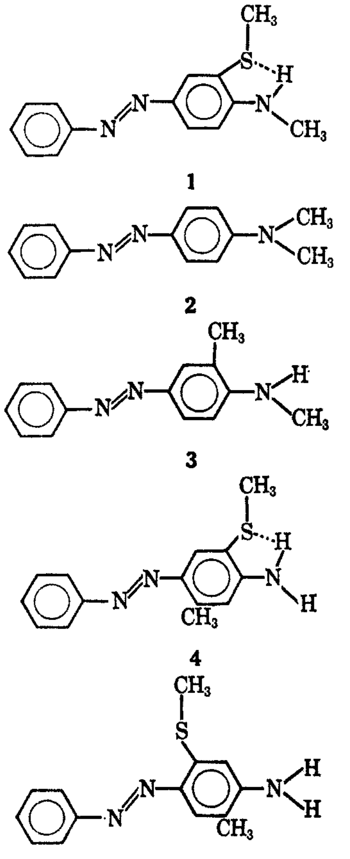
Chart I



3 hr. Ethyl acetate was added carefully; then 300 ml water was added. The layers were separated and the ether layer was dried over Na_2SO_4. The residue from the ether layer was fractionally distilled to yield 17.0 g (75%) of N-methyl-2-methylmercaptoaniline: bp 64° (0.06 mm); infrared spectrum 3386 s, 3066 m, 2984 m, 2920 s, 2865 m, 2812 m, 1591 s, 1500 s, 1454 s, 1427 s, 1317 s, 1286 m, 1166 m, 1017 w, 1031 m, 966 w, 740 m cm^{-1} (pure liquid); nmr spectrum (Varian A-60, hexamethyldisiloxane internal reference, pure liquid) δ 2.20 (3 H), 2.82 (3 H), 4.8 (1 H), 6.49 (triplet, 2 H), 7.1 (multiplet, 2 H).

3-Methylmercapto-N-methyl-4-aminoazobenzene (1).—2-Methylmercaptoaniline was converted to its ω-methyl sulfonate by the procedure of Miller, *et al.*[7] This product was coupled with diazotized *p*-aminobenzoic acid to give 4′-carboxy-3-methylmercapto-4-aminoazobenzene ω-methylsulfonate, which was hydrolyzed in alcoholic alkali[7] to yield 4′-carboxy-3-methylmercapto-4-aminoazobenzene, mp 219°. Acetic acid was added to the hydrolysis mixture to complete precipitation of the dye, which was filtered and washed with water. Recrystallization from acetic acid gave a sample for analysis. *Anal.* Calcd for $C_{14}H_{13}N_3O_2S$: C, 58.53; H, 4.56; N, 14.63; S, 11.14. Found: C, 58.27; H, 4.89; N, 14.03; S, 11.06. This compound (102 g) was dissolved in 1500 ml of 10% KOH and heated on a steam bath. When the temperature reached 60°, 225 g of $Na_2S_2O_4$ was added in 50-g portions. The mixture was heated for another 0.5 hr, 1000 ml of 11 *N* KOH was added, and the mixture was cooled and extracted with three 500-ml portions of a 1:1 mixture of ether and benzene. The extract was dried over Na_2SO_4 and evaporated to give 40.5 g of solid 2-methylmercapto-1,4-phenylenediamine, mp 93°. This diamine (7.7 g, 0.05 mole) was coupled with 5.5 g of nitrosobenzene.[8] The product was chromatographed on alumina with 30% benzene in hexane (Skellysolve B); 7.8 g of 3-methylmercapto-4-aminoazobenzene (64%) was obtained. Only 0.37 g of presumed 2-methylmercapto-4-aminoazobenzene was found. Rechromatography of the 3-methylmercapto-4-aminoazobenzene on a longer column with 15% benzene in hexane, followed by evaporation of solvent and removal of the last traces of solvent in a vacuum desiccator over mineral oil gave an oil which was analyzed. *Anal.* Calcd for $C_{13}H_{13}N_3S$: C, 64.19; H, 5.39; N, 17.27; S, 13.15. Found: C, 64.08; H, 5.29; N, 17.24; S, 12.94. This compound was formylated by the procedure described above. When the benzene was removed from the reaction product, treatment of the residue with ether effected instantaneous crystallization to a solid mass. This was filtered, washed with ether, and air dried to give beautiful, orange crystals in yields of 60–70%, mp 139°. The N-formyl-3-methylmercapto-4-aminoazobenzene was methylated with methyl iodide and KOH by the procedure of Ishikawa, *et al.*,[8] to give 1 in 80% yield after alumina chromatography. *Anal.* Calcd for $C_{14}H_{15}N_3S$: C, 65.36; H, 5.88; N, 16.33; S, 12.44. Found: C, 65.56; H, 5.95; N, 16.38; S, 12.47. Compound 1 was a thick oil which, when highly purified and cooled at −20° for several days, solidified to crystals which melted at 46°; for the infrared spectrum see ref 4.

