1.4768. *Anal.* (Literature cited) Found: C, 79.3; H, 12.3.

Anal. Calcd. for $C_{14}H_{26}O$: C, 79.93; H, 12.46; MR_D, 64.66. Found (our values): C, 80.00; H, 12.55; MR_D, 64.14.

The 2,4-dinitrophenylhydrazone of VI melted at 107–108° after crystallization from dilute ethanol.

Anal. Calcd. for $C_{20}H_{30}N_4O_4$: N, 14.36. Found: N, 14.43.

The oxime of VI melted at 146.5–148° (cor.) after crystallization from dilute ethanol; literature[7] m.p. 152° (uncor.). *Anal.* (Literature cited, ref.[7]) Calcd. for $C_{14}H_{27}NO$: C, 74.66; H, 12.00; N, 6.23. Found (our values): C, 74.60; H, 12.21; N, 6.17. *Anal.* Calcd. for $C_{14}H_{27}NO$: N, 6.26. Found (our value): N, 6.31.

2,2,4-Trimethyl-4-cyclohexylpentane (IV).—Compound VI, 21 g., was reduced to the hydrocarbon by the modified Wolff–Kishner[14] method using 10 g. of potassium hydroxide, 75 ml. of diethylene glycol, and 7.5 ml. of 85% hydrazine hydrate. A 51% yield of hydrocarbon was obtained, n^{20}D 1.4650, whose infrared spectrum was practically identical to that of compound IV obtained by dehydration of II followed by hydrogenation.

Reactions of Compound V. Sulfuric Acid and Benzene.—The procedure of Ipatieff and Corson[4] was followed using 10 g. of V, 16 g. of benzene and 19 g. of 96% sulfuric acid. The reaction mixture was maintained at 50–60° for 4 hours. The organic layer was separated, extracted with 5% sodium hydroxide, washed with water and dried. The product was distilled at 5 mm. on a Piros–Glover micro column, giving the following fractions: (a) 83–91° 0.3 ml., n^{20}D 1.4890; (b) 92–93°, 3.0 ml., n^{20}D 1.4938; (c) 93–94°, 2.9 ml., n^{20}D 1.4940. A composite sample of fractions (b) and (c) was analyzed by means of infrared spectra; found 94 ± 3% pure compound V.

Hydrogen Fluoride and Benzene.—Compound V, 8 g., 125 ml. of benzene and 30 g. of hydrogen fluoride were stirred for an hour in a copper reactor maintained at 0°. The organic layer was separated, washed with 5% potassium hydroxide followed by water, and dried. Distillation on a Piros–Glover micro column at 4 mm. gave the following fractions: (a) 83–88°, 0.3 ml., n^{20}D 1.4900; (b) 88–90°, 0.9 ml., n^{20}D 1.4938; (c) 90–91°, 4.7 ml., n^{20}D 1.4942. A composite sample of fractions (b) and (c) was submitted for infrared analysis; found 95 ± 3% pure compound V.

Ferric Chloride and Benzene.—The procedure of Ipatieff and Corson[4] was followed using 10 g. of V, 88 g. of benzene and 6 g. of freshly prepared anhydrous ferric chloride.[15] The mixture was refluxed with stirring for 4 hours; hydrogen chloride was evolved. The reaction mixture was then washed with 5% hydrochloric acid followed by water until the washings were neutral. After drying, the product was distilled at 3 mm. on a Piros–Glover micro column. Fractions collected: (a) 78–86°, 0.6 ml., n^{20}D 1.4910; (b) 86–87°, 1.5 ml., n^{20}D 1.4938; (c) 87–88°, 5.8 ml., n^{20}D 1.4942. Fraction (a) and a composite sample of (b) and (c) were submitted for infrared analysis; found fraction (a) contained 90% compound V. The composite sample was about 98% pure compound V.

Microanalyses were performed by J. Sorensen and C. Brauer, Northwestern University.

EVANSTON, ILLINOIS

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

[15] H. F. Walton, "Inorganic Preparations," Prentice-Hall Publishers, Inc., New York, N. Y., 1948, p. 113.

