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LEAD TETRAACETATE OXIDATION OF UNSATURATED CARBOXYLIC ACIDS. THE EFFECT OF LITHIUM CHLORIDE

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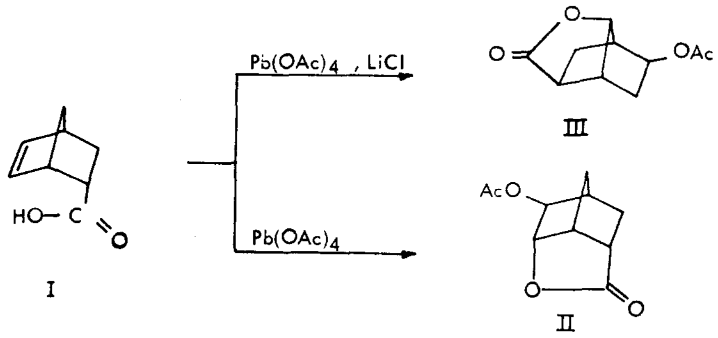
In the preceding communication we reported that lead tetraacetate oxidation of various olefinic carboxylic acids caused formation of the corresponding acetoxy lactone. This result was unexpected in that similar treatment of saturated carboxylic acids leads to efficient decarboxylation[2].

Since it has been shown that halide ion strongly catalyses the decarboxylation of lead carboxylates[3], it appeared of interest to apply the "halodecarboxylation" oxidative conditions to unsaturated carboxylic acids. Our principal objective was to learn whether acetoxy lactone formation would prevail under these circumstances, or, alternatively, whether decarboxylation might occur as a result of the catalytic effect of the halide ion.

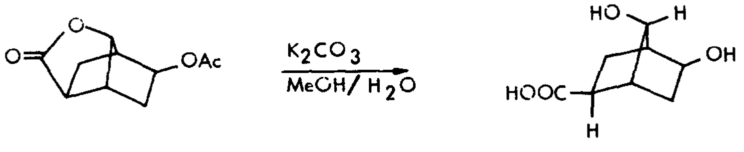
Treatment of endo-5-carboxybicyclo [2,2,1] hept-2-ene (I) with lead tetraacetate (1.5 molar equivalents) and lithium chloride (10 molar equivalents) in benzene caused no decarboxylation, but rather high yield (70%) formation of an acetoxy lactone (III) isomeric with the one formed in the absence of added halide ion, namely, (II).



Structure III for this lactone of m.p. 116-116.5°, νc = 0, 1725, 1780 cm^{-1}, is assigned on the basis of the following physical and chemical evidence. The high resolution mass spectrum showed a relatively weak molecular ion at m/e 196 (0.5%) but a stronger peak at m/e 136 (44%). This mass corresponds to loss of acetic acid. Furthermore, metastables derive from this mass: m * 85.7, 136 → 108 + 28; m * 62.23, 136 → 92 + 44; m * 57.8, 108 → 79 + 29. The first two transformations correspond to fragmentation of the lactone ring in P CH$_3$COOH by loss of CO and CO$_2$, respectively.

The loss of acetic acid, either thermally or upon electron impact, strongly indicates the presence of the unit -CH$_2$-CHOCOCH$_3$. Similar mass spectral studies on related norbornyl acetates indicate that the Bredt's rule restriction for thermal loss of acetic acid also obtains in electron impact decompositions[4].

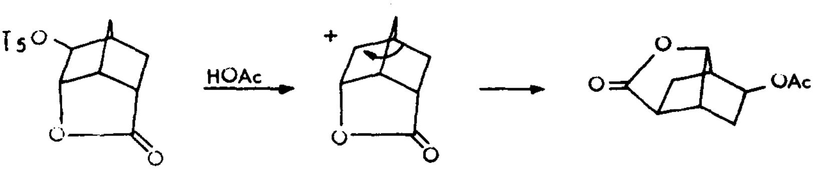
Further evidence for structure III was obtained from an examination of its n.m.r. spectrum at 100 Mc/sec. The proton at C$_7$ appears as doublet at 4.86 p.p.m. (from TMS in CDCl$_3$); J_{1-7} and J_{4-7} amount to 1.8 c.p.s.; $J_{7-6\,\underline{en}}$ and $J_{7-5\,\underline{en}}$ is 2.0 c.p.s. The endo proton at C$_3$ appears at 4.70 p.p.m. as a doublet with $J_{3\underline{en}-2\underline{en}}$ of 3.0 c.p.s. In the higher field portion of the spectrum the presence of two sets of geminal methylene protons at C_2 and C_5 is clearly indicated. The methyl peak appears at 1.90 p.p.m. as a sharp singlet. Hydrolysis of acetoxy lactone III yielded dihydroxy acid IV:



