The Reduction of Methyl Cyclopropyl Ketone to Methylcyclopropylcarbinol

By V. A. Slabey and P. H. Wise

In the course of an investigation of the syntheses of alkylcyclopropanes from methyl cyclopropyl ketone it was necessary to prepare a quantity of methylcyclopropylcarbinol. The reduction of methyl cyclopropyl ketone with sodium and ethanol[1] was found to be unsatisfactory because of the low yields of carbinol obtained. Methylcyclopropylcarbinol of good purity was obtained in good yield by the use of lithium aluminum hydride, but the method was abandoned because of the difficulties encountered in applying it to large-scale work.

Catalytic reductions were considered most desirable because of their applicability to preparations of any size. Consequently, reductions with hydrogen in the presence of Raney nickel and copper chromite catalysts were attempted. Hydrogenation with Raney nickel was found to yield nearly equal quantities of methylcyclopropylcarbinol and pentanol-2, as well as unconverted ketone. In the presence of a barium-promoted copper chromite catalyst, hydrogenation of the ketone at 150° and 1500 to 2000 p.s.i. of hydrogen gave a 76% yield of the desired carbinol which was contaminated with a close-boiling impurity believed to be pentanol-2. When the temperature was reduced to 100°, however, the yield of methylcyclopropylcarbinol increased to 90%, and ring cleavage to yield pentanol-2 was no longer evident. No difficulty was experienced in determining when the reaction was complete, because hydrogen consumption dropped to virtually nothing as soon as sufficient hydrogen to convert carbonyl to carbinol was absorbed (Fig. 1).

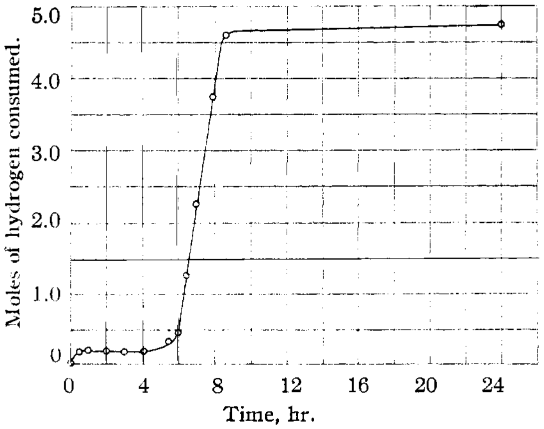

Fig. 1.—Rate of hydrogenation of 5 moles of methylcyclopropyl ketone at 100° in the presence of copper chromite catalyst.

The physical constants, carbon–hydrogen analysis, and infrared spectrum were determined on a center cut of the product obtained from the copper chromite reduction at 100°. These data are presented in Tables I and II.

Table I

Physical Constants and C–H Analysis of Methylcyclopropylcarbinol

M. p., °C., −31.04; b. p., °C., at 760 mm., 122.51; n^{20}_D, 1.43160; d^{20}, g./ml., 0.88860. Carbon, %, calcd. 69.7. Found: 69.8. Hydrogen, %, calcd. 11.7. Found: 11.8.

Table II

Infrared Absorption Maxima of Methylcyclopropylcarbinol

λ, microns	% Transmission[a]	λ, microns	% Transmission[a]
2.98	38	8.62	66
3.38	39	9.05	23
4.90	65[b]	9.22	30
5.24	56[b]	9.53	28
6.08	60[b]	9.78	26
6.87	60	10.10	45
7.08	51	10.64	16
7.26	54	10.90	64
7.79	62	11.31	63
7.95	51	12.14	48[c]
8.36	68		

[a] 1:10 dilution in carbon tetrachloride. [b] Undiluted. [c] 1:10 dilution in carbon disulfide.

The use of copper chromite as a catalyst for 1,2-hydrogenation of "conjugated" cyclopropane systems appears to be generally applicable.[2] Copper chromite has previously been used to hydrogenate the "conjugate" isopropenylcyclopropane to isopropylcyclopropane.[3]

Experimental

The methyl cyclopropyl ketone[4] was fractionated and only center-cut material was used in this work (n^{20}_D 1.4250–1.4252).

