[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Reductions at Metal Surfaces. II. A Mechanism for the Clemmensen Reduction[1]

BY JAMES H. BREWSTER

RECEIVED OCTOBER 30, 1953

Alcohols, chlorides and olefins are not significantly reduced to saturated hydrocarbons in homogeneous media under conditions suitable for Clemmensen reduction of the corresponding carbonyl compounds. In competitive reductions cyclohexanone is reduced more rapidly than is cyclopentanone. These findings indicate that the slow step in the reaction is coördination of the carbonyl carbon atom with the metal surface. A mechanism correlating this reaction with those described in part I and permitting an interpretation of "abnormal" Clemmensen reductions is presented.

The Clemmensen reduction[2] of a carbonyl group to a methyl or methylene group by means of zinc amalgam and hydrochloric acid is of theoretical interest because it corresponds to the addition of four electrons and four protons to the carbonyl group. Using the "nascent hydrogen,"[3] "metal atom addition"[4] and "electron–proton"[5] theories of active metal reductions, an alcohol would seem to be required as an intermediate in such a process. On the other hand, the chemisorption mechanism[6] pictures the solid metal as an "electron pump," obviating the need for free, partially reduced intermediates; the detailed mechanisms presented in part I furthermore suggest that alcohols would not be formed to any great extent in strongly acid medium.

Hydrogenolysis of an alcohol or of a chloride formed from the alcohol by reaction with hydrochloric acid and zinc chloride, indeed, appears to be a *possible* pathway for the Clemmensen reduction of *phenyl* ketones.[7,8] On the other hand, the use of aliphatic alcohols as solvents for the reaction[2] and the reduction of some hydroxyketones without loss of the hydroxy group[9] suggests that alcohols may not be intermediates in the reduction of *aliphatic* carbonyl compounds.

It has now been found that aliphatic alcohols and chlorides are not reduced, in homogeneous solution, under conditions suitable for reduction of the corresponding carbonyl compounds. Thus, 2-octanone in 50% methanol yielded 45% of *n*-octane, about 7% of octenes and 20% of recovered ketone. Under the same conditions, 2-octanol yielded no detectable paraffin, about 4% of octenes and 81% of recovered octanol. These results were not changed by varying the reaction conditions; the ketone showed no catalytic effect on the reduction of the alcohol. Similar results were obtained in attempted reductions of cyclopentanol, cyclohexanol, 1-heptanol, cyclohexyl chloride and 2-octyl chloride (the latter two in 75–80% acetic acid to ensure homogeneity of the liquid phase). Traces of alcohols (ceric nitrate test[10]), halide (Beilstein test[11]) and acetates (hydroxamic acid test[12]) were sometimes found in the recovered ketones; olefins were detected by changes in volume and refractive index of hydrocarbon fractions after treatment with cold concentrated sulfuric acid. These results show that alcohols and chlorides, while often formed as by-products, are not important as intermediates in Clemmensen reductions of aliphatic ketones. Evidence that free carbonium ions are not intermediates is provided by the fact that the *saturated* products from the reduction of pinacolone[8,13] and pivalophenone[8] have unrearranged carbon skeletons.

In competitive reductions cyclohexanone is reduced more rapidly than is cyclopentanone. The results of two reductions of equimolar mixtures of the two ketones, in homogeneous medium, are summarized in the table. In both cases the material not recovered as cycloparaffin or as ketone was distributed in several high-boiling fractions, apparently complex mixtures of di- and trimolecular condensation products. Counting these products, the material balances are of the order of 95%. In each case the material balance defect of cyclopentanone is too small to account for the differences in the yields of the two cycloparaffins.

TABLE I

COMPETITIVE REDUCTION OF 1:1 CYCLOPENTANONE–CYCLOHEXANONE

Reacn. time, min.	Product	C_5H_8O, %	$C_6H_{10}O$, %
ca. 45 (I)	Cyclane	10.7	29.7
	Cycloketone	79.1	53.5
	Material balance	89.8	83.2
	Defect	10.2	16.8
ca. 60 (II)	Cyclane	20.1	44.7
	Cycloketone	64.8	25.0
	Material balance	84.9	69.7
	Defect	15.1	30.3

This result indicates that the slow step in the reaction is one in which the carbonyl carbon atom changes its coördination number from three to four.[14] For the reasons stated above, this cannot correspond to the formation of either an alcohol or a

---

(1) Presented at the XIIth Congress of Pure and Applied Chemistry, New York, N. Y., September, 1951.

(2) E. L. Martin, in "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 155.

(3) A. Baeyer, *Ann.*, **269**, 145 (1892).

(4) R. Willstätter, F. Seitz and E. Bumm, *Ber.*, **61**, 871 (1928).

(5) H. Burton and C. K. Ingold, *J. Chem. Soc.*, 2022 (1929).

(6) See part I, THIS JOURNAL, **76**, 6361 (1954).

(7) E. L. Martin, *ibid.*, **58**, 1438 (1936).

(8) See part III, *ibid.*, **76**, 6368 (1954).