[CONTRIBUTION FROM THE ROLLIN H. STEVENS MEMORIAL LABORATORY OF THE DETROIT INSTITUTE OF CANCER RESEARCH]

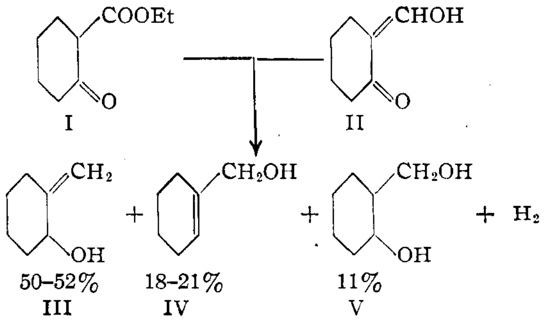
Reduction of Some Enolizable β-Dicarbonyl Compounds to Unsaturated Alcohols by Lithium Aluminum Hydride. I. Monocyclic β-Ketoesters and α-Hydroxymethylene Ketones[1]

BY ANDRE S. DREIDING AND JOHN A. HARTMAN

RECEIVED APRIL 15, 1952

The lithium aluminum hydride reduction of four β-dicarbonyl compounds was found to give primarily unsaturated alcohols 2-Methylenecyclohexanol and 1-cyclohexenemethanol were the main products of the reduction of both 2-carbethoxycyclohexanone and 2-hydroxymethylenecyclohexanone. A small amount of 2-hydroxymethylcyclohexanol was also formed. The corresponding results were obtained with the related compounds in the five-membered ring series. The structures of the unsaturated alcohols were proven by their reactions and in some cases by alternative synthesis. A mechanism is suggested.

The action of lithium aluminum hydride on partially enolized β-dicarbonyl compounds has been reported to give low yields of the 1,3-diols as the only organic products.[2] While the evolved hydrogen has been determined quantitatively,[3] the nature of the major product(s) has not been reported. Our investigation showed that an excess of lithium aluminum hydride in boiling ether reduced 2-carbethoxycyclohexanone (I), and the structurally related 2-hydroxymethylenecyclohexanone (II), to give a mixture of 2-methylenecyclohexanol (III), 1-cyclohexenemethanol (IV) and 2-hydroxymethylcyclohexanol (V) in a 5:2:1 ratio. The physical properties and the derivatives of III and IV are shown in Table I.



The evidence for the structural assignments is as follows: Catalytic reduction followed by chromic acid oxidation of 2-methylenecyclohexanol (III) afforded a 73% yield of 2-methylcyclohexanone (VIII). Ozonization gave a 27% yield of formal-

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[1] (a) A part of this work was presented at the 118th Meeting of the American Chemical Society. (b) This work was supported in part by a Research and Development Contract between the Detroit Institute of Cancer Research and the United States Atomic Energy Commission. Additional support was provided by institutional grants from the Michigan Cancer Foundation, the American Cancer Society, Inc., and the S. S. Kresge Foundation.

[2] M. Viscontini and C. Ebnoeter, *Helv. Chim. Acta*, **34**, 116 (1951); C. S. Marvel and H. W. Hill, Jr., THIS JOURNAL, **73**, 481 (1951); V. Boekelheide and S. Rothchild, *ibid.*, **71**, 879 (1949), and E. Buchta and H. Bayer, *Ann.*, **71**, 227 (1951).

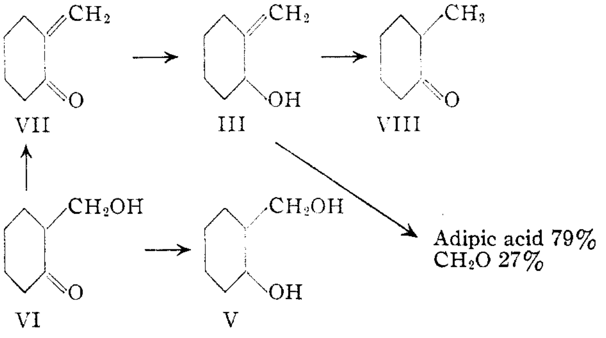
[3] J. A. Krynitsky, J. E. Johnson and H. W. Carhart, THIS JOURNAL, **70**, 486 (1948); F. A. Hochstein, *ibid.*, **71**, 305 (1949).

TABLE I

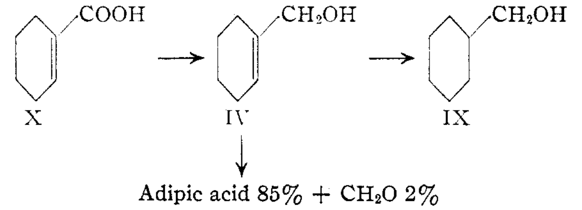
	III	IV	XIII	XIV
B.p., °C.	81–85 (27 mm.)[a]	98–99 (27 mm.)[g]	85–86 (68 mm.)	95–96 (68 mm.)[o]
$n^{25}\text{D}$	1.4883	1.4905	1.4750	1.4851
Derivative	M.p., °C.	M.p., °C.	M.p., °C.	M.p., °C.
α-Naphthylurethan	126.4–127.5[b]	125–125.4[h]		
Phenylurethan	71.4–72.4[c]	96.6–97.5[i]	82.6–83.6[l]	55–56[p]
3,5-Dinitrobenzoate	86.5–87.5[d]	100–100.5[j]	62.2–65.2[m]	99.8–101[q]
p-Nitrobenzoate	61–62.5[e]		84.8–85.8[n]	75.0–75.6[r]
Dibromide	75–76[f]	61.4–62[k]		

