

Substituted Aromatic and Aliphatic Sulfonic Esters

DANIEL A. SCOLA¹ and JOHN S. ADAMS, Jr.

Monsanto Research Corp., Boston Laboratories, Everett, Mass. 02149

Several substituted aromatic and aliphatic sulfonic esters were prepared and characterized.

IN A PROGRAM designed to test novel compounds for herbicidal activity, several aromatic and aliphatic sulfonic esters were synthesized (1, 3) by reactions of the appropriate sulfonyl chloride (or fluoride) with the alcohol or phenol in the presence of a base: $\text{RSO}_2\text{Cl} + \text{R}'\text{OH} \rightarrow \text{R}-\text{SO}_2-\text{OR}'$ ($\text{R}, \text{R}' = \text{alkyl or aryl}$).

Yields, melting or boiling points, and elemental analyses of compounds prepared are summarized in Table I. Characteristic infrared spectral data are listed in Table II. The infrared spectra are consistent with the reported structures.

EXPERIMENTAL

Except for *N*-acetylsulfanilyl fluoride, all reactants were obtained commercially and were used without further purification. Melting points were taken on a Thomas-Hoover melting point apparatus and are uncorrected.

Infrared spectra were recorded with a Perkin-Elmer Model 21 spectrophotometer in a potassium chloride matrix (for solids) or as a liquid film between sodium chloride prisms.

General Procedure (3). The sulfonic esters were prepared by the addition of excess pyridine (0.646 mole) to a solution of the sulfonyl chloride (0.323 mole) in the reacting alcohol (0.350 mole) at 0°C., over a 2- to 3-hour period. The mixture was diluted with a mixture (1000 ml.) of ice and dilute hydrochloric acid, followed by extraction with ether (3 × 200 ml.). The combined ether extracts were washed with water and 10% sodium bicarbonate solution, and then dried (Na_2SO_4). After removal of the solvent by evaporation under diminished pressure, the residue was purified by distillation or by recrystallization, as indicated in Table I.

1-Methylbutyl *N*-Acetylsulfanilate (1). A solution of 0.49 mole of *N*-acetylsulfanilyl fluoride, m.p. 174.5–6.5°C. (2), in ether (200 ml.) was added with cooling to 0.49 mole of sodium 1-methylbutyl oxide [made from 2-pentanol + Na under N_2 (1)] in ether (200 ml.) and stirred under

Table I. Substituted Aromatic and Aliphatic Sulfonic Esters ($\text{R}-\text{SO}_2\text{O}-\text{R}'$)

No.	Compound	R	R'	Yield, %	M.P. or B.P., °C.	Analysis {		
						Calcd. Found		
						% C	% H	% S
1	2,5-Dichlorophenyl <i>p</i> -bromobenzenesulfonate	BrC_6H_4-	$\text{Cl}_2\text{C}_6\text{H}_3-$	60 ^a	116–18	37.7 38.0	1.8 1.8	8.4 8.8
2	1-Methylbutyl <i>N</i> -acetylsulfanilate	$\text{CH}_3\text{CONHC}_6\text{H}_4-$	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}-$ CH_3	63 ^b	oil	54.7 55.0	6.7 6.7	11.2 11.2
3	2-Nitrobutyl <i>p</i> -toluenesulfonate	$\text{CH}_3\text{C}_6\text{H}_4-$	$\text{CH}_3\text{CH}_2-\text{CH}-\text{CH}_2-$ NO_2	12 ^c	52–3	48.4 48.7	5.5 5.5	11.7 11.9
4	3-Methoxy-1,3-dimethylbutyl <i>p</i> -bromobenzenesulfonate	BrC_6H_4-	$(\text{CH}_3)_2\text{C}-\text{CH}_2\text{CH}-$ OCH_3 CH_3	55 ^d	oil	44.5 45.2	5.5 5.8	9.1 8.4
5	<i>p</i> -Iodophenyl <i>p</i> -bromobenzenesulfonate	BrC_6H_4-	IC_6H_4-	53 ^e	126–8	32.8 32.3	1.8 1.7	7.3 7.5
6	2-Chloroethyl ethanesulfonate	CH_3CH_2-	$\text{ClCH}_2\text{CH}_2-$	39 ^f	63–4/0.09 mm.	27.7 27.6	5.3 5.0	18.6 19.0
7	2,3-Dichloropropyl ethanesulfonate	CH_3CH_2-	$\text{ClCH}_2\text{CH}-\text{CH}_2-$ Cl	44	102–4.5/0.4 mm.	27.2 26.9	4.6 4.5	

