

*Citation:*

J. Böeseken & W.D. Cohen, On the reduction of aromatic ketones, in:  
KNAW, Proceedings, 16 I, 1913, Amsterdam, 1913, pp. 91-99

**Chemistry.** — "*On the reduction of aromatic Ketones*". By Prof. J. BOESEKEN and W. D. COHEN. (Communicated by Prof. A. F. HOLLEMAN).

1. This research originated in the observation by one of us that in the reduction of benzophenone by aluminium amalgam in 80% alcohol, therefore in a neutral medium, are formed considerable quantities of benzopinacone in addition to benzhydrole. As according to statements in the literature which are supported by our own observations, benzophenone may be quantitatively converted into benzhydrole by zinc dust in a faintly alkaline alcoholic solution, whereas reduction in an acid solution causes the formation of pinacone<sup>1)</sup> (or of the pinacoline secondarily resulting there from) it struck us that a systematic research as to the progressive change of this reduction would not be devoid of interest.

In the reduction of benzophenone may be formed, besides alcohol and pinacone, also diphenylmethane. KLAGES and ALLENDORF<sup>2)</sup> have even succeeded in obtaining a quantitative yield of this hydrocarbon by means of sodium and ethyl alcohol. Evidently this total reduction takes place owing to a powerful action in a concentrated alkaline medium. Presumably, stress must be laid here on the nature of the reduction agent because on using zinc dust in a strongly alkaline alcoholic solution benzhydrole is formed almost exclusively, whereas on using aluminium amalgam diphenylmethane may be detected. Working according to MONTAGNE's<sup>3)</sup> directions with zinc dust we have obtained from 25 grams of benzophenone 25 grams of crude hydrole which was practically odourless consequently free from diphenylmethane.

With magnesium amalgam (obtained by heating 2 grams of Mg with 200 grams of Hg) was obtained, in absolute alcohol solution, mainly benzhydrole besides a little diphenylmethane, but no pinacone.

As magnesium and aluminium stand nearer to sodium than zinc, this result is not astonishing.

In order not to complicate the reaction too much we have tried to avoid the formation of diphenylmethane as much as possible.

As reduction agents we have chosen: zinc dust and aluminium, the latter in the form of amalgam in so far as it concerned the reduction in a neutral or acid medium.

Again, when using the latter metal we have avoided a too power-

<sup>1)</sup> LINNEMANN Ann **133**, 6

<sup>2)</sup> Berichte **31**, (1898).

<sup>3)</sup> Recueil **25**, 402 (1906).

fully acid or alkaline reaction, because diphenylmethane is then also formed.

As solvent we selected in all cases a liquid containing 80% ethyl alcohol to which the acid, alkali, etc. was eventually added.

In 80% alcohol benzophenone is practically insoluble whilst the hydrole is readily soluble therein, so that the determination of the two substances in a mixture is a simple matter.

Solubility of pinacone: Shaken in a thermostat for one day at 25°.

In supersaturated solution 100 cc. retained 0.124 gram.

„ unsaturated „ „ „ dissolved 0.110 „

The solubility of benzhydrole =  $\pm 35$  grams.

We have also ascertained that the solubility of pinacone is not appreciably influenced by quantities of hydrole up to 5 grams.

The *modus operandi* was very simple. Quantities of 5 grams of benzophenone were boiled for some time in a reflux apparatus, with the requisite amounts of the reduction agent, in 50 cc. of 80% alcohol; the solution was filtered hot, the residue was extracted with small quantities of boiling 80% alcohol, the filtrate made up to 100 cc. and then shaken at 25° for one day.

In 50 cc. of the solution the hydrole was determined by evaporation. The residue was tested as to its purity by the determination of its odour, melting point, and crystal-habit.

This evaporation was always carried out in the same manner, for the hydrole is somewhat volatile; for instance, if the evaporation lasts 30 minutes, 12 mg. of benzhydrole get lost.

For this loss a correction was made as well as for the pinacone eventually present.

