did not reduce Tollens reagent, nor did it yield a derivative with 2,4-dinitrophenylhydrazine.

**Cyclopropylglyoxal.**—Acetic acid (17 cc.), water (15 cc.), dioxane (375 cc.) and selenium dioxide (66 g.) were mixed and heated on a steam-bath until solution was complete. Methyl cyclopropyl ketone (50 g.) was then added; the solution was heated for five hours and then allowed to stand overnight. The solution was decanted from the gray deposit of selenium, dioxane was removed under reduced pressure, and the residue was distilled through a column (15 × 1.5 cm.) packed with glass helices. The product (24.7 g.), a light yellow-green liquid with a sharp odor, boiled at 40–41° (10 mm.), and had $n^{20}\text{D}$ 1.481. A center cut was taken for analysis.

*Anal.* Calcd. for $C_5H_6O$: C, 61.21; H, 6.16. Calcd. for $C_5H_6O\cdot H_2O$: C, 51.7; H, 6.9. Found: C, 57.45; H, 6.52.

A sample, prepared as above but with omission of acetic acid, was analyzed. Found: C, 55.67; H, 6.47. The substance was therefore a mixture of cyclopropylglyoxal and its hydrate. On standing overnight, the product polymerized, but the monomer could be recovered by distillation of the polymer with a trace of phosphorus pentoxide. The glyoxal reduced Tollens solution, and formed a 2,4-dinitrophenylhydrazone which crystallized from ethanol in orange-red needles melting at 173–173.5°.

*Anal.* Calcd. for $C_{11}H_{10}O_5N_4$: C, 47.48; H, 3.62. Found: C, 47.47; H, 3.76.

**Cyclopropylglycolic Acid.**—Crude cyclopropylglyoxal (9.3 g.) was dissolved in water (50 cc.), the solution was cooled (0°), and aqueous sodium hydroxide (4 g. in 50 cc.) was added with stirring. The mixture was kept at 0° for three hours, then allowed to stand at room temperature for 18 hours. The light yellow solution was concentrated to 20 cc. under reduced pressure and thoroughly extracted with ether. The aqueous layer was acidified with dilute sulfuric acid and continuously extracted with ether for 48 hours. The extract was dried (magnesium sulfate), the solvent was removed, and the residue was crystallized from chloroform–petroleum ether. The white needles melted at 77.5–78.5° and weighed 3.1 g.

*Anal.* Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94; neut. equiv., 116.1. Found: C, 51.75; H, 7.16; neut. equiv., 117.3, 117.7.

The *p*-bromophenacyl ester crystallized from aqueous ethanol, formed white needles which melted at 93–93.5°.

*Anal.* Calcd. for $C_{13}H_{13}O_4Br$: C, 49.86; H, 4.18. Found: C, 49.90; H, 4.21.

The acid (1 g.) and potassium permanganate (2.5 g.) were dissolved in water (50 cc.) and the solution was allowed to stand at room temperature for three days. Excess permanganate and manganese dioxide were reduced with sodium bisulfite and the clear solution was concentrated under reduced pressure to a small volume. The solution was acidified and extracted with ether; solvent was removed from the extract and the residual liquid acid was converted into the *p*-bromophenacyl ester melting at 71–72° alone or when mixed with the *p*-bromophenacyl ester of cyclopropanecarboxylic acid.