(9) E. Clemmensen, *Ber.*, **47**, 681 (1914); R. E. Marker and E. J. Lawson, THIS JOURNAL, **61**, 852 (1939); R. E. Lutz and L. Small, *J. Org. Chem.*, **4**, 220 (1939).

(10) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 3rd Edition, John Wiley and Sons, Inc., New York, N. Y., p. 96.

(11) *Idem.*, *ibid.*, p. 55.

(12) N. D. Cheronis and J. B. Entrikin, "Semimicro Qualitative Organic Analysis," Thomas Y. Crowell Co., New York, N. Y., 1947, p. 121.

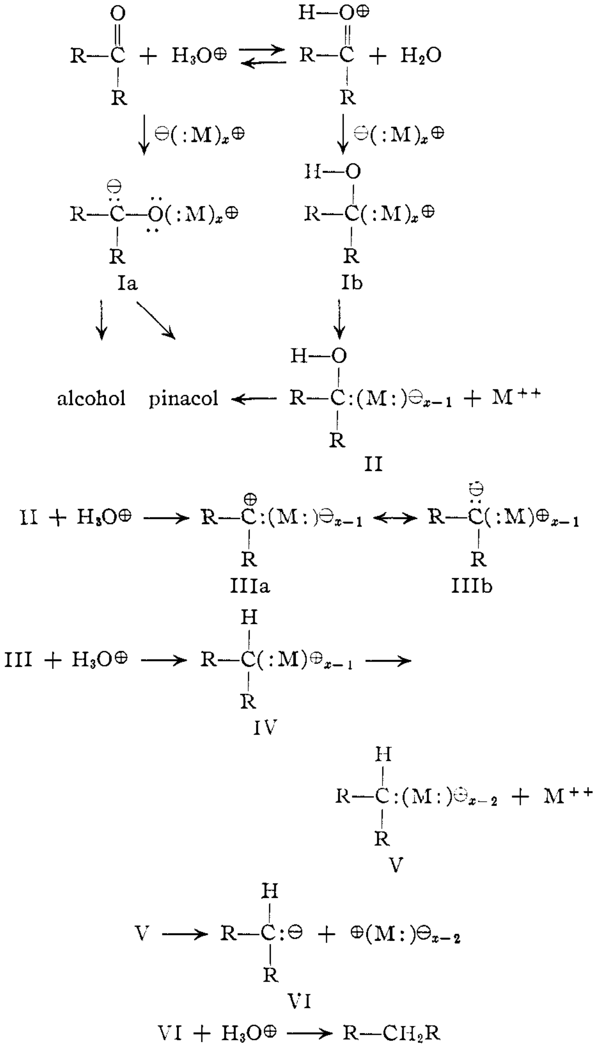
(13) J. P. Wibaut, H. Hoog, S. L. Langendijk, J. Overhoff and J. Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939).

(14) H. C. Brown, R. S. Fletcher and R. B. Johannesen, THIS JOURNAL, **73**, 212 (1951).

carbanion and must, therefore, correspond to coordination with dissolved metal atoms or the metal surface. It seems unlikely that dissolved zinc atoms could survive in strongly acidic medium, nor if they could survive, would there be any need for amalgamation of the zinc.

The following mechanism accounts for the facts known about the Clemmensen reduction and permits a detailed correlation of this reaction with other reductions at active metal surfaces.[6,15]

Strongly acidic conditions are necessary for this reaction. It is, first of all, necessary that the weakly basic ketone be sufficiently protonated[16] that Ib be formed to the exclusion of Ia, an intermediate in the formation of alcohols[6] and thus of chlorides and olefins. This would be especially important in reductions of phenyl ketones and of sterically hindered ketones where the formation of Ia would be more strongly favored.[6,8] Of particular importance is the function of acid in promoting the formation of III, thus hindering pinacol formation[6]; note here the resonance-stabilizing function of the massive metal. The use of dilute solutions or of an extracting solvent[2] would also hinder pinacol formation as well as reduce the amount of acid-catalyzed condensations. Amalgamation of the zinc serves to raise its hydrogen overvoltage[17] to the point where it could survive as a reducing agent in the strongly acidic medium. The hydrogen halides appear to be the only strong mineral acids the anions of which are not reduced by zinc amalgam.



$$R-\underset{\underset{R}{|}}{\overset{\overset{O}{\|}}{C}} + H_3O^{\oplus} \rightleftharpoons R-\underset{\underset{R}{|}}{\overset{\overset{H-O^{\oplus}}{\|}}{C}} + H_2O$$

$$\downarrow {}^{\ominus}(:M)_x^{\oplus} \qquad\qquad \downarrow {}^{\ominus}(:M)_x^{\oplus}$$

$$\underset{\text{Ia}}{R-\underset{\underset{R}{|}}{\overset{\ominus}{C}}-\ddot{O}(:M)_x^{\oplus}} \qquad \underset{\text{Ib}}{R-\underset{\underset{R}{|}}{\overset{\overset{H-O}{|}}{C}}(:M)_x^{\oplus}}$$

$$\text{alcohol} \quad \text{pinacol} \longleftarrow \underset{\text{II}}{R-\underset{\underset{R}{|}}{\overset{\overset{H-O}{|}}{C}}:(M:)^{\ominus}_{x-1}} + M^{++}$$

$$\text{II} + H_3O^{\oplus} \longrightarrow \underset{\text{IIIa}}{R-\underset{\underset{R}{|}}{\overset{\oplus}{C}}:(M:)^{\ominus}_{x-1}} \longleftrightarrow \underset{\text{IIIb}}{R-\underset{\underset{R}{|}}{\overset{\ominus}{\ddot{C}}}(:M)^{\oplus}_{x-1}}$$

