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OXIDATIVE DECARBOXYLATION OF EXO- AND ENDO-2-CARBOXYBORNANE WITH LEAD TETRA-ACETATE.

G.E.Gream and D.Wege

Department of Organic Chemistry, University of Adelaide, Adelaide, South Australia.

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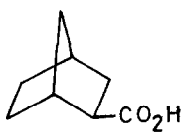
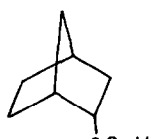
The mechanism of the oxidative decarboxylation of aliphatic acids with lead tetra-acetate has received considerable attention in recent years (1-4). As a result of a study of the action of the above reagent and pyridine on exo- and endo-2-norbornane carboxylic acids (I and II respectively) in benzene and acetonitrile as solvents, Corey and Casanova (1) concluded that the reaction for both acids proceeded via the classical norbornyl cation (III). These authors recognised, however, the possibility that the reactions may have involved initial homolytic decarboxylations followed by fast electron transfers from the norbornyl radical (IV) to give the cation III. Compelling evidence for such a two-step mechanism, i.e. homolysis followed by rapid formation of the carbonium ion, at least in other systems, has been recently presented by Kochi (3), and Davies and Waring (4).



I



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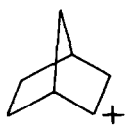
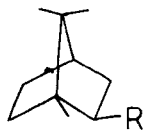


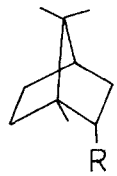
III

IV

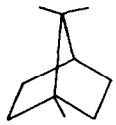
In an attempt to gain further insight into the nature of the mechanism of oxidative decarboxylation with lead tetra-acetate of acids in the norbornyl series, we have carried out an investigation of this reaction with exo- and endo-2-carboxybornane (V and VI, respectively) (5). Our reasons for believing that such a study could be informative were twofold. A. The presence of bornane (VII) in the reaction mixture would be evidence for the formation, at least in part, of the bornyl radical (VIII).Berson and co-workers (7,8) have shown that bornane is the major product formed from the above radical. Of particular importance is the fact that this radical does not undergo skeletal change in the temperature range in which the oxidative decarboxylations are carried out (7). B. The nature of the products derived from carbonium ion precursors could give information as to the precise nature of these cationic intermediates.



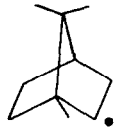
V, R = CO_2H
X, R = CH_2OH
XV, R = $OCOCH_3$



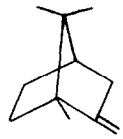
VI, R = CO_2H
XI, R = CH_2OH
XVI, R = $OCOCH_3$



VII



VIII



IX

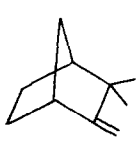
Although de Botton (9) prepared the optically pure exo- and endo-2-carboxybornanes by carbonation of the Grignard reagent of optically pure bornyl chloride, the precedure was long and gave a very poor yield of the exo isomer. Accordingly, alternative methods for the preparation of the optically active acids were investigated. (+)-endo-Acid (VI), $[\alpha]_D^{20}$ +16.8 (benzene), was conveniently obtained by Flautt and Erman's procedure (10) for the preparation of the inactive acid. For the preparation of optically pure exo-2-carboxybornane (V), (+)-camphor was converted into 2-methylenebornane (IX) (11) by a Wittig reaction. Oxidative hydroboration of the olefin with disiamylborane (12) gave a mixture (9:1, 59%) of the carbinols (X and XI, respectively) which was oxidised with Jones' reagent (13) to give an acidic mixture containing the desired exo-acid (75%) and the endo-acid (25%). Pure (-)-exo -2-carboxybornane, $[\alpha]_D^{18}$ - 95 (benzene) was isolated from the mixture via its (+)-bornylamine salt (9).

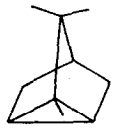
Initial attempts to carry out the oxidative decarboxylations in acetic acid containing sodium acetate were abandoned when it was found that the endo-acid underwent reaction only slowly under these conditions, and that the initially formed products were apparently consumed in secondary reactions with the lead tetra-acetate (14).

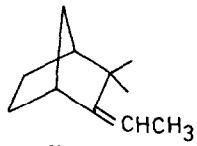
The reactions of the acids V and VI were therefore carried out under conditions described by Corey and Casanova (1), i.e. in benzene containing pyridine as catalyst. It was found that both acids underwent reaction qualitatively at the same rate and gave the same products and in essentially the same proportions (15) when the number of equivalents of the

reagent were the same. The proportions of the products depended, however, on the amount of lead tetra-acetate used since the major product, camphene (XII), readily underwent secondary reactions with the reagent (16).

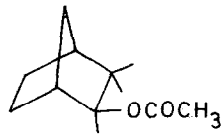
With 1.25 equivalents of lead tetra-acetate, both acids gave mixtures (ca. 60 - 75 %) which consisted of tricylene (XIII, 2%), camphene (XII, 53-57%), 8-methylcamphene (XIV, 3-4%), isobornyl acetate (XV, 11-13%), bornyl acetate (XVI, 5-6%), acetate of camphene hydrate (XVII, 9%), acetate A (2%), acetate B (5-6%), and acetate C (5-6%).* 8-Methylcamphene and the acetates A, B and C were shown to be secondary products formed from camphene by the action of lead tetra-acetate. The camphene obtained from these oxidative decarboxylations had a high optical purity; that from the exo-acid showed $[\alpha]_D^{19}$ +109° (benzene), lit.(17) $[\alpha]_D$ -117.5° (toluene) while that obtained from the endo-acid showed $[\alpha]_D^{20}$ + 112 (benzene).