[a] (Reported,[16] b.p. 92–94° at 15 mm.) [b] Needles from ethanol. *Anal.* Calcd. for $C_{18}H_{19}NO_2$: C, 76.85; H, 6.81; N, 4.98. Found: C, 77.00; H, 7.00; N, 5.45. [c] Needles from petroleum ether, m.p. not raised by chromatography. *Anal.* Calcd. for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.06. Found: C, 72.93; H, 7.40; N, 6.22 (reported[16] m.p. 61–62° and 96°). [d] Prisms from petroleum ether. *Anal.* Calcd. for $C_{14}H_{14}N_2O_6$: N, 9.15. Found: N, 9.17. [e] Fine needles from ethanol. *Anal.* Calcd. for $C_{14}H_{15}NO_4$: N, 5.36. Found: N, 5.21. [f] Flat prisms from petroleum ether. *Anal.* Calcd. for $C_7H_{12}Br_2O$: Br, 58.76. Found: Br, 58.88 [g] Reported[17] b.p. 92–94° at 15 mm. [h] Needles from petroleum ether. *Anal.* Calcd for $C_{18}H_{19}NO_2$: C, 76.85; H, 6.81; N, 4.98. Found: C, 77.24; H, 7.10; N, 5.13. Mixed m.p. with *b* depressed to 103–111°. [i] Needles from petroleum ether. *Anal.* Calcd. for $C_{14}H_{17}NO_2$: C, 72.69; H, 7.41; N, 6.06. Found: C, 73.04; H, 7.36; N, 6.12 (reported[17] m.p. 96°). [j] Fine needles from petroleum ether. *Anal.* Calcd. for $C_{14}H_{14}N_2O_6$: N, 9.15. Found: N, 9.08. [k] Needles from petroleum ether. *Anal.* Calcd. for $C_7H_{12}Br_2O$: Br, 58.76. Found: Br, 59.05. [l] Short needles from petroleum ether. *Anal.* Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 72.08; H, 7.01; N, 6.40. [m] Plates from petroleum ether. *Anal.* Calcd. for $C_{13}H_{12}N_2O_6$: C, 53.42; H, 4.14; N, 9.59. Found: C, 53.38; H, 4.21; N, 9.31. [n] Prisms from petroleum ether. *Anal.* Calcd. for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 63.11; H, 5.60; N, 5.80. [o] Reported[27] b.p. 66° at 11 mm., $n^{21}\text{D}$ 1.4770. [p] Needles from petroleum ether. *Anal.* Calcd. for $C_{13}H_{15}NO_2$: C, 71.86; H, 6.96; N, 6.45. Found: C, 71.74; H, 7.02; N, 6.46 (reported[27] m.p. 64–65°). [q] Needles from petroleum ether. *Anal.* Calcd. for $C_{13}H_{12}N_2O_6$: C, 53.42; H, 4.14; N, 9.59. Found: C, 53.68; H, 4.40; N, 9.21. [r] Yellow plates from petroleum ether. *Anal.* Calcd. for $C_{13}H_{13}NO_4$: C, 63.15; H, 5.30; N, 5.67. Found: C, 62.92; H, 5.22; N, 5.66 (reported[33] m.p. 36–37°).

dehyde (as its dimedone derivative)[4] and a 79% yield of adipic acid. An alternative synthesis of III consisted of the lithium aluminum hydride reduction of 2-methylenecyclohexanone (VII) which was prepared by the dehydration of 2-hydroxymethylcyclohexanone (VI). The infrared spectrum[5] of III showed the characteristic peaks at 9.1–9.2 μ (secondary hydroxyl group)[6] and at 11.1–11.2 μ (double bond of type $R_2C{=}CH_2$).[7]

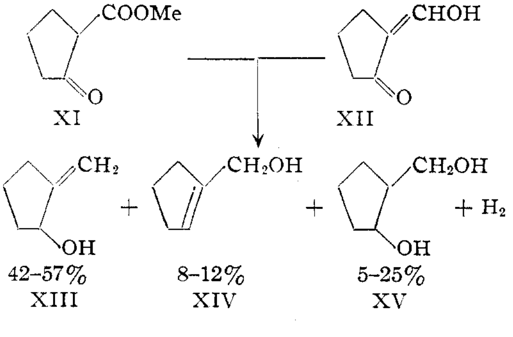


Reduction of 1-cyclohexenemethanol (IV) gave cyclohexanemethanol (IX) while ozonization resulted in an 85% yield of adipic acid and only 2% of formaldehyde. An authentic sample of IV was prepared by the lithium aluminum hydride reduction of 1-cyclohexenecarboxylic acid (X). The infrared spectrum of IV, obtained from I or II, indicated that it may have been contaminated with a small amount of III but showed a characteristic broad band at 9.5–10.0 μ (primary hydroxyl group)[6] and two peaks at 12.0 and 12.5 μ, one of which was possibly due to the double bond ($R_2C{=}CHR$).[7]



An alternative preparation of 2-hydroxymethylcyclohexanol (V) was accomplished by the lithium aluminum hydride reduction of 2-hydroxymethylcyclohexanone (VI). Nitric acid oxidation of V from the two different sources gave good yields of adipic acid.

