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Nucleophilic Substitution of Alkyl (or Aryl) Imidomethyl Sulfones. A New Convenient Synthesis of Alkane(or Arene)sulfinates

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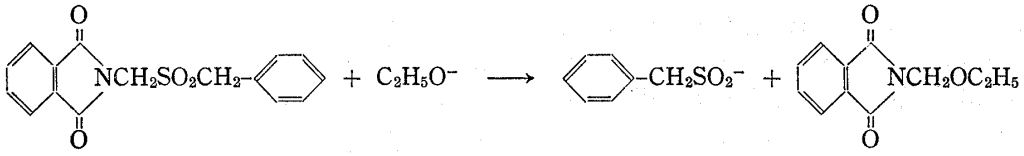
Convenient syntheses of sodium alkane- and arenesulfinates in high yields and purities have been provided by nucleophilic substitution reactions of alkyl phthalimidomethyl sulfones and aryl succinimidomethyl sulfones, respectively, with ethoxide or thiolates.

Keywords——nucleophilic substitution; alkyl imidomethyl sulfide; aryl imidomethyl sulfide; alkyl imidomethyl sulfone; aryl imidomethyl sulfone; alkanesulfinate; arenesulfinate; alkyl benzyl sulfone; arenesulfinic acid; cmc

Methods available for the synthesis of alkane- and arenesulfinates include treatment of organometallic compounds with sulfur dioxide,[2] reduction of organic sulfonyl chlorides with zinc or sodium sulfite,[2] oxidation of thioalcohols with *m*-chloroperoxybenzoic acid,[3] reaction of diazonium compounds with sulfur dioxide,[2] and base-induced cleavage of organic sulfones.[2] However, in these methods the work-ups encounter complication arising from side reactions and further reactions owing to the instability of the sulfinates, particularly, alkane analogs. The method of the cleavage of sulfones to alkali metal alkane- and arenesulfinates has been improved by using more reactive sulfones such as 1,2-dialkyl(or diaryl)sulfonylethanes,[4] 3-alkyl(or aryl)sulfonylpropanenitriles[5] and ethyl 3-alkyl(or aryl)sulfonylacrylates;[5] however, in these methods yields and purity of the products are not sufficiently high. The previous communication[6] describes a new convenient method for the synthesis of sodium alkanesulfinates from alkyl phthalimidomethyl sulfones. We now wish to report synthesis of not only alkanesulfinates but also arenesulfinates by this method in detail.

Hetero-functional groups, *i.e.* chloro, bromo, hydroxy and ethoxy, linking phthalimido-(or succinimido)methyl have been well documented readily to suffer substitution by nucleophiles. We have found that benzyl phthalimidomethyl sulfone smoothly reacts with sodium ethoxide in ethanol to give sodium phenylmethanesulfinate in high yield. The only moderate



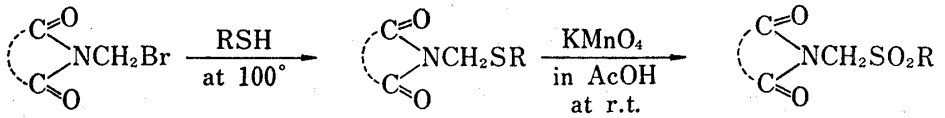
solubility of the N-(ethoxymethyl)phthalimide in benzene renders separation of the sodium phenylmethanesulfinate easy. Using a slight excess of ethoxide, clear separation to give the two products in both nearly quantitative amounts was achieved by benzene extraction. Sodium phenylmethanesulfinate thus obtained as a solid powder insoluble in benzene showed

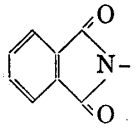
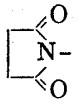
1) Location: *2-2-1 Oshika, Shizuoka 422, Japan.*
2) W.E. Truce and A.M. Murphy, *Chem. Rev.*, **48**, 69 (1950).
3) W.G. Filby, K. Günther, and R.D. Penzhorn, *J. Org. Chem.*, **38**, 4070 (1973).
4) *a*) C.S. Marvel and R.S. Johnson, *J. Org. Chem.*, **13**, 822 (1948); *b*) W.M. Ziegler and R. Conner, *J. Am. Chem. Soc.*, **62**, 2596 (1940); R. Otto, *J. Prakt. Chem.*, **30**, 176 (1884); *idem, ibid.*, **30**, 185 (1884); *idem, ibid.*, **30**, 208 (1884); *idem, ibid.*, **30**, 321 (1884).
5) W.E. Truce and F.E. Roberts, Jr., *J. Org. Chem.*, **28**, 593 (1963).
6) M. Uchino, K. Suzuki, and M. Sekiya, *Synthesis*, **1977**, 794.