2-Methylmercapto-5-methyl-4-aminoazobenzene (4).—Potassium hydroxide (6.5 g) was dissolved in 100 ml of absolute ethanol. Methanethiol (4.8 g) was added, followed by 3-nitro-4-chlorotoluene (Aldrich, 17.2 g, 0.10 mole). The mixture was refluxed for 3 hr, then diluted to 500 ml with water. The product was extracted with two 200-ml portions of 20% benzene in hexane. Removal of the solvent left a dark red-black mass, which was leached with boiling hexane. Upon cooling, yellow, oily crystals separated from the hexane. Recrystallization from 30 ml of 95% ethanol gave 6.4 g (34%) of 3-nitro-4-methylmercaptotoluene, mp 75°. This was reduced by Kuhn's procedure[9] in quantitative yield (5.4 g) to 2-methylmercapto-5-methylaniline. The ω-methylsulfonate was prepared as for 2-methylmercaptoaniline, coupled in the same way with diazotized *p*-aminobenzoic acid, and the coupling product was similarly hydrolyzed to give a 40% yield of 4′-carboxy-2-methylmercapto-5-methyl-4-aminoazobenzene. This compound (2.0 g) was reduced with $Na_2S_2O_4$ as before to give 2-methylmercapto-5-methyl-1,4-phenylenediamine (0.49 g, 44%, mp 89°). The diamine (0.42 g, 0.0025 mole) was dissolved in a mixture of 2.3 ml of absolute ethanol and 0.45 ml of glacial acetic acid. Nitrosobenzene (0.27 g) was added, and the mixture was allowed to stand for 3 days at room temperature, then made alkaline with 2% NaOH and extracted with ether. The residue from the ether extract was chromatographed on alumina. Compound 4 (0.35 g, 55%, mp 67°) was eluted first, followed by compound 5 (0.03 g, 5%). *Anal.* Calcd for N-methyl derivative of 4 ($C_{15}H_{17}N_3S$): C, 66.40; H, 6.32; N, 15.49; S, 11.79. Found: C, 66.45; H, 6.36; N, 15.42; S, 11.70.

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Cerium(IV) Oxidation of Organic Compounds. III. Preparation of Cyclopropanecarbaldehyde from Cyclopropanemethanol[1a-c]

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We wish to report a convenient and efficient oxidative synthesis of cyclopropanecarbaldehyde (1). We have found that an aqueous solution 1 *N* in ceric ammonium nitrate oxidizes cyclopropanemethanol (2) to 1 in 64% isolated yield. The reaction occurs rapidly (5–15 min) under mild conditions (75°) and affords a simple,

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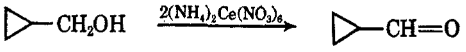

2 1

one-step preparation of 1 from commercially available starting materials.

Several other methods are known for the preparation of 1. Of the few known oxidative routes to 1,[2-5] only the copper-catalyzed air oxidation of cyclopropanemethylamine gives 1 in greater than 50% yield.[5] However, this method is experimentally more complex than the cerium(IV) oxidation. Good yields of 1 are obtained by several reductive methods.[6-10] A summary of the known routes to 1 is presented in Table I. It is apparent from inspection of the table that the yield of 1 obtained by the cerium(IV) oxidation is as high as that obtained by any other method. Although the starting materials for the other methods may be less expensive than those for the cerium(IV) oxidation, the extremely simple procedure for the isolation of 1 from the cerium(IV) oxidation of 2 makes this method attractive.

