

James L. Kelley*, Ed W. McLean and K. F. Williard

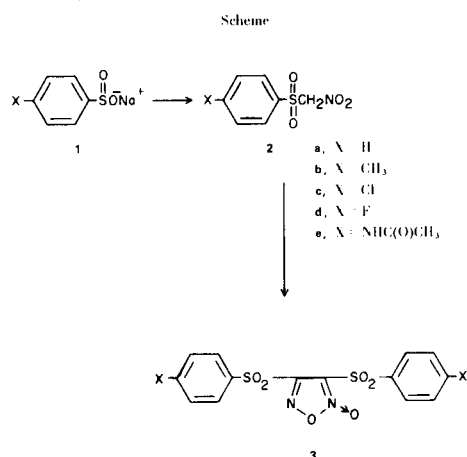
Wellcome Research Laboratories, Research Triangle Park, North Carolina 27709

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The synthesis of some symmetrically substituted bis(arylsulfonyl)furoxans from aryl nitromethyl sulfones is reported.

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A wide variety of synthetic methods are known for the preparation of furoxans in general which encompass intramolecular and intermolecular cyclizations as well as rearrangement reactions (1,2). Synthetically useful preparations of bis(arylsulfonyl)furoxanes such as **3** (Scheme),



however, have been described only from (arylsulfonyl)acetic acids by the action of nitric acid (3), from sodium *p*-toluenesulfinate and chloropicrin (3), or from aryl diazomethyl sulfones and dinitrogen trioxide (4). Bis(4-toluenesulfonyl)furoxan has also been isolated as one of three products from tosyldiazomethane and nitrosyl chloride (5) and as a minor product from nitromethyl *p*-tolyl sulfone and sodium nitrite (6). We report here a new and convenient synthesis of bis(arylsulfonyl)furoxans (**3**) by reaction of aryl nitromethyl sulfones with nitric acid in acetic acid.

When **2a** (Scheme) was treated with nitric acid in acetic acid at ambient temperature no reaction occurred. When the temperature was raised to 60-65° for 1 hour, **3a** was obtained in high yield. These same conditions were used successfully in the preparation of **3b-3e** (Table II). Not even with the 4-acetylamino phenylsulfone (**3e**) was concomitant nitration of the aromatic ring detected. The starting aryl nitromethyl sulfones (**2**) were prepared by a modification of the method of Zeilstra and Engberts (7) from sodium arylsulfonates and nitromethane. We found the use of a nitrogen atmosphere to be of no advantage and that sodium methoxide could be conveniently substituted for potassium *t*-butoxide.

This procedure provides a simple and efficient synthesis of symmetrical bis(arylsulfonyl)furoxans from readily available sodium arylsulfonates *via* aryl nitromethyl sulfones.

EXPERIMENTAL

Melting points were taken in capillary tubes on a Mel-Temp block and are uncorrected. Each analytical sample had its ir and nmr spectra compatible with the assigned structure and moved as a single spot on tlc. The analytical samples gave combustion values for C, H and N within 0.4% of the theoretical.

Preparation of Aryl Nitromethyl Sulfones (**2**).

To a stirred, ice cold mixture of 0.10 mole of sodium methoxide in 475 ml. of DMF was added dropwise a solution of 0.22 mole of nitromethane in 25 ml. of DMF. After 0.5 hour, 0.10 mole of the sodium arylsulfinate and 0.10 mole of iodine was added to the white mixture. The orange reaction mixture was then stirred at ambient temperature overnight, after which a concentrated solution of sodium sulfite in water was added until the dark color had disappeared. The reaction was poured over 1 l. of ice water and acidified with dilute hydrochloric acid. The precipitate was collected, dissolved in 300 ml. of benzene, washed with three 100 ml. portions of water, dried (magnesium sulfate) and spin evaporated *in vacuo* to give the crude product. This material generally contained a contaminant which remained at the origin on tlc on silica gel with ethyl acetate-hexanes:1-2, but the material was quite satisfactory for the next reaction. Recrystallization from the appropriate solvent gave the analytical samples.

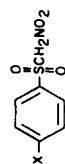
Preparation of Bis(arylsulfonyl)furoxans (**3**).

A stirred mixture of 0.10 mole of **2**, 70 ml. of acetic acid, and 35 ml. of 90% nitric acid were heated at 60-65° for 1 hour. The cooled reaction mixture was poured over 600 ml. of ice water, and the resultant precipitate was collected and recrystallized.

