Method D. The perchloric salts were made by adding 70% perchloric acid to solutions of the appropriate methylene heterocycles in acetic acid or in alcohol. Upon cooling, the salt precipitates. In some cases, ether is added to facilitate the isolation of the salts.

Reduction of Nitro Compounds to Amines

Method E. A mixture of 0.01 mole of the nitro compounds and 2 grams of sodium sulfide in 50 ml of alcohol was heated at reflux for 8 hr. A little insoluble material was filtered off, and the filtrate was reheated and diluted with H_2O until turbid and then chilled. The solid was collected and crystallized.

Preparation of Pyridine Derivatives

Method F. A solution of 0.01 mole of the methylenepyran (**13, 14, 15**) in 125 ml of acetic acid and 10 grams of ammonium carbonate was heated until the reaction mixture became light red (2–3 hr). After cooling, the solid was collected and recrystallized.

Condensation to Methine Dyes

Method G. A mixture of 0.01 mole of the perchlorate salt **4** and 0.01 mole of the *p*-dimethylaminobenzaldehyde or *p*-dimethylaminocinnamaldehyde in 25 ml of acetic anhydride was refluxed for 1 hr, cooled, and the dye was collected and recrystallized.

Method H. A mixture of 0.01 mole of the perchlorate salt **4** and 0.01 mole of the pyrone in 10 ml of phosphoryl chloride was heated on the steam bath for 1 hr. The reaction mixture was poured slowly into 100 ml of MeOH, and 5 ml of 70% $HClO_4$ was added. After cooling, the dye was collected and recrystallized.

Literature Cited

(1) Sagura, J. J., Van Allan, J. A., U.S. Patent 3,178,362 (1965).
(2) Schofield, K., *J. Chem. Soc.*, **1949**, p 2408.
(3) Van Allan, J. A., Farid, S., Reynolds, G. A., Chang, S. Chie, *ibid.*, **38**, 2834 (1973).
(4) Van Allan, J. A., Reynolds, G. A., *J. Heterocycl. Chem.*, **11**, 395 (1974).

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Halogenation of Arylsulfonylacetamides

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The bromination of 2-(*p*-toluenesulfonyl)acetamide (I) at 25–30° results in the formation of 2-bromo-2-(*p*-toluenesulfonyl)acetamide (VI); at 90–100° the product is 2,2-dibromo-2-(*p*-toluenesulfonyl)acetamide (VII). The structures assigned by Tröger and Hille are incorrect.

Tröger and Hille reported that halogenation of arylsulfonylacetamides gives *N*-halogenated products. The bromination of 2-(*p*-toluenesulfonyl)acetamide (I) was examined in detail. Tröger and Hille (*1*) reported that bromination of I at 25–30° gives *N*-bromo-2-(*p*-toluenesulfonyl)acetamide (II); at 90–100° the product is *N*-bromo-2-bromo-2-(*p*-toluenesulfonyl)acetamide (III). Chlorination of 2-(phenylsulfonyl)acetamide (IV) was reported to give *N*-chloro-2,2-dichloro-2-(phenylsulfonyl)-acetamide (V).

These structural assignments are incorrect. Bromination of I in acetic acid at 25–30° results in the formation of 2-bromo-2-(*p*-toluenesulfonyl)acetamide (VI); at 90–100° the product is 2,2-dibromo-2-(*p*-toluenesulfonyl)-acetamide (VII), and bromination of IV at 90–100° gives 2,2-dibromo-2-(phenylsulfonyl)acetamide (VIII). Monobromination of IV was not described by Tröger and Hille. Chlorination of IV in acetic acid does not give V as they reported. The product is 2,2-dichloro-2-(phenylsulfonyl)acetamide (IX) from chlorination of IV with either sulfuryl chloride or chlorine gas in acetic acid. No trichloro derivative was obtained even by chlorination of IV for 5 hr in acetic acid at 95–100°.

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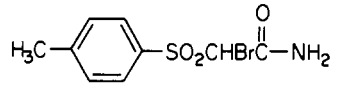
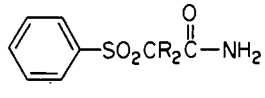


VI



VIII R = Br
IX R = Cl

The pmr spectrum of VI has absorption in DMSO-d_6 of δ 2.46 (S, 3H, $ArCH_3$), 5.86 (S, 1H, $-\overset{|}{C}HBr$), 7.4–8.0 ($AA'BB'$, 4H, ArH), and in CD_3CN of δ 2.46 (S, 3H, $ArCH_3$), 5.40 (S, 1H, $-\overset{|}{C}HBr$), 6.5 (vbs, 2H, NH_2), 7.4–8.0 ($AA'BB'$, 4H, ArH) and is consistent with the assigned structure.

The pmr spectrum of VIII was observed in DMSO-d_6, CD_3CN, and dioxane. In all three cases, the only signals observed were the 5H aromatic multiplet and a broad signal for the NH_2 protons. No signal was observed in the region expected for $-SO_2CHBrCO$. The pmr spectrum of VII is similar to that of VIII. No signal for a proton in the 2-position was observed, indicating that geminal bromine substitution has taken place.

The ^{13}C spectrum in DMSO-d_6 of VIII showed the expected absorption at 162.5 (C=O), 136.4 (C—SO_2 and para aromatic carbons), 133.0, 129.9 (ortho and meta aromatic carbons), and 72.9 ($-SO_2-\overset{*}{C}-CO$) ppm vs. tetramethylsilane. The signal at 72.9 ppm remained a singlet during off resonance ^1H decoupling, verifying that there is no hydrogen on that carbon.

The pmr spectrum in DMSO-d_6 of IX shows typical phenyl absorption as a multiplet in the 7.4–8.1 ppm re-

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.

Literature Cited

(1) Troger, J., Hille, W., *J. Prakt. Chem.*, **2**, 200 (1905).

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

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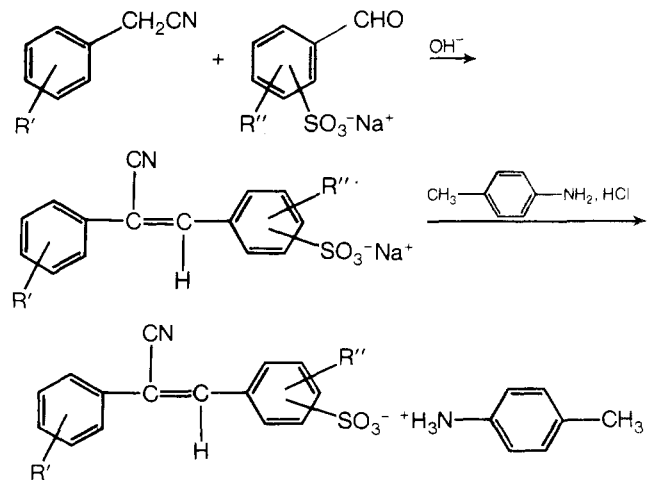
Some *p*-toluidine salts of substituted α-phenylcinnamonitrile sulfonic acids are synthesized via base-catalyzed condensations of substituted phenylacetonitriles and benzaldehyde sulfonic acid sodium salts, followed by reaction of the resulting products with *p*-toluidine in aqueous acid media. A summary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