,900	1560, 1440, 1420	Aromatic C=C	69	21.3	CF_3
	240.5	30,500	1380, 1183	—SO_2O—	133	100.0	Loss of $SO_2OCH_2C_3F_7$
	285	6.860	1230, 1130	—C_3F_7	197	17.0	Loss of $OCH_2C_3F_7$
	294	7,450	1050, 1017, 963, 918		396	58.6	M^-, $C_{12}H_7F_7O_3S_2$
	303	6,570	843, 762. . .				

^{a} Assignment: ($H—C \equiv C—SO_2$)

Table II. NMR Data

Solvent, C_6D_6; external reference, tetramethylsilane

	Chemical Shifts, C.P.S.					
Compound	*H2*	*H3*	*H4*	*H5*	*H6*	*H7*
I	470.1	. . .	496.2	434.9	427.5	439.0
II	429.6	475.8	. . .	470.1	406.9	448.0
III	489.3	. . .	493.8	438.2	435.0	454.1
IV	441.7	474.3	. . .	475.4	425.5	463.9

	Chemical Shifts, C.P.S.								
	J_{23}	J_{26}	J_{37}	J_{45}	J_{46}	J_{47}	J_{56}	J_{57}	J_{67}
I	. . .	0.4	. . .	8.4	1.1	0.8	7.3	1.0	8.3
II	5.6	0.5	0.9	. . .	. . .	. . .	7.7	0.9	8.2
III	. . .	0.4	. . .	7.9	1.2	0.8	7.1	1.0	7.8
IV	5.7	0.5	0.9	. . .	. . .	. . .	7.7	0.9	8.2

purity 99.3% after distillation] by the method of Bergmann and Shani (*1*). The product was a yellow oil, 6.4 grams (crude yield, 95%). Distillation in vacuo afforded 5.9 grams (88% yield) of III, a pale yellow oil, b.p. 127–29° C. (0.2 mm.), n_D^{20} 1.48511, showing a single peak by GLC.

Anal. Calcd. for $C_{12}H_7F_7O_3S_2$: C. 36.38; H. 1.78. Found: C, 36.02; H, 1.83.

Benzo[*b*]thiophene-4-(2,2,3,3,4,4,4-heptafluorobutyl)sulfonate IV. The preparation of IV was identical with that of III. A crude yield of 94% was obtained. Vacuum distillation afforded an 86% yield of IV, a pale yellow oil, b.p. 136–140° C. (0.5 mm.) n_D^{20} 1.49178, showing a single peak by GLC.

Anal. Calcd. for $C_{12}H_7F_7O_3S_2$: C, 36.38; H, 1.78. Found: C, 36.37; H, 1.78.

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