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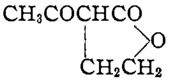
## Cyclopropanes. IX.[1] Methyl Cyclopropyl Ketone

BY LEE IRVIN SMITH AND EDGAR R. ROGIER

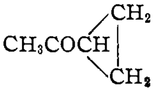
Preparation of methyl cyclopropyl ketone (III) in fairly large amounts *via* the published procedures is difficult and time-consuming. Preliminary to the researches reported in this series of papers, an investigation of the methods for preparation of the ketone was carried out. The best route to the ketone involves conversion of α-acetobutyrolactone (I) to 5-chloro-2-pentanone (II) (61–67%) by action of constant boiling hydrochloric acid[2] and conversion of II to the ketone (III) (74–78%) by action of dry, powdered potassium hydroxide.[3]



I

$CH_3CO(CH_2)_3Cl$

II



III

### Experimental Part

**5-Chloro-2-pentanone (II).**—A solution of hydrochloric acid (38%, 450 cc.) in water (500 cc.) was added to α-acetobutyrolactone (512 g., 4 moles).[4] The mixture was shaken for a short time until homogeneous, and then allowed to stand at room temperature until evolution of carbon dioxide almost ceased (two to three hours). The flask was then equipped with a separator and an efficient reflux condenser and the mixture was brought to the boiling point (open flame). The constant boiling hydrochloric acid in the distillate (lower layer) was continuously returned to the flask; the product (upper layer) was removed. Distillation was continued until the distillate did not contain appreciable amounts of II (four to five hours). The product was dried (magnesium sulfate) and distilled under reduced pressure. The distillate, a colorless liquid (293–320 g., 61–67%), boiled at 50–51° (8 mm.). Only a few drops of fore-run and a very small amount of residue were obtained.

**Methyl Cyclopropyl Ketone (III).**—Powdered potassium hydroxide (400 g., 90%, technical, flakes ground in a mortar) was placed in a 5-l. 3-necked round-bottomed flask equipped with a Hershberg stirrer, dropping funnel and reflux condenser. A thermometer was suspended through the condenser and fixed so that the bulb was just above the stirrer. Stirring was begun, and 5-chloro-2-pentanone (II) (595 g., 4.93 moles) was added as follows: 200 cc. of the chloroketone at such a rate that the temperature was maintained at 65–75°, then 50 cc. of water all at once, followed by another 200 cc. of the chloroketone at 65–75°, then 50 cc. of water, and finally the remainder of the chloroketone at 65–75°. Stirring was continued while the temperature was maintained at about 65° for two hours and then allowed to fall to 30°. The mixture was cooled (ice-bath), water (400–500 cc.) was added, and then dilute sulfuric acid until the mixture was neutral. The ketone layer was extracted with two 400-cc. portions of ether, the combined ether extracts were dried (magnesium sulfate), the solvent was removed, and the residual liquid was added to the bulk of the ketone. The product was distilled through a column (45 × 1.8 cm.) packed with small bent pieces of wire screening. The distillate (306–326 g., 74–78%) boiled at 110–111°.

All of the procedures reported in the literature for this re-

TABLE I

REACTION CONDITIONS AND REAGENTS FOR PREPARATION OF III

| Reactant | Reagent and conditions | Yield, % |
|---|---|---|
| II | KOH, dry, powdered | 74–78 |
| II | $LiNH_2$ in boiling ether | Trace |
| II | $LiNH_2$ in boiling benzene | None |
| II | KOH, 50% aqueous, warm | 44 |
| II | Collidine at 140° | None |
| 5-Bromo-2-pentanone | KOH, water[a] | 46 |
| 5-Bromo-2-pentanone | KOH in dry methanol | None |
| 5-Bromo-2-pentanone | $NaOCH_3$ in dry methanol | None |

[a] M. Idzkowska and E. Wagner, *J. Russ. Phys. Chem. Soc.*, **30**, 259 (1897); *Chem. Centr.*, 69, II, 474 (1898).

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(1) Paper VIII, L. I. Smith and E. R. Rogier, THIS JOURNAL, **73**, 4047 (1951).

(2) Modification of the procedure of S. E. Forman, British Patent 601,803; *C. A.*, **42**, 7787 (1948).

(3) Modification of the procedures of N. D. Zelinski and E. F. Dengin, *Ber.*, **55**, 3354 (1922).

(4) We wish to thank Dr. Max Tishler and Dr. Earl Pierson, of Merck and Company, Inc., for their generous gifts of this compound.

action as well as several others, were tried. The results are summarized in Table I.

