The compounds $RSO_4 \cdot Zr(SO_4)_2$ are soluble in a small quantity of water but are hydrolyzed when heated with an excess of water. The cobalt and manganese compounds are colored pink and light yellow, respectively; the remaining three are white in color. The yield of these compounds varies between 60 and 75%. If alkali sulfate was used in place of bivalent metallic sulfate no precipitate was obtained.

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# Small-Ring Compounds. V. Synthesis of Cyclopropanecarboxaldehyde by the MacFadyen–Stevens Reduction

BY JOHN D. ROBERTS

The MacFadyen–Stevens reduction appears to be generally applicable only to the synthesis of aromatic or heterocyclic aldehydes[1] and, in view of the general similarity between the physical and chemical behavior of cyclopropane rings and unsaturated groups,[2] it was of interest to determine whether cyclopropanecarboxaldehyde could be obtained from cyclopropanecarboxylic acid by this method.

Treatment of cyclopropanecarboxylic benzenesulfonhydrazide with sodium carbonate in ethylene glycol at 165° resulted in the formation of cyclopropanecarboxaldehyde which was isolated in 16% yield as the 2,4-dinitrophenylhydrazone. The yield was not as high as those which are customarily obtained in the synthesis of aromatic aldehydes (42–87%)[1a] but was comparable with the yields in some heterocyclic aldehyde preparations (20–23%).[1b]

## Experimental

**Ethyl Cyclopropanecarboxylate.**—The procedure was patterned after that of Thielepape.[3] A mixture of 100 g. (1.16 moles) of cyclopropanecarboxylic acid,[2] 100 g. (2.2 moles) of absolute ethanol, 150 g. of benzene and 1 ml. of concentrated sulfuric acid was placed in the boiler of a Soxhlet extractor and 50 g. (0.80 mole) of calcium carbide was placed in the thimble. The liquid was heated to rapid refluxing with an electric mantle. After thirty-six hours, the volatile material in the boiler was distilled rapidly at 10 mm. into a Dry Ice-cooled receiver. The distillate was fractionated through a 30-cm. Vigreux column and yielded 112 g. (84%) of ethyl cyclopropanecarboxylate, b.p. 133–133.5° (lit., 132.4–132.6°,[4a] 133°[4b]).

**Cyclopropanecarboxylic Hydrazide.**—A mixture of 30 g. (0.26 mole) of ethyl cyclopropanecarboxylate and 30 g. of hydrazine hydrate was refluxed for twelve hours and then placed in a vacuum desiccator over sulfuric acid for several days. The crude solid hydrazide (26 g.) was recrystallized from benzene containing a small amount of ethanol and yielded 22.4 g. (85%) of material having m.p. 96–99°.

*Anal.* Calcd. for $C_4H_8ON_2$: C, 47.98; H, 8.05. Found: C, 48.39; H, 7.79.

**Cyclopropanecarboxylic Benzenesulfonhydrazide.**—Benzenesulfonyl chloride (35 g., 0.20 mole) was added dropwise to a water-cooled, stirred solution of 20 g. (0.20 mole) of cyclopropanecarboxylic hydrazide in 50 ml. of pyridine. After the addition was complete, the mixture was stirred for an hour at room temperature and then poured into ice water. The solid was collected, washed well with water and recrystallized from acetic acid-water. The yield of the benzenesulfonhydrazide was 41.3 g. (86%), m.p. 167–169°.

*Anal.* Calcd. for $C_{10}H_{12}O_3N_2S$: C, 49.98; H, 5.03. Found: C, 50.42; H, 5.08.

**Cyclopropanecarboxaldehyde 2,4-Dinitrophenylhydrazone.**—A mixture of 2.0 g. of cyclopropanecarboxylic benzenesulfonhydrazide and 50 ml. of ethylene glycol was heated to 165° and 2 g. of anhydrous sodium carbonate added all at once. After about a minute, the evolution of gas ceased and the mixture was cooled to room temperature. After dilution with water and acidification with 6 *N* hydrochloric acid, an excess of 2,4-dinitrophenylhydrazine reagent[5] was added and the resulting solid collected. The crude product was recrystallized from ethanol-ethyl acetate and yielded 0.33 g. (16%) of material having m.p. 185–186.5°. A further recrystallization raised the m.p. to 190–190.6° (lit.,[6] 186–187.5°). The recrystallized material did not depress the m.p. of an authentic sample (m.p. 187–190°) prepared by Dr. R. H. Mazur using cyclopropanecarboxaldehyde obtained from the Oppenauer oxidation of cyclopropylcarbinol.

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[1] (a) J. S. MacFadyen and T. S. Stevens, *J. Chem. Soc.*, 584 (1936); (b) C. Niemann, R. N. Lewis and J. T. Hays, THIS JOURNAL, **64**, 1678 (1942); (c) C. Niemann and J. T. Hays, *ibid.*, **65**, 482 (1943).

[2] *Cf.* J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2509 (1951) for references.

[3] E. Thielepape, *Ber.*, **66**, 1454 (1933).

[4] (a) P. Bruylants, *Bull. soc. chim. Belg.*, **38**, 133 (1929); (b) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948).

[5] R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1948, p. 97.

[6] C. L. Wilson, THIS JOURNAL, **69**, 3002 (1947).

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# Methylene Diisocyanate[1]

BY RHODA ROESCH AND MARVIN H. GOLD

Although several $\alpha,\omega$-polymethylene diisocyanates are well known, the simplest member of the series, methylene diisocyanate has never been described. The compound is readily derived from malonyl hydrazide.[2]

**Experimental.**—Malonyl azide was prepared from malonyl hydrazide essentially as described by Curtius.[3] The azide was extracted several times from the aqueous solution with alcohol-free chloroform and then the chloroform solution was dried 15 to 20 hours over anhydrous sodium sulfate. (Calcium chloride as a drying agent was found to have a deleterious effect and produced polymer.) During the drying operation the chloroform solution was stored at low temperatures in order to minimize decomposition of the azide. Then the sodium sulfate was removed by filtration and the dry chloroform solution transferred to a previously dried boiling flask. A dry reflux condenser connected to a calcium chloride drying tube was attached and the reaction mixture was carefully heated on a water-bath at 40–45° for three to five hours. (The temperature must be raised with caution as it is possible for a violent exothermic reaction to set in.) Then the reaction temperature was again raised to 50–55° for another two hours. In order to complete the decomposition another three-hour heating period at the reflux temperature (64°) is generally satisfactory. The chloroform was then removed under vacuum and the residue distilled. The methylene diisocyanate boiled at 37–38° (14 mm.) in 36 to 42% yields, leaving behind a small amount of high boiling polymeric residue.

*Anal.*[4] Calcd. for $C_3H_2N_2O_2$: C, 36.74; H, 2.05; N, 28.57. Found: C, 37.10; H, 1.96; N, 27.95.

A phenylurea derivative was prepared by reaction with aniline in chloroform solution to give a product melting at 238–240°.

*Anal.* Calcd. for $C_{15}H_{16}N_4O_2$: N, 19.71. Found: N, 20.32.

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[1] This work was performed under Contract with the Office of Naval Research.

[2] Curtius, Schöfer and Schwan, *J. prakt. Chem.*, **51**, 180 (1895).

[3] Curtius, *ibid.*, **52**, 210 (1895).

[4] Analysis by Dr. A. Elek, Los Angeles, Calif.