^a Recrystallized from absolute alcohol. ^b A tan solid, which on removal of last traces of solvent in vacuo, reverted to an orange syrup. ^c Recrystallized from butanol-ligroin. ^d The oil was not distilled. It contained impurities of starting alcohol, as indicated by infrared analysis. ^e n_D^{20} 1.4556. ^f Analyzed for chlorine: calcd., 32.1; found, 32.6.

¹ Present address: United Aircraft Research Laboratories, East Hartford, Conn. 06108

Table II. Characteristic Infrared Absorptions of Substituted Aromatic and Aliphatic Sulfonic Esters

No.	Aromatic CH Stretch, Cm. ⁻¹	Aliphatic CH Stretch, Cm. ⁻¹	Aromatic C=C Stretch, Cm. ⁻¹	—SO ₂ —O Absorption, Cm. ⁻¹	CH-out-of-Plane Deformation, Cm. ⁻¹	Other Characteristic Absorption, Cm. ⁻¹
1	3070	...	1640 1570 1470	1370 1180	910 820	C—Cl 700
2	3040	2940	1600 1570	1360 1170	825	O —C— 1650 NH 3340
3	3040	2900	1600 1550 ^a	1360 1190	790 805 828	—NO ₂ 1550 ^a 1360
4	3070	2940	1580 1470	1360 1180	805 825	—OCH ₃ 1070
5	3070	2940	...	1370 1200	805	...
6	...	2940	...	1360 1160	...	C—Cl 705
7	...	2940	...	1360 1160	...	C—Cl 680 720

^aAbsorptions for the NO₂ group fall in the same region as the absorption for aromatic C=C and —SO₂—O functions. Therefore, definite assignments cannot be made.

nitrogen for 15 hours at 25°C. After filtering off the NaF, the filtrate was washed with 100 ml. of 5% hydrochloric acid, twice with saturated sodium carbonate solution, twice with cold water, dried (Na₂SO₄), filtered, and treated twice with Norit A. Ether was removed, leaving 89 grams (63%) of tan solid. On drying in vacuo at 50°C., this solid liquefied to an orange syrup.

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Carboxylation of Substituted Phenols in *N,N*-Dimethylamide Solvents at Atmospheric Pressure

WILLIAM H. MEEK and CHARLES H. FUCHSMAN

Ferro Chemical Division, Ferro Corp., P. O. Box 46349, Bedford, Ohio 44146

A series of substituted phenols were carboxylated at atmospheric pressure in the presence of strong base, in *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and *N,N*-dimethylpropionamide solvents.

IN CONNECTION with recently increasing interest in substituted salicylic acids of demonstrable fibrinolytic (33, 34) and protein-bonding (4, 31) activity, and interest in substituted *p*-hydroxybenzoic acids as intermediates in the production of light-stabilizers for polyolefins (7), modified methods for the carboxylation of phenols were investigated recently. In the course of the present study, which centered on the use of certain amide solvents as reaction media, the authors learned of related work done by Hirao and coworkers on dimethylformamide and other nonprotonic high-boiling solvents (10–15). The present work on carboxylation of phenols with different and generally greater substitution than those studied by Hirao has led to observations

which differ from those reported by the Japanese investigators for simpler phenols, and may thus contribute to a more general insight into the carboxylation process in the synthesis of aromatic hydroxy acids.

The reaction consists, essentially, of the treatment of the phenol with carbon dioxide at atmospheric pressure in a highly basic environment in an *N,N*-dimethylalkanoamide—e.g., dimethylacetamide—at temperatures typically in the range 165° to 180°C. The basic environment can be provided by first converting the phenol to the corresponding alkali metal phenoxide, or by adding sodium methoxide in slight excess to the mixture of the solvent and phenol. As an alternate to carbon dioxide, the carbox-