Anal. Calcd. for C_6H_7NS: N, 11.2; S, 25.6. Found: N, 11.4; S, 26.0.

This compound must be analyzed immediately since it is hydrolyzed rapidly by the moisture in the air. One sample which was allowed to stand for two days had only 9.73% nitrogen. This same sample was allowed to stand for several weeks and at that time had only 5.07% nitrogen.

An attempt to prepare a picrate of this compound gave only the picrate of methylamine, m. p. and mixed m. p. 209–211° uncor.

Anal. Calcd. for $C_7H_8N_4O_7$: C, 32.31; H, 2.96. Found: C, 32.01; H, 3.07.

Reaction of 2-Thenylamine Hydrochloride and Hexamethylenetetramine.—One mole (140 g.) of hexamethylenetetramine in 500 ml. of water was heated to boiling in a flask equipped for distillation. To this boiling mixture, one mole, 113 g., of 2-thenylamine[3] in 100 g. of 36% hydrochloric acid and 200 ml. of water was added dropwise over a period of approximately ninety minutes. 2-Thiophenealdehyde, 15 g., was obtained from the distillate after this period of time. The reaction was stopped at this point, not because the aldehyde formation had stopped, but in order that the insoluble yellow oily layer could be investigated. The *p*H of the reaction mixture was approximately 6 at this point as determined by Hydrion paper. After cooling to 20°, 150 ml. of concd. hydrochloric acid was added. The *p*H changed from 6 to approximately 4 during this addition but the yellow oil did not dissolve. Extraction with ether yielded 90 g. of a bright yellow oil which when distilled gave 10 g. of 2-thiophenealdehyde. The remaining material, b. p. 116–124.5 (0.8 mm.), was identified as I, N,N'-di-(2-thenyl)-1,3-diazacyclobutane.[2]

Acknowledgment.—The authors are grateful to Dr. D. E. Badertscher for his advice and interest in this problem and to Dr. Seymour L. Meisel for the preparation of N-methyl-2-thenaldimine and determination of its properties in connection with another phase of this problem.

Summary

A convenient synthesis of several 2-thiophenealdehydes is described in which the aminomethylation intermediates, the N-(2-thenyl)-formaldimines, undergo a prototropic shift and are hydrolyzed to the corresponding aldehydes. The reaction is complicated by side reactions and N-methyl- and N,N-dimethyl-2-thenylamines are also isolated.

PAULSBORO, N. J. RECEIVED SEPTEMBER 10, 1948

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Small-Ring Compounds. III. Synthesis of Cyclobutanone, Cyclobutanol, Cyclobutene and Cyclobutane[1]

BY JOHN D. ROBERTS AND CHARLES W. SAUER[2,3]

The formation of methylenecyclobutane from the reaction of pentaerythrityl bromide with zinc represents one of the simplest methods for the synthesis of a cyclobutane derivative in good yield from readily available starting materials. This reaction, which was discovered by Gustavson[4] and studied by a large number of other investigators,[5] gives methylenecyclobutane along with lesser amounts of 2-methyl-1-butene and spiropentane. Derfer, Greenlee and Boord[6] have extended the scope of the reaction considerably by showing that 1,1,1-tri-(bromomethyl)-alkanes react with zinc to give alkenyl- and alkylidenecyclobutanes.

Methylenecyclobutane has been converted to cyclobutanone in 30–36% yield by ozonization[7] and in small yield by oxidation with potassium permanganate in aqueous acetone[8] or *via* reduction of the corresponding nitrosite.[9] Other methods for the preparation of cyclobutanone, with the exception of the reaction of ketene with diazomethane,[10] involve at least five steps from available starting materials and give over-all yields of less than 10%.[11]

In the present work, methods for the preparation of cyclobutanone from methylenecyclobutane were investigated. Ozonization was not attempted because of the relative difficulty of adapting this procedure to large-scale laboratory operation. Satisfactory yields of cyclobutanone were obtained from methylenecyclobutane by oxidation to 1-(hydroxymethyl)-1-cyclobutanol and cleavage of the glycol with lead tetraacetate. Gustavson[4] has previously obtained 1-(hydroxymethyl)-1-cyclobutanol in 40% yield by oxidation of methylenecyclobutane with dilute aqueous potassium permanganate. In the present investigation, 80–83% yields were achieved by performic acid oxida-

---

(1) Earlier papers in this series, THIS JOURNAL, **67**, 1281 (1945); **68**, 843 (1946).