The lithium aluminum hydride reduction, with an excess of the reagent, of the corresponding five-membered ring compounds, 2-carbomethoxycyclopentanone (XI) and 2-hydroxymethylenecyclopentanone (XII), gave qualitatively analogous results, *i.e.*, 2-methylenecyclopentanol (XIII), 1-cyclopentenemethanol (XIV) and 2-hydroxymethylcyclopentanol (XV) were formed. The physical properties and the derivatives of XIII and XIV are shown in Table I.



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(4) C. F. Seidel, H. Schinz and L. Ruzicka, *Helv. Chim. Acta*, **32**, 1739 (1949), reported a maximum of 34% for compounds with a semicyclic double bond.

(5) We are grateful to Mr. Bruce Scott of Parke, Davis and Co. for the measurement and interpretation and to Dr. G. B. B. M. Sutherland of the University of Michigan for a discussion of the spectra.

(6) N. B. Colthup, *J. Opt. Soc.*, **40**, 397 (1950), and G. B. B. M. Sutherland, private communication.

(7) D. Barnard, L. Bateman, A. J. Harding, H. P. Koch, N. Sheppard and G. B. B. M. Sutherland, *J. Chem. Soc.*, 915 (1950).

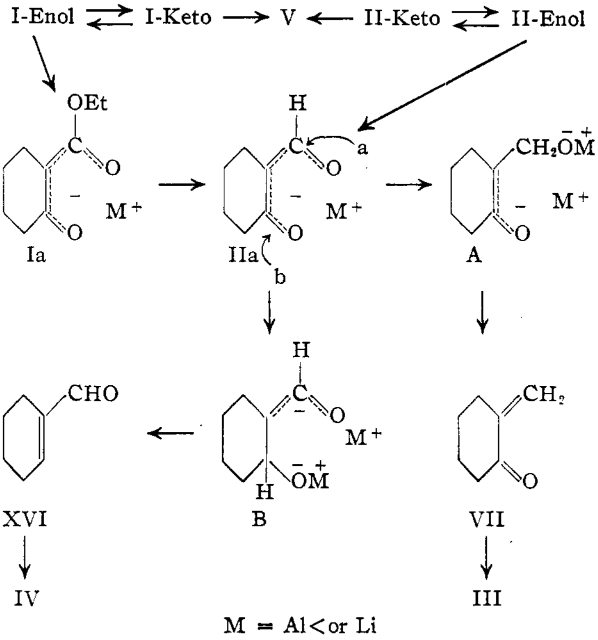
The evidence for these structures was again based on hydrogenation, oxidation, ozonization and an alternative synthesis of XIV. The reduction of XIII followed by oxidation gave 2-methylcyclopentanone, while ozonization resulted in a 24% yield of formaldehyde. The infrared spectrum of XIII was similar to that of III in the above mentioned respects.

The catalytic reduction of 1-cyclopentenemethanol (XIV) gave cyclopentanemethanol. An authentic sample of XIV was prepared from 1-cyclopentenecarboxylic acid. The infrared spectrum of a sample of XIV obtained from XI or XII indicated the presence of some XIII but was otherwise similar to the spectrum of IV.

The formation of unsaturated alcohols in these reductions cannot be explained by postulating a normal reduction to the glycol and subsequent dehydration of V during the isolation since V was formed in good yield from VI under identical conditions. The following postulated course of the reaction, which is similar to the one proposed for the action of the phenyl Grignard reagent on dihydroresorcinol,[8] would account for the observed products and is consistent with the indicated experiments.

