

## CATALYTIC ACTION OF REDUCED COPPER ON PINACONES.

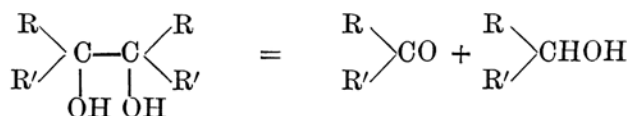
By Shozo YAMAGUCHI.

Received February 3, 1926. Published April 28, 1926.

In the recent articles<sup>(1)</sup> on the catalytic action of reduced copper on oximes, it was already stated by the present writer that reduced copper heated at 200° acts on the oximes to promote, on the one hand, reduction like reduced nickel, and on the other, Beckmann's rearrangement, and the latter action was noticed to be similar to that of dilute sulphuric acid on oximes.

Hence, it may naturally be anticipated that the reduced copper is also capable, under certain conditions, of exercising a catalytic influence on the transformation of pinacones into pinacolines, which was actually observed by many investigators in the case of the action of dilute sulphuric acid on pinacones.

According to W. Thorner and Th. Zincke<sup>(2)</sup>, the pinacones derived from benzophenone and acetophenone, when heated above their melting points (280°–300°), decomposed completely into the corresponding ketone and alcohol, as is shown in the following scheme :



It seems, therefore, an interesting problem from the view point of the contact action, to see what chemical change would take place when these pinacones come into contact with reduced copper heated at about 200°. The present experiment was undertaken to study the catalytic action of this metal and moreover to obtain some facts which might throw some light upon the mechanism of the pinacolone transformation.

1. **Benzophenon-pinacone.** The pinacone of m.p. of 168°–169°, which was prepared from benzophenone by reduction with zinc and sulphuric acid in an alcohol solution, according to the directions of Ed. Linnemann,<sup>(3)</sup> and W. Thorner and Th. Zincke<sup>(4)</sup>, was passed on reduced copper heated at 200°. The reaction products remained almost entirely on the catalyst, due to their non-volatility, was treated with chloroform and separated from the catalyst by filtration. The product, thus obtained, amounted to 8 gr. (from 10 gr. of the

(1) This journal, 1 (1926), 35 and 54.

(2) *Ber.*, 13 (1880), 641.

(3) *Lieb. Ann.*, 133 (1865), 26.

(4) *Ber.*, 10 (1877), 1473.

pinacone), and was ascertained to be composed of 7 gr. of pure benzophenone pinacolone with a m.p. of 177°–179°, after being purified by the method suggested by C. Paar<sup>(1)</sup>. On analysis, it gave the following results :

0.1122 gr. subst. gave 0.3674 gr. CO<sub>2</sub> and 0.0576 gr. H<sub>2</sub>O. (Found : C=89.30 ; H=5.74. C<sub>26</sub>H<sub>20</sub>O requires C=89.63 ; H=5.77%).

For confirmation, 4 gr. of the pinacolone have converted, by hydrolysis with an alkali solution, into 3 gr. of pure triphenyl methane (m.p. 92°–93°) and 1.0 gr. of pure benzoic acid (m.p. 121°), and both substances were confirmed by the determination of the chemical and physical properties and also by the elementary analyses :

0.1135 gr. of the hydrocarbon gave 0.3867 gr. CO<sub>2</sub> and 0.0687 gr. H<sub>2</sub>O. (Found : C=92.92 ; H=6.77. C<sub>19</sub>H<sub>16</sub> requires C=93.42 ; H=6.58%). 0.1099 gr. of the acid gave 0.2773 gr. CO<sub>2</sub> and 0.0502 gr. H<sub>2</sub>O. (Found : C=68.70 ; H=5.11. C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> requires C=68.84 ; H=4.92%).

Thus, the pinacolone which was obtained by the contact action of reduced copper on benzophenone pinacone, was confirmed to be the same substance which was previously obtained by other chemists<sup>(2)</sup> from the same pinacone by means of acetyl chloride, benzyl chloride, dilute sulphuric acid, oxalic acid and concentrated hydrochloric acid heated above 200°.

**2. Acetophenone-pinacone.** Applying the contact action of reduced copper at 130°–140° on 13 gr. of acetophenone-pinacone, m.p. 120°, prepared from acetophenone<sup>(3)</sup>, 6.6 gr. of liquid and 4 gr. of solid reaction products were obtained.

The liquid reaction product consisted, on distillation, of the following fractions :

140°–160°, trace ; 160°–205°, 3.0 gr. ; Residue, 2.4 gr.

The second fraction was confirmed to consist mainly of acetophenone by oximiration with hydroxylamine, and the residue as well as the solid reaction product above mentioned were noticed to be composed mostly of the pinacone (m.p. 120°) unchanged in the reaction.

In the second reaction of the pinacone carried out at higher temperature such as 180° and 200°, no other chemical reaction than that mentioned above, could be observed.

(1) *Ber.*, 17 (1884), 911.

(2) W. Thorner and Th. Zincke, loc. cit.

C. Paar, Loc. Cit.

E. Erlenmeyer, *Ber.*, 14 (1881), 322.

U. Nef, *Lieb. Ann.*, 318 (1901), 37 ; 335 (1904), 243.

H. Meerwein, *Lieb. Ann.*, 376 (1910), 152 ; 396 (1913), 200 ; 405 (1914), 129 ; 417 (1918), 225 ; 419 (1919), 121.

F. Henrich, "Theorien der Organischen Chemie," 5 Auflage (1924) p. 444."

(3) *Ber.*, 10 (1877), 1714.

Such a difference in the behavior of the pinacones toward reduced copper heated at about 200°, would be ascribed either to the chemical affinity between two tertiary carbons of the pinacone molecule or to some other reason, and further experiments are required to discover an explanation which will cover the facts underlying the pinacoline transformation, one of the most interesting problems in modern organic chemistry.

September 1925.

Laboratory of Organic and Bio-chemistry.

College of Science, Kyoto Imperial University.

---