(2) An abstract of a thesis submitted in partial fulfillment of the requirements for the Degree of Doctor of Philosophy.

(3) Present address: Arthur D. Little, Inc., Cambridge, Mass.

(4) Gustavson, *J. prakt. Chem.*, [2] **54**, 97, 104 (1896); Gustavson and Bulatoff, *ibid.*, [2] **56**, 93 (1897).

(5) See Marrian, *Chem. Rev.*, **43**, 149 (1948), for a number of leading references.

(6) Derfer, Greenlee and Boord, THIS JOURNAL, **67**, 1863 (1945); **71**, 175 (1949).

(7) Bauer and Beach, *ibid.*, **64**, 1142 (1942), cite unpublished work by Whitmore and Williams; *cf.* Williams, Ph.D. Thesis, Pennsylvania State College, 1941, and Krimmel, Ph.D. Thesis, Pennsylvania State College, 1945.

(8) Filipow, *J. Russ. Phys.-Chem. Soc.*, **46**, 1141 (1914); *J. prakt. Chem.*, [2] **93**, 162 (1916).

(9) Demjanow, *Ber.*, **41**, 915 (1908); Demjanow and Dojarenko, *J. Russ. Phys.-Chem. Soc.*, **49**, 193 (1917); *Ber.*, **55**, 2727 (1922).

(10) (a) Lipp and Köster, *Ber.*, **64**, 2823 (1931); (b) Lipp, Buchkremer and Seeles, *Ann.*, **499**, 1 (1932); (c) Benson and Kistiakowsky, THIS JOURNAL, **64**, 80 (1942).

(11) (a) Kishner, *J. Russ. Phys.-Chem. Soc.*, **37**, 106 (1905); (b) **39**, 922 (1907); (c) Demjanow and Dojarenko, *Ber.*, **40**, 4393 (1907); (d) **41**, 43 (1908); (e) **55**, 2737 (1922); (f) Demjanow, *J. Russ. Phys.-Chem. Soc.*, **61**, 1861 (1929); (g) Demjanow and Shuikina, *J. Gen. Chem.* (*USSR*), **5**, 1213 (1935); (h) Demjanow and Telnow, *Bull. acad. sci. URSS, Classe sci. math. nat. sci. chim.*, 529 (1937); (i) Curtius and Grandel, *J. prakt. Chem.*, [2] **94**, 359 (1916); (j) Wagner, Ph.D. Thesis, Pennsylvania State College, 1941.

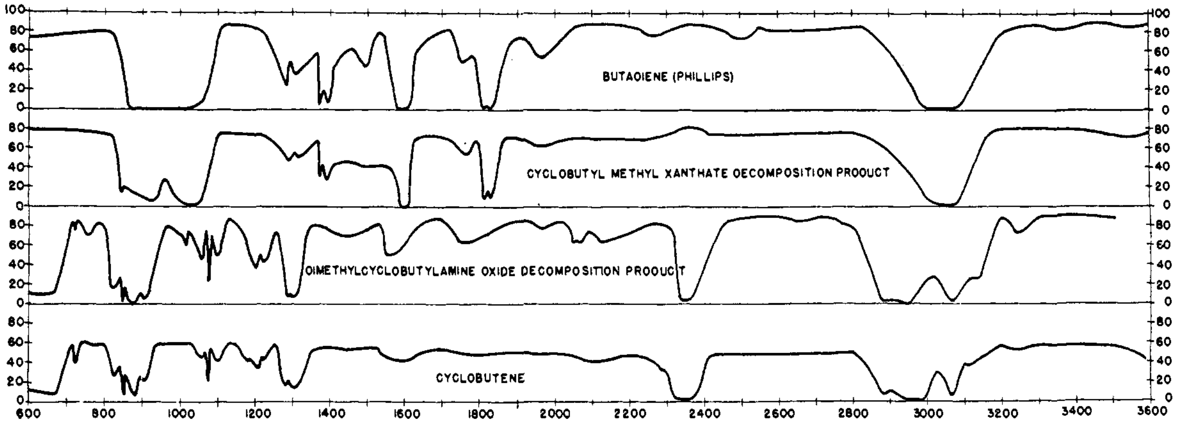
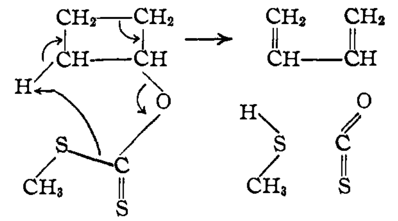