It is likely that the enolized portions of I and II react with lithium aluminum hydride to form the enolate salts Ia and IIa along with hydrogen, while the non-enolic portions are reduced in the "normal" fashion to the diols. This interpretation receives some support from a comparison of the yield of hydrogen[3] with that of combined unsaturated alcohols: from I, H_2 93%, Δ-alcohols 73%; from II, H_2 94%, Δ-alcohols 68%; from XI, H_2 56%, Δ-alcohols 50%; from XII, H_2 80%, Δ-alcohols 69%. Furthermore, replacement of the active hydrogen in I and II with a "C" methyl group causes the lithium aluminum hydride reduction to result in a high yield of the diols under similar conditions.[9]

The ethoxy group in Ia may be replaced by hydrogen to give IIa, which would then be intermediate in the reduction of both I and II. This assumption is in accord with the observed formation of the same proportion of III and IV in the two reductions. The salt IIa could now suffer a hydride attack at either position a or b to give the intermediates A or B, respectively. Since A and B are simple enolates they would be resistant to further lithium aluminum hydride reduction (see below). Each, however, might be expected to lose an oxygen by analogy with the base catalyzed dehydration of aldols.[10] The resulting 2-methylenecyclohexanone (VII) and 1-cyclohexenecarboxaldehyde (XVI) would be further reduced to III and IV, respectively, in the presence of excess hydride. The formulation of the last two steps is consistent with the observation that the partial reduction of II yielded 20% of 1-cyclohexenecarboxaldehyde (XVI) and much viscous material, which might well have resulted from the dimerization of VII,[11] and with the fact that the lithium aluminum hydride reduction of VII gave III.



The postulated reduction of an enolate salt is contrary to the generally accepted notion that enolates resist attack by the reagent.[12] That some *simple enolates* indeed do resist such a reduction was shown by the almost quantitative recovery of 2-methylcyclohexanone (VIII) from a lithium aluminum hydride treatment of its sodium enolate. However, the sodium enolate of 2-carbomethoxycyclopentanone (XI) yielded mostly unsaturated alcohols (XIII and XIV), which demonstrates that *enolates of some β-dicarbonyl compounds* are attacked by the reagent.

Experimental[13]

Lithium Aluminum Hydride Reduction of 2-Hydroxymethylenecyclohexanone (II).—To a stirred solution containing 27 g. (0.71 mole) of lithium aluminum hydride in 400 cc. of dry ether was added dropwise a solution of 80 g. (0.63 mole) of 2-hydroxymethylenecyclohexanone (II)[14] in 80 cc. of dry ether. The addition required three hours and care was exercised to avoid the building up of pressure formed by the liberated hydrogen. The mixture was refluxed for 30 minutes followed by the careful decomposition of the excess hydride with water. Approximately 300 cc. of 20% aqueous Rochelle salt was added to complex the alumina,[15] the ethereal layer was separated and the aqueous layer extracted twice with ether. The combined ethereal solutions were washed with saturated sodium chloride solution, dried over magnesium sulfate and concentrated. The colorless residue was fractionated at reduced pressure through a Widmer column to give the following fractions: 2-methylenecyclohexanol (III), b.p. 81–85° and 27 mm., n^{25}_{D} 1.4883 (reported[16] b.p. 84–85° at 13 mm., n^{20}_{D} 1.4843), yield 35.6 g. (50%); 1-cyclohexenemethanol (IV), b.p.

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[8] G. F. Woods and I. W. Tucker, THIS JOURNAL, **70**, 2174 (1948).

[9] Ann Voltman, this Laboratory, unpublished results. See also the last reference in footnote 2.

[10] E. R. Alexander, "Ionic Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 180.

[11] C. Mannich, *Ber.*, **74B**, 554 (1941).

[12] W. G. Brown, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 473.

[13] All analyses were performed by Micro-Tech Laboratories, Skokie, Ill. The melting points are not corrected.

[14] Pl. A. Plattner, P. Treadwell and C. Scholz, *Helv. Chim. Acta*, **28**, 771 (1945).

[15] R. Nystrom and W. G. Brown, THIS JOURNAL, **70**, 3736 (1948).

[16] M. Mousseron, F. Winternitz and J. Jullien, *Bull. soc. chim.*, 80 (1947), and *ibid.*, 883 (1948); M. Mousseron and R. Jaquier, *ibid.*, 106 (1951).

98–99° and 27 mm., n^{25}D 1.4905 (reported[17] b.p. 92–94° at 15 mm.), yield 13.0 g. (18%); and 2-hydroxymethylcyclohexanol (V), b.p. 87–90° and 1 mm., n^{25}D 1.4920 (reported[16] b.p. 114–115° at 14 mm., n^{20}D 1.4923), yield 8.8 g. (10.7%).

Lithium Aluminum Hydride Reduction of 2-Carbethoxycyclohexanone (I).—The reduction of 100 g. (0.58 mole) of I[18] with 33 g. (0.84 mole) of lithium aluminum hydride in 500 cc. of dry ether was carried out as described in the first experiment. The product was fractionated at reduced pressure and the three constituents were separated: 2-methylenecyclohexanol (III), b.p. 78.5–80° at 23 mm., n^{25}D 1.4878, yield 34 g. (52%); 1-cyclohexenemethanol (IV), b.p. 95–96° at 23 mm., n^{25}D 1.4905, yield 14 g. (21%); and 2-hydroxymethylcyclohexanol (V), b.p. 148–151° at 23 mm., yield 8.2 g. (11%).

