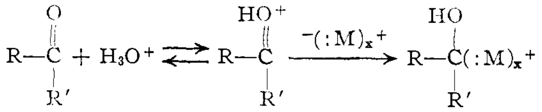
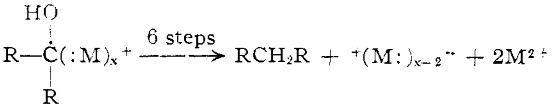
assumes the bond formation between carbon and *massive* metal



$$R{-}\overset{\overset{O}{\|}}{\underset{\underset{R'}{|}}{C}} + H_3O^+ \rightleftarrows R{-}\overset{\overset{HO^+}{\|}}{\underset{\underset{R'}{|}}{C}} \xrightarrow{^-(:M)_x{}^+} R{-}\overset{\overset{HO}{|}}{\underset{\underset{R'}{|}}{C}}(:M)_x{}^+$$

Electrons are transferred to carbon through this bond with dissolution of metal ion from the *massive* metal into the solution



$$R{-}\overset{\overset{HO}{|}}{\underset{\underset{R}{|}}{\dot{C}}}(:M)_x{}^+ \xrightarrow{\text{6 steps}} RCH_2R + {}^+(M:)_{x-2}{}^{-} + 2M^{2+}$$

This mechanism has many features in common with the concept of the free-electron model of the metal and hence with the electrochemical mechanism of the reduction. As explained above, this theory cannot readily account for the fact that the first step of Clemmensen reduction involves two-electron reduction with exclusion of one-electron reduction. The author's hypothesis involves the reaction of carbonyl compound with *zinc atom* as the essential step of Clemmensen reduction: this theory accounts for the fact that electrons are transferred *in pairs* from metal to carbonyl compound

$$RR'CO \xrightarrow{2e^-} \text{carbonium ion} \xrightarrow{2e^-} RCH_2R'$$

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# Studies on the Mechanism of Clemmensen Reduction. II. Evidence for the Formation of an Intermediate Carbonium Ion

BY TADAAKI NAKABAYASHI*

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The initial stages of Clemmensen reductions of acetophenone and *t*-butyl phenyl ketone were studied at 60°. The saturated and the unsaturated (and, in the case of *t*-butyl phenyl ketone, rearranged) hydrocarbons are formed from these ketones directly, not by way of the corresponding alcohols. This result suggests that a carbonium ion is the intermediate in Clemmensen reduction.

It has often been stated that in Clemmensen reduction the carbonyl compound is reduced to hydrocarbon by way of the corresponding alcohol. Steinkopf and Wolfram[1] found benzyl alcohol in the reduction product of benzaldehyde and regarded this alcohol as an intermediate of the reduction. They also detected styrene, di-, tri- and polystyrene in the reduction product of acetophenone and considered them to be products of dehydration of the intermediate 1-phenylethanol. Phenylglyoxalic acid gives mandelic acid instead of phenylacetic acid. Martin[2] showed that benzyl alcohol and benzyl chloride give toluene under "Clemmensen's conditions" and concluded that the alcohol and the chloride are intermediates in this reaction. Recently Brewster and co-workers[3] stated that alcohol is an important intermediate in the reduction of aromatic carbonyl compound or sterically hindered ketone but is not in the reduction of aliphatic compounds.

These authors, however, did not prove the intermediacy of alcohol kinetically and, in some cases, did not even prove the formation of the alcohol in the course of Clemmensen reduction. Sometimes the formation of unsaturated product was regarded as evidence for the formation of alcohol. To ascertain the nature of the intermediates of this reaction the author studied the early stages of the reductions of some aromatic ketones under mild conditions avoiding any secondary changes of the reaction products.