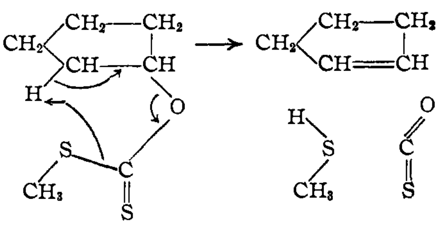
Fig. 1.—Infrared spectra.

tion using a modification of the procedure employed by Roebuck and Adkins[12] for the preparation of *trans*-cyclohexandiol-1,2. A 39% yield was obtained in a single experiment using hydrogen peroxide in *t*-butyl alcohol.[13] Oxidation of the glycol with lead tetraacetate in methylene chloride solution gave yields of cyclobutanone up to 90%. Periodate oxidation of the glycol was not successful. The over-all yield of cyclobutanone from pentaerythritol was 40%.

Cyclobutane was obtained from cyclobutanone in 82% yield by the Huang-Minlon[14] modification of the Wolff–Kishner reduction.[15] Reduction of cyclobutanone to cyclobutanol was achieved in 90–100% yields using lithium aluminum hydride.[16]

The direct dehydration of cyclobutanol to cyclobutene does not appear to be feasible. Dojarenko[17] has reported that cyclobutanol is converted largely to propylene and butadiene over alumina at 360–390°. In the present work the indirect Tschugaeff method was investigated since this procedure has been shown to give olefins from alcohols in many cases with little skeletal rearrangement.[18] Cyclobutanol was converted to O-cyclobutyl S-methyl xanthate by successive treatments in diethyl ether with sodium hydride,[19] carbon disulfide and methyl iodide. The xanthate ester was pyrolyzed by dropwise addition to boiling diphenyl. The sodium hydroxide-insoluble gaseous product was shown to be quite pure 1,3-butadiene by comparison of its infrared spectrum (Fig. 1) with the infrared spectra of authentic samples of cyclobutene (prepared by the method of Willstätter and von Schmaedel[20]) and 1,3-butadiene. Application of the Tschugaeff method to cyclopentanol, investigated as a model case, resulted in a 70% yield of the normal dehydration product, cyclopentene, which was isolated as the dibromide. The abnormal behavior of the cyclobutyl xanthate ester as compared with the corresponding cyclopentyl ester on pyrolysis may be due to a different mode of reaction available only to the former ester. In this formulation the 2,3-bond of the cyclobutane ring is considered to be cleaved as an integral part of the pyrolysis reaction.





For the preparation of cyclobutene, cyclobutanone was converted to cyclobutyldimethylamine by reductive amination with excess methylamine followed by methylation of the resulting cyclobutylmethylamine with formaldehyde and formic acid. The procedure for the reductive amination was similar to that used by Hancock and Cope[21] for the preparation of isopropylaminoethanol while the methylation procedure was that of

---

[12] "Organic Syntheses," Vol. 28, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 35.

[13] Milas and Sussman, THIS JOURNAL, 58, 1302 (1936).

[14] Huang-Minlon, *ibid.*, 68, 2487 (1946).

[15] For discussion of earlier methods for the preparation of cyclobutane see Cason and Way, *J. Org. Chem.*, 14, 31 (1949).

[16] Nystrom and Brown, THIS JOURNAL, 69, 1197 (1947).

[17] Dojarenko, *J. Russ. Phys.-Chem. Soc.*, 58, 1, 16, 27 (1926).

[18] Hückel, Tappe and Leguthe, *Ann.*, 543, 191 (1939); Stevens and Richmond, THIS JOURNAL, 63, 3132 (1941).

[19] Sodium hydride appears to be considerably superior to other reagents for forming the alkoxide in this preparation.

[20] Willstätter and von Schmaedel, *Ber.*, 38, 1992 (1905).

[21] "Organic Syntheses," Vol. 26, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 38.