97% of sulfinate content by titration with potassium permanganate and was identified as dibenzyl sulfone by reaction with benzyl chloride. By a similar procedure, benzyl succinimidomethyl sulfone gave somewhat lower yield (87%) of sodium phenylmethanesulfinate.

For extention to synthesis of a variety of alkanesulfinates we prepared nine alkyl phthalimidomethyl sulfides and oxidized them with potassium permanganate to the corresponding sulfones (Table I).

Table I. Synthesis of Imidomethyl Sulfides and Sulfones

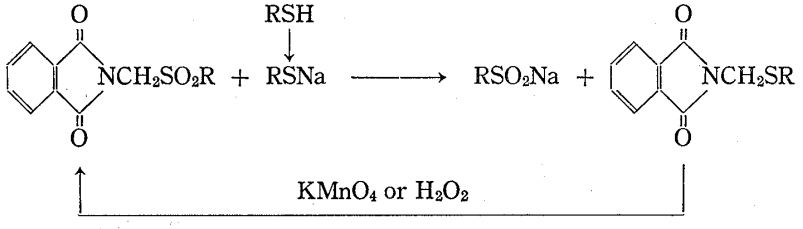


Imide residue	R	Yield (%) Sulfide	Yield (%) Sulfone
	$C_6H_5CH_2$–	84	89
	$CH_3(CH_2)_4$–	75	75
	$(C_2H_5)_2CH$–	78	81
	$(CH_3)_2CHCH(CH_3)$–	80	83
	$CH_3(CH_2)_5$–	81	89
	$CH_3(CH_2)_6$–	72	81
	$CH_3(CH_2)_7$–	75	84
	$CH_3(CH_2)_{11}$–	73	95 (85)[a]
	$CH_3(CH_2)_{13}$–	85	Quant.
	$CH_3(CH_2)_{15}$–	83	96
	C_6H_5–	93	83
	p-$CH_3C_6H_4$–	94	Quant.[a]
	p-ClC_6H_4–	90	90
	p-$NO_2C_6H_4$–	Quant.	Quant.[a]
	β-$C_{10}H_7$-	84	90
	$C_6H_5CH_2$–	70	96

a) H_2O_2 in AcOH at 100° for 2 hr.

By the same procedure as shown above the reaction of these alkyl phthalimidomethyl sulfones with sodium ethoxide gave almost quantitative yields of sodium alkanesulfinates, which are 94—98% pure as determined by titration with potassium permanganate. In the case of higher alkanesulfinates, *i.e.* dodecanesulfinate, tetradecanesulfinate and hexadecanesulfinate, every most portion (84—90%) of them precipitated as fine crystals from the reaction solution, thus simple filtration gave the sulfinates in pure state.

The substitution reaction of alkyl phthalimidomethyl sulfones can also be carried out with sodium alkanethiolates in ethanol. In this case, the resultant alkyl phthalimidomethyl sulfides may be recycled upon oxidation with potassium permanganate. Due to the higher



nucleophilicity of the thiolates relative to the ethoxide, the reaction proceeds much more rapidly as can be seen in Table II. Separation of alkanesulfinates from alkyl phthalimidomethyl sulfides can be similarly carried out by benzene extraction. The sodium alkanesulfinates were identified by conversion to alkyl benzyl sulfones (Table III).

Table II. Sodium Alkanesulfinates prepared

R	Method[a]	Reaction time (hr)	Yield (%)
$C_6H_5CH_2$–	A	7	98
	B	3	93
$CH_3(CH_2)_4$–	A	5	92
	A	1	Quant.
$(C_2H_5)_2CH$–	A	3.5	Quant.
$(CH_3)_2CHCH(CH_3)$–	A	5	Quant.
$CH_3(CH_2)_5$–	A	5	92
$CH_3(CH_2)_6$–	A	6	Quant.
$CH_3(CH_2)_7$–	A	6	95
$CH_3(CH_2)_{11}$–	A	10	Quant.
	B	1	Quant.
$CH_3(CH_2)_{13}$–	A	15	Quant.
	B	2	Quant.
$CH_3(CH_2)_{15}$–	A	20	Quant.
	B	3	Quant.

a) Method A: using EtONa as a reagent. B: using RSNa as a reagent.