XII


XIII



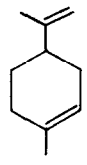
XIV



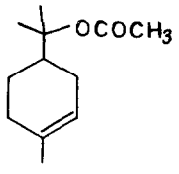
XVII

* The analyses were carried out by vapour phase chromatography using a 300' Ukon capillary column.

Camphene (XII) and the acetate of camphene hydrate (XVII) must be derived from cationic species, and not the bornyl radical (VIII), since their formation has involved rearrangement of the original bornane structure. Tricyclene (XIII) has been detected as a very minor product from the bornyl radical (7,8) as well as from cationic intermediates (6). Significantly however, bornane (VII) could not be detected in the mixtures under analytical conditions in which 0.5% could have been readily determined. It is therefore concluded that the free bornyl radical was not formed, and that the isobornyl and bornyl acetates (XV and XVI, respectively) are also formed from carbonium ion species. Also noteworthy was the absence of limonene (XVIII) and α-terpinyl acetate (XIX) in the mixtures. The formation of these two compounds might have been expected if a "hot" bornyl cation (18) had been formed.



XVIII



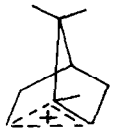
XIX

The proportions of the three acetates XV, XVI and XVII formed directly from the two acids are shown in Table I. Of particular interest is the finding that the ratio of isobornyl to bornyl acetate is always ca. 68 : 32. To our knowledge this is the highest ratio of bornyl to isobornyl derivative formed in carbonium ion reactions of isobornyl and bornyl derivatives (19).

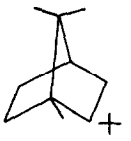
TABLE I

Acid	Equivs $Pb(OAc)_4$	Acetates Formed (%)			Ratio $\frac{XV}{XVI}$
		XV	XVI	XVII	
(-)-exo-	1.04	41	20	39	67 : 33
(+)-endo-	1.02	40	19	41	68 : 32
(±)-endo	1.16	44	21	35	68 : 32
Mixt(57:43) (-)-exo + (+)-endo	1.25	44	21	35	68 : 32

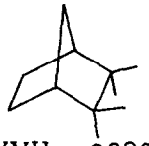
As derivatives of borneol, i.e. attack from the endo direction, have not been observed in reactions believed to proceed through the non-classical camphenehydro-isobornyl cation (XX) (6), the formation of bornyl acetate is believed to result from the classical bornyl cation (XXI). If the latter species were, however, the only reactive carbonium ion present, a much higher ratio (perhaps greater than 9 : 1) of bornyl to isobornyl acetate may have been expected since the syn-7 methyl group causes the exo side to be the more hindered (20). We believe therefore that the initially formed classical ion (XXI) is to a large extent converted into the non-classical ion (XX) (21). Further support for the intervention of the latter species comes from the fact that the acetate of camphene hydrate (XVII) was not contaminated by the epimeric methylcamphenilyl acetate (XXII). The analytical conditions were such that 1 % of the latter in the former could have been easily detected.



XX



XXI



XXII $OCOCH_3$

As already mentioned, the absence of bornane (VII) in the reaction mixtures indicates that the products were entirely formed via carbonium ion species, a result which is accord with Corey and Casanova's conclusions (1) in the case of the unsubstituted acids I and II. If the initial decarboxylation step in V and VI involves a preliminary homolysis as suggested by Kochi's work (3), the intermediate radical must be oxidised in a very fast step, probably one in which the lead (III) species is reduced before it has departed from the sphere of the bornyl radical.

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14. The structures of two epimeric lactones formed as secondary products have been elucidated by G.E.Gream and D. Wege, Tetrahedron, 22, 2583 (1966).

15. In its reaction with lead tetra-acetate, the exo-acid is in part epimerised to the endo isomer. An investigation of the extent of epimerisation and the rates of reaction of the two acids is planned.

16. Some products of reaction of camphene with lead tetra-acetate have been reported: reference 14; and T.Wolinsky, J.Org.Chem., 26, 704 (1961), and references therein.

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19. A higher ratio (2:3) of endo to exo substitution in a norbornyl derivative has been observed in the acetolysis of 7-keto-exo-2-norbornyl p-toluenesulphonate by P.G.Gassman and J.L.Marshall, Tetrahedron Letters, 4073 (1965); J.Amer.Chem.Soc., 87, 4648 (1965), ibid, 88, 2822 (1966).

20. The report by A.F.Thomas and B.Willhalm Tetrahedron Letters, 1309 (1965) that camphor undergoes base catalysed deuterium exchange at the exo-3 position shows however that the assumption that reagents, other than those reacting with postulated non-classical cations, will attack at the endo-2 (or 3) position in norbornyl derivatives possessing bulky syn-7 substituents is not without its pitfalls.

21. Recently, one of us (6) expressed the view that although the kinetic evidence presented so far for the existence of non-classical ions in the norbornyl series seemed to be valid for the π-route only, and not for the σ-route to such ions, the most compelling evidence for their existence was stereochemical. In accepting Brown's interpretation (23, 24) of the Goering-Schewene diagram, i.e. the factor that is responsible for the exo to endo rate ratios in norbornyl derivatives is also responsible for the stereoselectivity of substitution, we realise that the use of the non-classical camphenehydro-isobornyl cation may be suspect unless convincing kinetic evidence for participation by the σ-route is forthcoming. We also believe, however, that Brown's "steric hindrance to ionisation" mechanism (23) requires more convincing evidence than that presented so far in order to establish its reality.

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