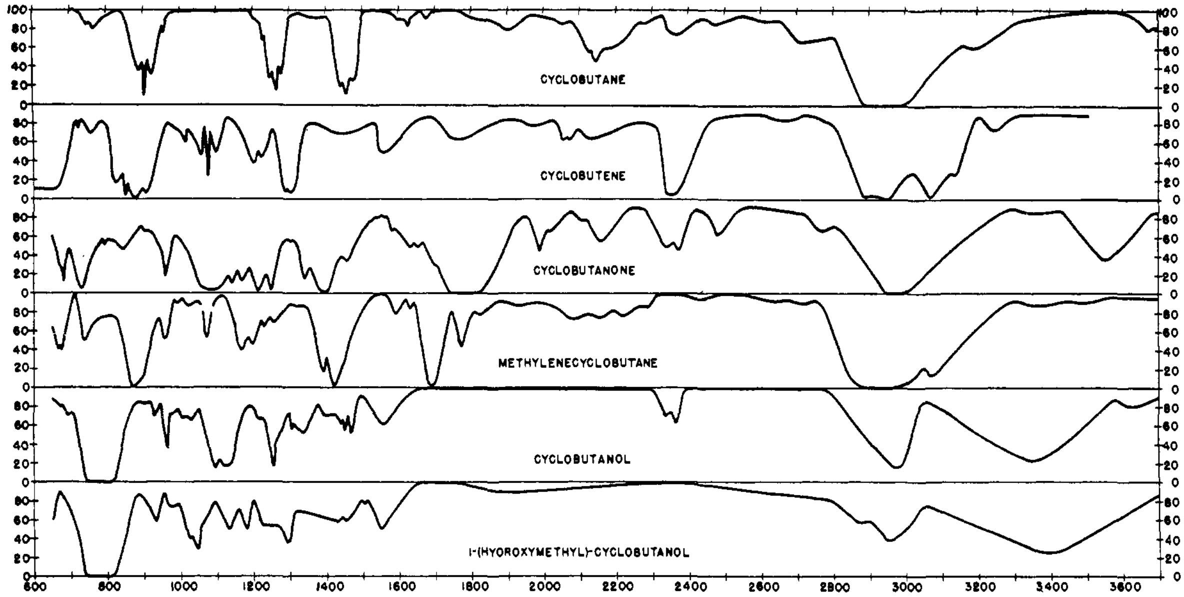


Fig. 2.—Infrared spectra.

Clarke, Gillespie and Weishaus.[22] Part of the cyclobutyldimethylamine was converted to cyclobutene through the quaternary iodide by the method of Willstätter.[20] Contrary to earlier reports[20,23] the cyclobutene obtained in this ways contained no appreciable amount of 1,3-butadiene (*cf.* infrared curves of Fig. 1). Cyclobutene, free of 1,3-butadiene, was also obtained from the pyrolysis of cyclobutyldimethylamine oxide by the method of Cope, Towle and Foster.[24] The amine oxide was prepared by oxidation of dimethylcyclobutylamine with 10% hydrogen peroxide. Cyclobutene was obtained by this method in 50–60% yields with recoveries of 28–30% of the starting material as cyclobutyldimethylamine. The yield of cyclobutene from the quaternary iodide is somewhat better (70%) and about 30% of cyclobutyldimethylamine is recovered.

Acknowledgment.—We are indebted to Dr. R. C. Lord, Jr., Mr. R. S. McDonald and Mr. E. Slowinski for the infrared determinations.

Experimental

Methylenecyclobutane.—The reaction of pentaerythrityl bromide with zinc is more easily controlled using the following procedure than the one described by Shand, Schomaker and Fischer.[25]

A solution of 10 g. of zinc bromide and 30 ml. of ethanol in 700 ml. of water was placed in a 3-l. three-necked creased flask equipped with a stainless-steel stirrer driven by a 1/4-h. p. 10,000 r. p. m. motor. One neck of the flask was equipped with a thermometer which extended into the solution and a 30-cm. air-cooled reflux condenser with a Claisen head at the top connected to a water-cooled spiral condenser. The receiver at the bottom of the spiral condenser was fitted with a Dry Ice-cooled condenser. Stirring was begun and 476 g. (7.3 gram atom) of zinc dust added. Purified pentaerythrityl bromide[26] (678 g., 1.75 moles) was placed in a 1-l. Erlenmeyer flask attached to the third neck of the creased flask by a rubber tube.[27] The contents of the reaction flask were heated to 90° and a portion of the bromide was added. The reaction began immediately and the remainder of the bromide was added portionwise as rapidly as permitted by the foaming of the mixture. The temperature was maintained at 90 ± 1° during the addition of the bromide and afterwards at 95° for one-half hour. The hydrocarbon which steam-distilled was washed with ice water and dried over calcium chloride. The yield of crude product was 102 g. (86%). Fractionation of the material from several runs through a 2 × 60 cm. glass-helix packed column gave a 70% yield (based on pentaerythrityl bromide) of methylenecyclobutane, b. p. 41.5–42°. No spiropentane could be isolated from the reaction products. The infrared spectrum of the methylenecyclobutane is given in Fig. 2.

