

Catalytic Action of Reduced Copper on Pinacones.

By

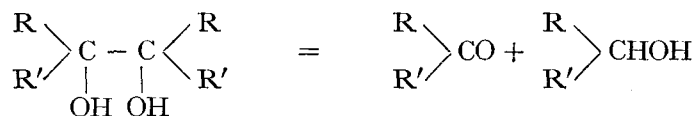
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(Received February 2, 1926)

In the recent article¹ 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., Zincke², the pinacones derived from benzophenone and acetophenone, when heated above their melting points (280°–300°), decomposed completely into the corresponding ketone and alcohol as will be 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

¹ These Memoirs, **9**, 427 (1926).

² Ber. D. Chem. Ges., **13**, 641 (1880).

pinacones come into contact with reduced copper heated at about 200° , and the present experiment was undertaken to learn the catalytic action of this metal and also to obtain some facts which might throw some light upon the mechanism of the pinacolone transformation.

1. BENZOPHENONE PINACONE.

The pinacone of a m.p. of 168° – 169° , prepared from benzophenone by reduction with zinc and sulphuric acid in an alcohol solution, according to the directions of Ed. Linnemann¹ and W. Thorner & Th. Zincke,² was passed on reduced copper heated at 200° , and the reaction products remained almost entirely on the catalyst, due to their non-volatility, treated with chloroform and separated from the catalyst by filtration. The product, thus obtained, amounted to 8 grm., from 10 grm. of the pinacone, which was ascertained to be composed of 7 grm. of pure benzophenone pinacolone with a m.p. of 177° – 179° , after being purified by the method suggested by C. Paar³.

On analysis, it gave the following results:

0.1122 grm. subst. gave 0.3674 grm. CO_2 and 0.0576 grm. H_2O

	C.	H.
Found.	89.30	5.74
Calc. for $\text{C}_{23}\text{H}_{20}\text{O}$	89.63	5.77

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

0.1135 grm. of the hydrocarbon gave 0.3867 grm. CO_2 and 0.0687 grm. H_2O .

	C.	H.
Found.	92.92	6.77
Calc. for $\text{C}_{19}\text{H}_{16}$	93.42	6.58

0.1099 grm. of the acid gave 0.2773 grm. CO_2 and 0.0502 grm. H_2O .

	C.	H.
Found.	68.70	5.11
Calc. for $\text{C}_7\text{H}_6\text{O}_2$	68.84	4.92

¹ Lieb. Ann., **133**, 26 (1865).

² Ber. D. Chem. Ges., **10**, 1473 (1877).

³ Ber. D. Chem. Ges., **17**, 911 (1881).

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 chemists¹ 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 gram of acetophenone-pinacone, m. p. 120°, prepared from acetophenone², 6.6 gram. of liquid and 4 gram. of solid reaction products were obtained.

The liquid reaction product consisted of the following fractions:

1. 140°—160° trace.
2. 160°—205° 3.0 gram.
3. Residue 2.4 gram.

And the second fraction was confirmed to consist mainly of acetophenone by oximiration with hydroxylamine, and the residue and also 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 differing from that mentioned previously could be observed.

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 pinacones molecule or to some other reason, and further experiments are required to discover an explanation which will cover the fact underlying the pinacolone transformation, one of the most interesting problems in modern organic chemistry.

Sep. 1925 Laboratory of Organic and Bio-chemistry.

¹ W. Thorner & Th. Zincke: *Loc. cit.* C. Paar: *Loc. cit.* E. Erlenmeyer: *Ber. D. Chem. Ges.*, **14**, 322 (1881). U. Nef: *Lieb. Ann.*, **355**, 243 (1904); **318**, 37 (1901); H. Meerwein: *Lieb. Ann.*, **376**, 152 (1910); **396**, 200 (1913); **405**, 129 (1914); **417**, 255 (1918); **419**, 121 (1919). F. Henrich: *Theorien der Organischen Chemie* 5 Auflage 1924 S. 444.

² *Ber. D. Chem. Ges.*, **10**, 1714 (1877).