Table III. Yield of Alkyl Benzyl Sulfones ($RSO_2CH_2C_6H_5$) prepared from Sodium Alkanesulfinates and Benzyl Chloride

R	Yield (%)
$C_6H_5CH_2$–	86
$CH_3(CH_2)_4$–	80
$(C_2H_5)_2CH$–	80
$(CH_3)_2CHCH(CH_3)$–	72
$CH_3(CH_2)_5$–	73
$CH_3(CH_2)_6$–	74
$CH_3(CH_2)_7$–	75
$CH_3(CH_2)_{11}$–	79
$CH_3(CH_2)_{13}$–	73
$CH_3(CH_2)_{15}$–	84

Higher stability of the metal salts of alkanesulfinic acids relative to the free acids has been reported;[4a] alkanesulfinic acids quickly suffer both disproportionation and air oxidation, and their magnesium salts slowly undergo air oxidation. Our test showed that sodium dodecanesulfinate as a sample in sealed tube filled with nitrogen showed no appreciable decomposition after storing one year. In view of easy isolation and high yield of sodium alkanesulfinates of high state of purity, the present method of sulfinates synthesis appears superior to the earlier methods. The first values (Table IV) of critical micelle concentration (cmc) of

Table IV. Critical Micelle Concentration of Sodium Alkanesulfinates and Sodium Alkanesulfates

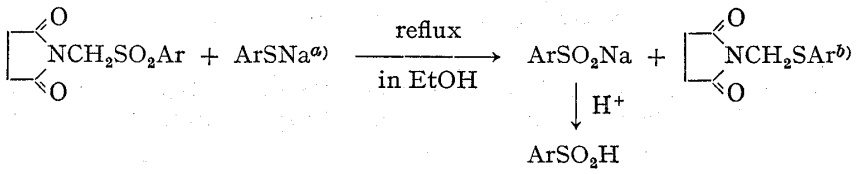
R	Critical Micelleconcentration[a] (mmol/l)	
	RSO_2Na	$ROSO_3Na$[b]
$CH_3(CH_2)_{11}$–	9.0	8.1
$CH_3(CH_2)_{13}$–	2.3	2.1
$CH_3(CH_2)_{15}$–	0.90	0.54

a) Determined by conductmetric determination at 50°.
b) H. Lange, *Kolloid-Z.*, **131**, 96 (1953).

the sodium higher alkanesulfinates measured by the conductmetric determination at 50° were nearly close to those of corresponding sodium alkanesulfates.

Attention was then drawn to synthesize arenesulfinates by a method similar to that described above for alkanesulfinates. Aryl succinimidomethyl sulfones (Table I), none of which has appeared in the literature, were synthesized instead of phthalimidomethyl analogs because the synthesis of the latter encountered difficulty in the oxidation of the sulfides with permanganate owing to their sparing solubility in acetic acid. By allowing phenyl succinimidomethyl sulfone to react with sodium thiophenolate in refluxing ethanol the reaction proceeded to give sodium benzenesulfinate and phenyl succinimidomethyl sulfide in both nearly quantitative yields. The latter may be recycled upon oxidation to the starting phenyl succinimidomethyl sulfone. The reaction was extended to synthesis of a variety of arenesulfinates from aryl succinimidomethyl sulfones prepared. Table V shows results of these experiments, in which the yields were determined as purified crystalline sulfinic acids. In view of these results, the present method provides practical applicability also for the synthesis of arenesulfinic acids.

Table V. Synthesis of Arenesulfinates



Ar	Reaction period (hr)	Yield[c] (%)
C_6H_5–	2	93
p–$CH_3C_6H_4$–	4	81
p-ClC_6H_4–	1	88
p-$NO_2C_6H_4$–	7	91
β-$C_{10}H_7$–	1	95

a) Molar ratio;  (0.02 mol): ArSNa=1:1.

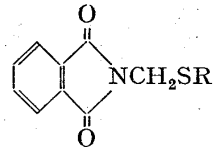
b) Obtained almost quantitatively.
c) Yield of free sulfinic acid.