Hydrogenation and Oxidation of 2-Methylenecyclohexanol (III).—The theoretical amount of hydrogen (466 cc.) was consumed in 40 minutes by 2.072 g. of III with 0.20 g. of Adams catalyst in 50 cc. of commercial absolute methanol at room temperature and atmospheric pressure. Purification of the product by evaporative distillation gave a colorless oil which was oxidized with chromic acid at room temperature to give an 86% yield of 2-methylcyclohexanone (VIII). The semicarbazone and 2,4-dinitrophenylhydrazone formed in better than 90% yields, m.p. 189–190° and 136–137° alone and when mixed with authentic samples of the respective derivatives of VIII.

Hydrogenation of 1-Cyclohexenemethanol (IV).—When the hydrogenation was performed on 2.07 g. of IV as described in the previous experiment it proceeded much more slowly and could only be brought to 84% completion. Isolation of the product and evaporative distillation at 90–100° (23 mm.) yielded 1.7 g. (80%) of cyclohexanemethanol (IX).

The α-naphthylurethan crystallized from absolute ethanol as long flat needles, m.p. 109.4–110.2°, alone and when mixed with this derivative of an authentic sample of cyclohexanemethanol.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.28; H, 7.47; N, 4.94. Found: C, 76.47; H, 7.51; N, 5.17.

Ozonization of 2-Methylenecyclohexanol (III).—A solution of 1.02 g. of III in 30 cc. of ethyl acetate was treated with ozone until the exit gases liberated iodine from aqueous potassium iodide. Refluxing the ozonide for one hour with 10 cc. of 30% hydrogen peroxide, removal of ethyl acetate by a stream of dry air and treatment of the semi-solid residue with 10 drops of concentrated nitric acid gave a 79% yield of crude adipic acid, m.p. 143–147°, not depressed by an authentic sample. In another experiment 1.016 g. of III was ozonized in a similar way with the exit gases passed through distilled water. The contents of the wash bottle were treated with dimedone, warmed and chilled to give 10 mg. of the dimedone derivative of formaldehyde as short needles, m.p. 190–190.4°. The ozonide was hydrogenated in the presence of Adams catalyst (50 mg.) at 0° and the product was treated with dimedone to give the same derivative as above, m.p. 188.5–190.5°, yield 0.664 g. in two crops, total yield 27%.

Ozonization of 1-Cyclohexenemethanol (IV).—A 1-g. sample of IV was ozonized and worked up for adipic acid as above; m.p. 148–150°, yield 1.1 g. (85%). Another 1-g. sample was ozonized and the formaldehyde was isolated as described above; yield 2%.

2-Methylenecyclohexanol (III).—To an ice-cold solution of 30 g. of thionyl chloride and 80 g. of dry pyridine in 200 cc. of dry ether was added, dropwise with stirring, 15 g. of 2-hydroxymethylcyclohexanone (VI)[19] diluted with an equal volume of dry ether. After two hours at ice-bath temperature, the mixture was poured on crushed ice and the aqueous layer separated and extracted with ether. The combined ethereal solutions were washed with saturated sodium bicarbonate, cold 10% sulfuric acid, 5% sodium hydroxide and saturated sodium chloride. After drying over magnesium sulfate, the concentrated residue was transferred to a 100-cc. flask containing 14 g. of mixed collidines. The flask was fitted with a capillary and a goose neck leading to another 100-cc. flask, which was chilled to −70° and connected to a vacuum line. The distillation flask was warmed slowly to 63° and 1 mm. and, after three hours, all the volatile components in the flask had distilled into the receiver and partly solidified. The cold distillate containing 2-methylenecyclohexanone, was taken up in ether and extracted in the cold with 10% sulfuric acid to remove the collidines. After brief drying over magnesium sulfate, the cold solution was added rapidly to a solution of 2 g. of lithium aluminum hydride in 250 cc. of dry ether. After isolating as described in the first experiment, the product was distilled to give 1.3 g. (10%) of III, b.p. 83–85° at 26 mm., n^{25}D 1.4893. The melting points of the dibromide (74.5–75°), α-naphthylurethan (123–125°) and the phenylurethan (70–71°) were not depressed on mixing with the same derivatives of III obtained from I or II. In one experiment the cold distillate containing VII was allowed to warm, when it first became a mobile liquid and then, at room temperature, set to a solid mass in an exothermic reaction. After crystallization from aqueous methanol, the hydrate of the dimer of 2-methylenecyclohexanone, m.p. 146–152°,[11] was obtained.