Pentaerythrityl benzenesulfonate failed to react with zinc dust in boiling 50% absolute ethanol in the presence of sodium iodide or sodium bromide.

1-(Hydroxymethyl)-1-cyclobutanol.—**A.** To an ice-cooled solution of 12 g. (0.176 mole) of crude methylenecyclobutane, 88 ml. (0.194 mole) of 7.5% hydrogen peroxide in *t*-butyl alcohol was added 1 ml. of a 0.5% solution of osmium tetroxide in *t*-butyl alcohol. The mixture was kept in a refrigerator for two days. At the end of this period, the solution gave a negative test for peroxide. The *t*-butyl alcohol was removed by distillation and the residue distilled under reduced pressure. The yield of the glycol, b. p. 78–85° (2 mm.), was 7.0 g. (39%).

Anal. Calcd. for $C_5H_8O_2$: C, 58.80; H, 9.86. Found: C, 59.10; H, 9.79.

B. To a stirred mixture of 600 ml. (13.4 moles) of 87% formic acid and 120 ml. (1.1 moles) of 35% hydrogen peroxide was added slowly 68 g. (1.0 mole) of purified methylenecyclobutane. The temperature of the reaction mixture was maintained at 20–30° with an ice-bath. The mixture was then allowed to stand at room temperature

---

[22] Clarke, Gillespie and Weisshaus, THIS JOURNAL, **55**, 4571 (1933).

[23] Heisig, *ibid.*, **63**, 1698 (1941).

[24] Cope, Towle and Foster, *ibid.*, **71**, 3929 (1949).

[25] Shand, Schomaker and Fischer, *ibid.*, **66**, 636 (1944).

[26] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 476.

[27] Fieser, "Experiments in Organic Chemistry," second edition, D. C. Heath and Co., New York, N. Y., 1941, p. 311.

overnight. The formic acid and water were removed by distillation on a steam-bath at water-pump pressure. The residue was treated with an ice-cold solution of 80 g. (2.0 moles) of sodium hydroxide in 150 ml. of water. The alkaline solution was warmed to 45°, allowed to cool and then extracted with methylene chloride in a continuous extractor for twenty-four hours. The methylene chloride was removed and the residue distilled. The yield of the glycol, b. p. 93° (5 mm.), was 83.2 g. (83%); n^{25}_{D} 1.4715. The infrared spectrum of the liquid product is shown in Fig. 2.

Cyclobutanone.—In a 1-liter creased flask equipped with a stainless-steel stirrer was placed 85.0 g. (0.833 mole) of 1-(hydroxymethyl)-1-cyclobutanol and 500 ml. of methylene chloride. One neck of the flask was closed with a stopper while the other was fitted with a vertical vapor extractor topped by a reflux condenser. The extractor tube held a large Soxhlet thimble containing 420 g. (0.948 mole) of crude lead tetraacetate. The stirrer was started and the mixture heated to reflux. The lead tetraacetate was extracted by the methylene chloride and carried into the solution of the glycol. When the extraction was complete, the mixture was refluxed and stirred for an hour and then allowed to stand overnight. Water (250 ml.) was added and the mixture steam-distilled until about 1 liter of steam-distillate was collected. The distillate was cooled in ice and neutralized with 40% sodium hydroxide solution and then continuously extracted with methylene chloride. Distillation through a 1.6 × 25 cm. glass-helix packed column 52.8 g. (90.5%) of cyclobutanone, b. p. 98–100°, n^{25}_{D} 1.4189. The infrared spectrum of the pure material (liquid) is given in Fig. 2. The product was identified by its 2,4-dinitrophenylhydrazone, m. p. 146–146.5° (lit., 132–133°,[10a] 146.3–146.7°,[6] 147–147.2°[28]) and semicarbazone, m. p. 206–207° dec. (lit., 201°[11b], 202°[29,11d], 202.6–203°,[6] 211–212°,[10a,11e,j] 212–212.5°,[28] 216°,[30] 221°).[11a]

Anal. (semicarbazone). Calcd. for $C_5H_9ON_3$: C, 47.23; H, 7.13. Found: C, 47.08; H, 7.25.