REFERENCES AND NOTES

- (1) K. L. Stuart, *Heterocycles*, **3**, 651 (1975).
- (2) J. H. Boyer in "Heterocyclic Compounds", Vol. 7, R. C. Elderfield, Ed., John Wiley and Sons, New York, N. Y., 1961, p. 462.
- (3) W. V. Farrar, *J. Chem. Soc.*, 904 (1964).
- (4) J. F. J. Engbersen and J. B. F. N. Engberts, *Synth. Commun.*, **1**, 121 (1971).
- (5) J. C. Jagt, I. van Buuren, J. Strating, and A. M. van Leusen, *ibid.*, **4**, 311 (1974).
- (6) J. J. Zeilstra and J. B. F. N. Engberts, *Synthesis*, 49 (1974).
- (7) J. J. Zeilstra and J. B. F. N. Engberts, *Rec. Trav. Chim.*, **93**, 11 (1974).

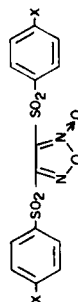
Table I
Physical Properties of Aryl Nitromethyl Sulfones



Compound	X	Recrystallization Solvent	M.p. °C	Yield, %	Formula	Calculated, %			Found, %		
						C	H	N	C	H	N
2a	H	Ethanol	76-77 (a)	44	C ₇ H ₇ NO ₄ S	41.78	3.51	6.96	41.45	3.55	6.84
2b	CH ₃	95% Ethanol	112-114 (b)	42	C ₈ H ₉ NO ₄ S	44.64	4.22	6.50	44.56	4.35	6.55
2c	Cl	Ethanol	138-139	39	C ₇ H ₆ ClNO ₄ S	35.68	2.57	5.95	35.67	2.62	5.93
2d (c)	F	Ethanol-water	89-90	46	C ₇ H ₆ FNO ₄ S	38.35	2.76	6.39	38.26	2.81	6.43
2e	NHC(O)CH ₃	Methanol	228-229	36	C ₉ H ₁₀ N ₂ O ₅ S	41.85	3.91	10.85	41.58	3.81	10.81

(a) W. E. Truce, T. C. Klingler, J. E. Paar, H. Feuer and D. K. Wu, *J. Org. Chem.*, **34**, 3104 (1969) report m.p. 150-150.5°; J. Troger and E. Nolte, *J. Prakt. Chem.*, **101**, 136 (1920) report dimorphic forms m.p. 151° and 69.72°. (b) Literature (7), m.p. 116.1-116.6°. (c) For the preparation of the starting sodium sulfinate see J. M. Dumont and P. Rumpf, *Bull. Soc. Chim. France*, 1213 (1962).

Table II
Physical Properties of Bis(arylsulfonyl)tuoroaxans



Compound	X	Recrystallization Solvent	M.p. °C	Yield, %	Formula	Calculated, %			Found, %		
						C	H	N	C	H	N
3a	H	Ethanol	155-157 (a)	85	C ₁₄ H ₁₀ N ₂ O ₆ S ₂	45.89	2.75	7.65	46.07	2.83	7.40
3b	CH ₃	Acetone-water	181-183 (b)	82	C ₁₆ H ₁₄ N ₂ O ₆ S ₂	48.72	3.58	7.10	48.67	3.59	7.16
3c	Cl	Ethyl acetate-ethanol	177-178 (c)	87	C ₁₄ H ₈ Cl ₂ N ₂ O ₆ S ₂	38.63	1.86	6.44	38.86	2.04	6.51
3d	F	Ethanol-ethyl acetate	182-183	24	C ₁₄ H ₈ F ₂ N ₂ O ₆ S ₂	41.78	2.01	6.96	41.90	2.08	6.82
3e	NHCOCH ₃	Ethanol	~220 (dec.)	45	C ₁₈ H ₁₆ N ₄ O ₈ S ₂ ·C ₂ H ₆ O (d)	45.62	4.21	10.64	45.54	4.18	10.55

(a) Literature (3) m.p. 126-127°; we have repeated the experimental conditions in reference 3 and obtained a product identical with **3a** by tlc, mixture m.p., ir, and nmr. (b) Literature (3,4) m.p. 183-184°. (c) Literature (3) m.p. 176°. (d) The presence of a molar equivalent of ethanol was supported in the nmr spectra.