## Experimental

**Materials.**—Acetophenone of reagent grade was rectified under reduced pressure and the distillate was purified by crystallization; m.p. 18.5–19.5°. It was distilled just before use. 1-Phenylethanol was prepared by Meerwein–Ponndorf reduction of acetophenone; b.p. 102–103° (20 mm.). *t*-Butyl phenyl ketone was prepared from *t*-butylmagnesium chloride and benzonitrile[4]; b.p. 66–68° (2 mm.). *t*-Butylphenylcarbinol was prepared from *t*-butylmagnesium chloride and benzaldehyde[5]; b.p. 74–75° (2 mm.). The phenylurethan of this alcohol was prepared in the following way. *t*-Butylphenylcarbinol was mixed with an equal volume of phenyl isocyanate and kept for 3 days at room temperature. The unreacted substances were removed by heating the product at 100° under 2 mm. pressure. The residual matter was dissolved in benzene, filtered, petroleum benzine was added to the filtrate, the precipitated crystals were collected, dissolved in benzene and precipitated with petroleum benzine. This process was repeated three times. The white crystals obtained in this way melted at 105.0–105.8°. 2-Methyl-3-phenyl-2-butene was prepared by dehydration of *t*-butylphenylcarbinol with sodium hydrogen sulfate; b.p. 73° (11mm.). Its infrared absorption spectrum[6] had peaks 7.26, 8.28, 8.83, 9.33, 9.74, 10.99, 11.21, 13.07, 14.22$\mu$. These peaks agreed with those reported by Brewster[3] except that at 11.21$\mu$. An additional peak at 7.75$\mu$ was reported by him. Neopentylbenzene was prepared from benzylmagnesium chloride and *t*-butyl bromide[7]; b.p. 82° (30mm.). Its infrared absorption spectrum had the following important peaks which agreed with those reported by Brewster[3]: 7.20, 7.31, 8.06, 8.31, 8.72, 9.27, 9.69, 11.14, 12.98, 13.93, 14.22$\mu$. Hydrochloric acid of G.

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(1) W. Steinkopf and A. Wolfram, *Ann.*, **430**, 113 (1923).

(2) E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

(3) J. H. Brewster and others, *ibid.*, **76**, 6368 (1954).

(4) A. Willemart, *Bull. soc. chim.*, [5] **2**, 867 (1935).

(5) G. Tsatsas, *Ann. chim.*, **1**, 342 (1946).

(6) The infrared spectra were recorded by A. Matsuda of Kyushu University with a Perkin-Elmer 112 infrared spectrophotometer.

(7) A. Bygden, *Ber.*, **45**, 479 (1912).

R. grade was distilled and diluted with redistilled water; 0.01% polyvinyl alcohol was added to it. Mercury was washed with dilute nitric acid and twice distilled; 2% zinc amalgam was prepared by dissolving granular zinc of analytical grade in it.

**Clemmensen Reduction of Acetophenone.**—A mixture of 50 ml. of 2.14 *N* hydrochloric acid, 10 ml. of 95% ethanol and 5 ml. (5.15 g.) of acetophenone was treated under hydrogen at 60° (thermostat) with 30 ml. of zinc amalgam (2% zinc) under vigorous stirring. Owing to the heat of reaction, the temperature of the mixture rose 1° higher than that of the thermostat. After 5 min., the upper layer was separated from the zinc amalgam, cooled immediately with water and neutralized with sodium hydroxide solution. The reaction products of six experiments were combined and extracted with ether. The ethereal solution was washed with water, dried with anhydrous sodium sulfate and concentrated. The residue was fractionated with a 15-cm. column into several fractions (30.9 g. of acetophenone was used in all):

| Fraction | B.p. °C. | B.p. Mm. | Yield, g. |
|---|---|---|---|
| a | 59–70 | 59 | 7.0 |
| b | 86–88 | 16 | 12.5 |
| c | 125–134 | 3 | 0.3 |
| d | 135–180 | 3 | 5.0 |
| e | Residue | | 0.8 |
| | | Total | 25.6 |

No halogen was detected in these fractions by Beilstein's method.

They were treated as follows.

Fraction a, colorless liquid. The styrene in this fraction was converted into dibromide by adding bromine in carbon tetrachloride under ice cooling, and the product was distilled; 0.4 g. of oil boiling near 135° was obtained. This was supposed to be ethylbenzene (b.p. 136°). Styrene dibromide melting at 73.0–74.5° was obtained by recrystallizing the residue from ethanol. Styrene also was identified by converting it into β-styrenephosphonic acid[8] by the action of phosphorus pentachloride at room temperature followed by hydrolysis. This fraction was shown to contain 68.2% of styrene by the KBr-KBrO$_3$ method[9] or 69.2% of styrene and 30.8% of ethylbenzene by means of gas chromatography.