## 2. *Reduction in a neutral medium.*

This was only possible with aluminium amalgam. This was prepared by shaking aluminium grit with 1%  $\text{HgCl}_2$  solution for 15 minutes at the ordinary temperature, filtering off rapidly and washing with 96% alcohol. It was then at once used for the reduction in the proportion of 10 grams of the aluminium to 5 grams of benzophenone.

The following figures were obtained: (see table page 93).

Hence, the result shows that the proportion in which hydrole and pinacone are formed is constant, namely 68% : 32%, independent of the time of the reduction.

Pinacone once formed is not reduced any further in a neutral solution within seven hours, so it cannot be considered as an intermediate product.

No. of experiment	Time of reduction	Benzhydrole formed	Remarks
1	1 uur	3.37 gr.	The residue on evaporation was odourless and melted at 68° hence contained no benzophenone and diphenylmethane. The insoluble part contained 1.55 grams of pinacone.
2	2 "	3.45 "	
3	3 "	3.41 "	
4	4 "	3.4 "	Preliminary experiments, where the solution after boiling was left for 24 hours. After filtering, the residue was washed with cold alcohol. The insoluble part contained 1.6 grams of pinacone.
5	5 "	3.2 "	
6	6 "	3.3 "	
7	7 "	3.4 "	

### 3. Reduction in a faintly acid medium.

#### A. With zinc dust.

After it had been ascertained that no appreciable change had taken place on boiling benzophenone with 80 % alcohol and zinc dust for 6 hours, the operation was repeated in a *current of carbon dioxide*.

After boiling 10 and 12 hours 4.19 and 4.00 grams of residue were obtained on evaporation; this however, melted just below 48° and had the usual properties of benzophenone. The remaining of the 5 grams was benzpinacone.

On again subjecting the residue a few times to the same process (in order to concentrate hydrole formed eventually) the quantity became less, namely 2.9 and 1 gram, but it remained benzophenone. The quantity of the product insoluble in 80% alcohol increased, it was pinacone, but not very pure.

With zinc dust in a very faintly acid medium the reaction therefore proceeds very slowly and with exclusive formation of pinacone.

This same result was also obtained when instead of carbon dioxide ammonium chloride was taken. 10 grams of zinc, 3 grams of  $\text{NH}_4\text{Cl}$  and 50 cc. of 80% alcohol were chosen for 5 grams of benzophenone.

The operation here had to be modified somewhat because the residue on evaporation contained zinc and nitrogen; it was boiled with hydrochloric acid (1 part of acid 1.19 — 1 part of water), washed and dried.

After boiling for 3½, 6 and 12 hours we obtained as a purified residue: 2.22, 1.87, and 0.99 gram of a substance melting below 48° and having a strong odour of benzophenone.

The insoluble part was a not very pure pinacone; after extraction with benzene and evaporation it melted at 170°.

In a somewhat stronger acid medium pinacone (pinacoline) was also obtained exclusively.

For this was used a mixture of 80% of alcohol and 20% of glacial acetic acid; quantities of 15 grams of zinc dust and 75 cc. of the acid mixture were chosen for 5 grams of benzophenone.

The reaction takes place more energetically and much zinc acetate is deposited. The liquid is therefore diluted with water and the remaining zinc rapidly dissolved by means of dilute HCl. A solid substance is now left which is shaken for a day with 100 cc. of 80% alcohol as directed above.

On boiling for 2 and 6 hours, respectively only 0.45 and 0.35 gram of a substance readily soluble in 80% alcohol had formed; its melting point was, however, situated below 25°; it did not crystallise in the shape of felt-like needles and had the typical odour of diphenylmethane; the residue consisted of pinacone.

Hence, the reduction proceeds in dilute acetic acid and zinc dust much more rapidly than in a nearly neutral medium, but otherwise in the same direction.

This result agrees with that of ZAGOMENNI<sup>1)</sup>, who obtained 92% of pinacone in glacial acetic acid solution.

