was washed with benzene. The filtrate and washings were combined and the solvent was removed under diminished pressure to yield a dark red oil. Crystallization of the oil from methanol as described was attempted, but was unsuccessful. The solution was therefore diluted with water and extracted with ether. The ether layer was washed and dried, and the solvent was evaporated. The residue was a red oil which partially solidified. This material was triturated with 20 ml. of benzene. The insoluble solid (IB) was removed by filtration.

The benzene filtrate was poured onto a column of 200 g. of activated alumina. The column was eluted with 2:8 hexane:ether, and then with ether. The early fractions yielded orange crystals which were combined and recrystallized from methylene chloride–hexane, m.p. 148–149°, wt. 0.27 g. (7%). The mixture melting point with authentic III was undepressed.

A small portion of the benzene-insoluble solid (IB) was recrystallized from methanol, m.p. 127–131° (lit.[3] m.p. 131.5°). The remainder of the crude IB was chromatographed on alumina with gradually increasing concentrations of methylene chloride in hexane, followed by pure ether. From the 4:6 hexane:methylene chloride fractions there was obtained a solid which was crystallized to yield IA as orange needles, m.p. 172.5–173.5°, wt. 0.20 g. From the ether fractions there was obtained material which after recrystallization gave III as colorless plates, m.p. 147–148.5°. The mixed melting point with authentic III was undepressed.

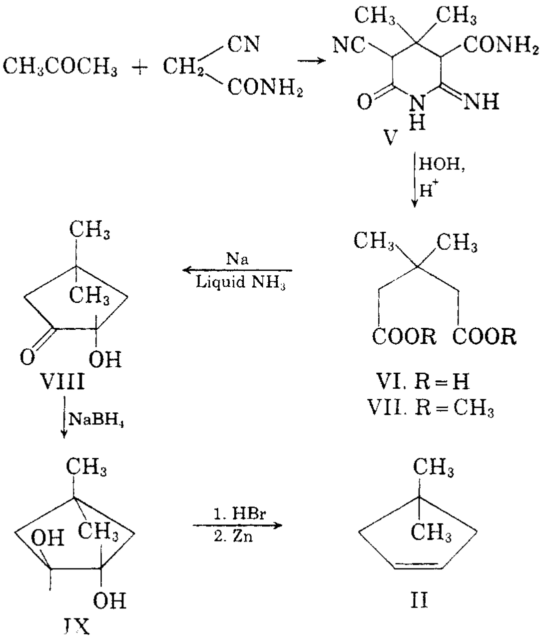
Department of Chemistry
Wayne State University
Detroit 2, Mich.

Synthesis of the *gem*-Dimethylcyclopentenes

Harold Kwart and John A. Ford, Jr.[1]

Received July 17, 1959

The two isomeric *gem*-dimethylcyclopentenes were required for an investigation in progress in these laboratories. A method of preparation of 2,2-dimethylcyclopentane (1) has been reported,[2] but apparently the conditions employed for obtaining a significant yield were very exacting. Kizhner[2] has described the formation of (I) by dehydrobromination of 1-bromo-2,2-dimethylcyclopentane, (III), which, as he indicated, resulted from a Demjanov type of rearrangement[3] of cyclobutyldimethyl carbinol (IV) on boiling with fuming hydrobromic acid. When we used 48% aqueous hydrobromic acid instead in the procedure of the Russian author, we obtained chiefly 1,2 dimethylcyclopentene and none of the desired bromo compound (III). Subsequently we found, however, that stirring (IV) with 48% hydrobromic acid at 20–30° (without heating) produced a good yield of (III). Furthermore, upon increasing the reaction time given by Kizhner[2] for the dehydrobromination of (III) we were able to raise the yield of (I) from 42 to 74%



Flow Diagram for Synthesis 3,3-Dimethylcyclopentene

The synthesis of the other isomer, 3,3-dimethylcyclopentene (II), has not been reported. This has now been achieved according to the reactions illustrated in the flow diagram.

The starting material, 5-carbamyl-3-cyano-4,4-dimethyl-6-imino-2-piperidone, (V), was made by condensation of acetone and cyanoacetamide.[4] (V) was hydrolyzed to 3,3-dimethylglutaric acid (VI) by a procedure analogous to that given by Thole and Thorpe.[5] Cyclization of the methyl ester[6] (VII) to 3,3 dimethylglutaroin (VIII) was effected by means of sodium in liquid ammonia. The structure of (VIII) was confirmed by the identity of its osazone with that from 1,1-dimethyl-3,4-cyclopentanedione.[7]

Reduction of (VIII) with sodium borohydride gave 1,1-dimethyl-*trans*-3,4-cyclopentanediol (IX). The trans structure was confirmed by the failure of (IX) to form a cyclic ketal with *p*-nitrobenzaldehyde[8] and the absence of any infrared evidence[9] for intramolecular hydrogen bonding.

