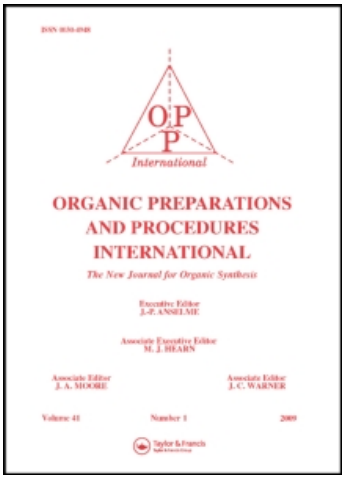

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A NOVEL SYNTHESIS OF SOME ARYLTHIOGLYCOLIC ACIDS

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A NOVEL SYNTHESIS OF SOME ARYLTHIOGLYCOLIC ACIDS

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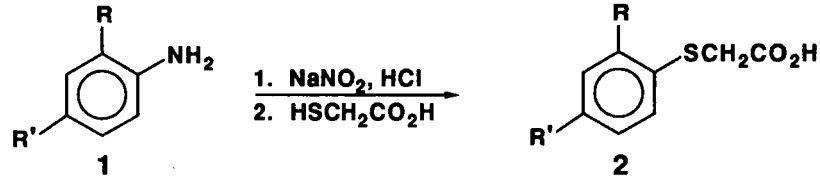
Substituted thioindoxyls are extensively used for the synthesis of vat dyestuff.[1,2] Of the many methods for their synthesis,[1,3] the most widely used is the cyclization of the appropriate arylthioglycolic acids.[4,5] Previous preparations of arylthioglycolic acids are laborious multi-step processes which consume large amounts of chemicals.[2,5,6] We now describe a simpler and more economical two-step procedure for the synthesis of arylthioglycolic acids in higher



yields than those previously reported. The products were identified by comparison with authentic samples and by their spectral data. We are currently investigating the utility of the reaction with amines bearing electron-donating groups.

EXPERIMENTAL SECTION

All melting points were determined in sealed capillaries. IR spectra were recorded on a Perkin-Elmer 1330 spectrometer. ^{1}H NMR spectra were obtained on a Varian EM-360 L at 60 MHz.

Typical Procedure. *o*-Fluorophenylthioglycolic Acid.- A mixture of *o*-fluoroaniline (11.1 g, 0.10 mole) and 27 ml conc. HCl was cooled to -10°; then about 60 g of crushed ice added and the mixture was then diazotized by the slow addition of a solution of $NaNO_2$ (8.97 g, 0.13 mole) in 20 ml of water. This cold solution of diazotized amine (CAUTION) was then added slowly to a stirred solution of thioglycolic acid (9.2 g, 0.10 mole) and the reaction mixture was refluxed for 2 hrs. The hot (100°) aqueous solution was decanted from the precipitated solid and allowed to come to room temperature. More of the product (2a) crystallized from the aqueous solution. The precipitated solid was again heated to 100° in water, and again the solution was decanted from the solid and allowed to

TABLE 1. Yields, mps and Elemental Analyses of 2

Compd	R	R'	mp. (°C)	lit. mp. (°C)	Yield (%)	Elemental Analyses Calcd	Found
2a	F	H	80-82	79[a]	35	C, 51.60	51.62
						H, 3.79	3.74
2b	Cl	H	117-118	117-118[b]	35	C, 47.41	47.45
						H, 3.48	3.51
2c	Cl	Cl	122-124	122-123[c]	33	C, 40.53	40.66
						H, 2.55	2.49
2d	Br	H	116-117	116-117[d]	33	C, 38.89	39.01
						H, 2.86	2.80
2e	H	Br	110-112	107[e],112[f]	34	C, 38.89	38.60
						H, 2.86	2.79
2f	I	H	103-106	112-113[g]	33	C, 32.67	32.54
						H, 2.40	2.45

a) N. Sharghi and I. Lalezari, J. Chem. Eng. Data, 8, 276 (1963); b) Ref. 5; c) H. Erdtman and G. Nilsson, Acta Chem. Scand., 3, 901 (1949); d) G. M. Oksengendler and Yu. E. Gerasimenko, J. Gen. Chem., USSR, 29, 919 (1959); e) P. Friedlander and A. Chwaia, Monatsh. Chem., 247 (1907); f) S. Claësson, Bull. Soc. Chim. France, [2], 23, 444 (1875); g) N. S. Dokunikhin and Y. Gerasimenko, J. Gen. Chem. USSR, 30, 1987 (1960).

TABLE 2. ^{1}H NMR and IR Data of 2

Cmpd	^{1}H NMR (δ, $CDCl_3$)	IR (C=O, KBr) (cm^{-1})
2a	10.40(s, 1 H); 7.35(m, 4 H); 3.75(s, 2 H)	1710
2b	9.92(s, 1 H); 7.35(m, 4 H); 3.85(s, 2H)	1703
2c	8.05(s, 1H); 7.40(m, 3 H); 3.70(s, 2 H)	1707
2d	8.50(s, 1 H); 7.40(m, 4 H); 3.75(s, 2 H)	1700
2e	9.57(s, 1 H); 7.40(m, 4 H); 3.64(s, 2 H)	1698
2f	8.17-7.35(m, 5 H); 3.85(s, 2 H)	1697

come to room temperature whereupon more solid crystallized from the aqueous solution. The same decantation process was repeated five more times. The various crops were combined and recrystallized from water to yield 6.51 g (35%) of product, mp. 80-82°. The same procedure was used for preparation of other compounds (2), which were identical to authentical samples (Table 1).

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REFERENCES

1. H. A. Lubs and A. L. Fox, U. S. Patent, 2,061,200 (1936); Chem. Abs., 31, 881 (1937).

2. W. Carpmael, Brit. Patent. 274,527 (1926); Chem. Abs., 22, 2277 (1928).

3. L. K. A. Rahman and R. M. Scrowston, J. Chem. Soc., Perkin Trans. 1, 385 (1984).

4. O. Dann and M. Kokorudz, Chem. Ber., 86, 1449 (1953).

5. C. E. Dalgliesh and F. G. Mann, J. Chem. Soc., 893 (1945).

6. W. Carpmael, Brit. Patent, 287,858 (1929); Chem. Abs., 23, 527 (1929).

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AN OPTIMIZED SYNTHESIS OF DIMETHYL 2,2'-DIHYDROXY-1,1'-BINAPHTHALENE-3,3'-DICARBOXYLATE AND OF METHYL 2,2'-DIHYDROXY-1,1'-BINAPHTHALENE-3-CARBOXYLATE

Submitted by (11/28/89)

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Many derivatives of 1,1'-binaphthalene-2,2'-diol are used as chiral auxiliaries in stereoselective organic reactions.[1] These compounds can be prepared by a variety of methods, the oxidative coupling of substituted 2-naphthols being the most direct. However, despite the fact that this reaction was recognized more than one hundred years ago[2] and studied many times since then, it suffers from several disadvantages: first, there is no reliable way to predict which oxidizing agent would be the best for a given substrate -an empirical approach based on analogy is unavoidable- and second, over-oxidation as well as other side-reactions[3] may often be a serious problem. Moreover, almost no attention has been paid to the possibility of preparing unsymmetrical binaphthols by oxidative cross-coupling of differently substituted 2-naphthols.[4] Thus a simple and mild procedure