

Citation:

J. Böeseken & W.D. Cohen, On the reduction of aromatic ketones. II., in:
KNAW, Proceedings, 16 II, 1913-1914, Amsterdam, 1914, pp. 962-968

Consequently the muscles that are in a state of tonus satisfy better the indispensable condition of rigor mortis, namely suffocation, than the atonic ones. The leg with tonus muscles also satisfies better the 2nd condition namely the condition of being influenced by the nerves.

For these muscles constantly receive indeed stimulants by way of reflection, whereas the other atonic leg remains without these stimulants. The consequence of both the more intense alteration of the chemical state and the influence of the reflection is that the leg of which the tonus-reflection track remains uninjured, stiffens sooner than the leg of which this reflection-track is interrupted at the posterior roots or near the Rami communicantes. We must thus consider the rigor mortis of the skeleton muscles as a last vital demonstration of the muscles under the influence of suffocation, whilst stimulants running along the tonus-reflection-track accelerate this process. That rigor mortis is a last (tonical) contraction of the muscles is apparent from the fact that the muscles that have lost their irritability in an atmosphere of oxygen, can no more stiffen or shorten under circumstances of suffocation.

Chemistry. — “*On the reduction of aromatic ketones*”. II. By Prof. J. BÖSEKEN and W. D. COHEN. (Communicated by Prof. A. F. HOLLEMAN).

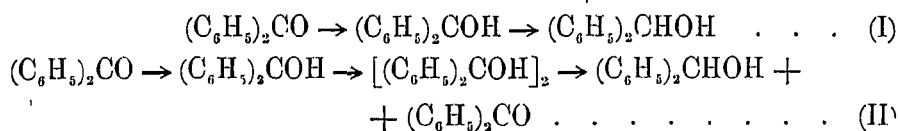
(Communicated in the Meeting of February 28, 1914).

In our previous communication on this subject ¹⁾ we have assumed that by reduction of the ketones the half pinacone molecule is in all cases the sole direct reduction product.

If, in the position where that partial molecule is formed, there are practically no OH-ions it polymerises immediately to pinacone.

In the presence of OH', however, there was always found benzhydrol and the question arose whether this was caused by direct reduction or by the transformation of the previously formed pinacone into benzophenone and benzhydrol by the OH-ions.

These alternatives may be represented by the schemes



¹⁾ Proc. XVI, 91 (1913).

If the latter is the case, the pinacones belonging to the ketones which, in a neutral or very faintly alkaline medium, give much hydrole must be decomposed by alkalis into a mixture of hydrole and ketone much more rapidly than those which in the same circumstances yield but little hydrole.

It may even be expected that the formation of hydrole and the splitting of the pinacone by alkalis will proceed in a strongly parallel manner.

This has now indeed proved to be the case. The greater the decomposition velocity of the pinacone by alkalis, the smaller the quantities formed in the reduction with aluminium amalgam.

With this is also proved that at the boundary layer of the amalgam is present an excess of OH-ions which is only accessible to the pinacone in its nascent state. If, for instance, pinacone is exposed to the action of aluminium amalgam and 80% alcohol, it is practically not attacked, moreover the proportion in which pinacone and hydrole are formed is nearly independent of the duration of the reduction. (1st communication p. 92).

The proportion of the quantities of pinacone and benzhydrole in which these are formed during the reduction of thirteen aromatic ketones with aluminium amalgam has been given in the 1st communication p. 98.

The decomposition velocity of the pinacones was determined by dissolving quantities of 0.5 gram in a mixture of 75 cc. of ether and 5 cc. of alcohol diluting this solution to 105 cc. with alcoholic solutions of potassium hydroxide of $N/0.42$, $N/0.042$ and $N/0.0042$ strength, respectively. The normalities of the solution thus become 0.1, 0.01, and 0.001.

These mixtures were kept for definite periods at 25°, then diluted with cold water, agitated a few times with ether, the ethereal solution was evaporated down rapidly and the residue digested with 80% alcohol at 25° in the manner described previously (l. c. p. 9) in order to get to know the quantities of undecomposed pinacone.