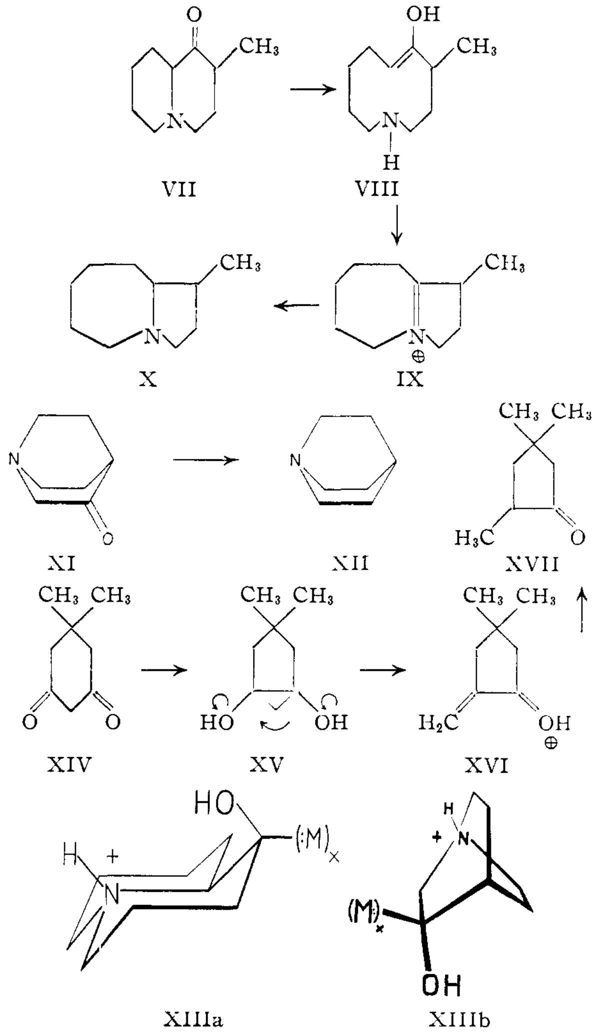
$$\text{III} + H_3O^{\oplus} \longrightarrow \underset{\text{IV}}{R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}(:M)^{\oplus}_{x-1}} \longrightarrow$$

$$\underset{\text{V}}{R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}:(M:)^{\ominus}_{x-2}} + M^{++}$$

$$\text{V} \longrightarrow \underset{\text{VI}}{R-\underset{\underset{R}{|}}{\overset{\overset{H}{|}}{C}}:^{\ominus}} + {}^{\oplus}(M:)^{\ominus}_{x-2}$$

$$\text{VI} + H_3O^{\oplus} \longrightarrow R-CH_2R$$

Clemmensen reduction of unsaturated ketones might be expected to parallel their reduction at other active metal surfaces,[6] giving mono- and bimolecular products in which the olefinic linkage has been reduced.[18] Reductive loss of α-substituents[19] could also occur.[6] The rearrangements of cyclic amino ketones (VII → X) on Clemmensen



VII VIII

X IX

XI XII XVII

XIV XV XVI

XIIIa XIIIb

---

[15] Shortly after the presentation of this paper, the author's attention was called to a similar mechanism, presented without supporting evidence; C. R. Noller, "Chemistry of Organic Compounds," W. B. Saunders Co., Philadelphia, Penna., 1951, p. 216. The author wishes to acknowledge Prof. Noller's priority.

[16] *Cf.* P. D. Bartlett, in H. Gilman, "Organic Chemistry, an Advanced Treatise," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 83-85.

[17] E. Newberry, *J. Chem. Soc.*, **109**, 1051 (1916).

[18] J. F. J. Dippy and R. H. Lewis, *Rec. trav. chim.*, **56**, 1000 (1937).

[19] T. B. Johnson and W. W. Hodge, THIS JOURNAL, **35**, 1014 (1913); E. Clemmensen, *Ber.*, **47**, 681 (1914); J. v. Braun and K. Weissbach, *ibid.*, **62**, 2416 (1929); K. Funke and J. Ristie, *J. prakt. Chem.*, **146**, 151 (1936); C. D. Hurd and G. W. Fowler, THIS JOURNAL, **61**, 249 (1939); W. T. Smith, *ibid.*, **73**, 1883 (1951).

reduction[20] are of particular interest; the conversion of 3-keto-quinuclidine (XI) to quinuclidine (XII)[20], *without rearrangement*, supports the view that C–N bond scission results from *trans* elimination (see XIIIa and XIIIb). The ring contraction of methone (XIV) on Clemmensen reduction[21] may occur by way of an internal pinacol (XV), dehydration and reduction of which would produce XVII, one of the major products.