Fraction b, colorless liquid, solidified on cooling and melted at 15–18°. By gravimetric analysis with 2,4-dinitrophenylhydrazine,[10] the acetophenone content was found to be 93.4%. Since the b.p. of 1-phenylethanol, which is expected from this reaction, is close to that of acetophenone, detection of 1-phenylethanol was attempted. The sample was refluxed with 1 g. of 3,5-dinitrobenzoyl chloride, 10 ml. of dry pyridine and 10 ml. of dry benzene for 1 hr. The intensely colored mixture was cooled, washed with dilute hydrochloric acid, then with sodium carbonate solution and finally with saturated sodium chloride solution. Some precipitate in the solution was filtered off and the solvent and acetophenone were removed. The dark resinous residue (0.5 g.) was purified by means of adsorption chromatography (column: SiO$_2$, 1 × 27 cm.; solvent benzene); 160 mg. of yellow sticky matter (it deposited some white crystals) and 100 mg. of crystals melting at 83–87°[11] were obtained. Because of the presence of sticky contaminant, further purification and exact m.p. determination of the crystals could not be accomplished However, the crystals were identified with 1-phenylethyl 3,5-dinitrobenzoate by means of paper chromatography (filter paper: No. 50 of Toyo Filter Paper Co.; solvent: *n*-hexane–acetone, 10:1); $R_f$ 0.81 at 12° in good agreement with that of an authentic sample of 1-phenylethyl 3,5-dinitrobenzoate (0.81). The existence of a small amount of 1-phenylethanol in this fraction was thus proved.

Fraction c, light yellow and viscous oil, on analysis gave 84.4% C, 7.68% H, corresponding to the formula $C_{16}H_{17 \cdot 4}O_{1 \cdot 24}$. This was supposed to be a mixture of acetophenone pinacol and pinacone. It gave no derivative when treated with hydroxylammonium chloride and sodium hydroxide. When the sample was oximated after being warmed with concentrated hydrochloric acid, white crystals melting at 147–150° were obtained, identified with the oxime of acetophenone pinacone[12] by mixed melting.

Fraction d, a light yellow and viscous oil, after one or two days deposited white crystals and formed a plastic mass. This fraction was dissolved in a small amount of benzene, petroleum benzine was added to it and the solution was cooled in ice. White crystals melting at 84–100° were obtained. The mother liquor was analyzed after removal of the solvent. Its composition was 82.4% C, 7.49% H, corresponding to the formula $C_{16}H_{17 \cdot 4}O_{1 \cdot 48}$, and hence it was supposed to be a mixture of acetophenone pinacol and pinacone. The solid was identified as acetophenone pinacol by warming it with concentrated hydrochloric acid and oximation. A benzene solution of the solid, when mixed with phenyl isocyanate, gave pinacone and *sym*-diphenylurea in accordance with the equation

$$\text{PhMeCOHCOHPhMe} + 2\ \text{PhNCO} \longrightarrow \text{Ph}_2\text{MeCCOMe} + (\text{PhNH})_2\text{CO} + \text{CO}_2$$

From these results, this fraction appeared to be composed of acetophenone pinacol and a small amount of pinacone.

Fraction c, a reddish-brown, transparent and brittle solid, was soluble in ethanol, acetic acid and benzene. Analysis of carbon and hydrogen gave 83.0% C, 7.49% H, corresponding to the formula $C_{16}H_{17 \cdot 2}O_{1 \cdot 36}$. It reacted with 0.380 equivalent of lead tetraacetate per C$_{16}$-unit. It also reacted with bromine but the bromine consumed could not be determined accurately. From the analytical data, this fraction was supposed to be a one-electron reduction product of acetophenone closely allied to acetophenone pinacol and pinacone.

**Reduction of 1-Phenylethanol with Zinc Amalgam and Hydrochloric Acid.**—The method was similar to that employed in the Clemmensen reduction of acetophenone; dissolved zinc and evolved hydrogen were measured. Initial concentrations were: 2.00 *N* hydrochloric acid, 2.03% zinc amalgam, 0.02 mole/l. 1-phenylethanol, temperature 60°. After 1 or 2 hours the amount of evolved hydrogen was equivalent to that of dissolved zinc, showing that 1-phenylethanol is not reduced under these conditions.