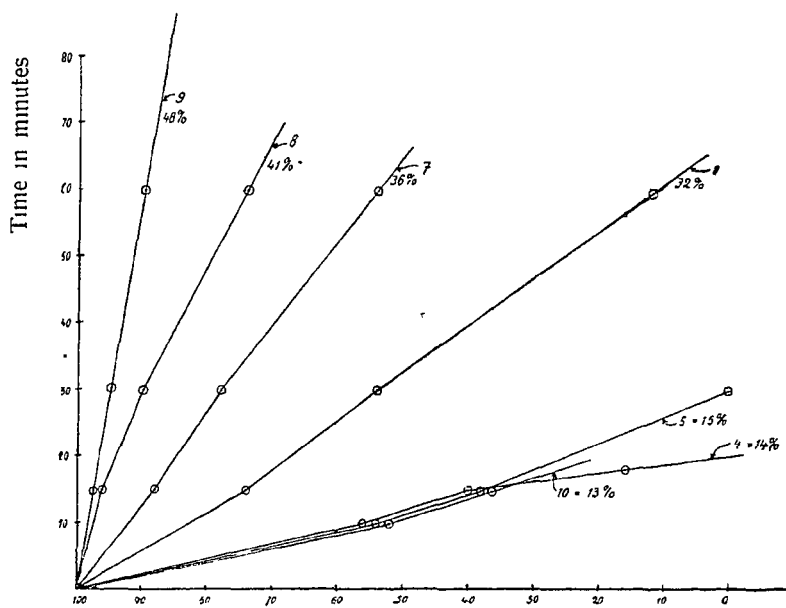
The subjoined table and graphic representations give a survey of the results obtained.

The numbers of the lines in the graphic representations appertain to the numbers with which the pinacones are indicated in the table; the percentages next to or below those numbers in the graphic representation indicate the quantities of pinacone formed from the respective ketones by reduction with aluminum amalgam in 80% alcohol.

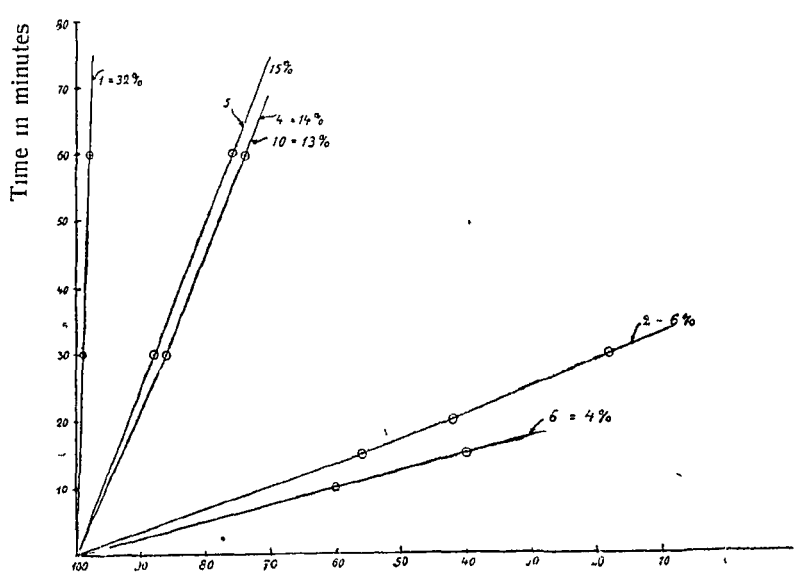
From the graphic representation of the pinacone decomposition, where, as observed above, are indicated the percentages of pinacone

which are formed in the reduction with aluminium amalgam, it follows that these two phenomena proceed indeed in a completely parallel manner.

Pinacone	NaOC ₂ H ₅ - approximate concentration.	Time of action in minutes.	Undecomposed pinacone in mgr.
1) pinacone from benzophenone	0.1	120	0
"	0.01	15	370
"	0.01	30	270
"	0.01	60	60
"	0.001	15	500
"	0.001	30	498
"	0.001	60	488
2) pinacone from 2.chlorobenzophen	0.1	120	0
"	0.01	15	0
"	0.01	30	0
"	0.001	15	280
"	0.001	20	210
"	0.001	30	90
3) pinacone from 3 chlorobenzophen	0.001	15	0
"	0.001	25	0
4) pinacone from 4 chlorobenzophen	0.01	10	280
"	0.01	15	200
"	0.01	23	80
"	0.01	30	0
"	0.001	30	430
"	0.001	60	370
5) pinacone from 4.bromobenzophen	0.01	10	270
"	0.01	15	190
"	0.01	30	0
"	0.001	30	440
"	0.001	60	380
6) pinacone from 4'chlorobenzophen	0.01	10	0
"	0.01	15	0
"	0.001	10	300
"	0.001	15	200
"	0.001	25	0
7) pinacone fr. 4 methoxybenzophen	0.01	15	440
"	0.01	30	390
"	0.01	60	270
"	0.001	30	} not attacked
"	0.001	60	
8) pinacone from 4 methylbenzophen	0.01	15	480
"	0.01	30	450
"	0.01	60	370
"	0.001	15	} not attacked
"	0.001	30	
"	0.001	60	
9) pinacone fr. 4,4' dimethylbenzoph.	0.01	30	475
"	0.01	60	450
"	0.01	90	430
"	0.001	60	} not attacked
"	0.001	120	
"	0.1	90	0
10) pinacone fr. 2'Cl 4 methylbenzoph.	0.01	10	260
"	0.01	15	180
"	0.01	30	0
"	0.001	30	430
"	0.001	60	370
11) pinacone fr. 4'Cl 4 methylbenzoph.	0.001	15	0
"	0.001	25	0

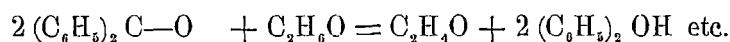


Percentage of unsplit pinacone
 Fig. 1.
 Decomposition of the pinacones in 0.01 n NaOC_2H_5 .