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[1] Abstracted from the doctorate thesis of John A. Ford, Jr., submitted to the University of Delaware in partial fulfillment of the requirements of the Ph.D. degree, June, 1958; present address, Eastman Kodak Co., Rochester 4, N. Y.

[2] N. Kizhner, *J. Russ. Phys. Chem. Soc.*, **40**, 999 (1908); *Chem. Abstr.*, **3**, 533 (1909).

[3] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," p. 486 *et, seq.*, Cornell University Press, Ithaca, N. Y. (1953).

[4] F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 430 (1911).

[5] F. B. Thole and J. F. Thorpe, *J. Chem. Soc.*, **99**, 434 (1911).

[6] G. Kommpa, *Ber.*, **32**, 1423 (1899).

[7] G. L. Blanc and J. F. Thorpe, *J. Chem. Soc.*, **99**, 2012 (1911).

[8] H. M. Walborsky and D. F. Loncrini, *J. Am. Chem. Soc.*, **76**, 5399 (1954).

[9] See for examples, L. P. Kuhn, *J. Am. Chem. Soc.*, **74**, 2492 (1952); **76**, 4323 (1954) and H. Kwart and G. C. Gatos, *J. Am. Chem. Soc.*, **80**, 881 (1958).

Treatment of (IX) with hydrogen bromide in glacial acetic acid gave 1,2-dibromo-4,4-dimethylcyclopentane (X), which was reacted with zinc dust to give (II). The structure of (II) was confirmed by ozonization and peroxidation to (VI).[10]

EXPERIMENTAL[11]

1-Bromo-2,2-dimethylcyclopentane (III). A mixture of 400 ml. of 48% aqueous hydrobromic acid and 100 g. (0.877 mol.) of cyclobutyldimethylcarbinol was stirred 3 hr. at 20–30° and the organic layer separated and boiled 1 hr. with a solution of 100 g. of potassium hydroxide in 250 ml. of water. The mixture was steam distilled. A volume of 600 ml. of distillate was collected and diluted with a liter of water. The organic layer was separated, dried with anhydrous calcium chloride, and distilled, giving 100 g. of pale yellow liquid, b.p. 157–164°, n_D^{20} 1.4792 (65%).

2,2-Dimethylcyclopentene (I). A solution of 94.0 g. (0.531 mol.) of (III), 140 g. of potassium hydroxide, and 850 ml. of absolute ethanol was refluxed 24 hr. and then diluted with a liter of water prior to steam distillation. A 600 ml. volume of distillate was collected, diluted with a liter of water and the organic layer separated, dried with anhydrous calcium chloride, and distilled to give 38 g. of colorless liquid (74%), b.p. 78–80°, n_D^{25} 1.4151.

5-Carbamyl-3-cyano-6-imino-4,4-dimethyl-2-piperidone (V). A mixture of 250 g. (2.97 mol.) of cyanoacetamide, 125 g. (2.15 mol.) of acetone, 50 ml. of piperidine, and 1 l. of water was allowed to stand with occasional shaking for 24 hr. The white solid was filtered, washed with cold water and dried at room temperature giving 261 g. of product (84%).

3,3-Dimethylglutaroin (VIII). In a flask previously flamed dry for 15 min. and swept with dry oxygen-free nitrogen for 0.5 hr. was placed 5 l. of anhydrous ether. A 5 l. volume of liquid ammonia was collected in the flask, a dry ice-acetone trap being used as the condenser. With vigorous stirring 67 g. (2.91 g. at.) of sodium was added in small pieces under nitrogen during a 20 min. period. To the deep blue solution was added dropwise over a 4 hr. period a solution of 125 g. (0.665 mol.) of (VII) in 500 ml. of anhydrous ether. The mixture was stirred an additional 2 hr. at −33°, and the ammonia was allowed to evaporate gradually overnight. To the resulting yellow suspension was added dropwise a solution of 250 ml. of methanol in 500 ml. of ether. The mixture was acidified with 3*N* hydrochloric acid. At this point the nitrogen flow was stopped. The ether layer was separated, the aqueous layer was extracted four times with a total of 800 ml. of ether, and the combined ether solutions were dried overnight with anhydrous calcium sulfate. After removal of the ether on a steam bath distillation of the residue gave 68 g. of colorless liquid, b.p. 68–70° (2 mm.) (80%); phenylosazone, orange needles from methanol, m.p. 167–169°.[7]