**Dehydration of 1-Phenylethanol.**—1-Phenylethanol solution (10 ml., 0.12 *M*) in 95% ethanol was mixed with 50 ml. of 2.12 *N* hydrochloric acid and the mixture was kept at 60° for 5 min. No styrene was found in the product by the KBr-KBrO$_3$ method.[9]

**Reaction of Styrene with Zinc Amalgam.**—A 0.02 *M* solution of styrene in 1.81 *N* hydrochloric acid (solvent: 13.3% aqueous ethanol) was shaken with 2% zinc amalgam in a hydrogen atmosphere at 60°. Evolved hydrogen and dissolved zinc were determined. After 30 min. of the reaction, styrene was not reduced at all.

**Clemmensen Reduction of *t*-Butyl Phenyl Ketone.**—The procedure was similar to that employed in the reduction of acetophenone. A mixture of 50 ml. of 2.02 *N* hydrochloric acid, 10 ml. of 95.6% ethanol, 5 ml. of *t*-butyl phenyl ketone and 30 ml. of 2% zinc amalgam at 60° was stirred for 15 min. under a gentle stream of nitrogen. The products of the six experiments were combined and treated as before. The following 3 fractions were obtained: fraction a, b.p. 66–76° (9 mm.), 4.5 g.; fraction b, b.p. 76–80° (4 mm.), 17.2 g.; fraction c, residue, 1.1 g.

These fractions were treated as follows: to fraction a, a colorless liquid, bromine in carbon tetrachloride was added under ice cooling and the product was distilled. No fraction corresponding to neopentylbenzene was obtained. The resulting dibromide was dissolved in acetic acid and the unsaturated hydrocarbon was regenerated by treating the dibromide with zinc dust; yield 2 g. It was oxidized at room temperature with a mixture of 3 g. of potassium bichromate, 10 ml. of concentrated sulfuric acid and 10 ml. of water. The resulting acetophenone was identified by converting it into the 2,4-dinitrophenylhydrazone. The existence of 2-methyl-3-phenyl-2-butene was thus confirmed. The content of this hydrocarbon determined by KBr-KBrO$_3$ method[9] with acetic acid as solvent was 93.5%. Constituents other than the alkene may be saturated hydrocarbon, *i.e.*, neopentylbenzene and/or 2-methyl-3-phenylbutane.

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(8) E. Bergmann and A. Bondi, *Ber.*, **63**, 1158 (1930).

(9) H. L. Johnson and R. A. Clark, *Anal. Chem.*, **19**, 869 (1947).

(10) H. A. Iddles and other workers, *Ind. Eng. Chem., Anal. Ed.*, **11**, 102 (1939).

(11) Reported 94–95°; R. E. Buckles and J. E. Maurer, *J. Org. Chem.*, **18**, 1585 (1953).

(12) M. p. of the oxime reported 151.5°; K. Shishido, H. Nozaki and O. Kurihara, THIS JOURNAL, **72**, 2270 (1950).

The infrared absorption spectrum of this fraction had the following important peaks: 7.26, *8.07*, 8.28, 8.83, 9.32, 9.74, *10.42*, 10.99, 13.07, *13.91*, 14.24$\mu$. Peaks other than the italicized ones agreed with those of 2-methyl-3-phenyl-2-butene. 2-Methyl-3-phenyl-2-butene prepared by the author had an additional peak at 11.21$\mu$, but this peak was not present in those reported by Brewster[3] and hence may be ascribable to a contaminant. Since the peaks at 8.07 and 13.91$\mu$ agreed with strong ones of neopentylbenzene, the main constituent of the saturated hydrocarbon may be neopentylbenzene. The small peak at 10.42$\mu$ may be assigned to *t*-butyl phenyl ketone (10.47$\mu$).[3] No peak corresponding to 2-methyl-3-phenylbutane[3] was present.