III IV

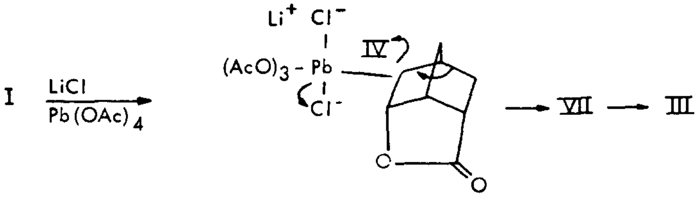
3 exo, 7 anti-Dihydroxynorbornane-6 exo carboxylic acid (IV), m.p. 157-58°, was converted with diazomethane to the methyl ester (V), m.p. 114-16°. The n.m.r. spectra of both IV and V showed the characterically narrow C_7 resonance peak as expected for small couplings involving protons 1, 4 and 5 endo; 6 endo. The C_3 endo proton in IV and V displayed the expected coupling pattern established for III.

Since lactone III may formally be regarded as a product of Wagner-Meerwein rearrangement of II proceeding from carbonium ion VII, the direct generation of this carbonium ion was attemped.



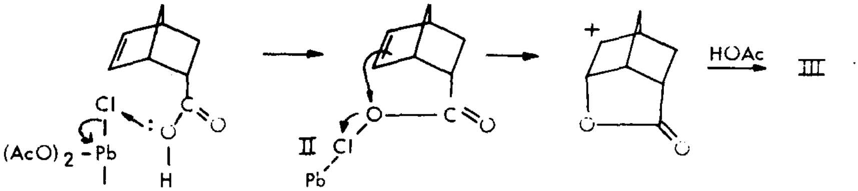
VI VII III

Acetolysis of tosylate VI does in fact yield III[5]. The reasonable assumption may be made that lithium chloride causes formation of carbonium VII. One interpretation of the action of lithium chloride in this system is that the transition state for carbonium ion formation in the cleavage of an intermediate such as VIII is stabilized electrostatically due to the presence of species such as $\mathrm{Li}_n^+\ \mathrm{Pb}^{\mathrm{IV}}(\mathrm{O_2R})_4\ \mathrm{Cl}_n^{-n}$, and also due to partially dissociated lithium chloride itself.

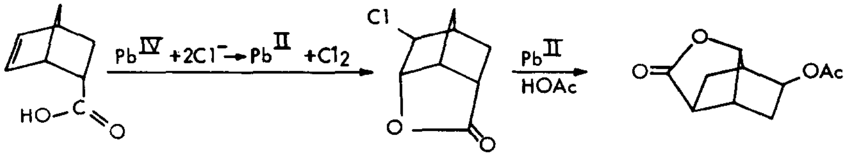


VIII

While this possible description is attractive, we have found that the free carboxyl group is necessary for formation of III in the LiCl-Pb(OAc)$_4$ oxidation of I. That is, LiCl-Pb(OAc)$_4$ oxidation of methyl endo-5-carboxybicyclo [2.2.1] hept-2-ene yields only the "unrearranged" lactone II. This result indicates that an acyl hypochlorite or its lead carboxylate equivalent may be involved:



VII



I IX III

A third reasonable mechanism which warrants consideration, but may be nonetheless rejected, involves the initial oxidation of chloride anion to chlorine by $Pb^{IV} \longrightarrow Pb^{II}$. The chlorine might then react with I to yield the chlorolactone (IX) Electrophilic catalysis by either Pb^{IV} or Pb^{II} could assist in removal of chloride anion with the eventual generation of carbonium ion VII.

It has been found, however, that halolactones are stable to either lead tetraacetate or lead tetraacetate-lithium chloride oxidation under the standard reaction conditions. Both Pb^{IV} and Pb^{II} species are present in these reactions.

Finally, the reaction (I → III) is uninhibited by oxygen, and chlorine is not produced in detectable amounts. These results are compatible with the proposed acyl hypohalite intermediate and its subsequent decomposition *via* an ionic pathway.

REFERENCES

1. R. M. Moriarty, H. G. Walsh, H. Gopal, *Tetrahedron Letters* (1966).
2. J. K. Kochi, *J. Am. Chem. Soc.*, **87**, 2500 (1965).
3. J. K. Kochi, *J. Org. Chem.*, **30**, 3265 (1965).
4. Unpublished results
5. The acetolysis of VI, which is extremely slow (*ca* 10^7 times at 25° slower than *exo* norbornyl p-toluenesulfonate), is the subject of a future communication.

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