Percentage of unsplit pinacone.
 Fig. 2.
 Decomposition of the pinacones in 0.001 n NaOC_2H_5 .

MONTAGNE¹⁾ found some years ago that a number of aromatic ketones are already reduced by boiling with alcoholic potassium hydroxide; it is very well possible that the strongly alkaline reaction of the medium increases the affinity of the ketone oxygen for the hydrogen of the alcohol molecules, so that also here half pinacone mols. are formed²⁾ as follows:



The phase of the entire pinacone mols. is very rapidly gone through in this case.

It speaks for itself that this powerful affinity influence of the medium will also make its action felt on other bonds in the molecule, so that the entire phenylgroup may be resolved or halogen atoms become "activated" as found by MONTAGNE, an action that ceases, or becomes less, when the entire C=O-group is saturated with hydrogen.

Conversely, this influence itself will be modified by the nature of the groups in the ketone and this the more so as the character of that group differs more from that of the hydrogen atoms. In fact, MONTAGNE has found that the aminobenzophenones are absolutely not affected by strong alcoholic potassium hydroxide.

3. This influence of the substituents on the stability of the central pinacone-C—C bond in regard to alkalis can now be readily deduced from our measurements (see graphic representation *A* and *B* and table).

If we take the ordinary benzpinacone as the starting point, it appears that the methyl- (9 and 8) and the methoxylgroup (7) in the para-position render the molecule stable, on the other hand the halogen atoms will render the said bond looser and this in the order para (4), ortho (2), meta (table N°. 3). The para-placed bromine atom (5) joins the chlorine atom; also in the pinacone from 4,4'-dichlorobenzophenone (6) the bond is considerably looser than in the pinacone from 4 chlorobenzophenone.

Whereas in the pinacone from 2 Cl 4'-methylbenzophenone the two influences, as might be expected, counteract each other (10) it appears that in the pinacone from 4 Cl 4'-methylbenzophenone (11) the methylgroup unexpectedly promotes the loosening action of the chlorine atom.

The method followed by us thus indicates the way to mutually

¹⁾ MONTAGNE, Recueil 27, 327 (1908).

MONTAGNE and MOLL VAN CHARENTE, R. 31, 298 (1912).

²⁾ We may also express this as follows: the oxygen activated by the alkali metal withdraws the hydrogen from the alcohol molecules.

compare the action of different substituents in a molecule on a definite bond of that same molecule. If we choose the decomposition velocity of one of the pinacones as unit, the ratio of the velocities of the other pinacones to this unit is then the measure of the relative lability.

Thus we obtain for the decomposition in N/0.01 sodium ethoxide:

for 4.4.4'.4'. tetramethylpinacone (9)	= 0.1
4.4'. dimethylpinacone (8)	= 0.18
4.4'. dimethoxypinacone (7)	= 0.45
	[pinacone (1) = 1.]
2.2'. diCl 4.4'. dimethyl ,, (10)	= 2.5
4,4'. dibromo ,, (5)	= 2.4
4.4'. dichloro ,, (4)	= 2.3

Moreover, owing to the nature of the measurements we cannot attach to these figures more value than to an approximate determination.

4. With regard to the relative reduction velocity of the ketones to pinacones these experiments tell us nothing. In order to get to know something about this we must reduce the different ketones under the same conditions, preferably in such a manner that nothing but the pinacone is formed.

This now may be effected by exposing to light a solution of the ketones in *absolute* alcohol when indeed a ready transformation into pinacone and aldehyde takes place ¹⁾.

As it concerns here the activation of the C-O-bond it is to be expected that the relative extent of the influence of the substituents in the benzene nucleus will show quite a different order than in the pinacone resolution. We will refer to this in a future communication.

Labor. Org. Chem. Techn. University.

Delft, February 1914.

¹⁾ This was stated long ago by CIAMICIAN and SILBER; we have pointed out in our previous communication that in this neutral, or at most very faintly acid medium no transformation of pinacone into hydrole is to be expected and that, therefore, the absence of hydrole in this case is again a proof that the reaction proper does not extend further than to the half pinacone molecule.