1-Cyclohexenemethanol (IV).—Thionyl chloride and pyridine dehydration of 2-carbethoxycyclohexanol[20] followed by saponification gave 1-cyclohexenecarboxylic acid (X), m.p. 33.5–35.8° from aqueous acetic acid (reported[21] m.p. 33–35°). The reduction of 2.5 g. of X with a 20% excess of lithium aluminum hydride was carried out as described above. The resulting 1-cyclohexenemethanol (IV) was evaporatively distilled at 125° and 23 mm., n^{25}D 1.4881, yield 2.0 g. (91%). The 3,5-dinitrobenzoate and the dibromide melted at 99.4–100° and 60.8–62°, respectively, alone and when mixed with the same derivatives of IV from the first experiment.

2-Hydroxymethylcyclohexanol (V).—The reduction of 20 g. (0.15 mole) of VI[19] was accomplished with 5 g. (0.13 mole) of lithium aluminum hydride as described in the first experiment. The crude diol (V) was distilled at 148–152° and 24 mm., n^{25}D 1.4882, yield 13 g. (64%). Cold oxidation of this product with nitric acid gave a 70% yield of adipic acid. Similar treatment of the diol from the first experiment gave a 78% yield of crude adipic acid.

Partial Reduction of 2-Hydroxymethylenecyclohexanone (II).—To a solution of 20 g. (0.16 mole) of II in 100 cc. of dry ether was added, with stirring, 40.5 cc. of an ethereal solution of 3.02 g. (0.079 mole) of lithium aluminum hydride (calculated by hydrogen evolution of an aliquot) at such a rate that the solvent refluxed gently (two hours). The mixture, which contained a light yellow precipitate, was allowed to stand overnight at room temperature. The addition of water produced no heat effect nor evolution of hydrogen, indicating no unused hydride. The ethereal solution was separated, extracted three times with 5% sodium hydroxide, dried over magnesium sulfate and concentrated. The colorless residue was distilled at reduced pressure and 1-cyclohexenecarboxaldehyde (XVI) was collected as a colorless oil with a benzaldehyde-like odor, b.p. 75–80° at 25 mm., yield 3.2 g. (20%); $\lambda_{\max}^{\text{alc}}$ 230 mμ, log ε 3.8 (reported[22] $\lambda_{\max}^{\text{alc}}$ 229 mμ, log ε 4.1). The 2,4-dinitrophenylhydrazone crystallized from ethyl acetate as fine reddish-orange needles, m.p. 217–219° dec. (reported[23] 219–220°). The semicarbazone crystallized from ethanol as clusters of colorless prisms, m.p. 219–220° (reported[23] 213–216°); $\lambda_{\max}^{\text{alc}}$ 260, 265 mμ, log ε 3.99, 4.02 (reported[22] $\lambda_{\max}^{\text{alc}}$ 260, 265 mμ, log ε 4.45, 4.50). A large amount of dark viscous material remained as a residue in the distillation of XVI.

Attempted Reduction of the Sodium Salt of 2-Methylcyclohexanone (VIII) by Lithium Aluminum Hydride.—The sodium salt of VIII[24] was prepared under nitrogen from 9.2 g. (0.082 mole) of VIII and 5 g. (0.22 mole) of sodium hydride in ether. After heating for five days the reaction appeared complete and the white thick suspension was treated with 2 g. (0.052 mole) of lithium aluminum hydride in 70 cc. of ether followed by refluxing for two hours. The product was isolated as described above. The concentrated residue, 8.5 g. (92% recovery by weight), showed a

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70% carbonyl content[25] as compared with a 90% carbonyl content of the starting material. Fractionation at atmospheric pressure gave 5.7 g. (73%) of VIII, b.p. 160–163°, n^{25}_{D} 1.4540. The carbonyl content of the distillate was 77 and 78% in duplicate runs. The melting point of the 2,4-dinitrophenylhydrazone was 135–137° and not depressed by an authentic sample of the same derivative of VIII.

Estimate of the Amount of Hydrogen Evolved by the Action of Lithium Aluminum Hydride on I, II, XI and XII.—Weighed amounts, 0.2–0.3 g., of the oils in 3–4 cc. of dry ether were added dropwise to an ethereal solution of lithium aluminum hydride in a closed system leading to a gas buret.[3] In the case of XII, the solid was lowered into the solution in a small beaker. The following yields of hydrogen were obtained in duplicate runs: acetoacetic ester 69, 68% (reported[3] 57, 74%); 2-carbethoxycyclohexanone (I) 91, 95%; 2-hydroxymethylenecyclohexanone (II) 94, 95%; 2-carbomethoxycyclopentanone (XI) 56, 56%; 2-hydroxymethylenecyclopentanone (XII) 80, 81%.