With sulphuric acid (80 cc. of 96% alcohol, 20 cc. of H<sub>2</sub>SO<sub>4</sub> 1—1) exactly the same result was obtained. After boiling for 2—4 hours, respectively there was obtained only 0.28—0.27 gram of a product: soluble in alcohol having the odour of orange peels and a very pale yellow colour with a low melting point; the part not soluble in alcohol was, presumably, mainly pinacoline.

#### *B. Reduction in a faintly acid medium with aluminium.*

Aluminium grit was not attacked by the above acetic acid-alcohol mixture (15 grams of Al, 75 cc. of acid mixture to 5 grams of benzophenone). Therefore, a little HgCl<sub>2</sub> was added which caused the reaction to set in. After three hours' boiling the product was treated as stated above; no hydrole could be detected, only a little of a pale yellow product soluble in alcohol and having an odour of orange-peels, all the rest consisted of pinacone. The melting point 165° also again pointed to formation of pinacoline. Contrary to the reduction in a neutral solution *no* hydrole is formed.

#### *4. Reduction in a faintly alkaline medium.*

##### *A. With zinc dust.*

For this was chosen a mixture of 50 cc. of 96 % alcohol, 25 cc.

<sup>1)</sup> B 14, 102 (1881),

of ammonia density 0.93 and 10 grams of zinc dust, which was boiled with 5 grams of benzophenone.

After 2 and 5½ hours' boiling, respectively 4.21—4.34 grams of pure hydrole were formed; the balance consisted of pinacone, which could be isolated by the extraction of the insoluble part with benzene.

After 2 hours nearly all the ammonia was boiled off; after 5½ hours it had quite disappeared.

*B. With aluminium amalgam.*

For 5 grams of ketone were taken 40 cc. of alcohol, 10 cc. of ammonia and 10 grams of aluminium amalgam and the whole was boiled until all the ammonia was expelled (3 hours). 4.81 grams of very beautiful benzhydrole and 0.21 gram of pure pinacone were obtained.

From this we notice that the reduction is almost independent of the metals and that the result is mainly governed by the reaction of the medium.

5. In a stronger alkaline medium with alcoholic sodium hydroxide not a trace of pinacone was obtained, with zinc dust as well as with aluminium; the product was very readily soluble in 80 % alcohol. During the aluminium reduction, which was particularly violent, a product was obtained having a pale yellow colour and which judging from the odour, contained a little diphenylmethane.

Let us tabulate the results obtained in the subjoined survey (also including sodium).

Medium	Zinc dust	Aluminium	Magnesium	Sodium
acetic acid	pinacone in presence of some diphenylmethane and pinacoline	pinacone	—	—
very faintly acid: carbonic acid, NH <sub>4</sub> Cl.	pinacone	—	—	—
neutral	—	pinacone 32% hydrole 68 "	—	—
faintly alkaline (NH <sub>3</sub> )	pinacone 15% hydrole 85 "	pinacone 4 " hydrole 96 "	—	—
strongly alkaline	hydrole	hydrole	hydrole	hydrole
in presence of diphenylmethane				

When we disregard the formation of diphenylmethane it is beyond all doubt that the formation of pinacone or benzhydrole is in the first instance dependent on the reaction of the medium.

The nature of the metal is apparently of secondary importance and can only exert an influence in so far as it yields OH-ions. (Magnesium, sodium).

So long as the reaction is acid, even ever so feeble, pinacone is exclusively formed; but no sooner do OH-ions occur than we notice the appearance of the hydrole.

This even takes place with aluminium-amalgam in 80 % alcohol where we may take it for granted that the liquid is practically neutral, although the possibility is not excluded that at the boundary layer of the metal a very small excess of OH is temporarily present.

If the excess of OH-ions is small we can still detect the pinacone in the presence of hydrole, but when it becomes more considerable pinacone is soon no longer present.

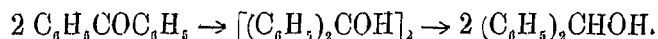
The cause of the non-occurrence of pinacone in strongly alkaline solutions is now very easy to explain. If we boil a solution of pinacone with sodium ethoxide it gets converted into a mixture of benzophenone and hydrole.

