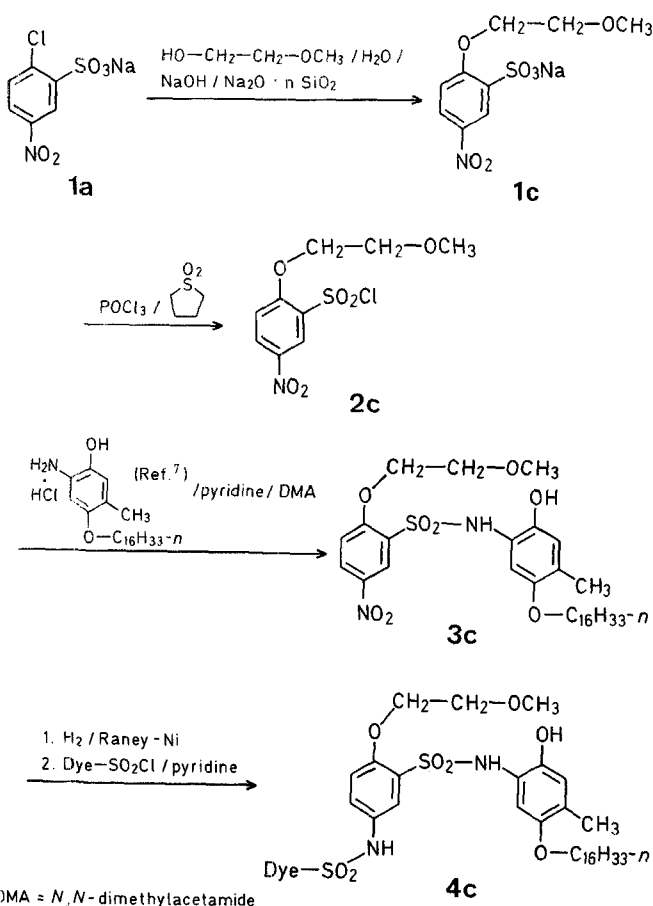


Treatment of arenesulfonic acid sodium salts (**1**) with phosphoryl chloride/sulfolane in acetonitrile (Conditions A) affords the corresponding arenesulfonyl chlorides (**2**) in 85–96% yields of isolated product. Other reaction conditions were examined for comparison. Addition of a catalytic amount of *N,N*-dimethylacetamide (Conditions B) accelerates the reaction and affords almost the same yields. (The system POCl_3 /*N,N*-dimethylacetamide has been found to be superior to the system POCl_3 /DMF in terms of chemoselectivity.) However, a large excess of *N,N*-dimethylacetamide (Conditions D) causes undesired coloration of the products and a decrease in yield. While several sodium arenesulfonates (e.g. **1b** and **1c**) can be converted into the chlorides (**2**) even in the absence of sulfolane (Conditions C), the reactions are slow and the yields are lower than with Conditions A and B. Moreover, no conversion of **1a** proceeds under Conditions C. These facts indicate that solvation of (intermediate) ionic species by sulfolane plays an important role in the reaction.

As an example of the synthetic application of the chlorination method described here, a sequence leading to *o*-sulfonylamino phenolic dye releasers (**4c**) is outlined in Scheme B, wherein Dye represents a dye moiety and the hexadecyloxy group is a ballst group^{2,6}. The reaction **1c**→**2c** is a key step in this sequence.



DMA = *N,N*-dimethylacetamide

Scheme B

2-Chloro-5-nitrobenzenesulfonyl Chloride (**2a**); Typical Procedures:

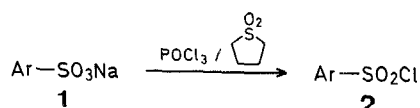
Conditions A: A mixture of sodium 2-chloro-5-nitrobenzenesulfonate (**1a**; 5.20 g, 0.02 mol), acetonitrile (10 ml), sulfolane (10 ml), and phosphoryl chloride (7.3 ml) is stirred at 68–72°C for 40 min. The mixture is then cooled to <5°C and cold water (50 ml) is added dropwise at <10°C. Stirring is continued at <10°C for 10 min and the precipitated crystalline product is isolated by suction, washed with water, and dried at the air; yield: 4.92 g (96%); m.p. 88–89°C.

A Convenient Preparation of Arenesulfonyl Chlorides from the Sodium Sulfonates and Phosphoryl Chloride/Sulfolane

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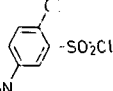
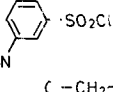
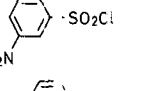
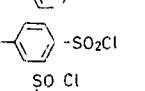
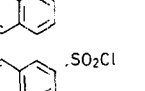
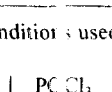
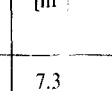
Aromatic sulfonyl chlorides (**2**) are useful intermediates for the syntheses of drugs¹ and of dye releasers in instant-color photography². Of the several known methods for the conversion of sulfonic acids into the sulfonyl chlorides³, the method using thionyl chloride/dimethylformamide is the usually employed one⁴. However, the resultant sulfonyl chlorides have been reported⁵ to form complexes with dimethylformamide so that in many cases the yields of sulfonyl chlorides are only low. We report here that the use of phosphoryl chloride/sulfolane (Scheme A) represents a convenient method for such chlorinations.



