gion (5H). Two broad singlets at 8.2 (1H) and 8.5 (1H), both of which exchange slowly with D_2O, are assigned to the NH hydrogens, confirming the unsubstituted amide character of the molecule.

Analysis of VIII and IX by mass spectrometry gives a fragmentation pattern which supports halogenation on the methylene carbon.

Compound VIII		Compound IX	
m/e	Relative intensity	*m/e*	Relative intensity
355	(37) M^+	267	(40) M^+
312	(23) M—CONH	224	(20) M—CONH
291	(18) $M—SO_2$	203	(20) $M—SO_2$
214	(2.9) $M—C_6H_5SO_2$	141	(100) $C_6H_5SO_2$
198	(2.9) CBr_2CO	110	(2.2) CCl_2CO
186	(14) $COBr_2$	98	(9.0) $COCl_2$
141	(100) $C_6H_5SO_2$	83	(10.0) $CHCl_2$

These results indicate that chlorination of 2-(*p*-toluenesulfonyl)acetamide gives 2,2-dichloro-2-(*p*-toluenesulfonyl)acetamide and bromination of 2-(β-naphthylsulfonyl)-acetamide gives 2,2-dibromo-2-(β-naphthylsulfonyl)acetamide rather than the *N*-halogenated structures assigned by Tröger and Hille.

These halogenated compounds on irradiation generate bromine, which may be utilized to oxidize leuco triphenylmethane dyes.

Experimental

The procedures described by Tröger and Hille (*1*) for the bromination and chlorination of the arylsulfonylacetamides were used for the preparation of VI, VIII, and IX. 2,2-Dichloro-2-(phenylsulfonyl)acetamide (IX) was also prepared as follows: A solution of 10 grams of 2-(phenylsulfonyl)acetamide in 50 ml of acetic acid and 30 ml of sulfuryl chloride was heated for 15 min on the steam bath, 50 ml of water was added, and the solid was collected and crystallized from ethyl acetate–ligroin to give 10.2 grams (77% yield) of IX, mp 144°.

Anal. Calcd for $C_8H_7Cl_2NO_3S$: C, 35.9; H, 2.6; Cl, 26.5; N, 5.2; S, 12.8. Found: C, 35.8; H, 2.4; Cl, 26.5; N, 5.2; S, 12.6.

The melting points and analytical data for the brominated products are given below.

VI, $C_9H_{10}BrNSO_3$: mp 176°

Anal. Calcd: C, 37.0; H, 3.4; N, 4.8; Br, 27.4. Found: C, 36.8; H, 3.7; N, 5.1; Br, 27.5.

VII, $C_9H_9Br_2NO_3S$: mp 124.

Anal. Calcd: C, 29.2; H, 2.2; N, 3.8; Br, 43.0. Found: C, 29.4; H, 2.1; N, 4.1; Br, 42.8.

VIII, $C_8H_7Br_2NSO_3$: mp 139.

Anal. Calcd: C, 26.8; H, 2.0; Br, 44.8. Found: C, 26.6; H, 1.9; Br, 44.5.

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Synthesis and Properties of *p*-Toluidine Salts of Substituted α-Phenylcinnamonitrile Sulfonic Acids

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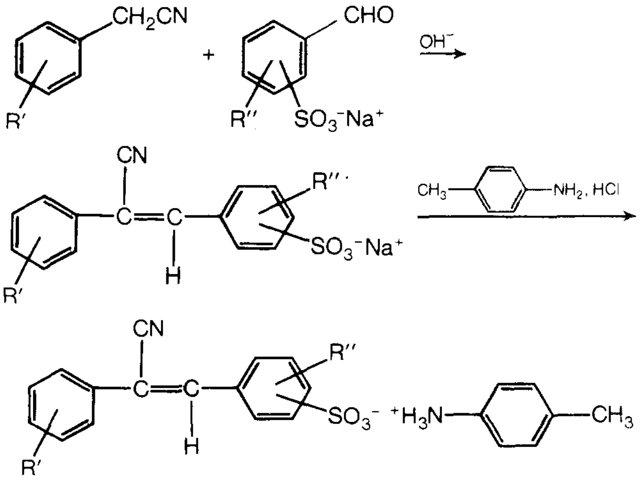
Some *p*-toluidine salts of substituted α-phenylcinnamonitrile sulfonic acids are synthesized via base-catalyzed condensations of substituted phenylacetonitriles and benzaldehyde sulfonic acid sodium salts, followed by reaction of the resulting products with *p*-toluidine in aqueous acid media. A summary of the physical properties of the new compounds is presented.

Interest in this laboratory in the use of α-phenylcinnamonitrile sulfonic acids as potential analytical reagents resulted in the synthesis of some model compounds (Table I). A literature search revealed that little if any information was available concerning the synthesis and physical properties of these substances.

