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INVESTIGATION OF THE PYROLYTIC DECARBOXYLATION OF CARBOXYLIC ACIDS WITH ^{14}C

MECHANISM OF THE FORMATION OF CAMPHOR FROM HOMOCAMPHORIC ACID

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THE oldest, but in many cases still practically used method to prepare ketones is based on the dry distillation of a salt of the respective carboxylic acid. Numerous conceptions have been proposed[1-5] with regard to the mechanism of the reaction. The most feasible suggestion seemed to be that of Nuenhoeffer and Paschke[2] according to which the reaction is taking place through a β-keto-carboxylic acid arising from a condensation process. According to Lee and Spinks[5] the most contestable point of this assumption is the fact that no explanation can be given in this way for the formation of diaryl ketones. In our opinion the reaction may be treated on a more uniform basis, if the formation of the respective alkyl cation is

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[1] E.Bamberger, Ber.Dtsch.Chem.Ges. 48, 3517 (1910).

[2] O.Neunhoeffer and P.Paschke, Ber.Dtsch.Chem.Ges. 72, 919 (1939)

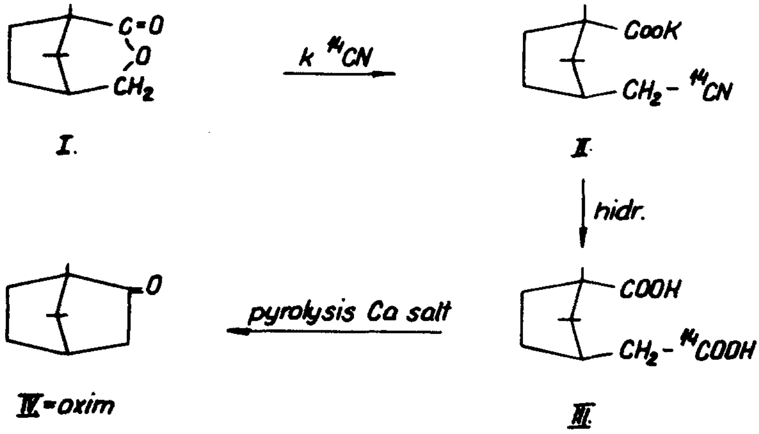
[3] A.L.Miller, N.C.Cook and F.C.Whitmore, J.Amer.Chem.Soc. 72, 2732 (1950).

[4] J.Bell and R.I.Reed, J.Chem.Soc. 1383 (1952)

[5] C.C.Lee and J.W.T.Spinks, J.Org.Chem. 18, 1079 (1953)

assumed to be the first step which is followed by a decarboxylation of the S_E2 type. Among the results of Lee and Spinks experiments, carried out with ^{14}C, the soundness of the data referring to the pyrolysis of calcium-1-^{14}C-acetate + calcium-phenylacetate given in full details has been disputed by Nefedov, Toropova and Skulski[6] on the basis of their own experiments with isotopes.

In order to test the mechanism assumed by Neunhoeffer and Paschke, our choice fell on a model in which one of the carbon atoms adjacent to a carboxyl group was a quarternary while the other a secondary one. In order to obtain a satisfactory isolability of the mixed ketone arising both carboxyl groups were built into the same molecule, and the origin of the emerging CO_2 has been determined by indication with ^{14}C. Accordingly the pyrolysis of the Ca-salt of homocamphoric acid, containing ^{14}C-carboxyl, adjacent to the secondary carbon atom, has been investigated The preparation of the compound was carried out as follows: the lacton



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[6] V.D.Nefedov,M.A.Toropova and I.A.Skulskij, Zs.Fiz.Him. 29, 2236 (1955)

ring of α-campholide (I), prepared according to Komppa,[7] was opened with $K^{14}CN$, then the obtained potassium salt of homocamphoric acid semi-nitrile (II) was subjected to acidic hydrolysis and transformed into the Ca-salt. Dry distillation of the product gives camphor (IV) which could be identified in form of its oxime. The scheme of preparation is given in the figure on page 20, the values of the activities in Table 1. The determination of the latter was carried out with a gas phase counter.

TABLE 1

Compound	Activity, μc/mM
II	17.2
III	17.2
IV-oxim	0.19

The results show clearly that in the course of the pyrolysis the activity passes entirely into the liberated CO_2. Even if steric factors, or the difference in the bonding energies of the carboxyl groups or in their tendency to produce acyl cations are taken into consideration, these cannot provide for such a significant difference in the behaviour of the two groups. The reaction, however, may be explained if we assume that, by the addition of the CH_2-group, attached to the carboxyl-group marked with ^{14}C, 3-carboxy-camphor is intermediately formed which then suffers

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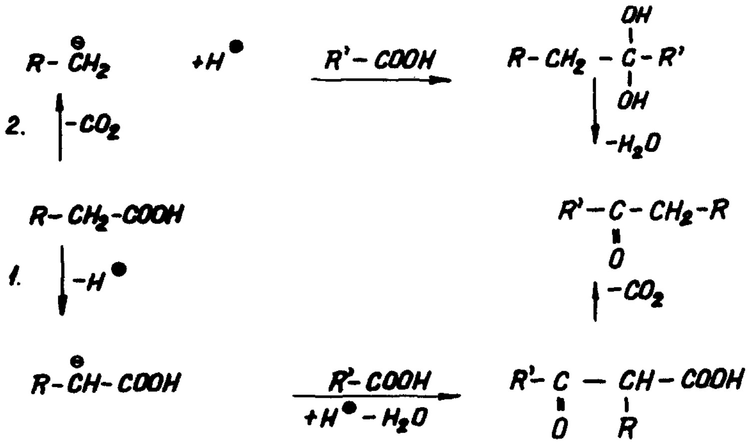
[7] G.Komppa, Ber.Dtsch.Chem.Ges. **41**, 4470 (1903)

decarboxylation under the conditions of the reaction. This means essentially the verification of the condensation mechanism in the case of our model.

We are of the opinion that in a general sense also this reaction may be considered as an anionic addition process. The formation of the carbanion may take place in two different ways: by splitting off of a proton, or else by the catalysed liberation of CO_2. In the former case the reaction will occur through a β-keto-carboxylic acid, in the latter through the alcoholate of a geminal diol.



Where a possibility for both reaction directions is given, the β-keto-carboxylic-acid mechanism will dominate, as shown by the experimental results of Lee and Spinks as well as of Nefedov, Toropova and Skluski. If there is no possibility to split off the proton, the reaction occurs by the other mechanism. Investigations are in course in this direction, with aromatic substituted carboxylic acids.