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# NEW COMPOUNDS

## Certain *n*-Dodecyl Sulfides

**2-*n*-Dodecylmercapto-2-methyl-4-pentanone.**—Following the procedure of Thompson,[1] anhydrous hydrogen chloride was passed through a solution of 17.2 g. (0.085 mole) of *n*-dodecyl mercaptan and 8.6 g. (0.088 mole) of mesityl oxide, initially at room temperature, for one and a half minutes. The exothermic reaction which resulted raised the temperature to 75°. The reaction mixture was heated at about 60° for three hours and, after standing two days, was distilled under reduced pressure. A fraction of 13.3 g. (52%) of pale yellow liquid was obtained, b.p. 176–178° (4 mm.), $n^{20}\text{D}$ 1.4694.

*Anal.* Calcd. for $C_{18}H_{36}OS$: C, 71.93; H, 12.08; S, 10.67. Found: C, 71.4; H, 12.1; S, 10.39.

**Methyl 3-*n*-Dodecylmercaptopropionate.**—This compound was prepared by the method of Hurd and Gershbein.[2] 86.1 g. (1.0 mole) of methyl acrylate was slowly added by means of a dropping funnel to a cold stirred mixture of 123 g. (0.608 mole) of *n*-dodecyl mercaptan and 0.5 g. of sodium methoxide. The exothermic reaction ensuing was kept at room temperature by means of an ice-bath. After the addition of the methyl acrylate, the mixture was stirred at room temperature for 16 hours. The filtered reaction mixture was then distilled under reduced pressure. There was obtained 149 g. (85%) of a colorless liquid, b.p. 162–163.5° (0.5 mm.), $n^{20}\text{D}$ 1.4660.

*Anal.* Calcd. for $C_{16}H_{32}O_2S$: C, 66.61; H, 11.18; S, 11.12. Found: C, 66.7; H, 11.3; S, 10.99.

***n*-Dodecyl *p*-Nitrobenzyl Sulfide.**—Ninety-four and seven-tenths grams (0.468 mole) of *n*-dodecyl mercaptan was added to a solution of 26.6 g. (approx. 0.468 mole of $NaOCH_3$) of sodium methoxide reagent in 400 ml. of methanol. To this was then added a solution of 101 g. (0.468 mole) 4-nitrobenzyl bromide in 600 ml. of warm methanol. The reaction mixture was refluxed four hours. Excess solvent was removed by distillation and the residue was poured into 800 ml. of cold water. The orange solid forming was filtered off and recrystallized twice from a mixture of methanol and benzene. A total of 96.7 g. (61%) of light yellow crystals was obtained, m.p. 31–33°.

*Anal.* Calcd. for $C_{19}H_{31}O_2SN$: S, 9.50. Found: S, 9.09.

***n*-Dodecyl *p*-Aminobenzyl Sulfide.**—An ethanol solution of 72.7 g. (0.216 mole) of *n*-dodecyl *p*-nitrobenzyl sulfide was refluxed with an excess of tin and hydrochloric acid for 16 hours. The solvent was removed by distillation. The orange residue solidified on cooling. It was taken into solution with methanol. The solution was made basic with sodium methoxide and was then poured into a liter of cold water. The yellow solid which separated was recrystallized from methanol. A pale yellow solid, m.p. 40°, was obtained.

*Anal.* Calcd. for $C_{19}H_{33}SN$: C, 74.21; H, 10.82; S, 10.43. Found: C, 74.7; H, 10.87; S, 10.05.