Fraction b, a colorless liquid, was composed mainly of *t*-butyl phenyl ketone, whose content was known to be 93.0% by gravimetric analysis with 2,4-dinitrophenylhydrazine.[10] This fraction was mixed with an equal volume of phenyl isocyanate and kept for one week at room temperature. The white crystals thus formed were collected and washed with benzene. The filtrate and benzene washing were combined, benzene and unreacted substances were removed by distillation and the residue was extracted with benzene. The benzene solution was concentrated, petroleum benzine was added to the concentrate and the mixture was cooled in ice to yield 0.5 g. of crystals melting at 100–102°. The melting point was 102.4–104° after recrystallization from a mixture of benzene and petroleum benzine. They were identified with the phenylurethan of *t*-butylphenylcarbinol by mixed melting. This fraction was thus shown to be composed mainly of unreacted *t*-butyl phenyl ketone and contain a small amount of *t*-butylphenylcarbinol.

Fraction c contained white needles, which were isolated using benzene and petroleum benzine as solvent; m.p. 176–177°. They may be the pinacol of *t*-butyl phenyl ketone.

*Anal.* Found: C, 80.82; H, 9.49. Calcd. for $(C_4H_9\text{-}COHC_6H_5)_2$: C, 81.0; H, 9.28.

**Reduction and Dehydration of *t*-Butylphenylcarbinol.**—By methods similar to those applied in the case of 1-phenylethanol, *t*-butylphenylcarbinol was shown not to be reduced or dehydrated under the condition of the reduction of *t*-butyl phenyl ketone.

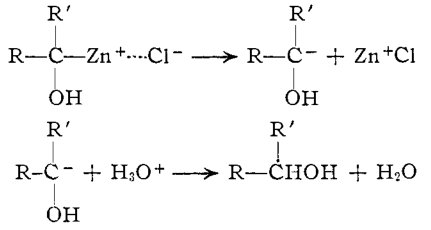
## Discussion

The Clemmensen reduction of acetophenone gives ethylbenzene, styrene and acetophenone pinacol as major products and 1-phenylethanol and acetophenone pinacone as minor products. Reduction and dehydration of 1-phenylethanol and reduction of styrene do not take place under the conditions used. It is evident that styrene and ethylbenzene are formed directly from acetophenone, not by way of a stable intermediate such as 1-phenylethanol or styrene. The same is true in the reduction of *t*-butyl phenyl ketone; neopentylbenzene and 2-methyl-3-phenyl-2-butene are formed directly from the ketone, not by way of the corresponding alcohol, *t*-butylphenylcarbinol. These results suggest that the intermediate in Clemmensen reduction is a carbonium ion which gives hydrocarbon on reduction or gives unsaturated or rearranged product without further reduction. This hypothesis is consistent with the conclusions of a kinetic study that the first step of this reaction is a formation of a complex composed of carbonyl compound, zinc atom and chloride ion leading to two-electron reduction of carbonyl compound.

An alternative point of view of the rearrangement is that a radical $R_3C\dot{C}HR'$ is formed, rearranges and undergoes disproportionation

$$R_3C\dot{C}HR' \longrightarrow R_2\dot{C}CHRR' \xrightarrow{\text{disproportionation}} R_2C{=}CRR'$$

This view cannot be supported for the following reasons: First, 2-methyl-3-phenylbutane was not detected in the reduction product of *t*-butyl phenyl ketone. Second, dimers of these radicals were not found in the reductions of acetophenone and *t*-butyl phenyl ketone. Third, since, as will be reported in part III, the formation of pinacol—which may be a result of dimerization of the radical $R\dot{C}OHR'$—is a different reaction from Clemmensen reduction, a stepwise reduction of radical type can hardly be considered. The small amounts of alcohol found in the reduction product of acetophenone and *t*-butyl phenyl ketone may be formed by



$$R\text{—}\underset{OH}{\overset{R'}{C}}\text{—}Zn^{+}\cdots Cl^{-} \longrightarrow R\text{—}\underset{OH}{\overset{R'}{C}}{}^{-} + Zn^{+}Cl$$

$$R\text{-}\underset{OH}{\overset{R'}{C}}{}^{-} + H_3O^{+} \longrightarrow R\text{—}\overset{R'}{C}HOH + H_2O$$

In some cases alcohol gives hydrocarbon under "Clemmensen's conditions," but, as the author's work indicates, this reaction forms a very minor part of Clemmensen reduction.

**Acknowledgment.**—The author is indebted to Dr. A. Matsuda, Kyushu University, for the infrared spectra.