2-Carbomethoxycyclopentanone (XI).—This ketoester was prepared from dimethyl adipate by the method described for the ethyl ester,[26] b.p. 109–111° (27 mm.), n^{25}_{D} 1.4582.

The 2,4-dinitrophenylhydrazone crystallized from absolute ethanol in long orange plates, m.p. 126–127°, sintering at 123°.

Anal. Calcd. for $C_{13}H_{14}N_4O_6$: N, 17.39. Found: N, 17.16.

Lithium Aluminum Hydride Reduction of 2-Carbomethoxycyclopentanone (XI).—The reduction was carried out as described in the first experiment. The crude product from 20 g. (0.14 mole) of the keto ester and 11 g. (0.29 mole) of lithium aluminum hydride in 400 cc. of dry ether was fractionated at reduced pressure into three components: **2-methylenecyclopentanol** (XIII), b.p. 85–86° (68 mm.), n^{25}_{D} 1.4750, yield 5.6 g. (42%); 1-cyclopentenemethanol (XIV), b.p. 95–96° (68 mm.), n^{25}_{D} 1.4851 (reported[27] b.p. 66° at 11 mm., n^{21}_{D} 1.4770), yield 0.9 g. (8%). The residue was evaporatively distilled at 160–165° (30 mm.) to give 2.5 g. (15%) of what is probably 2-hydroxymethylcyclopentanol (XV), n^{25}_{D} 1.4825 (reported[28] b.p. 127.5° at 9 mm., n^{20}_{D} 1.4828). The aqueous layer was continuously extracted for two days with ether to give an additional 1.7 g. (10%) of the diol (XV).

In another experiment, 20 g. (0.12 mole) of the crude sodium salt from the Dieckmann condensation in preparing XI was added to 10 g. (0.26 mole) of lithium aluminum hydride in 200 cc. of dry ether. The mixture of XIII and XIV was distilled without efficient fractionation, b.p. 79–84° at 52 mm., n^{25}_{D} 1.4773, yield 5.9 g. (50%).

Lithium Aluminum Hydride Reduction of 2-Hydroxymethylenecyclopentanone (XII).—The reduction of 13 g. (0.11 mole) of XII was accomplished by the addition of the solid ketone[29] (XII, m.p. 77°) to a solution of 10 g. (0.26 mole) of lithium aluminum hydride in one liter of dry ether. The product was isolated as above to give the following: 2-methylenecyclopentanol (XIII), b.p. 77–80° at 50 mm., n^{25}_{D} 1.4769, yield 6.4 g. (57%); 1-cyclopentenemethanol (XIV), b.p. 92–95° at 50 mm., n^{25}_{D} 1.4853, yield 1.3 g. (12%). Evaporative distillation of the residue at 160–170° (30 mm.) gave 0.70 g. (5%) of what is probably XV. Continuous extraction of the aqueous layer gave no further product.

Ozonization of 2-Methylenecyclopentanol (XIII).—A total of 24% of the dimedone derivative of formaldehyde was obtained when XIII was ozonized as described for III.

Hydrogenation and Oxidation of 2-Methylenecyclopentanol (XIII).—These reactions were carried out as described for III which gave a 34% over-all yield of the semicarbazone of 2-methylcyclopentanone, m.p. 187° (reported[30] m.p. 187.2°). A portion of the semicarbazone was heated for a few minutes in a solution of 2,4-dinitrophenylhydrazine in 50% sulfuric acid. Crystallization of the **2,4-dinitrophenylhydrazone of 2-methylcyclopentanone** from ethanol gave orange needles, m.p. 159–159.5°.

Anal. Calcd. for $C_{12}H_{14}N_4O_4$: C, 51.79; H, 5.07; N, 20.14. Found: C, 52.28; H, 5.01; N, 20.35.

Hydrogenation of 1-Cyclopentenemethanol (XIV).—A 59% yield of cyclopentanemethanol was obtained by a slow catalytic reduction and evaporative distillation of the product at 90° and 30 mm. The phenylurethan crystallized from petroleum ether in short needles, m.p. 108–108.5° (reported[31] m.p. 110°).

1-Cyclopentenemethanol (XIV).—The reduction of 1-cyclopentenecarboxylic acid,[32] m.p. 119–120°, with an excess of lithium aluminum hydride gave an 83% yield of XIV by evaporative distillation at 160–170° (atmospheric pressure), n^{25}_{D} 1.4785. The melting points of the *p*-nitrobenzoate (74.5–75.5°) and the phenylurethan (56.3–57.5°) were not depressed on admixture of the same derivatives obtained from XI. (Reported for *p*-nitrobenzoate m.p. 36–37°[33] and for phenylurethan m.p. 64–65°.[27])

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