Experimental[7]

Synthesis of Alkyl (or Aryl) Imidomethyl Sulfides (Table I) General Procedure——Alkyl (or Aryl) imidomethyl sulfides listed in Table I were synthesized according to the method[8] reported for the synthesis of benzyl phthalimidomethyl sulfide. An equimolar mixture of N-(bromomethyl)phthalimide (or -succinimide) and alkane (or arene) thiol was heated at about 100° with stirring until evolution of HBr ceased. The resulting oily or solid material was washed with aq. $NaHCO_3$ and subjected to vacuum distillation *via* benzene extraction or recrystallization. Yields of the products are recorded in Table I, and spectral and analytical data in Tables VI and VII.

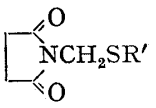
Synthesis of Alkyl (or Aryl) Imidomethyl Sulfones (Table I) General Procedure——To a saturated solution of 0.05 mol of alkyl (or aryl) phthalimido(or succinimido)methyl sulfide in acetic acid (100—1400 ml), 0.06 mol of powdered potassium permanganate was added in small portions with stirring at room temperature. Stirring was continued overnight. The precipitated sulfone was collected by filtration, washed with cold

7) All melting points and boiling points are uncorrected. Infrared (IR) spectra were recorded on a Hitachi EPI-G2 spectrophotometer. NMR spectra were taken with a JEOL-C-60-H spectrophotometer (60 MHz). Chemical shift values are given in δ (ppm) relative to tetramethylsilane as an internal standard. The following abbreviations are used: s=singlet, d=doublet, t=triplet, q=qualtet, m=multiplet.
8) H. Böhme and A. Müller, *Arch. Pharm.*, **296**, 54 (1963).

TABLE VI. Spectral and Analytical Data of 

R	bp (°C) (mmHg)	mp (°C)	IR ν_{max}^{KBr} (cm^{-1}) C=O	NMR (δ in $CDCl_3$)					Analysis (%) Calcd. (Found)		
				Aromatic protons	$>NCH_2S-$	Alkyl protons (J=Hz)					
						CH_3-	$-CHnS-$	Others	C	H	N
$CH_3(CH_2)_4-$	160—162 (0.15)	40—41	1775 1716	7.94—7.42	4.62	0.85 t(5)	2.64, 2H t(7)	2.32—1.03 6H, m	63.85 (64.13)	6.50 (6.51)	5.31 (5.30)
$(C_2H_5)_2CH-$	166—168 (0.09)	34—37	1778 1710	7.92—7.47	4.60	0.93 t(6)	3.05—2.57 1H, m	1.80—1.16 4H, m	63.85 (63.79)	6.50 (6.51)	5.31 (5.22)
$(CH_3)_2CHCH(CH_3)-$	149—152 (0.07)	44—47	1778 1710	7.90—7.47	4.62	1.23, 3H, d(6) 0.90, 6H, d(7)	3.17—2.57 1H, m	2.17—1.38 1H, m	63.85 (63.86)	6.50 (6.49)	5.31 (5.27)
$CH_3(CH_2)_5-$	168—169 (0.03)	29—31	1776 1721	8.33—7.53	4.77	0.87 t(6)	0.72, 2H t(6)	1.83—1.03 8H, m	64.95 (64.48)	6.90 (6.77)	5.04 (5.11)
$CH_3(CH_2)_6-$	171—173 (0.05)	34—36	1772 1720	8.08—7.58	4.78	0.88 t(5)	2.72, 2H t(5)	1.78—1.08 10H, m	65.94 (65.90)	7.26 (7.16)	4.80 (4.82)
$CH_3(CH_2)_7-$	177—178 (0.04)	45—47	1772 1722	8.04—7.67	4.75	0.85 t(6)	2.72, 2H t(6)	1.67—1.05 12H, m	66.85 (66.83)	7.58 (7.53)	4.58 (4.58)
$CH_3(CH_2)_{11}-$	188—191 (0.008)	63—65 Leaflets (petr. ether)	1774 1726	8.00—7.67	4.76	0.86 t(6)	2.71, 2H t(6)	1.71—1.08 20H, m	69.76 (69.71)	8.64 (8.63)	3.87 (3.82)
$CH_3(CH_2)_{13}-$	—	66—67 Prisms (iso-Pr_2O)	1774 1722	8.02—7.62	4.76	0.89 t(6)	2.70, 2H t(6)	1.85—1.08 24H, m	70.91 (70.76)	9.06 (8.98)	3.60 (3.60)
$CH_3(CH_2)_{15}-$	—	70—71 Needles (iso-Pr_2O)	1772 1722	8.00—7.65	4.75	0.90 t(6)	2.72, 2H t(6)	1.78—1.08 28H, m	71.90 (72.05)	9.41 (9.47)	3.35 (3.31)
$C_6H_5CH_2-$	—	113—114[a] Prisms (MeOH)	1770 1712	8.00—6.98	4.54	—	3.87, 2H m	—	67.82 (67.59)	4.64 (4.62)	4.94 (4.92)

a) lit.[9] mp 108°.