The compounds were synthesized via base-catalyzed condensations of substituted phenylacetonitriles and benzaldehyde sulfonic acid sodium salts as shown in Scheme 1. The resulting product, a substituted sodium α-phenylcinnamonitrile sulfonate (I), usually precipitated from solution upon cooling. When this did not occur,



SCHEME I

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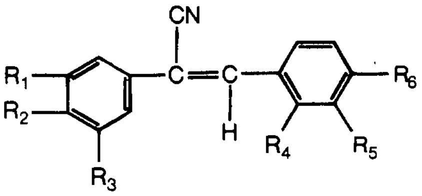
Table I. p-Toluidine Salts of Substituted α-Phenylcinnamonitrile-Sulfonic Acids



Compd	R_1	R_2	R_3	R_4	R_5	R_6	Mp, °C	Yield,[a] %
1	H	H	H	SO_3-tol^{+}[b]	H	H	215–216	76
2	H	H	H	H	SO_3-tol^{+}	OCH_3	249–251	72
3	H	OCH_3	H	SO_3-tol^{+}	H	H	269–271	80
4	H	OCH_3	H	H	SO_3-tol^{+}	OCH_3	245–247	82
5	OCH_3	OCH_3	H	SO_3-tol^{+}	H	H	218–223	75
6	OCH_3	OCH_3	H	H	SO_3-tol^{+}	OCH_3	238–240	80
7	OCH_3	OCH_3	OCH_3	SO_3-tol^{+}	H	H	173–175	85
8	OCH_3	OCH_3	OCH_3	H	SO_3-tol^{+}	OCH_3	244–247	82
9	H	Br	H	SO_3-tol^{+}	H	H	273–275	80
10	H	Br	H	H	SO_3-tol^{+}	OCH_3	265–267	78
11	H	C_6H_5	H	SO_3-tol^{+}	H	H	253–258	70
12	H	C_6H_5	H	H	SO_3-tol^{+}	OCH_3	263–268	75

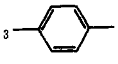
[a] No attempt was made to optimize yield. Yields are based on starting nitrile and aldehyde. [b] Tol^{+} = $^{+}NH_3$—  —CH_3.

Table II. Summary of Physical Properties of p-Toluidine Salts of Substituted α-Phenylcinnamonitrile-Sulfonic Acids

					Fluorescence			
Compd	Anal Calcd	Anal Found	Uv EtOH, λ_{max}, nm	Ir, ν_{max}, cm^{-1}	Solid[a]	Soln[b] excit max	Soln[b] emiss max	Rel fluoresc. QRU[c]
1	C, 67.33 H, 5.13 N, 7.13	C, 67.48 H, 5.25 N, 7.11	303 (ϵ = 20,000)	2240 (CN) 1175 (sulfonate) 1050 (sulfonate)	Violet	...	[d]	...
2	C, 65.40 H, 5.21 N, 6.64	C, 65.24 H, 5.29 H, 6.57	327 (ϵ = 17,700)	2240 (CN) 1275 (arom. ether) 1100 (arom. ether) 1170 (sulfonate) 1040 (sulfonate)	Violet	...	[d]	...
3	C, 65.40 H, 5.21 N, 6.63	C, 65.29 H, 5.26 N, 6.55	333 (ϵ = 20,000)	2240 (CN) 1250 (arom. ether) 1090 (arom. ether) 1170 (sulfonate) 1020 (sulfonate)	Bluish white	375	425	0.009
4	C, 63.71 H, 5.30 N, 6.19	C, 63.54 H, 5.40 N, 6.11	350 (ϵ = 45,000)	2240 (CN) 1270 (arom. ether) 1100 (arom. ether) 1200 (sulfonate) 1040 (sulfonate)	Blue	...	[d]	...
5	C, 63.69 H, 5.34 N, 6.19	C, 63.78 H, 5.38 N, 6.17	345 (ϵ = 15,000)	2240 (CN) 1240 (arom. ether) 1095 (arom. ether) 1175 (sulfonate) 1025 (sulfonate)	Bluish white	370	465	0.204
6	C, 62.24 H, 5.39 N, 5.80	C, 62.15 H, 5.42 N, 5.85	358 (ϵ = 30,000)	2220 (CN) 1280 (arom. ether) 1095 (arom. ether) 1170 (sulfonate) 1020 (sulfonate)	Greenish yellow	...	[d]	...
7	C, 62.22 H, 5.43 H, 5.80	C, 62.32 H, 5.50 N, 5.70	325 (ϵ = 17,000)	2240 (CN) 1260 (arom. ether) 1095 (arom. ether) 1140 (sulfonate) 1030 (sulfonate)	Greenish yellow	375	455	0.090
8	C, 60.92 H, 5.50 N, 5.46	C, 60.77 H, 5.56 N, 5.43	351 (ϵ = 17,000)	2225 (CN) 1280 (arom. ether) 1095 (arom. ether) 1195 (sulfonate) 1040 (sulfonate)	Greenish yellow	...	[d]	...

