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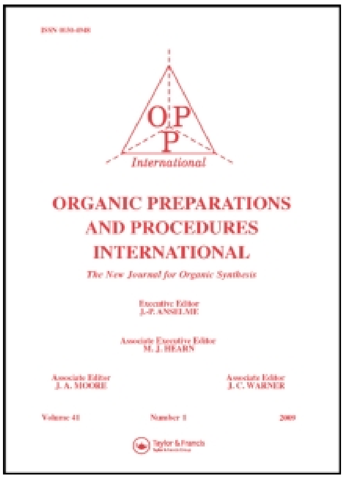

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FURTHER APPLICATIONS OF THE NOVEL SYNTHESIS OF ARYLTHIOGLYCOLIC ACIDS

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FURTHER APPLICATIONS OF THE NOVEL SYNTHESIS OF ARYLTHIOGLYCOLIC ACIDS

Submitted by
(11/28/94)

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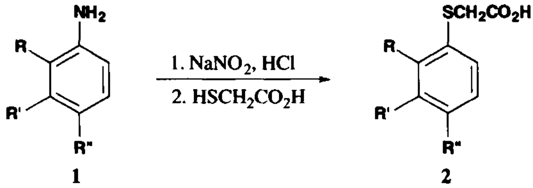
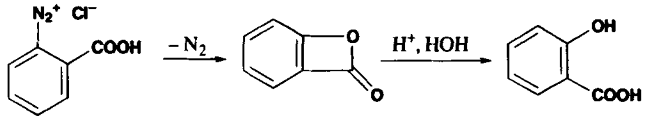
We previously reported a more efficient two-step procedure for the synthesis of arylthioglycolic acids which are used for the cyclization to thioindoxyls. The utility of this process has now been extended to aryl groups bearing electron-donating and -withdrawing groups.



a) R = R' = R" = H b) R = CH_3, R' = R" = H c) R = R' = H, R" = CH_3
d) R = R' = CH=CHCH=CH, R" = H e) R = R" = H, R' = NO_2
f) R = R' = H, R" = CO_2H

Treatment of the diazonium salts of aniline, substituted anilines (**1**) and α-naphthylamine (**1d**) with thioglycolic acid (**2**) gave the corresponding arythioglycolic acids in variable yields (Table). However, anilines substituted with electron-donating groups such as hydroxy and methoxy failed to yield the thioglycolic acids under the same conditions. Surprisingly, the product of the reaction of anthranilic acid was **not** the anticipated *o*-carboxyphenylthioglycolic acid but salicylic acid, possibly generated *via* the lactone as shown below.



If this reaction had occurred by direct attack of water on the diazonium salt, phenol derivatives should also have been formed, instead of the observed products, with the other diazonium salts.

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. Elemental analyses were carried out with a Leco-CHN-600 instrument.

Typical Procedure. *o*-Tolylthioglycolic Acid.- A mixture of *o*-toluidine (10.72 g, 0.10 mol) and 27 mL of conc. HCl was cooled to -10°; then about 60 g of crushed ice was added and the mixture was the diazotized by the slow addition of a solution of sodium nitrite (8.97 g, 0.13 mol) in 20 mL of water. The cold solution of the diazotized amine (CAUTION!) was then added cautiously and slowly to a stirred solution of thioglycolic acid (9.12 g, 0.10 mol) and the reaction mixture was heated at reflux for 2 hrs. The hot aqueous solution was decanted from the precipitated solid and allowed to cool to room temperature. More of the product (**2a**) crystallized from the aqueous solution. It was collected and boiled again in water. This process was repeated six more times and the solid crops were combined and recrystallized from water to yield 4.0 g (22%) of product, mp. 103-105°.

TABLE. Yield, mps and ^{1}H NMR Spectral Data of Compounds **2**

Cmpd	Yield (%)	mp. (°C)	lit mp. (°C)	^{1}H NMR (δ, CDCl$_3$)
2a	30	57-60	59-61[a]	8.3 (s, 1H), 7.3 (m, 5 H), 3.6 (s, 2 H)
2b	22	103-105	106-107[b]	9.5 (s, 1H), 7.2 (m, 4 H), 3.6 (s, 2 H), 2.4 (s, 3H)
2c	20	95-97	85-86[c]	9.6 (s, 1H), 7.4 (m, 4 H), 3.6 (s, 2 H), 2.3 (s, 3H)
2d	29	108-110	107[d,e]	8.3-7.3 (s, 8H), 3.7 (s, 2 H)
2e	60	130-132[f]	—	8.8 (broad, 1 H), 8.3-7.5 (m, 4 H), 3.9 (s, 2 H) [δ (CD$_3$)$_2$CO]
2f	85	222-225	>250[g]	8.1 (broad, 2H), 7.9 (d, 2 H), 7.5 (d, 2 H), 3.9 (s, 2 H) [δ (CD$_3$)$_2$CO]

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