explosion and without change in phenolic yields.

(7) Vedejs (ref 1) reported that MoO_5–H_2O–HMPA may be unstable when stored at room temperature. We stored this complex for 2 weeks and there was no indication of any instability. However, if the complex was exposed to air for 2–3 days it absorbed moisture and was exceedingly difficult to recrystallize.

(8) All compounds **1a–4a** were compared with the authentic samples for TLC, IR, NMR and melting point data.

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A Convenient Synthesis of 1-Bromo-8-iodonaphthalene and 1,8-Dibromonaphthalene from 8-Bromo-1-naphthoic Acid

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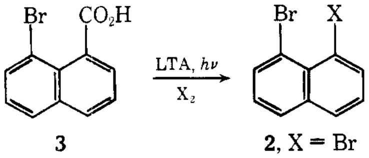
1,8-Dihalonaphthalenes, especially those containing bromine and/or iodine, are important intermediates for the preparation of naphthalene-based heterocycles and other naphthalene derivatives. Fieser and Seligman[2] prepared several 1,8-disubstituted naphthalenes from 1,8-diaminonaphthalene employing a modified stepwise diazotization procedure.[3] This method is time consuming and does not give satisfactory results.[4] Direct tetraazotization of 1,8-diaminonaphthalene is useful for preparing 1,8-diiodonaphthalene (1)[5] but does not give good yields of 1,8-dibromonaphthalene (2)[4] and is not a feasible route to mixed dihalonaphthalenes.

A synthesis of 2 using the Hunsdiecker reaction on 8-bromo-1-naphthoic acid (3) was reported[4] and 1-bromo-8-iodonaphthalene (4) has been prepared by treating 8-bromo-1-naphthoic acid with red mercuric oxide and iodine.[6a] For large scale preparations of these compounds both routes have disadvantages: the former requires expensive silver salts and the latter gives modest yields (28%).

Since our work requires that we have ready access to all three dihalonaphthalenes, 1, 2, and 4, we investigated all of the reported methods for making these compounds in order to find the most reliable and efficient routes. The diazotization procedures[2] for preparing 2 and 4 gave yields varying from 0 to 30%. These reactions are apparently very sensitive to the state of the catalyst. We were not successful in finding a way to make it consistently active.

Although we found the tetraazotization procedure[5] useful for preparing 1,[7] we could not extend this method to 2, an observation consistent with that made earlier.[4] Our efforts to improve the yields of the mercuration–iodination reaction[6a] to produce 4 were unsuccessful. When we substituted iodine monochloride for iodine we isolated no product from the reaction mixture.

We did find that lead tetraacetate (LTA) induced halodecarboxylation, a procedure usually inefficient for aromatic acids,[8] is a convenient route to both 2 and 4 from 3.



3

2, X = Br
4, X = I

We have found the yields consistently good for 4 (≥75%, isolated) using LTA, halogen, and 3. The yields of 2 run lower (~50%, isolated) but are still in the useful range.

Attempts to extend this method to making 1, 2, 3, and 8-iodonanaphthoic acid (5) from 1,8-naphthalenedicarboxylic acid (6) failed using pure benzene and pure tetrahydrofuran solvent systems.

Experimental Section

Melting points were determined on a Thomas-Hoover Mel-Temp melting point apparatus and are corrected. Infrared spectra were taken on a Perkin-Elmer Infracord 137 using pressed KBr pellets. NMR spectra were obtained from a Varian A60-A spectrometer in $CDCl_3$ with Me_4Si as internal standard. IR, NMR, and mass spectra of 4 and 2 are consistent with the assigned structures.

1-Bromo-8-iodonaphthalene (4). In a three-necked 1-L round-bottom flask equipped with heating mantle, reflux condenser, magnetic stirrer, and a syringe needle for bubbling N_2 through the solution were placed 750 mL of dry benzene and 14 g of 8-bromo-1-naphthoic acid.[9] This slurry was warmed to near reflux to dissolve 3. Nitrogen was bubbled through the solution and moist lead tetraacetate freshly made from 57 g of Pb_3O_4 in 98 mL of glacial acetic acid and 32 mL of acetic anhydride[10] was added to give a deep red solution. The solution was irradiated with a 275-W sunlamp and turned yellow after 5 min. Iodine was added in small portions with time allowed between additions for the iodine color to discharge. Large amounts of lead salts precipitated during the addition of the iodine. When the iodine color did not discharge after 15 min of irradiation, the reaction was assumed to be complete and the light was turned off. The red solution was cooled, filtered, and washed with saturated sodium thiosulfate solution. The resulting yellow benzene solution was dried with anhydrous $MgSO_4$ and filtered, and the solvent was removed in vacuo. The brown solid obtained was placed on a 10 × 5 cm column of alumina (Alcoa F-20, neutral, activated) and eluted with hexane as one large fraction. Removal of the hexane gave 13.6 g (75%) of a pale yellow solid, mp 92–93 °C (lit. mp[6] 91–92 °C). A second run on the same scale produced 13.7 g (76%) of 4.

1,8-Dibromonaphthalene (2). The procedure was the same as that for 4 with the exception that bromine was added in small portions by syringe. Six grams of 8-bromo-1-naphthoic acid (3) gave 4.5 g (66%) of a pale yellow solid after chromatography on alumina with hexane, mp 82–85 °C. Recrystallization from ethanol gave 3.4 g (50%) of an off-white solid, mp 104–105 °C.[6a,b] A second run on 4 g of 3 gave 1.8 g (40%) after recrystallization, mp 104–105 °C (lit. mp 109–110[2] and 106–108 °C[6]).

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