Cyclobutane.—A 200-ml. flask containing a mixture of 7.0 g. (0.1 mole) of cyclobutanone, 10 ml. of 85% hydrazine hydrate, 50 ml. of Carbitol and a solution of 14 g. (0.3 mole) of potassium hydroxide in 50 ml. of Carbitol was attached to a 12 × 250 mm. Vigreux column the top of which was connected to a Dry Ice-cooled trap. The flask was heated in an oil-bath and the evolved cyclobutane collected in the trap. The heating was continued until no water distilled from the reaction mixture with the bath at 200°. The cyclobutane was distilled through a short Vigreux column with an ice-cooled reflux condenser, b. p. 12.5°; yield 4.6 g. (82%). The infrared spectrum of the gaseous material is shown in Fig. 2. A similar procedure gave an 86% yield of cyclopentane from cyclopentanone.

Cyclobutanol.—Cyclobutanone (30 g., 0.43 mole) was added dropwise to a stirred suspension of 5 g. (0.125 mole) of lithium aluminum hydride in 200 ml. of dry ether. After the addition was complete the mixture was refluxed for one hour. Sufficient 10% sulfuric acid was added slowly with stirring to dissolve the solids and the cyclobutanol was extracted with ether. Distillation through a 16 × 250 mm. glass-helix packed column, gave, other than diethyl ether: 8.6 g., b. p. 121–125°, and 19.1 g., b. p. 125°, of cyclobutanol. The combined yield was 90%. The pure material showed n^{25}_{D} 1.4347. The infrared spectrum of the liquid is shown in Fig. 2.

Cyclobutyl phenylurethan was prepared from cyclobutanol and phenyl isocyanate; m. p. 130.6–131.2° (lit.,[31] 110–111°) after recrystallization from hexane.

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85. Found: C, 69.35; H, 6.78.

A similar lithium aluminum hydride reduction of cyclopentanone gave an 85% yield of cyclopentanol.

O-Cyclobutyl S-Methyl Xanthate.—The procedure for this preparation was similar to that employed by Whitmore and Simpson.[32]

To a stirred suspension of 3.5 g. (0.146 mole) of sodium hydride in 100 ml. of dry ether was added dropwise 8 g. (0.11 mole) of cyclobutanol. The mixture was refluxed for three hours and then treated successively with 9.7 g. (0.135 mole) of carbon disulfide and 19.2 g. (0.135 mole) of methyl iodide. After each addition, the mixture was refluxed for three hours. Water was added to dissolve the solids, the ether layer was separated and dried over magnesium sulfate. The ether, excess carbon disulfide and methyl iodide were removed and the cyclobutyl methyl xanthate distilled under reduced pressure. The yield was 14.3 g. (84%), b. p. 67° (1.5 mm.).

Anal. Calcd. for $C_6H_{10}OS_2$: C, 44.41; H, 6.21. Found: C, 44.37; H, 6.43.

O-Cyclopentyl S-methyl xanthate, b. p. 88° (2.5 mm.), was prepared by a similar procedure in 90% yield.

Anal. Calcd. for $C_7H_{12}OS_2$: C, 47.69; H, 6.86. Found: C, 47.66; H, 6.93.

Pyrolysis of O-Cyclobutyl S-Methyl Xanthate.—The xanthate ester (1.84 g., 0.011 mole) was added to boiling diphenyl and the evolved gases collected over concentrated sodium hydroxide solution to dissolve the carbon oxysulfide and methyl mercaptan formed in the pyrolysis. The residual gas amounted to 250 ml. Comparison of the infrared spectrum (Fig. 1) of the gas with that of a sample of 1,3-butadiene (Phillips Petroleum Company, "Special Purity") showed the product to be apparently pure 1,3-butadiene. Pyrolysis of 13.5 g. (0.077 mole) of O-cyclopentyl S-methyl xanthate by the same procedure gave cyclopentene which was isolated as the dibromide, b. p. 75° (17 mm.). The yield of the dibromide was 12.2 g. (70%).