During the reduction in an alkaline medium the pinacone generated will be continuously converted into the above mixture of which the keton will be again reduced, so that finally all will have been converted into hydrole.

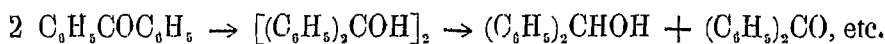
Apparently the latter, in strongly alkaline liquids, becomes the only direct reduction product.

That this, however, cannot be the case is shown from the course of the reduction in a feebly alkaline medium where also pinacone may be retained.

In a neutral solution much larger quantities of pinacone may be retained and owing to the fact that they are not reduced any further we have already come to the conclusion that pinacone cannot be an intermediate reaction product as the following scheme might express:



In an alkaline solution, pinacone can be, incidentally, an intermediate product owing to a secondary reaction:



We might assume that, apart from this secondary hydrole formation, a direct addition of an entire molecule of hydrogen to the ketone takes place under the influence of the OH-ions. Then however it would be strange that in presence of an excess of OH-ions,

however small, pinacone was still formed and retained because now two causes would cooperate to retard the formation of pinacone.

It appears to us as the most probable that the direct reduction product is in all cases the *half pinacone molecule* which afterwards:

1. will polymerise to pinacone which remains unchanged in a neutral solution and resolves into hydrole and ketone in an alkaline solution; the ketone can then again be attacked.

2. will possibly, be further reduced to hydrole and diphenylmethane.

We base this conception, besides on the above experiments from which appears a predilection for the formation of pinacone, also on observations as to the behaviour of mixtures of benzophenone and absolute alcohols and other substances in direct sunlight.

CIAMICIAN and SILBER<sup>1)</sup> have in this way obtained pinacone quantitatively from benzophenone and ethyl alcohol, we have been able to confirm this result with a series of other alcohols<sup>2)</sup>. Not a trace of hydrole is formed in these neutral liquids *absolutely free from hydroxyl-ions*.

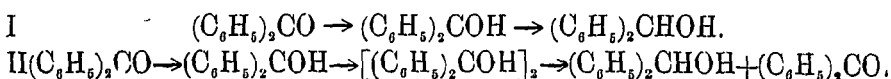
With benzyl alcohol and with ether the two Italian chemists found, besides pinacone, substances such as  $(C_6H_5)_2COHCHC_6H_5OH$  and  $(C_6H_5)_2COHCHCH_3OC_2H_5$ , whose formation, like that of pinacone may be explained in the simplest manner by a primary addition of one hydrogen-atom to the ketone-oxygen which will here be followed immediately by an attachment of the molecular residues to the carbon of the CO-groups.

Hence, in the above formulated assumption it has been taken for granted that the half pinacone molecule  $(C_6H_5)_2COH$  is the sole real intermediate product.

It is now very well possible that this, in an alkaline solution, is straightway reduced to hydrole (2).

But it is, however, also not excluded that the polymerisation to pinacone takes place, also in alkaline solution, with such velocity that this latter product is formed first also in these circumstances, then to be secondary converted into hydrole in the manner suggested above.

The two alternatives may be represented as follows:



If the latter is the case it is to be expected that the ketones which yield pinacones that are rapidly resolved by OH-ions into a mixture

<sup>1)</sup> B 33, 2911; 36, 1577; 43, 1536; 44, 1557.

<sup>2)</sup> This research will become the subject of a further communication.



of ketone and hydrole will yield on reduction in a (OH-containing) neutral medium a slight amount of pinacone.

In order to verify this experimentally we have commenced by reducing a series of ketones by means of aluminium amalgam in 80 % alcohol.