Table II. Continued

					Fluorescence			
Compd	Anal Calcd	Anal Found	Uv EtOH, λ_{max}, nm	Ir, ν_{max}, cm^{-1}	Solid[a]	Soln[b] excit max	Soln[b] emiss max	Rel fluoresc. QRU[c]
9	C, 56.05 H, 4.03 N, 5.95	C, 55.82 H, 4.11 N, 5.83	306 (ϵ = 11,000)	2240 (CN) 1175 (sulfonate) 1020 (sulfonate) 620 (C-Br)	Violet	...	[d]	...
10	C, 55.08 H, 4.19 N, 5.58	C, 54.83 H, 4.35 N, 5.45	346 (ϵ = 30,000)	2225 (CN) 1180 (sulfonate) 1040 (sulfonate) 625 (C-Br)	Blue	...	[d]	...
11	C, 71.80 H, 5.13 N, 5.98	C, 71.94 H, 5.14 N, 6.08	325 (ϵ = 9,000)	2220 (CN) 1175 (sulfonate) 1030 (sulfonate)	Blue	...	[d]	...
12	C, 69.87 H, 5.22 N, 5.62	C, 69.86 H, 5.30 N, 5.65	342 (ϵ = 19,500)	2220 (CN) 1280 (arom. ether) 1100 (arom. ether) 1180 (sulfonate) 1040 (sulfonate)	Bluish white	...	[d]	...

[a] Ascertained by visual observation of the dry powder when exposed to uv light from a long wavelength uv lamp. [b] Measurements were recorded on an Aminco-Bowman spectrophotofluorometer using ethanol as solvent. [c] Quinine Reference Unit, see ref. 2. [d] Denotes that no fluorescence was observed in ethanolic solution.

vacuum distillation of the solvent yielded the crude product. Because satisfactory elemental analyses could not be obtained for these desired products, they were further characterized as their *p*-toluidine salts (II) as shown in Scheme 1 and Table I. These salts crystallize readily and have sharp and characteristic melting points (*1*).

Table II presents a summary of the physical properties of the *p*-toluidine salts. There was special interest in the fluorescence of these compounds since previous experience with other types of α-phenylcinnamonitriles had shown that such substances possessed good fluorescent intensity in solution (*2*). Fluorescent measurements were performed by visual examination of the dry powder using long wavelength ultraviolet light (Ultra-Violet Products, Inc., San Gabriel, Calif.) and by determination of the excitation and emission maxima of the compounds in ethanol using a spectrophotofluorometer. Although all the compounds possessed varied fluorescent intensities in the solid state, only compounds 3, 5, and 7 showed fluorescence in ethanol solution. A comparison of the fluorescent intensity of compounds 3, 5, and 7 to quinine sulfate via the quinine reference unit (QRU) was performed (*2*). It was concluded that these compounds possessed only moderate to weak fluorescence compared to quinine sulfate.

Experimental

Melting points were taken in open capillary tubes with a Thomas-Hoover apparatus; they are uncorrected. Uv spectra were determined in ethanol solution by means of a Perkin-Elmer Model 202 spectrophotometer. Ir spectra were obtained with a Perkin-Elmer Model 467 spectrophotometer. Fluorescence spectra were determined with an Aminco-Bowman spectrophotofluorometer equipped with a X-Y recorder; spectra were uncorrected. Microanalyses were performed by Atlantic Microlab, Inc., Atlanta, Ga.

Preparation of substituted sodium α-phenylcinnamonitrile sulfonates. Five ml of a 10% aqueous potassium hydroxide solution was added to a solution of 0.02 mole of the appropriate phenylacetonitrile and 0.02 mole of the properly substituted benzaldehyde sulfonic acid sodium salt in 50 ml of ethanol stirred at 50°C. The solution was then heated for an additional 5 min, cooled, and the precipitate was collected and dried. In those cases where no precipitation occurred, the ethanolic solution was evaporated on a rotary evaporator to near dryness, and the residue collected and dried.

Preparation of p-toluidine salt derivatives. Derivitization of each sulfonate was achieved by reaction with *p*-toluidine in aqueous acid media to yield the *p*-toluidine salts of the sulfonic acids (*1*). The salts were recrystallized using either ethanol or ethanol–water mixtures.

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