Reduction with Sodium and Ethanol.—Fourteen gram atoms (322 g.) of sodium in 0.25-inch cubes was added piecewise to 5 moles (420 g.) of methyl cyclopropyl ketone, 1500 ml. of ethanol and 500 ml. of water in a 3-liter flask equipped with a mercury-seal stirrer and a reflux condenser. During the addition of the sodium the reaction mixture was cooled to 10 to 15° by means of an ice-bath. When the addition was completed, the reactants were allowed to warm to room temperature to permit complete dissolution of the sodium. The mixture was then hydrolyzed by slowly adding 2 liters of cold water. The products were extracted from the water layer with ether and dried over anhydrous sodium sulfate. The dried ether solution was fractionated to yield 181 g., 42% yield, of methylcyclopropylcarbinol, b. p. 120–122°.

Reduction with Lithium Aluminum Hydride.—Five moles of methyl cyclopropyl ketone was added to a solution of approximately 2 moles (76 g.) of lithium aluminum hydride in 2 l. of dry ether in accordance with a previously described procedure.[5] The reaction mixture was stirred overnight and then hydrolyzed by the addition of 200 ml. of water and subsequently 1800 ml. of 10% sulfuric acid

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(1) Michiels, *Bull. Sci. Acad. Roy. Belgium*, 11 (1912).

(2) Unpublished work, this Laboratory.

(3) Slabey, Wise and Gibbons, This Journal, **71**, 1518 (1949).

(4) U. S. Industrial Chemicals, Inc., 60 E. 42nd Street, New York, N. Y.

(5) Nystrom and Brown, This Journal, **69**, 1197 (1947).

solution. The ether layer was washed with saturated sodium bicarbonate solution, dried over "Drierite," and fractionated to yield 291 g. of carbinol, b. p. 121–122°. An additional 38 g. of carbinol was obtained by re-working the fore-run fractions; total yield was 76%.

Catalytic Reduction with Raney Nickel.—Five moles of methyl cyclopropyl ketone, 200 ml. of ethanol and approximately 25 g. of Raney nickel were sealed in a 1.25-l. rocking autoclave, and hydrogen was admitted to 1200 p. s. i. at room temperature. The reactants were gradually heated to 90° at which temperature hydrogenation began. Maximum temperature reached was 125°. The hydrogenation was stopped when the theoretical amount of hydrogen had been consumed. The product was fractionated to yield 46 g. of unconverted ketone, 131 g. of pentanol-2, and 145 g., 34% yield, of methylcyclopropylcarbinol, b. p. 120–122°.

Catalytic Reduction with Copper Chromite.—Three hydrogenations were run in essentially the same manner as follows with the exception of a difference in temperature: Five moles of methyl cyclopropyl ketone and 42 g. of a commercial barium-promoted copper chromite catalyst[6] were sealed into the previously mentioned hydrogenation vessel, and hydrogen was admitted to 1750 p. s. i. at room temperature. The reactants were heated to 100°, and after an induction period of about five hours, hydrogenation began. The reaction was completed within about four hours as indicated by the hydrogen consumption dropping to virtually nothing. With the exceptions of about 20 g. of fore-run the product consisted of 390 g., 90% yield of methylcyclopropylcarbinol, b. p. 121–122°. The 3,5-dinitrobenzoate was prepared, m. p. 88.5–89.0° (uncor.). *Anal.* Calcd. for $C_{12}H_{12}O_6N_2$: N, 10.00. Found: N, 9.86.

When the hydrogenation was carried out at 120°, the yield of carbinol was 374 g., or 87%. At 150° the yield was 326 g., 76% yield of carbinol, b. p. 118–120°. From the refractive index it was evident that a close-boiling impurity of lower index than methylcyclopropylcarbinol was present. The impurity was assumed to be pentanol-2.

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(6) E. I. du Pont de Nemours, Ammonia Division, Wilmington, Delaware.

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Preparation of Organopolysiloxanes from Sodium Trimethylsilanolate[1,2]

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The availability of trimethylsilanol in good yield and high purity from the controlled hydrolysis of trimethylfluorosilane, and its rapid and complete reaction with sodium to give sodium trimethylsilanolate,[3] led to a study of the latter as an intermediate for further synthesis.