The subjoined table gives a survey of the results concerned :

Ketone (5 grams)	m.p. ketone	Quantity of hydrole		m.p. hydrole	Quantity of pinacone <sup>1</sup>		m.p. pinacone
		in gr.	in %		in gr	in %	
Benzophenone	48°	3.40	68	67°5	1.60	32	178°—180°
4 methoxybenzophenone	62°	3.22	64	60°	1.84	36	158°—160°
4 methylbenzophenone	55°	2.94	59	48°	2.07	41	164°—165°
4,4' dimethylbenzophenone	94°	2.58	52	67°—68°	2.40	48	180°—181°
4 Bromobenzophenone	81°	4.22	84	64°—65°	0.73	15	169°—170°
4 Chloro4'meth.benzoph.	118°	4.96	100	67°5	0.04		
2 Chloro4'meth.benzoph.	99.°5	4.35	87	67°	0.65	13	175°—176°
2 Chlorobenzophenone	45.°5	4.77	85	67°5	0.29	6	174°—175°
3 Chlorobenzophenone	81°	4.87	97	1)	0.12	2	
2,4' dichlorobenzophenone	52°	4.87	97	1)	0.14	3	
4,4' dichlorobenzophenone	144.°5	4.82	96	89°	0.19	4	180°
2,4,2',4' tetrachl.benzophen.	78°	5.0	100	100°	0.01		
4 Chlorobenzophenone	76°	4.27	85	78°5	0.72	14	179°

Disregarding a few irregularities, the following is now apparent from this table :

1. The methoxy- and methyl group appear to promote in a slight degree the formation of pinacone.

2. Halogen in the nucleus favours in a high degree the formation of the hydrole so that, particularly with plural substitution, the formation of pinacone is nearly, or entirely, prevented.

3. The position of the substituent in the nucleus does not appear to be of considerable influence on the proportion in which hydrole and pinacone are generated ; on the other hand the nature of the group entered seems to be of more importance.

Hence, many important differences may be observed in the relation

<sup>1)</sup> These hydroles have low melting points ; as only small quantities were at our disposal we did not succeed obtaining them in a perfectly pure condition.

pinacone: hydrole, which are dependent on the group introduced.

It is to be expected that these differences will continue to exist also in another medium provided this remains neutral, for instance when we reduce with aluminium amalgam in another saturated alcohol. This indeed proved to be the case.

Ketone	Solvent	Formed hydrole
Benzophenone	C <sub>2</sub> H <sub>5</sub> OH	68%
	CH <sub>3</sub> OH	68 "
o-Chlorobenzophenone	C <sub>2</sub> H <sub>5</sub> OH	94 "
	CH <sub>3</sub> OH	93 "

On the other hand it was ascertained that a ketone which in a neutral solution gave almost exclusively hydrole, yet yielded in a feebly acid solution nothing else but pinacone.

2 grams of *pp'* di-chlorobenzophenone yielding in a neutral solution with AlHg 96 % of hydrole gave with zinc dust and the acetic acid-alcohol mixture 1.99 grams of pure pinacone m. p. 180°.

0.1820 and 0.1926 gram gave 0.2060 and 0.2207 gram AgCl

Calculated for C<sub>12</sub>H<sub>8</sub>O<sub>2</sub>Cl<sub>4</sub> 28.1 % Cl (Found 28.0—27.7).

This also agrees with the assumption that the formation of pinacone, in the absence of OH-ions and in this method of reduction, takes place very much more rapidly than that of other possible reduction products and that the hydrole formation in a neutral medium must be attributed to the presence of OH-ions at the boundary layer.

The measurement of the velocity with which some pinacones are converted into the mixture of ketone and hydrole will be the subject of a following communication.

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*Delft, May 1913.*

**Chemistry.** — "*Equilibria in ternary systems*". VIII. By Prof. SCHREINEMAKERS.

Let us now consider the case when a liquid *L* is saturated with the solid compounds *F* and *F'* and at the same time in equilibrium with a vapour *G*. As the system *F* + *F'* + *L* + *G* contains the three components in four phases it is monovariant; hence we can consider the vapour pressure of the system and the composition of *L* and *G* as functions of the temperature.

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