Table VII. Spectral and Analytical Data of 

R′	bp (°C) (mmHg)	Appearance (recryst. solvt.) and mp (°C)	IR ν_{max}^{KBr} (cm^{-1}) C=O	NMR (δ in $CDCl_3$) Aromatic protons (J=Hz)	NMR (δ in $CDCl_3$) >NCH_2S– (s)	NMR (δ in $CDCl_3$) –CH_2CH_2– (s)	NMR (δ in $CDCl_3$) Others	Analysis (%) Calcd. (Found) C	H	N
C_6H_5–	166—169 (0.4)	47—49	1776 1696	7.05—7.55 m	4.73	2.54	—	59.71 (59.80)	5.01 (5.09)	6.33 (6.44)
p-$CH_3C_6H_4$–	—	Prisms (EtOH) 71—73	1776 1700	7.16, 2H, d(8) 7.44, 2H, d(8)	4.70	2.64	2.34 CH_3–	61.26 (61.26)	5.57 (5.62)	5.95 (5.93)
p-ClC_6H_4–	—	Prisms (EtOH) 94—96	1770 1702	7.25, 2H, d(8) 7.45, 2H, d(8)	4.82	2.67	—	51.67 (51.74)	3.94 (4.01)	5.48 (5.33)
p-$NO_2C_6H_4$–	—	Leaflets (AcOEt) 110—112	1772 1700	7.62, 2H, d(8) 8.19, 2H, d(8)	5.00	2.76	—	49.62 (49.47)	3.79 (3.69)	10.52 (10.34)
β-$C_{10}H_7$–	—	Plates (AcOEt) 103—104	1762 1700	7.34—8.05 m	4.91	2.60	—	66.40 (66.31)	4.83 (4.82)	5.16 (5.17)
$C_6H_5CH_2$–	172—174 (0.2)	—	1778[a] 1706[a]	6.98—7.42 m	4.41	2.45	3.80 –SCH_2ph	61.25 (61.21)	5.57 (5.51)	5.95 (5.70)

a) Liquid film.

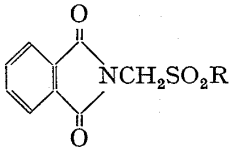
water and dried. The filtrate, after the remaining potassium permanganate color was quenched by addition of $NaHSO_3$, was evaporated under reduced pressure. An additional sulfone was obtained by washing the resulting residue with water. The combined crystals were recrystallized from appropriate solvent (Tables VIII and IX) and weighed.

An alternative oxidation method using H_2O_2 was utilized for the preparation of some sulfones (Table I). To a saturated solution of the sulfide (0.05 mol) in acetic acid, 10 ml (0.1 mol) of 35% H_2O_2 was added dropwise with stirring at steam bath temperature. After heating for additional 2 hr, crystals deposited in the cooled solution were collected by filtration, washed with water, dried and recrystallized. The filtrate was concentrated under reduced pressure and the resulting solid residue, after washed with water, was recrystallized.

Yields of the sulfones are shown in Table I and their physical, spectral and analytical data in Tables VIII and IX. Except benzyl phthalimidomethyl sulfone, previously prepared by the oxidation with monoperoxyphthalic acid, they have not been reported.

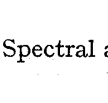
Synthesis of Sodium Alkanesulfinates General Procedure Method A: Reaction with Sodium Ethoxide ——To a solution of sodium ethoxide prepared from 0.51 g (0.022 mol) of metal sodium and 65 ml of ethanol, 0.02 mol each of the alkyl phthalimidomethyl sulfones prepared above was added and the mixture was refluxed with stirring under a stream of nitrogen until the starting sulfone disappeared (even in the case of sparingly soluble sulfone, the mixture was brought into homogeneous solution at the end of the reaction). Ethanol was removed under reduced pressure. N-(Ethoxymethyl)phthalimide was extracted from the resulting solid with several portions of benzene. Sodium alkanesulfinate obtained as a insoluble powder was weighed nearly quantitative. Yields of sodium alkanesulfinates thus obtained are shown in Table II. The products are 94—98% pure as determined by titration with potassium permanganate. For identification they were converted into the corresponding alkyl benzyl sulfones by the reaction with benzyl chloride in boiling ethanol. Spectral and analytical data of these sulfones thus obtained are shown in Table X. Removal of solvent from the foregoing benzene solution gave quantitative amount of N-(ethoxymethyl)phthalimide which was recrystallized from ethanol to give prisms, mp 87—89° (lit.[8] mp 83°).