Cyclobutyldimethylamine—Cyclobutanone (21 g., 0.30 mole) was dissolved in 102 ml. of a 5.9 *M* solution of methylamine in absolute alcohol. The mixture was allowed to stand overnight and then shaken with hydrogen at 10–35 lb. per sq. in. over previously reduced platinum oxide catalyst. The theoretical quantity of hydrogen was absorbed in two hours. The excess methylamine was removed by distillation and the residue cooled, then acidified with 45 ml. of concentrated hydrochloric acid. The hydrogenation catalyst was separated by filtration and the alcohol and water removed from the filtrate by distillation under reduced pressure. The sirupy residue was heated with 75 ml. of 87% formic acid and 75 ml. of 35% formaldehyde solution on a steam-bath until a vigorous evolution of carbon dioxide began. The flask was removed from the bath until the gas evolution subsided, after which heating was continued overnight. The next day, 15 ml. more of 35% formaldehyde solution was added and the mixture was heated under reflux for four hours. The excess formaldehyde and formic acid were removed under reduced pressure and the residue was dissolved in 75 ml. of water. A solution of 40 g. of sodium hydroxide in 60 ml. of water was added dropwise with stirring and the liberated amine extracted with xylene. The xylene extracts were combined, dried over sodium hydroxide and distilled from sodium. The yield of cyclobutyldimethylamine, b. p. 97–100°, was 22.4 g. (75.5%).

In an attempt to isolate **cyclobutylmethylamine** from a reductive amination using 35 g. (0.5 mole) of cyclobutanone and methyl Cellosolve instead of ethyl alcohol as solvent, 29.7 g. of product, b. p. 84.5–88°, was isolated which was apparently a stable hydrate of the amine.

Anal. Calcd. for $C_5H_{11}N \cdot H_2O$: C, 58.21; H, 12.70; neut. eq., 103.1. Found: C, 57.62; H, 12.74; neut. eq., 105.8.

Methylation of the hydrated amine with formic acid and formaldehyde gave dimethylcyclobutylamine, b. p. 98–100°, in good yield.

Cyclobutyldimethylamine picrate was prepared from the amine and picric acid in benzene and recrystallized from isopropyl alcohol; m. p. 193.5–195° (dec.).

---

[28] Buchman, Schlatter and Reims, THIS JOURNAL, **64**, 2701 (1942).

[29] Demjanow, *Ber.*, **40**, 4393, 4961 (1907).

[30] Zelinsky and Gutt, *ibid.*, **40**, 4744 (1907).

[31] Demjanow and Dojarenko, *ibid.*, **40**, 2594 (1907).

[32] Whitmore and Simpson, THIS JOURNAL, **55**, 3809 (1933).

Anal. Calcd. for $C_{12}H_{16}N_4O_7$: C, 44.14; H, 5.13. Found: C, 43.90; H, 4.91.

The **picrylsulfonate** was obtained from amine and picrylsulfonic acid in isopropyl alcohol. After recrystallization from ethanol containing a little water, the melting point was 194.5–195° (dec.).

Anal. Calcd. for $C_{12}H_{16}N_4O_9S$: C, 36.73; H, 4.11. Found: C, 36.97; H, 4.22.

Cyclobutene from Cyclobutyltrimethylammonium Hydroxide.—Willstätter and von Schmaedel[20] prepared cyclobutene from cyclobutyltrimethylammonium hydroxide but did not give experimental details.

To 10 g. (0.1 mole) of cyclobutyldimethylamine dissolved in 100 ml. of ether was added 16.5 g. (0.11 mole) of methyl iodide. Heat was evolved and the quaternary iodide began to crystallize at once. The mixture was allowed to stand in a refrigerator overnight. The yield of the quaternary iodide was quantitative.

A solution of 25 g. (0.1 mole) of the quaternary salt in 100 ml. of water was shaken with 0.30 mole of freshly prepared silver oxide for two hours. The mixture was filtered and concentrated under reduced pressure. The sirupy quaternary hydroxide was added dropwise to a flask heated to 140° with an oil-bath. The pressure within the flask was maintained at 50 mm. The evolved gases were bubbled through a 1 *N* solution of hydrochloric acid and then condensed in a Dry Ice-cooled trap. The contents of the trap were allowed to evaporate into a gas holder. The yield of cyclobutene calculated from the gas volume was 0.073 mole (73%). The infrared spectrum of the product is shown in Figs. 1 and 2.

The contents of the hydrochloric acid bubbler were made basic and extracted with xylene. The xylene extracts were dried over sodium hydroxide and distilled from sodium. The recovery of cyclobutyldimethylamine, b. p. 98–102° was 2.8 g. (23%).