In the present work sodium trimethylsilanolate was found to readily undergo Williamson type reactions with diethyldichlorosilane, ethyltrichlorosilane and silicon tetrachloride, according to the general equation

$$R_xSiCl_{4-x} + (4 - x)(CH_3)_3SiONa \longrightarrow R_xSi[(CH_3)_3SiO]_{4-x} + (4 - x)NaCl$$

By this method there were synthesized diethyldi-(trimethylsiloxy)-silane (I), ethyltri-(trimethylsiloxy)-silane (II), and tetra-(trimethylsiloxy)-silane (III). Alternate names by the siloxane nomenclature are somewhat more cumbersome, *i. e.*, 1,1,1,5,5,5-hexamethyl-3,3-diethyltrisiloxane (I).

$(C_2H_5)_2Si[OSi(CH_3)_3]_2$ (I)

$C_2H_5Si[OSi(CH_3)_3]_3$ (II)

$Si[OSi(CH_3)_3]_4$ (III)

Compounds I and II are new organopolysiloxanes of a type not readily obtained in good yields by other methods which comprise cohydrolysis of the appropriate pair of monomers. Compound III was previously prepared in 27% yield by the cohydrolysis of ethyl orthosilicate and trimethylethoxysilane with aqueous sodium hydroxide.[4]

In the present work compound III was also prepared by reaction of trimethylsilanol with ethyl orthosilicate in the presence of a small amount of sodium.

$$4\,(CH_3)_3SiOH + (C_2H_5O)_4Si \longrightarrow Si[OSi(CH_3)_3]_4 + 4\,C_2H_5OH$$

TABLE I

PHYSICAL PROPERTIES

Compound no.		I	II	III[a,b]
Calcd. mol. wt.		264.5	324.5	384.7
B. p., °C. (733 mm.)		187	206	220
Ref. index, $n^{20}D$		1.4005	1.3944	1.3895
Density in g./ml.	0°	0.8751	0.8756	0.8854
	20°	.8399	.8582	.8677
	60°	.8035	.8209	.8298
Mol. ref., found[c]		76.43	90.54	105.09
Mol. ref., calcd.[d]		76.90	90.75	104.80
Viscosity, centipoises	0°	2.020	2.723	4.235
	20°	1.441	1.896	2.868
	60°	0.841	1.067	1.503

[a] Melting point, *ca.* −60°. [b] Constants reported previously for compd. III (ref. 4) are $n^{25}D$ 1.3865, b. p. 91° (9 mm.). In a private communication Dr. M. J. Hunter informs us that the density given in ref. 4 should be changed to d^{25} 0.8630. [c] Calculated by the Lorentz–Lorenz equation. [d] Calculated by the method of Warrick, THIS JOURNAL, 68, 2455 (1946).

In Table I are listed the three organopolysiloxanes and some of their physical properties.

Comparison of compounds I and II with the previously reported octamethyltrisiloxane and methyl-(trimethylsiloxy)-silane,[5] respectively, shows that boiling points, densities and refractive indices are greater in compounds I and II by amounts approximating those to be expected from the substitution of ethyl for methyl.

A more interesting comparison is given by the highly-branched compound III and its linear isomer, dodecamethylpentasiloxane.[5] In compound III, boiling point, refractive index and density are

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(1) XXIV in a series on organosilicon chemistry. For Paper XXIII see THIS JOURNAL, **71**, 3056 (1949).

(2) Taken in part from a thesis submitted by L. Q. Green to the Graduate School of The Pennsylvania State College in partial fulfillment of the requirements for the M.S. degree.

(3) Sommer, Pietrusza and Whitmore, THIS JOURNAL, **68**, 2282 (1946).

(4) Wright and Hunter, *ibid.*, **69**, 803 (1947).

(5) Patnode and Wilcock, *ibid.*, **68**, 358 (1946); Hunter, Warrick, Hyde and Currie, *ibid.*, **68**, 2284 (1946).