In every run with dodecyl phthalimidomethyl sulfone, tetradecyl phthalimidomethyl sulfone and hexadecyl phthalimidomethyl sulfone, most portion of the corresponding sodium alkanesulfinate (84—90%)

TABLE VIII. Spectral and Analytical Data of 

R	Appearances (recryst. solvt.) and mp (°C)	IR ν_{max}^{KBr} (cm^{-1})		NMR (δ in $CDCl_3$)					Analysis (%) Calcd. (Found)		
		$-SO_2-$	C=O	Aromatic protons	$>NCH_2SO_2-$	Alkyl protons (J=Hz) CH_3-	$-CHnSO_2-$	Others	C	H	N
$CH_3(CH_2)_4-$	Prisms (MeOH) 110—111	1332 1137	1782 1718	8.10—7.70	4.94	0.91 t(6)	3.12, 2H t(8)	2.10—1.24 6H, m	56.93 (57.13)	5.80 (5.83)	4.74 (4.68)
$(C_2H_5)_2CH-$	Needles (AcOEt) 111—112	1344 1133	1784 1716	7.91—7.60	4.82	1.05, 6H t(6)	3.16—2.72 1H, m	2.12—1.62 4H, m	56.93 (57.05)	5.80 (5.89)	4.74 (4.73)
$(CH_3)_2CHCH(CH_3)-$	Needles (MeOH) 104—106	1322 1132	1784 1725	7.97—7.57	4.87	1.37, 3H, d(7) 1.01, 6H, d(7)	3.27—2.83 1H, m	2.87—2.40 1H, m	56.93 (57.23)	5.80 (5.80)	7.74 (4.71)
$CH_3(CH_2)_5-$	Plates (MeOH) 119—121	1332 1140	1784 1728	8.15—7.65	4.92	0.88 t(6)	3.10, 2H t(6)	2.05—1.20 8H, m	58.23 (58.53)	6.19 (6.20)	4.53 (4.65)
$CH_3(CH_2)_6-$	Plates (MeOH) 104—106	1336 1139	1783 1732	8.17—7.71	4.96	0.90 t(6)	3.16, 2H t(6)	2.03—1.22 10H, m	59.42 (59.41)	6.55 (6.52)	4.33 (4.32)
$CH_3(CH_2)_7-$	Plates (MeOH) 110—112	1334 1140	1782 1724	8.15—7.65	4.95	0.91 t(6)	3.15, 2H t(6)	2.00—1.15 12H, m	60.51 (60.59)	6.87 (6.92)	4.15 (4.10)
$CH_3(CH_2)_{11}-$	Plates (MeOH) 114—115	1332 1140	1782 1726	8.15—7.65	4.92	1.00 t(6)	3.12, 2H t(7)	1.95—1.15 20H, m	64.09 (64.16)	7.93 (7.99)	3.55 (3.51)
$CH_3(CH_2)_{13}-$	Leaflets (MeOH) 112—113	1334 1139	1783 1724	8.10—7.68	4.93	0.89 t(6)	3.13, 2H t(6)	2.20—1.09 24H, m	65.53 (65.38)	8.37 (8.36)	3.32 (3.31)
$CH_3(CH_2)_{15}-$	Prisms (MeOH) 110—111	1332 1138	1782 1724	8.08—7.64	4.91	0.89 t(6)	3.08, 2H t(6)	2.18—1.04 28H, m	66.78 (67.09)	8.74 (8.86)	3.11 (3.10)
$C_6H_5CH_2-$	Prisms (AcOEt) 188—189[a]	1320 1140	1780 1720	7.96—7.08	4.80	—	4.32, 2H s	—	60.94 (60.80)	4.15 (4.08)	4.44 (4.42)

a) lit.[8] mp 180°.