**Bis-(2-*n*-dodecylmercaptoethyl) Ether.**—To 57 g. (1 mole of $NaOCH_3$) of sodium methoxide reagent in 300 ml. of methanol was added 202 g. (1 mole) of *n*-dodecyl mercaptan. To the resultant mercaptide solution was added slowly 71.5 g. (0.5 mole) of $\beta,\beta'$-dichlorodiethyl ether in such a manner as to produce gentle refluxing of the methanol solvent from the heat of the reaction. After the addition, the reaction mixture was refluxed 20 minutes and then was poured into 500 ml. of cold water. The white solid that formed was filtered off and recrystallized from a mixture of methanol and isopropyl alcohol. A total of 130 g. (55%) of a white waxy solid was obtained, m.p. 31–32°.

*Anal.* Calcd. for $C_{28}H_{58}OS_2$: C, 70.82; H, 12.31; S, 13.50. Found: C, 70.6; H, 12.4; S, 13.2.

***n*-Dodecyl $\beta$-Hydroxyethyl Sulfide.**—To 28.2 g. (0.495 mole of $NaOCH_3$) of sodium methoxide reagent in 300 ml. of methanol was added 100 g. (0.495 mole) of *n*-dodecyl mercaptan. The resultant mercaptide solution was cooled to 5° with an ice–salt-bath. About 28 g. (0.65 mole) of ethylene oxide, previously cooled to 0°, was then added to the mechanically stirred solution over a period of 45 minutes, the reaction temperature being kept below 10°. Another 3 g. of ethylene oxide was added but there no longer was any exothermic reaction. The mixture was stirred an additional 15 minutes and was then poured into a concentrated hydrochloric acid–ice mixture. The upper organic layer was separated, combined with the ether extract of the aqueous layer, and dried over anhydrous sodium sulfate. The solvent was removed and the product was distilled under reduced pressure. There was obtained 55.8 g. (46%) of a colorless liquid, b.p. 168–175° (3 mm.). Redistillation gave a middle fraction, b.p. 145° (1.2 mm.), which solidified on standing; m.p. 28.5°.

*Anal.* Calcd. for $C_{14}H_{30}OS$: C, 68.22; H, 12.27; S, 13.01. Found: C, 68.1; H, 12.2; S, 12.8.

**Bis-(*n*-dodecylmercapto)-methane.**—Anhydrous hydrogen chloride was passed at a moderate rate into a mixture of 7.5 g. (0.25 mole $CH_2O$) of trioxane and 101 g. (0.5 mole) of *n*-dodecyl mercaptan at room temperature for a period of 90 minutes. The contents of the flask solidified as a white mass. This was allowed to stand overnight after which time it was washed thoroughly with water and dried. The yield of the mercaptal was nearly quantitative. It was readily recrystallized from isopropyl alcohol, giving white plate-like crystals, m.p. 42.5°.

*Anal.* Calcd. for $C_{25}H_{52}S_2$: C, 72.04; H, 12.58; S, 15.39. Found: C, 71.8; H, 12.6; S, 15.2.

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[1] R. B. Thompson, U. S. Patent 2,492,334 (1949).

[2] C. D. Hurd and L. L. Gershbein, This Journal, **69**, 2332 (1947).

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## Derivatives of Cyclohexanecarboxylic Acid

Two derivatives of cyclohexanecarboxylic acid have been prepared.

**S-Benzylthiuronium cyclohexanecarboxylate** was prepared in the usual fashion, from acid obtained from the Eastman Kodak Company. The melting points were determined with Anschütz thermometers in a Hershberg melting-point apparatus. A sample recrystallized from ethanol for analysis melted at 155–156°.

*Anal.* Calcd. for $C_{15}H_{22}N_2O_2S$ (mol. wt. 294.41): C, 61.19; H, 7.53; N, 9.52. Found: C, 61.19; H, 7.21; N, 9.67.

***p*-Bromophenacyl cyclohexanecarboxylate** was prepared in the usual fashion. A sample recrystallized from ethanol for analysis melted at 90–91°.

*Anal.* Calcd. for $C_{15}H_{17}BrO_3$ (mol. wt. 325.21): C, 55.42; H, 5.27. Found: C, 55.55; H, 5.37.

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