Scheme A

Conditions B: To a stirred suspension of sodium 2-chloro-5-nitrobenzenesulfonate (**1a**; 5.20 g, 0.02 mol) in acetonitrile (10 ml) and sulfolane (10 ml) is added phosphoryl chloride (7.3 ml) and then *N,N*-dimethylacetamide (0.5 ml). The mixture is stirred at 68–72°C for 15 min, then cooled to <5°C, and worked up as described above; yield: 4.92 g (96%).

Table. Arenesulfonyl Chlorides (**2**)

| 2 | Product | React. conditions ^a | Yield [%] | | m.p. [°C] | |
|---|---|--------------------------------|-----------|----------------|---|---|
| | | | found | reported | found | reported |
| a |  | A | 96 | 88–89° | 89–90° ⁸ | |
| | | | B | 96 | | |
| | | | C | — ^b | | |
| | | | D | 43 | | |
| b |  | A | 95 | 62–63° | 61° ³ | |
| | | | B | 95 | | |
| | | | C | 89 | | |
| c |  | A | 96 | 73–74° | C ₁₀ H ₁₀ ClNO ₆ S (295.6) | |
| | | | B | 95 | | |
| | | | C | 85 | | |
| d |  | A | 87 | 70–71° | 71° ³ | |
| | | | B | 84 | | |
| e |  | A | 96 | 52–53° | 51° ³ | |
| | | | B | 95 | | |
| f |  | A | 94 | 38–42° | 42° ⁹ | |
| | | | B | 90 | | (66–67°) ^c (66–67°) ^c |
| g |  | A | 85 | 71–72° | 75–76.5° ⁴ | |
| | | | B | 91 | | |

^a Conditions used for 0.02 mol of substrate **1**:

| | PCl ₅ [ml] | sulfolane [ml] | acetonitrile [ml] | <i>N,N</i> -dimethylacetamide [ml] | temperature [°C] | time [min] |
|---|-----------------------|----------------|-------------------|------------------------------------|------------------|------------|
| A | 7.3 | 10 | 10 | 0 | 68–72° | 40–60 |
| B | 7.3 | 10 | 10 | 0.5 | 68–72° | 15–30 |
| C | 7.3 | 0 | 20 | 0.5 | 70–75° | 120 |
| D | 7.3 | 0 | 20 | 7.3 | 50–55° | 90 |

^b No reaction after 7 h.

^c m.p. after recrystallization.

Sodium 2-(2-Methoxyethoxy)-5-nitrobenzenesulfonate (**1c**):

A mixture of sodium 2-chloro-5-nitrobenzenesulfonate (**1a**; 52 g, 0.1 mol), sodium silicate (Na₂O · nSiO₂, n ≈ 2; 10.0 g), and 2-methoxyethanol (120 ml) is stirred at 60°C and a mixture of sodium hydroxide (10.0 g), water (10 ml), and 2-methoxyethanol (17 ml) is added dropwise over a 10 min period. Stirring is continued at 60–63°C for 3 h, the mixture is diluted with methanol (80 ml), and filtered. The filter cake is washed with methanol (20 ml) and the combined filtrates are poured into a mixture of toluene (300 ml) and 2-propanol (80 ml). The precipitated crystalline product is isolated by suction, washed with 2-propanol, and dried at 85°C; yield: 57.4 g (96%); m.p. 238–239°C.

2-(2-Methoxyethoxy)-5-nitrobenzenesulfonyl Chloride (**2c**):

This compound is prepared using Conditions A; yield: 96%; m.p. 73–74°C.

| | | | | |
|---|-------|---------|--------|--------|
| C ₁₀ H ₁₀ ClNO ₆ S | calc. | C 36.56 | H 3.41 | N 4.71 |
| (295.6) | found | 36.45 | 3.32 | 4.58 |

M.S.: *m/e* = 295 (M⁺), 260 (M⁺ – Cl), 228 (M⁺ – Cl – CH₃OH), 185 (M⁺ – O – CH₂ – CH₂ – OCH₃).

¹H-N.M.R. (CDCl₃/TMS): δ = 8.81 (d, 1H, *J* = 3 Hz, 6-H); 8.53 (dd, 1H, *J* = 3 Hz, 9 Hz, 4-H); 7.36 (d, 1H, *J* = 9 Hz, 3-H); 4.5 (m, 2H, Ar–O–CH₂); 3.9 (m, 2H, CH₂–OCH₃); 3.43 ppm (s, 3H, OCH₃).

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² S. Fujita, S. Ono, H. Hayashi, *Brit. Pat. Application* 2000505 A (1979).

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⁴ H. H. Bosshard, R. Mory, M. Schmid, H. Zollinger, *Helv. Chim. Acta* **42**, 1653 (1959).

⁵ J. D. Albright, E. Benz, A. E. Lanzilotti, L. Goldman, *Chem. Commun.* **1965**, 413.

⁶ The dye releasers are oxidized to the corresponding *o*-quinone monosulfonylimines in photographic developing processes and then hydrolyzed to release diffusible dyes; see: S. Fujita, *Yuki Gosei Kagaku Kyokai-Shi* **39**, 331 (1981); *J. Chem. Soc. Chem. Commun.* **1981**, 425.

⁷ For the synthesis of the *o*-aminophenol derivatives, see: K. Koyama, Y. Maekawa, M. Miyakawa, *U. S. Patent* 4055428 (1977) ≡ *German Patent (DOS)* 2613005 (1976), Fuji Photo Film Co.; *C. A.* **87**, 31917 (1977).

S. Fujita, K. Koyama, Y. Inagaki, *Synthesis* **1982**, 68.

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