TABAB IX. Spectral and Analytical Data of 

R′	Appearace (recryst. solvt.) and mp (°C)	IR ν_{max}^{KBr} (cm^{-1}) $-SO_2-$	IR ν_{max}^{KBr} (cm^{-1}) C=O	NMR (δ in $CDCl_3$) Aromatic protons (J=Hz)	NMR (δ in $CDCl_3$) $>NCH_2SO_2-$ (s)	NMR (δ in $CDCl_3$) CH_2CH_2- (s)	NMR (δ in $CDCl_3$) Others	Analysis (%) Calcd. (Found) C	H	N
C_6H_5-	Needles (AcOEt) 138—139	1332 1141	1792 1720	7.38—8.10 m	4.90	2.79	—	52.16 (52.27)	4.38 (4.36)	5.53 (5.54)
p-$CH_3C_6H_4-$	Needles (EtOH) 138—140	1325 1137	1775 1706	7.37, 2H, d(8) 7.78, 2H, d(8)	4.88	2.77	2.46 CH_3-	53.92 (54.08)	4.90 (4.92)	5.24 (5.30)
p-ClC_6H_4-	Prisms (AcOEt) 179—181	1338 1131	1782 1714	7.67, 2H, d(8) 7.96, 2H, d(8)	5.26	3.16	—	45.92 (45.97)	3.50 (3.55)	4.87 (4.76)
p-$NO_2C_6H_4-$	Leaflets ($C_6H_5NO_2$) 255—257	1340 1136	1786 1706	8.29, 2H, d(8) 8.60, 2H, d(8)	5.25	3.06	—	44.30 (44.32)	3.38 (3.37)	9.39 (9.32)
β-$C_{10}H_7-$	Needles (MeOH) 158—159	1332 1140	1788 1710	7.56—8.60 m	4.99	2.75	—	59.39 (59.67)	4.32 (4.36)	4.62 (4.66)
$C_6H_5CH_2-$	Prisms (EtOH) 143—144	1340 1150	1770 1708	7.12—7.58 m	4.61	2.78	4.30 $-SO_2C\underline{H}_2ph$	53.92 (54.13)	4.90 (4.94)	5.23 (5.28)

deposited in the reaction solution on cool as a colorless crystals and collected by filtration. The sulfinates thus obtained were pure enough, giving satisfactory microanalysis. Sodium dodecanesulfinate, *Anal.* Calcd for $C_{12}H_{25}NaO_2S$: C, 56.12; H, 9.99. Found: C, 56.22; H, 9.83. Sodium tetradecanesulfinate, *Anal.* Calcd. for $C_{14}H_{29}NaO_2S$: C, 59.33; H, 10.56. Found: C, 59.12; H, 10.28. Sodium hexadecanesulfinate, *Anal.* Calcd. for $C_{16}H_{33}NaO_2S$: C, 61.75; H, 10.78. Found: C, 61.56; H, 10.64. Treatment of the foregoing filtrate as described above gave N-(ethoxymethyl)phthalimide and additional sodium alkanesulfinate.

Method B: Reaction with Sodium Thiolates——Each of alkyl phthalimidomethyl sulfones (0.02 mol) was added to the corresponding thiolate solution prepared from 0.46 g (0.02 mol) of clean cut sodium and 0.02 mol of thiol in 65 ml ethanol, and the mixture was refluxed with stirring under a stream of nitrogen. After disappearance of the starting sulfone on TLC, the reaction solution was cooled. In the run with pentyl phthalimidomethyl sulfone, the reaction solution was worked up by a procedure similar to that described in the method A, to give sodium pentanesulfinate and pentyl phthalimidomethyl sulfide. In the run with benzyl phthalimidomethyl sulfone, a most portion of benzyl phthalimidomethyl sulfide was precipitated in the reaction solution, and in the runs with dodecyl, tetradecyl and hexadecyl derivatives, both the sulfinate and the sulfide were precipitated. The mixture of the sulfinate and the sulfide obtained by filtration and by concentration of the filtrate was separated by extraction with benzene. Identification of these products thus obtained were made by comparisons of their IR spectra with those of the authentic specimens obtained in the foregoing. Permanganate titration of the sulfinates obtained showed 95—98% purity. Results are summarized in Table II.

Synthesis of Sodium Arenesulfinates General Procedure——Reaction was carried out by refluxing a solution of 0.02 mol of aryl succinimidomethyl sulfone and equimolar amount of the corresponding sodium arenethiolate in 65 ml ethanol. By the same procedure as described in the method A, sodium arenesulfinate and aryl succinimidomethyl sulfide were obtained. By acidification of an aqueous solution of sulfinate by hydrogen chloride arenesulfinic acid was obtained. Results are summarized in Table V. Physical data of the sulfinic acids are shown in Table XI.