Experimental

Zinc amalgams were prepared throughout in the following way: The desired weight of zinc (Baker and Adamson, reagent, 20 mesh, granular) was placed in the reaction flask and covered with twice its weight of water. A volume of 37% hydrochloric acid equal to 5% of that of the water was added with vigorous swirling. After about one-half minute, the calculated amount of mercuric chloride was added in one portion and the flask was closed with a ground joint stopper and shaken vigorously; hydrogen evolution ceased almost at once. The mixture was shaken at 5-minute intervals over a half-hour period and the water was decanted. The amalgam was washed twice with water and then once with the reaction solvent and used at once.

Comparative Reductions of Aliphatic Alcohols and the Corresponding Carbonyl Compounds.[22]—A 5% amalgam was prepared from 78 g. (1.2 g. atoms) of zinc and 5.2 g. of mercuric chloride. To this was added 180 ml. of methanol, 120 ml. of 37% hydrochloric acid, 60 ml. of water and 0.15 mole of the alcohol or carbonyl compound. *n*-Heptyl alcohol was not wholly soluble in this reaction mixture, so an additional 50 ml. of methanol was added in reductions of *n*-heptyl alcohol and *n*-heptaldehyde.

The homogeneous reaction mixture was heated under reflux for four hours; volatile materials entrained by the hydrogen formed during the reaction were condensed in two Dry Ice–trichloroethylene traps. Only in the reduction of cyclopentanone did any appreciable amount of condensable material pass through the water-cooled condensers; the material in this case was caught wholly in the first of the two traps. It is of interest that the acidic solutions of the ketones rapidly turned a very deep clear cherry-red in color as the reaction mixture was warmed and that this color disappeared within about 45 minutes, leaving a wholly colorless solution.

At the end of the heating period the reaction mixture was cooled in ice and diluted with 200 ml. of water. If any hydrocarbon layer separated it was collected, washed with salt water, dried over magnesium sulfate and distilled separately through a narrow bore two-foot Vigreux column with a heated jacket and under a reflux ratio of about 16 to 1. Small fractions were taken and analyzed by refractive index assuming additive *volumes* in the case of mixtures of similar materials. In several cases it was found advantageous to use cumene (b.p. 150–152°) as a distillation "chaser."

The acidic mother liquor was neutralized with 40% sodium hydroxide, saturated with salt and steam-distilled. The distillate was distilled through a large unheated Vigreux column to remove the methanol. The pot residue was saturated with salt and distilled or extracted with ether to recover unreacted alcohol or carbonyl compound. The ether solution was dried over magnesium sulfate and distilled through the column used for the distillation of the hydrocarbons to remove all low-boiling constituents. The pot residue was then distilled at atmospheric pressure or, with the higher boiling materials, at 13 mm. and the product collected in a large number of fractions and analyzed by refractive index.

The presence of olefins in the hydrocarbon fractions was detected by washing each fraction with cold concentrated sulfuric acid and observing changes in volume and refractive index of the undissolved (if any) material. Chlorides were detected by means of the Beilstein test,[11] alcohols by reaction with permanganate or ceric nitrate[10] and carbonyl compounds by reaction with 2,4-dinitrophenylhydrazine.

Cyclopentanone[23a] (b.p. 127–128°, $n^{20}\mathrm{D}$ 1.4372, 12.6 g.) gave 4.1 g. (37%) of cyclopentane (b.p. 48–49°, $n^{20}\mathrm{D}$ 1.4068 (lit. b.p. 49.3°, $n^{20}\mathrm{D}$ 1.4068[24a]).

Cyclopentanol[25] (b.p. 136–136.5°, $n^{20}\mathrm{D}$ 1.4530, 12.8 g.) gave less than 0.2 g. of material boiling below 100°. Recovery of the alcohol was rather poor (6.9 g., 54%) due to its solubility characteristics.

Cyclohexanone (Eastman Kodak, redistilled, b.p. 152–158°, $n^{20}\mathrm{D}$ 1.4503, 14.7 g.) gave 7.2 g. of hydrocarbon boiling in ten fractions between 78 and 82°, $n^{20}\mathrm{D}$ 1.4269–1.4302 (after washing with sulfuric acid, $n^{20}\mathrm{D}$ 1.4265) corresponding to mixtures containing a total of 6.5 g. (51%) of cyclohexane (b.p. 80.7°, $n^{20}\mathrm{D}$ 1.4264[24b]) and 0.7 g. (6%) of cyclohexene (b.p. 83°, $n^{20}\mathrm{D}$ 1.4465[24c]).

Cyclohexanol (Eastman Kodak, redistilled, b.p. 155–156°, m.p. 23.5–24°, 14.9 g.) gave less than 0.2 g. of material boiling below 100° and 9.4 g. (62.6% recovery) of cyclohexanol (b.p. 154–157°, m.p. 23–24°).