Cyclobutene from Cyclobutyldimethylamine Oxide.—To an ice-cooled stirred mixture of 20 ml. of 35% hydrogen peroxide and 50 ml. of water was added 10 g. (0.1 mole) of cyclobutyldimethylamine at such a rate as to keep the temperature of the reaction mixture below 10°. The solution was allowed to warm to room temperature and left overnight. Platinum foil was added to decompose the excess peroxide and the solution was concentrated under reduced pressure.

The sirupy amine oxide was decomposed at 160° as described above for cyclobutyltrimethylammonium hydroxide. The yields of cyclobutene were 50–60%. From 28–32% of cyclobutyldimethylamine, b. p. 98–102°, was recovered from the hydrochloric acid bubbler. The infrared spectrum of the cyclobutene prepared from the amine oxide pyrolysis is shown in Fig. 1.

Cyclobutyldimethylamine oxide picrylsulfonate was prepared from the amine oxide and picrylsulfonic acid in isopropyl alcohol; m. p. 168.8–169.5°, after recrystallization from isopropyl alcohol.

Anal. Calcd. for $C_{12}H_{16}O_{10}N_4S$: C, 35.29; H, 3.95. Found: C, 35.24; H, 4.06.

Summary

Cyclobutanone has been prepared in good yield by hydroxylation of methylenecyclobutane with performic acid and cleavage of the resulting glycol with lead tetraacetate.

Cyclobutanone has been converted to cyclobutane by the Wolff–Kishner reaction, cyclobutanol by reduction with lithium aluminum hydride, and cyclobutyldimethylamine by reductive amination with methylamine followed by methylation with formaldehyde and formic acid.

O-Cyclobutyl S-methyl xanthate on pyrolysis gives 1,3-butadiene. Under similar conditions, O-cyclopentyl S-methyl xanthate gives cyclopentene.

Cyclobutene, free of 1,3-butadiene, was prepared by the pyrolysis of cyclobutyltrimethylammonium hydroxide and cyclobutyldimethylamine oxide.

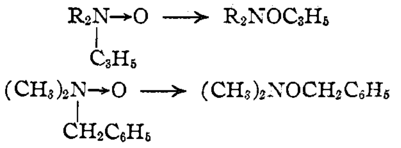
CAMBRIDGE 39, MASS. RECEIVED APRIL 12, 1949

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Thermal Decomposition of Amine Oxides to Olefins and Dialkylhydroxylamines[1,2]

BY ARTHUR C. COPE, THEODORE T. FOSTER AND PHILIP H. TOWLE

A number of allyldialkylamine oxides and benzyldimethylamine oxide recently have been shown to rearrange to trialkylhydroxylamine derivatives on heating at temperatures of 80 to 165°, with migration of the allyl and benzyl groups from nitrogen to oxygen.[3] In extending this work, it has



$$\underset{\displaystyle C_3H_5}{R_2N{\rightarrow}O} \longrightarrow R_2NOC_3H_5$$

$$\underset{\displaystyle CH_2C_6H_5}{(CH_3)_2N{\rightarrow}O} \longrightarrow (CH_3)_2NOCH_2C_6H_5$$

been found that N,N-dimethyl-(α-phenylethyl)-amine oxide (I) does not rearrange in this manner on heating, but undergoes an entirely different type of reaction, forming styrene and N,N-dimethylhydroxylamine. This paper reports an investigation of the thermal decomposition of several amine oxides, homologs of I, which was undertaken to obtain information concerning the scope and nature of the elimination reaction leading to olefins. Mamlock and Wolffenstein[4] have reported that tri-*n*-propylamine oxide decomposes on heating into propylene and N,N-di-*n*-propylhydroxylamine, but the reaction has received little attention.

N,N-Dimethyl-(α-phenylethyl)-amine oxide (I) was prepared by oxidation of the tertiary amine with 35% aqueous hydrogen peroxide at room temperature, and the excess hydrogen peroxide was decomposed catalytically in the presence of platinum foil. Preparation of the picrate of I from an aliquot of the aqueous solution showed that the

---

[1] Supported in part by the Office of Naval Research under Contract N5ori-07822, Project Designation NR-055-96.

[2] Presented in part at the St. Louis meeting of the American Chemical Society, Division of Organic Chemistry, September 7, 1948.

[3] Cope and Towle, THIS JOURNAL, **71**, 3423 (1949).

[4] Mamlock and Wolffenstein, *Ber.*, **33**, 159 (1900).