Table X. Spectral and Analytical Data of $RSO_2CH_2C_6H_5$

R	Appearance (recryst. soovt.) and mp (°C)	IR ν_{max}^{KBr} (cm^{-1}) $-SO_2-$	NMR (δ in $CDCl_3$) Aromatic protons	$PhCH_2-$ (s)	Alkyl protons (J=Hz) CH_3-	$-CHnSO_2-$	Others	Analysis (%) Calcd. (Found) C	H
$CH_3(CH_2)_4-$	Needles (EtOH) 97—98[a]	1320 1121	7.40	4.22	0.88 t (6)	2.86, 2H, t (6)	1.97—1.17 6H, m	63.68 (63.67)	8.01 (8.07)
$(C_2H_5)_2CH-$	Plates (petr. ether) 39—41	1344 1131	7.38	4.20	1.03 t (7)	2.93—2.38 1H, m	2.13—1.58 4H, m	63.68 (63.63)	8.01 (8.10)
$(CH_3)_2CHCH(CH_3)-$	Plates (petr. ether) 37—39	1304 1123	7.35	4.20	1.25, 3H, d(7) 1.05, 6H, d(7)	3.00—2.20 2H, m		63.68 (63.70)	8.01 (8.10)
$CH_3(CH_2)_5-$	Needles (petr. ether) 56—57	1322 1123	7.38	4.21	0.86 t (6)	2.82, 2H, t (6)	1.90—1.20 8H, m	64.96 (64.92)	8.38 (8.46)
$CH_3(CH_2)_6-$	Plates (petr. ether) 63—64	1322 1125	7.51	4.21	0.88 t (6)	2.85, 2H, t (6)	1.95—1.15 10H, m	66.10 (66.30)	8.71 (8.85)
$CH_3(CH_2)_7-$	Plates (petr. ether) 65—66	1319 1125	7.48	4.17	0.87 t (6)	2.82, 2H, t (6)	1.83—1.17 12H, m	67.12 (67.44)	9.01 (9.16)
$CH_3(CH_2)_{11}-$	Plates (iso-Pr_2O) 77—78	1320 1127	7.51	4.20	0.85 t (6)	2.80, 2H, t (6)	1.83—1.17 20H, m	70.32 (70.53)	9.93 (10.16)
$CH_3(CH_2)_{13}-$	Plates (iso-Pr_2O) 81—83	1320 1125	7.50	4.20	0.85 t (6)	2.81, 2H, t (6)	1.85—1.15 24H, m	71.54 (71.66)	10.29 (10.25)
$CH_3(CH_2)_{15}-$	Plates (iso-Pr_2O) 83—85	1321 1125	7.52	4.21	0.85 t (6)	2.80, 2H, t (6)	1.85—1.16 28H, m	72.58 (72.59)	10.59 (10.64)
$C_6H_5CH_2-$	Prisms (EtOH) 145—146[b]	1320 1120	7.26	4.07	—	4.07, 2H, s	—	68.26 (68.39)	5.73 (5.81)

a) lit. mp 101—101.5° [R.C. Krug, J.A. Rigney, and G.R. Tichelaar, *J. Org. Chem.*, **27**, 1305 (1962)].
b) lit. mp 151° [J.A. Smythe, *J. Chem. Soc.*, **101**, 2071 (1912)].

Table XI. Physical Data of $ArSO_2H$

Ar	mp (°C) (lit. mp)	Appearance (recryst. solvt.)	IR ν_{max}^{KBr} (cm^{-1}) S=O
C_6H_5-	77—78 (85)[a]	Needles (H_2O)	1088
p-$CH_3C_6H_4-$	87—89 (86—87)[a]	Needles (H_2O)	1074
p-ClC_6H_4-	98—99 (99)[b]	Needles (H_2O)	1081
p-$NO_2C_6H_4-$	125—127 (120)[c]	Leaflets (H_2O)	1080
β-$C_{10}H_7-$	94—96 (105)[d]	Needles (H_2O)	1070

a) S. Krishna and H. Singh, *J. Am. Chem. Soc.*, **50**, 792 (1928).
b) M.E. Hanke, *J. Am. Chem. Soc.*, **45**, 1321 (1923).
c) E. Fromm and J. Witmann, *Ber.*, **41**, 2269 (1098).
d) L. Gattermann, *Ber.*, **32**, 1136 (1899).

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