TABLE I

METHODS OF PREPARATION OF CYCLOPROPANECARBALDEHYDE

Substrate[a]	Reagent	Yield of aldehyde, %	Ref
RCH_2OH	$(NH_4)_2Ce(NO_3)_6$	64[b]	*c*
RCH_2OH	CrO_3	30[b]	2
RCH_2OH	H_2O_2, Fe(II)	30–37[d]	3
RCH_2OH	Al(O-*i*-Pr)$_3$	20[d]	4
RCH_2NH_2	O_2, Cu	54–57[b]	5
RCN	$LiAlH_4$	48[b]	6
RCN	LiAlH(OEt)$_3$	69[e]	7
RCN	LiAlH(O-*n*-Bu)$_3$	66,[b] 89[e]	7
RCOCl	LiAlH(O-*t*-Bu)$_3$	42[e]	8
$RCONC_2H_4$	$LiAlH_4$	60,[b] 67[e]	9
$RCON(CH_3)_2$	$LiAlH_2(OEt)_2$	78[e]	10
$RCON(CH_3)_2$	LiAlH(OEt)$_3$	67[e]	10
$RCONC_5H_{10}$	$LiAlH_4$	20[b]	6
$RCONHNHSO_2Ph$	Na_2CO_3	16[e]	*f*

[a] R = cyclopropyl. [b] Isolated yield. [c] This work. [d] Yield by glpc. [e] Yield from 2,4-dinitrophenylhydrazone derivative. [f] J. D. Roberts, *J. Am. Chem. Soc.*, **73**, 2959 (1951).

Experimental Section

To 8.07 g (0.112 mole) of cyclopropanemethanol (2) (Aldrich Chemical Co.) was added a solution of 136.5 g (0.241 mole) of ceric ammonium nitrate (G. F. Smith Chemical Co.) in 250 ml of water. The cloudy, deep red solution was heated on a steam bath until it was colorless (5–15 min). (The cloudiness can be avoided by filtering the ceric ammonium nitrate solution through a sintered-glass funnel prior to its addition to 2.) The solution was cooled, saturated with sodium chloride, and transferred to a separatory funnel. Water (400 ml) was added[11] and the solution was extracted four times with 50-ml portions of methylene chloride.[12] The combined methylene chloride layers were dried over a mixture of magnesium sulfate and sodium bicarbonate. The volume of the methylene chloride solution was reduced to 50–60 ml by distillation through a 30-cm Vigreux column at atmospheric pressure. A quantity of 4 ml of bromobenzene was added to the residue and the residue was distilled through a 20-cm vacuum-jacketed column packed with glass helices into a receiver flask cooled in an ice–acetone bath. A quantity of 6.1 g of material was isolated, bp 97–99° (760 mm) [lit.[9] bp 97–100° (740 mm)], which was 82.6% (by weight) 1 (0.027 mole) and 17.4% methylene chloride as shown by nmr. The yield of 1 was 64%. In a similar experiment, 4.85 g of a mixture composed of 93% (by weight) 1 and 7% methylene chloride was isolated. The yield of 1 was 57%.[13] Glpc determination of the amount of 1 in the methylene chloride layer showed that little product was lost in the distillation.

A 0.5-g-scale reaction was carried out as before except that sodium chloride and the addition of extra water were omitted in the isolation procedure. Glpc analysis of the methylene chloride layer indicated that the yield of 1 was comparable with that obtained in the original procedure.

We have found that aqueous acetic acid[1c] and aqueous acetonitrile are useful solvents for cerium(IV) oxidations of water-insoluble compounds.

Registry No.—1, 1489-69-6; 2, 2516-33-8.

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[11] Water was added to facilitate the separation of the organic and aqueous layers.

[12] The use of ether as extractant led to lower yields.

[13] Attempts to isolate 1 by preparative glpc on a Carbowax 20 M/Chromosorb P column resulted in only 30–40% yields of 1.

Structure of the Product of Condensation of Aromatic 1,2-Diamines with Aromatic 1,2-Dicarboxaldehydes[1]

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Ried and co-workers have reported[2] structures 1b–4b as products of the condensations of *o*-phenylenediamine (5), 2,3-naphthylenediamine (6), and 1,2-naphthylenediamine (7), with *o*-phthalaldehyde (8) and 2,3-naphthalenedicarboxaldehyde (9). (see Chart I).

The postulation of these structures appears in doubt, in view of the chemical[3] and recent spectroscopic[4] confirmation of ·*o*-benzylene-2,1-benzimidazole (10) as the product obtained by the condensation of Thiele and Falk[5] of 5·2HCl with 8. Also, structure 1b has recently been questioned[3c] on the basis of analogy with the assignment[3c] of structure 10 to the compound of Thiele and Falk. However, even if 10 is correct, it should not be concluded that the reactions involving *free* amines 5, 6, and 7 give 1a–4a and not 1b–4b. Whereas condensation of 5·2HCl with 2 moles of benzaldehyde has been shown to give 1-benzyl-2-phenylbenzimidazole (11),[4,6] N,N′-dibenzylidene-*o*-phenylene-

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[1] Grateful acknowledgment is made to the Foundation for the Advancement of Graduate Study in Engineering of Newark College of Engineering for support of this work.

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