***n*-Heptaldehyde** (Eastman Kodak, redistilled, b.p. 151–152°, $n^{20}\mathrm{D}$ 1.4131, 17.1 g.) gave 2.5 g. of material boiling, between 90 and 97°, $n^{20}\mathrm{D}$ 1.3898–1.3892. This corresponds to a mixture of 0.4 g. (2.7%) of 1-heptene (b.p. 93.1°, $n^{20}\mathrm{D}$ 1.3999[26a]) and 2.1 g. (14%) of *n*-heptane (b.p. 98.4°, $n^{20}\mathrm{D}$ 1.3877).[26b] In addition to 1.7 g. (10%) of *n*-heptaldehyde, there was obtained 7 g. of a much higher-boiling mixture (b.p. 125–140° (13 mm.)) containing some unidentified solid material.

***n*-Heptanol**[23b] (b.p. 174–176°, $n^{20}\mathrm{D}$ 1.4240, 17.4 g.) gave less than 0.1 g. of material boiling below 140°, but 13.7 g. (78.7%) of *n*-heptyl alcohol, b.p. 77–78.5° (13 mm.), $n^{20}\mathrm{D}$ 1.4243, was recovered.

2-Octanone (Paragon, redistilled, b.p. 171–172°, $n^{20}\mathrm{D}$ 1.4160, 19.2 g.) gave 8.0 g. of hydrocarbon, b.p. 119–123°, $n^{20}\mathrm{D}$ 1.4003 (ten fractions). This corresponds to a mixture of *n*-octane (b.p. 125.8°, $n^{20}\mathrm{D}$ 1.3976[26c]; 7.7 g., 45%) and probably 2-octene (b.p. 125, $n^{20}\mathrm{D}$ 1.4137[26d], 1.3 g., 7.5%). In addition, 3.9 g. (20%) of 2-octanone (b.p. 61–68° (13 mm.), $n^{20}\mathrm{D}$ 1.4160) was recovered for a material balance of 72.5%.

2-Octanol (Paragon, purified *via* its phthalate ester, b.p. 176–177°, $n^{20}\mathrm{D}$ 1.4265) gave 0.7 g. (4%) of a hydrocarbon (b.p. 118–123°, $n^{20}\mathrm{D}$ 1.4120–1.4130) which was wholly soluble in cold concentrated sulfuric acid and thus probably a mixture of 1-octene (b.p. 122.5°, $n^{20}\mathrm{D}$ 1.4103[26e]) and 2-octene (b.p. 125°, $n^{20}\mathrm{D}$ 1.4137[26d]). There was recovered, in addition, 15.9 g. (81.5%) of 2-octanol (b.p. 176–178°, $n^{20}\mathrm{D}$ 1.4263). This result is not noticeably changed by the use of 68.3 g. (1.05 g. atoms) of zinc, 20.4 g. (0.15 mole) of zinc chloride, 90 ml. (about 0.9 mole) of 37% hydrochloric acid, 90 ml. of water and 180 ml. methanol–a mixture corresponding to that which would be formed if all of the ketone were reduced first to the alcohol. Runs in which 3–30% of ketone were present always gave considerably less *n*-octane than would be expected from the amount of *ketone* used.

Comparative Reductions of Chlorides and Ketones.—A 5% amalgam was prepared from 52 g. (0.8 atom) of zinc and covered with 480 ml. of acetic acid. To this was added 0.2 mole of the ketone or chloride and 160 ml. of 37% hydrochloric acid. The mixture was heated under reflux for four hours. Two Dry Ice traps were used to condense entrained hydrocarbons. The reaction mixture was decanted from the zinc, diluted with water and steam distilled. The distillate was neutralized with sodium bicarbonate solution, saturated with salt and extracted with ether. The ether extract was dried over magnesium sulfate and distilled, the fractions being analyzed by refractive index as before. Traces of esters were found[12] in the high-boiling fractions in most instances.

---

(20) (a) V. Prelog and R. Seiwerth, *Ber.*, **72**, 1103, 1638 (1939); (b) G. R. Clemo and co-workers, *J. Chem. Soc.*, 1989 (1937); 2095 (1949); *Chemistry and Industry*, 856 (1949); (c) N. J. Leonard and co-workers, THIS JOURNAL, **71**, 3089, 3094, 3098, 3100 (1949); **72**, 3632, 4931 (1950); **73**, 5210 (1951); **74**, 1704, 2871, 4620 (1952); **75**, 1674 (1953). The gross outline of this mechanism is due to Prelog and Clemo.

(21) A. W. Day and R. P. Linstead, *J. Chem. Soc.*, 1063 (1935).

(22) All experimental boiling points uncorrected. All melting points corrected.

(23) (a) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 192; (b) p. 304; (c) p. 189.

(24) (a) G. Egloff, "Physical Constants of Hydrocarbons," Vol. II, Reinhold Publishing Corp., New York, N. Y., 1939, p. 54; (b) p. 78; (c) p. 324.

(25) C. R. Noller and R. Adams, THIS JOURNAL, **48**, 1084 (1926).

(26) (a) Ref. 24, Vol. I, p. 200; (b) *ibid.*, p. 40; (c) p. 49; (d) p. 215; (e) p. 214; (f) p. 38; (g) p. 196.

