this procedure together with yields from specific runs are listed in Table III.

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Oxidation of Nitrosoaromatic Compounds with Peroxytrifluoroacetic Acid[1]

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The previously unreported oxidation of *o*-dinitrosobenzene into *o*-dinitrobenzene has now been observed using peroxytrifluoroacetic acid.[2] Similar oxidations of 4-methyl-1,2-dinitrosobenzene into 4-methyl-1,2-dinitrobenzene and *p*-dinitrosobenzene into *p*-dinitrobenzene have occurred.

3-Nitro- and 3,5-dinitro-1,2-dinitrosobenzene, diphenylfuroxan, and the fused ring molecules, 1,2-dinitrosonaphthalene and 9,10-dinitrosophenanthrene apparently are not oxidized under similar conditions by peroxytrifluoroacetic acid into nitro derivatives and may be recovered. Poor recovery of the fused ring compounds indicates ring oxidation and degradation. Attempts to oxidize 4-chloro-5-methoxy-1,2-dinitrosobenzene with this reagent result in extensive destruction.

Peroxytrifluoroacetic acid oxidizes nitrosobenzene to nitrobenzene and catalyzes a self-condensation to *p*-nitrosodiphenylhydroxylamine.[3] Oxidation is predominant at higher temperatures and the condensation is predominant at lower temperatures.

$$C_6H_5NO \xrightarrow{F_3CCO_3H} C_6H_5NO_2 + p\text{-}ONC_6H_4N(C_6H_5)OH$$

EXPERIMENTAL

Oxidation of nitrosobenzene. To a solution of 3.21 g. (0.03 mol.) of nitrosobenzene in 25 ml. of methylene chloride, maintained at 5–10° with an ice bath, was added over a period of 45 min. with good stirring a solution of 1.2 ml. (0.04 mol.) of 90% hydrogen peroxide in 15 ml. (0.20 mol.) of trifluoroacetic acid. After the addition the solution was stirred another 15 min. at 5–10° and poured into 100 ml. of ice water. The mixture was made alkaline with solid sodium bicarbonate and allowed to stand for 4 hr. before the precipitated solid was collected, washed with 75 ml. of ether and air dried. The weight of crude yellow-brown *p-nitroso-N,N-diphenylhydroxylamine*, m.p. 138–141° dec. (lit.[3] m.p. 147–152° dec.), was 1.12 g. (35%). Recrystallization twice from aqueous ethanol (Norit) yielded 0.35 g. of yellow-brown solid, m.p. 137–138° (dec.).

A sample of the crude product dissolved in boiling aqueous ethanol was treated with zinc dust until the yellow color was discharged. After treating the mixture with Norit it was filtered and rapidly cooled. Grey platelets (which darkened in air) of *p*-aminodiphenylamine, m.p. 75–76° (lit.[4] m.p. 75°), separated from the solution. An attempt to carry out this reduction with sulfur dioxide as previously reported[3] allowed recovery of starting material.

The ether and methylene chloride layer of the filtrate from the oxidation reaction was separated and the aqueous phase was extracted with two 25-ml. portions of ether. The organic layer and the ether extracts were combined, washed with 25 ml. of water, and dried over anhydrous sodium sulfate. The solvent was removed, followed by distillation of a trace of a blue-green liquid (assumed to be nitrosobenzene), which was not isolated. Finally, 0.91 g. (25%) of nitrobenzene, b.p. 209–210°, n_D^{25} 1.5474, distilled as a dark yellow liquid. Redistillation gave a product b.p. 208–209°, n_D^{25} 1.5487, 0.63 g. (17%).

In another experiment nitrosobenzene was dissolved in 50 ml. of methylene chloride and, to the gently refluxing solution, a solution of hydrogen peroxide in trifluoroacetic acid was added over a period of 30 min. After refluxing another 15 min., the red-brown solution was poured into 150 ml. of ice water and worked up in the manner outlined above except that after filtering and washing the solid product with 25 ml. of cold methylene chloride, the combined filtrate and wash was steam distilled. The aqueous phase of the steam distillate was separated and extracted with two 15-ml. portions of methylene chloride. The combined extracts and methylene chloride layer of the distillate were dried over anhydrous sodium sulfate. By distillation of this solution there was obtained 1.31 g. (35.5%) of nitrobenzene, b.p. 208–210°, n_D^{25} 1.5484. The crude dry *p*-nitroso-*N*,*N*-diphenylhydroxylamine filtered from the reaction mixture weighed 0.49 g. (15%), m.p. 120° (dec.). Recrystallization from aqueous ethanol furnished 0.25 g. (8%) of material, m.p. 128–132° (dec.).

Oxidation of 1,2-dinitrosobenzene. To a solution of 2.70 g. (0.12 mol.) of the dinitroso compound in 15 ml. (0.20 mol.) of trifluoroacetic acid was added with stirring 1.7 ml. (0.06 mol.) of 90% hydrogen peroxide. The solution was heated to reflux and the heat of reaction was sufficient to maintain reflux for a few minutes. After a total reflux time of 45 min. the solution was poured into 200 ml. of ice water, the crude yellow precipitate of *o*-dinitrobenzene was filtered, washed with water, and recrystallized from dilute ethanol as light yellow needles, m.p. and mixture m.p. 118–119° (lit.[5] m.p. 116–116.5°), 0.71 g. (21%). Comparable yields of *o*-dinitrobenzene were obtained when the reaction was carried out in the presence of urea, a scavenger for oxides of nitrogen, either at room temperature for 17 hr. or at reflux for 1 hr.

In a similar manner, 3,4-dinitrosotoluene was oxidized into dinitrotoluene, m.p. and mixture m.p. 58–59°,[6] in 15% yield and *p*-dinitrosobenzene into *p*-dinitrobenzene, m.p. and mixture m.p. 174–175°,[5] in 92% yield.

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