TABLE II

PROPERTIES OF 1,3,5-TRINITROBENZENE ADDUCTS OF INDOLE-3-ACETIC ACID AND OF SEVERAL ESTERS OF INDOLE-3-ACETIC ACID

Trinitrobenzene derivative of	M.p., °C.	Color	Formula	Analyses, % Calcd. C	H	N	Found C	H	N
Indole-3-acetic acid	199 dec.	Orange	$C_{16}H_{12}N_4O_8$	49.5	3.1	14.4	49.7	2.9	14.4
Methyl ester	135	Yellow	$C_{17}H_{14}N_4O_8$	50.8	3.6	13.9	50.8	3.6	13.6
Ethyl ester	88	Yellow	$C_{18}H_{16}N_4O_8$	51.9	3.9	13.5	51.9	3.8	13.4
n-Propyl ester	111	Yellow	$C_{19}H_{18}N_4O_8$	53.0	4.2	13.0	53.2	4.4	13.2
n-Butyl ester	101	Yellow	$C_{26}H_{20}N_4O_8$	54.1	4.5	12.6	54.4	4.4	12.8
n-Amyl ester	96	Yellow	$C_{21}H_{22}N_4O_8$	55.0	4.8	12.2	54.9	5.0	12.1

Preparation of the Addition Products.[5]—One millimole of the indole-3-acetic acid derivative and one millimole of 1,3,5-trinitrobenzene were dissolved in 10 ml. of hot absolute ethanol and placed in the refrigerator to cool. The crystals which formed were recrystallized once from absolute ethanol and dried at room temperature *in vacuo* over phosphorus pentoxide prior to analysis. The properties of these derivatives are shown in Table II.

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[5] J. J. Sudborough, *J. Chem. Soc.*, **109**, 1339 (1916).

DEPARTMENTS OF AGRICULTURAL CHEMISTRY
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A Preparative Method for Thiosemicarbazones of Aromatic Aldehydes[1]

BY BRUNO PUETZER, WILLIAM E. HAMLIN[2] AND LEON KATZ

In the course of experiments designed to prepare chemotherapeutically active thiosemicarbazones a new method was sought which would eliminate the use of thiosemicarbazide. It has been found that an aqueous solution of hydrazinium thiocyanate will react with aromatic aldehydes in the presence of acetic acid to give the respective thiosemicarbazones directly. The products listed in Table I were prepared this way and compared with products made from the aromatic aldehyde and thiosemicarbazide.

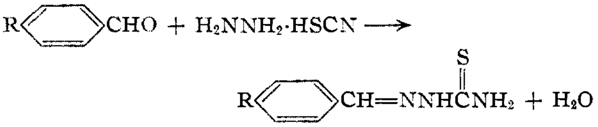

TABLE I

BENZALDEHYDE THIOSEMICARBAZONES

Benzaldehyde	Yield, %	M. p., °C., dec. [a]	[b]
4-CH_3CONH	86	234–236	235–236
4-$(CH_3)_2$N	97	211–214	214–215
4-OH	88	229–231	231–232
2-OH	81	220–223	228–229
4-NO_2	86	247–249	257–259

[a] Material isolated directly from reaction mixture, not recrystallized. [b] Recrystallized material prepared by condensation of thiosemicarbazide and the respective benzaldehyde. All melting points were uncorrected.

Experimental

Preparation of Hydrazinium Thiocyanate Solution.—Into a 4-l. beaker were charged 485 g. (5.0 moles) potassium thiocyanate, 425 g. (95% real, 2.50 moles real) dihydrazine sulfate, and 1 l. of water. The mixture was stirred and heated to 95° in 20 minutes, held at 95° five minutes, and cooled to 10° in three-quarter hour. The white slurry of potassium sulfate was collected on a Büchner funnel containing a thin bed of filter-cel, sucked well and the cake washed with 50 ml. of water. The volume of the filtrate was 1335 ml., equivalent to 0.00375 mole of hydrazinium thiocyanate per ml. This solution was used without further analysis.

4-Dimethylaminobenzaldehyde Thiosemicarbazone.—Into a 500-ml. three-necked flask equipped with a glas-col mantle, sealed stirrer, reflux condenser and thermometer were charged 28.5 g. (0.191 mole) of dimethylaminobenzaldehyde and 150 ml. of glacial acetic acid. This mixture was stirred and heated to 100°. Ninety-five ml. of the hydrazinium thiocyanate solution described above (0.356 mole) was heated to 100° and added to the acetic acid solution. After five minutes a red precipitate began to appear. The slurry was held at 95–100° for one hour longer, cooled to 10°, and filtered through a Büchner funnel. The cake was washed with 500 ml. of water and dried *in vacuo* at 65° for 15 hours. The weight of solid, m.p. 211–214° dec., was 40.7 g. An additional 0.5 g. of material was obtained from the filtrate.

As a solvent for the aromatic aldehydes ethanolic acetic acid of varying composition can be employed. A series of experiments were run with 4-acetylaminobenzaldehyde to determine the optimum usage of hydrazinium thiocyanate. An excess of 25–50% appeared to give the optimum yields.

Fractional crystallization from glacial acetic acid of the thiosemicarbazone formed from 4-nitrobenzaldehyde led to the isolation of a small quantity of azine; m.p. 307–309°. *Anal.* Calcd. for $C_{14}H_{10}O_4N_4$: C, 56.38; H, 3.36; N, 18.78. Found: C, 56.50; H, 3.30; N, 18.97.

SCHENLEY LABORATORIES, INC.
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[1] After the completion of this work a report by Stig Sunner (*C. A.*, **45**, 548b (1951)) appeared which described the reaction of hydrazinium thiocyanate with acetone to yield acetone thiosemicarbazone. At least two products were formed in this reaction whereas we obtained only the respective thiosemicarbazone under the conditions described in the experimental section with the exception of 4-nitrobenzaldehyde. In this case less than 5% of azine was isolated.

[2] The Upjohn Co., Kalamazoo, Mich.

The Double Sulfates of Zirconium and the Bivalent Metals

BY S. R. PATEL

A series of compounds of the type $RSO_4 \cdot Zr(SO_4)_2$ (where R = a bivalent metal) has been prepared (Table I). The compound $MgSO_4 \cdot Zr(SO_4)_2$ a typical example, was obtained by heating together 0.1 g. of zirconium nitrate (=0.04 g. zirconia) and 0.025 g. to 0.4 g. of $MgSO_4 \cdot 7H_2O$ in 40 cc. of sulfuric acid (sp. gr. 1.79). A clear solution was first obtained from which on further concentration a precipitate separated which after washing free from adhering sulfuric acid with absolute alcohol and then drying at 230° agreed with the formula $MgSO_4 \cdot Zr(SO_4)_2$.

TABLE I

R	Calcd., % R	Zr	SO_4	Found, % R	Zr	SO_4
Mg	6.024	22.59	71.39	5.58	22.73	71.60
Zn	14.70	20.50	64.79	15.11	20.18	65.05
Cd	22.85	18.55	58.60	22.63	18.51	58.54
Co	13.45	20.81	65.75	13.82	20.71	66.05
Mn	12.65	21.00	66.36	12.48	21.19	66.52

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.

THE ROYAL INSTITUTE OF SCIENCE
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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).

DEPARTMENT OF CHEMISTRY
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CAMBRIDGE 39, MASSACHUSETTS
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Methylene Diisocyanate[1]

BY RHODA ROESCH AND MARVIN H. GOLD

Although several α,ω-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.

AEROJET ENGINEERING CORPORATION
AZUSA, CALIF.
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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.