Cyclohexanone (19.6 g.) yielded 4.5 g. (27.9%) of cyclohexane, b.p. 77–80°, $n^{20}\mathrm{D}$ 1.4265.[24b]

Cyclohexyl chloride[23c] (b.p. 136–138°, $n^{20}\mathrm{D}$ 1.4619) yielded less than 0.2 g. of material boiling at 70–120°, but 19.5 g. (82%) of cyclohexyl chloride, b.p. 135–138°, $n^{20}\mathrm{D}$ 1.4620, was recovered. Reductions in which zinc chloride was present at the start gave similar results. Reduction with 5–20% of cyclohexanone present gave only small amounts of cyclohexane containing olefinic material.

2-Octanone (19.4 g., 0.15 mole) was heated for four hours in a mixture of 640 ml. of acetic acid and 160 ml. of 37% hydrochloric acid with a 5% amalgam made from 78 g. (1.2 g. atoms) of zinc. The mixture was worked up in the same way as the mixtures from the reduction of cyclohexanone. There was thus obtained 10.6 g. (62%) of *n*-octane (b.p. 118–122°, $n^{20}\mathrm{D}$ 1.3976) and 4 g. (21%) of 2-octanone (b.p. 170–175°, $n^{20}\mathrm{D}$ 1.4160).

2-Octyl chloride,[6] b.p. 171–173°, $n^{20}\mathrm{D}$ 1.4267, gave, under the same conditions, about 1 g. (nine fractions) of unsaturated hydrocarbon, b.p. 116–125°, $n^{20}\mathrm{D}$ 1.4081–1.4139, probably a mixture of octenes. The higher-boiling product, b.p. 165–173°, 72–85° (13 mm.) (eight fractions), $n^{20}\mathrm{D}$ 1.4248–1.4160, appeared to be a mixture of 8.6 g. (38%) of 2-octyl chloride and 7.9 g. (31%) of 2-octyl acetate, $n^{20}\mathrm{D}$ 1.4141.[27]

Competitive Reduction of Cyclopentanone and Cyclohexanone.—A 5% amalgam of zinc was prepared from 130 g. (2.0 g. atoms) of zinc. A freshly prepared homogeneous solution of 42.0 g. (0.5 mole) of cyclopentanone and 49.1 g. (0.5 mole) of cyclohexanone in a mixture of 600 ml. of water and 600 ml. of 37% hydrochloric acid was added to the zinc amalgam as quickly as possible. The mixture was heated strongly with an electric mantle until refluxing started and then heated under moderate reflux for 45 minutes (I) or one hour (II). Two Dry Ice traps were attached to the condenser during the heating period. The solution turned first a clear yellow in color, then cloudy brown; after about one-half hour a bright yellow volatile organic layer separated from the almost colorless solution. At the end of the heating period the solution was cooled in an ice-salt mixture, the condenser and traps being left attached to the flask.

The organic layer, which contained a suspended white solid, was separated from the aqueous layer by means of a chilled separatory funnel. The small amount of liquid in the first of the Dry Ice traps was added to this material. The traps, condenser, flask, unreacted zinc amalgam and separatory funnel (but not the solution) were washed serially with two 20-ml. portions of cumene (b.p. 150–152°). The cumene rinse was added to the organic layer and the combined material (fraction A) was dried over magnesium sulfate.

Immediately after separation of the two layers of the reaction mixture the aqueous layer was chilled strongly in ice-salt. After fraction A had been set aside to dry, the aqueous layer was neutralized to litmus with about 400 ml. of ice-cold 40% sodium hydroxide solution. The warm solution was saturated with salt and cooled to 10°; it was then extracted with three 100-ml. portions of ether. The combined ether extract was washed with 50 ml. of ice-water, which was added to the aqueous layer and dried quickly over magnesium sulfate. The ether was stripped off by distillation through an unheated three-foot Vigreux column under a reflux ratio of about twenty-to-one. The aqueous layer was rapidly steam distilled until the distillation temperature was 101°, using flame heating toward the end of the distillation. The distillate (about 400 ml.) was saturated with salt and extracted with the recovered ether in three portions. The combined ether extract was dried and distilled as before; the aqueous solution was steam distilled as before. The distillate (100 ml.) was saturated with salt and extracted with the recovered ether; the ether extract was distilled as before. The residues of the ether distillations were combined (fraction B).

In the first runs made, fraction A was analyzed by distillation through a narrow two-foot heated Vigreux column under a reflux ratio of about sixteen-to-one. The product boiling below 140° was collected in 10 to 20 fractions. The fractions boiling between 48° and 80° were found to be free of olefins and were analyzed by refractive index as ideal mixtures of cyclopentane (b.p. 49.3°, $n^{20}\mathrm{D}$ 1.4068, d^{20}_4 0.746[24a]) and cyclohexane (b.p. 80.7°, $n^{20}\mathrm{D}$ 1.4265, d^{20}_4 0.778[24b]). The higher boiling fractions gave negative tests for halides, alcohols and ketones and were therefore analyzed as mixtures of cyclohexane and cumene ($n^{20}\mathrm{D}$ 1.4915, d^{20}_4 0.8623[28]). Results obtained in this way did not differ significantly from those obtained later by distillation of fraction A through a miniature Podbielniak Heli-Grid high temperature distillation apparatus rated at about seventy theoretical plates.