1,1-Dimethyl-trans-3,4-cyclopentanediol (IX). A solution of 58 g. (0.45 mol.) of (VIII) in 50 ml. of absolute ethanol was added slowly with stirring to a solution of 15 g. (0.40 mol.) of sodium borohydride in 400 ml. of absolute ethanol. The solution was refluxed 2 hr., cooled, poured into 500 ml. of 6*N* sulfuric acid, the alcohol removed by steam distillation, and the residue extracted for 24 hr. with ether in a continuous liquid-liquid extractor. After drying with anhydrous potassium carbonate the ethereal solution was concentrated on a steam bath and the residue distilled at 93–96° (0.7 mm.). The white solid distillate was recrystallized from benzene to give 28 g. of (IX), m.p. 96–97° (48%).

Anal. Calcd. for $C_7H_{14}O_2$: C, 64.57; H, 10.83. Found: C, 64.36; H, 10.78.

An attempt to prepare a cyclic ketal with *p*-nitrobenzaldehyde[8] gave back only starting material. The infrared spectrum showed only one hydroxyl band[9] which occurred at 3620 cm.$^{-1}$

1,2-Dibromo-4,4-dimethylcyclopentane (X). A solution of 40.0 g. (0.308 mol.) of (IX), 2 ml. on conc. sulfuric acid, 200 g. of glacial acetic acid and 900 g. of 30–32% hydrogen bromide in glacial acetic acid (Eastman Kodak white label) was allowed to stand 8 hr. at room temperature and then heated 4 hr. at 100°. An additional 100 g. of the hydrogen bromide–glacial acetic acid reagent was added and the mixture heated another 4 hr. at 100°. The solution was cooled and poured into ice water. The organic layer was separated and the aqueous layer extracted three times with a total of 600 ml. of petroleum ether, b.p. 30–60°. The combined organic solutions were washed with saturated bicarbonate solution until effervescence ceased and then dried overnight with anhydrous sodium sulfate. The solvent was removed on a steam bath and the residue distilled to give 69.0 g. of colorless liquid, b.p. 65–67° (1 mm.) (88%), n_D^{20} 1.5053.

Anal. Calcd. for $C_7H_{12}Br_2$: C, 32.84; H, 4.69; Br, 62.4. Found: C, 32.78; H, 4.64; Br, 59.6.

3,3-Dimethylcyclopentene (II). To 130 g. of zinc dust in 600 ml. of boiling ethanol was added with stirring 130 g. (0.508 mol.) of (X) during 1.5 hr. The mixture was refluxed overnight, diluted with an equal volume of water and steam distilled. A volume of 800 ml. of distillate was collected, saturated with salt, and the organic layer separated and dried with anhydrous calcium chloride. Distillation gave 42.4 g. of (II) (87%), b.p. 74–75°, n_D^{22} 1.4160.

Anal. Calcd. for C_7H_{12}: C, 87.42; H, 12.58. Found: C, 86.09; H, 12.34.

Ozonization of (II). A solution of 3.14 g. (0.0326 mol.) of (II) in 100 ml. of purified carbon tetrachloride[12] was ozonized at 0–5° and then the solution concentrated to 20 ml. under water pump vacuum. After dilution to 100 ml. with glacial acetic acid the solution was added dropwise with stirring during 15 min. to a solution of 25 g. of 30% hydrogen peroxide, 1 ml. of conc. sulfuric acid, and 70 ml. of water. The mixture was refluxed 4 hr. and evaporated to 10 ml. under water pump vacuum. The residual solution was diluted with 50 ml. of water, extracted with ether, and the ether solution decolorized with norite and dried with anhydrous sodium sulfate. Evaporation and recrystallization from benzene gave 1.47 g. (28%) of (VI), m.p. 98–100°. A second recrystallization from benzene gave 1.35 g., m.p. and m.m.p. with (VI) 100–102°.

Acknowledgment. We are indebted to Mr. E. Sarasohn for translation of the Russian literature pertinent to this work and to the E. I. duPont de Nemours and Co., Inc. for a fellowship to one of us (J. A. F.) during the course of this research. We are also obliged to Mr. M. Hackett for valuable assistance in carrying out several procedures.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF DELAWARE
NEWARK, DEL.

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[10] The infrared and Raman spectra of both (I) and (II) on samples we have synthesized by the above procedures have been extensively studied by H. C. Beachell and W. Jones in these laboratories. The as yet unpublished results of their work and the spectral assignments they ascertained appear to be quite consistent with the structures we have assumed for (I) and (II).

[11] All melting point and boiling points given are uncorrected.

[12] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Second Edition, Longmans, Green and Co., New York, N. Y., 1951, p. 174.