The still-pot residue was distilled under vacuum to remove cumene (b.p. 45° (15 mm.)). The clear yellow residual oil (2–5 g.) was transferred while hot to a flask where it partially crystallized. The still-pot was rinsed with petroleum ether which was added to the semisolid residue, causing further separation of white solid. This solid has been found, by chromatography on alumina, to contain at least four different materials which have not as yet been fully characterized.

Fraction B was analyzed by distillation through a narrow-bore two-foot heated Vigreux column under a reflux ratio of sixteen-to-one. The material boiling at 125–152° was collected in five to ten fractions; it was found to be free of halides (Beilstein test).[11] The higher boiling fractions gave increasingly strong ceric nitrate tests (for alcohols).[10] The highest boiling fraction, b.p. 150–152°, appeared to be a mixture of cyclohexanone (b.p. 152–153°) and cyclohexanol (b.p. 155–156°) which could not be separated by the still used, though separable from cyclopentanone. In several runs, very small fractions were collected in the range 150–152°; they showed no change in refractive index. These fractions were analyzed by refractive index by comparison with synthetic mixtures and found to contain 5–10% of the alcohol. The lower boiling fractions were analyzed as mixtures of cyclopentanone, and the cyclohexanone–cyclohexanol mixture by refractive index, using synthetic mixtures. A typical analysis is shown in Table II. The residue from the distillation of fraction B was distilled in a small flask under reduced pressure. The first high-boiling fraction (*cf.*, *e.g.*, B14) probably contains bimolecular condensation products, such as 2-cyclohexenylcyclohexanone (b.p. 136–138° (10 mm.))[29] (compare B14 in Table II), and their reduction products, such as 2-cyclohexylcyclohexanone (b.p. 137° (13 mm.)[30]), the corresponding cyclopentanone derivatives and the products of mixed condensations. The next fraction may contain trimolecular derivatives. These complex mixtures were not investigated in detail.

TABLE II

DISTILLATION OF FRACTION IIB

No.	Temp., °C	Press.	Wt., g.	$n^{0}\mathrm{D}$	Weight C_5H_8O	Weight $C_6H_{10}O$–$C_6H_{12}O$
B6	125–128	Atm.	12.53	1.4373	12.44	0.09
B7	128–131	Atm.	7.84	1.4390	6.85	0.99
B8	131–136	Atm.	5.49	1.4412	4.03	1.46
B9	136–141	Atm.	3.21	1.4445	1.61	1.60
B10	141–146	Atm.	3.18	1.4480	0.86	2.32
B11	146–149	Atm.	4.12	1.4510	0.14	3.98
B12	149–152	Atm.	0.86	1.4520	...	0.86
B13	150–152	Atm.	0.95	1.4520	...	0.95
B14	130–140	13 mm.	1.48			
B15	170–172	1 + 2 mm.	1.96			
B16	Residue		1.50			
				Total	25.93	12.25
				Yield, %	63.2	24.9

The forerun of the distillation of fraction B contained some ether and gave a strong ketone test. This material was dissolved in alcohol and treated with a solution prepared by dissolving 20 g. of 2,4-dinitrophenylhydrazine in 100 ml. of concentrated sulfuric acid and diluting successively with 150 ml. of water and 250 ml. of ethanol. The mixture was heated and the crystals were collected by filtration of the hot solution. In this way 2–3 g. of the 2,4-dinitrophenylhydrazone of cyclopentanone (m.p. 143.5–144.0°, lit.[31] m.p. 144–145°) could be obtained. A further crop of 2–3 g. of less pure derivative (m.p. 135–138°) could be obtained

---

[27] R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **105**, 830 (1914).

[28] Reference 24, Vol. III, p. 81.

[29] G. A. R. Kon and J. H. Nutland, *J. Chem. Soc.*, 3101 (1926).

[30] J. V. Braun and H. Ritler, *Ber.*, **55**, 3792 (1922).

[31] J. D. Roberts and C. Greene, THIS JOURNAL, **68**, 214 (1946).

from the cooled filtrate. A single recrystallization from ethanol raised the melting point to 143.5–144.0°. The weight of derivative so obtained generally corresponded to an additional 3–5% recovery of cyclopentanone. A summary of two experiments carried out in this way is found in Table I.

W. LAFAYETTE, INDIANA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

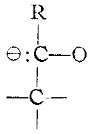
Reductions at Metal Surfaces. III. Clemmensen Reduction of Some Sterically-hindered Ketones

BY JAMES H. BREWSTER, JOAN PATTERSON AND DELMER A. FIDLER

RECEIVED OCTOBER 30, 1953

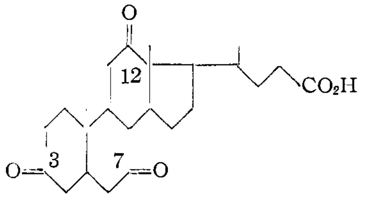
Pinacolone is reduced slowly and with difficulty to neohexane; tetramethylethylene could not be detected in the reaction product. Under the same conditions pinacolyl alcohol is converted to tetramethylethylene. Nearly equivalent amounts of neopentylbenzene and 2-methyl-3-phenyl-2-butene are formed in the reduction of pivalophenone; no 2-methyl-3-phenylbutane is produced under these conditions. Phenyl-*t*-butylcarbinol also forms neopentylbenzene and 2-methyl-3-phenyl-2-butene; in this case the latter predominates. The olefin is not reduced under these conditions. Benzopinacolone is reduced to tetraphenylethylene; no *unsym*-tetraphenylethane could be detected in the product. These results lend support to some of the conclusions of parts I and II. They also indicate that a phenyl ketone can be reduced by way of the corresponding alcohol, without intervention of the chloride or of a carbonium ion.

Reductions of carbonyl compounds by means of active metals appear to involve coördination of a metal surface with the carbonyl group to form I in neutral or alkaline medium or II in acidic medium.[1] In the presence of proton donors I reacts to form an alcohol; II can react to form a pinacol or be reduced to a hydrocarbon, as in the Clemmensen reduction.[2] Hindrance to the formation of II should make normal Clemmensen reduction difficult and might permit other reactions, involving alcohols as intermediates, to become important.

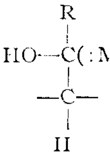


$$\ominus{:}\overset{\displaystyle R}{\underset{\displaystyle -\overset{|}{\underset{|}{C}}-}{C}}{-}O(:M)_x^{\oplus}$$

I

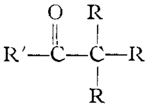


IV



$$HO{-}\overset{\displaystyle R}{\underset{\displaystyle -\overset{|}{\underset{|}{C}}-}{C}}(:M)_x^{\oplus}$$

II



$$R'{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}\overset{\displaystyle R}{\underset{\displaystyle R}{C}}{-}R$$

IIIa, $R' = R = -CH_3$
b, $R' = R = -C_6H_5$
c, $R' = -C_6H_5$; $R = -CH_3$

Substituents *alpha* to the carbonyl group should hinder the formation of II. It is reported, without details, that pinacolone (IIIa) is reduced to only a small extent under "Clemmensen conditions."[3] The carbonyl group at the 3-position of dehydrocholic acid (IV) is reduced more easily than are the keto groups at the more highly hindered 7- and 12-positions.[4] In the present work, the reduction of pinacolone with excess 10% zinc amalgam in aqueous hydrochloric acid was found, qualitatively, to be much more difficult than the reduction of unbranched aliphatic ketones.[2] Neohexane (usually about 14%) was the only hydrocarbon product formed at the end of eight hours[5]; about 50% of the starting ketone usually was recovered. The nature of the zinc, the extent of amalgamation and the presence of impurities in the acid had no effect on these results. Pinacolyl alcohol was not reduced under these conditions but was dehydrated to tetramethylethylene. These findings constitute further evidence that neither the alcohol nor the chloride derived from it are intermediates in Clemmensen reductions in the aliphatic series[2]; in this case, at least, the chloride would have had a rearranged carbon skeleton. The absence of olefin in the reaction product is evidence that the formation of an alcohol from IIIa is difficult under these conditions.

Competition between reactions proceeding through intermediates I and II would be expected to be more pronounced in the series of aryl ketones. Here, the positive charge of the protonated ketone V is delocalized and the resonance of V would be diminished in the formation of II. On the other hand, the unprotonated ketone should form an intermediate such as I more readily since the carbanionic structure VI can be stabilized by resonance. In accord with these conclusions, Clemmensen found that under some conditions (see below) styrene, rather than ethylbenzene, was the chief reduction product of acetophenone.[6] In the case of benzopinacolone (IIIb), the rearranged olefin, tetraphenylethylene, is the only hydrocarbon product formed.[7]

---

(1) Part I, THIS JOURNAL, **76**, 6361 (1954).

(2) Part II, *ibid.*, **76**, 6364 (1954).

(3) J. P. Wibaut, H. Hoog, S. L. Langendijk, J. Overhoff and J. Smittenberg, *Rec. trav. chim.*, **58**, 329 (1939).

(4) (a) W. Borsche, *Ber.*, **52**, 1353 (1919); (b) H. Wieland and O. Schlichting, *Z. physiol. Chem.*, **150**, 267 (1925).

(5) It was originally reported, J. H. Brewster, XIIth Congress of Pure and Applied Chemistry, New York, N. Y., Sept., 1951, that tetramethylethylene was formed as a by-product in this reduction. The pinacolone used in this work was a *redistilled* commercial sample; when this sample was further purified by *rectification* it gave no olefin in numerous attempts to repeat the earlier work. Pinacolone prepared by rearrangement of pinacol hydrate likewise gave no olefin. It has, unfortunately, proved impossible to check the hypothesis that the original sample of ketone contained some pinacolyl alcohol.

(6) E. Clemmensen, *Ber.*, **46**, 1837 (1913).

(7) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923). We have confirmed this finding; the infrared spectrum of the product contained none of the characteristic peaks of an authentic sample of *unsym*-tetraphenylethane.