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SELECTIVE OXIDATION OF n-ALKANES WITH LEAD TETRAACETATE

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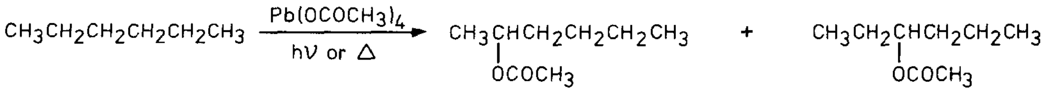
Abstract Alkanes, when treated with lead tetraacetate under thermal or photochemical conditions, undergo a slow but highly selective oxidation to form secondary acetates.

The n-alkanes are normally considered to be inert to mild oxidants, and with strong oxidants, mixtures of products are usually obtained, with considerable chain fragmentation[1] This is because the initial products have greater susceptibility to oxidation than the original alkanes. The problem of producing selective oxidation of alkanes is thus a very difficult one.

Lead tetraacetate has been used to oxidize a wide range of organic substances[2] but it has previously been reported that it is unreactive with alkanes[3] This is true if conventional reaction times of a few hours are used, but it has now been established that significant reaction takes place if prolonged times are used.

In a typical experiment, n-hexane (25 g) and lead tetraacetate (140 g) in acetic acid (200 ml) were heated at 80°, with stirring, for 18 days. At the end of this period no oxidant remained. The mixture was added to ice, and the oily layer (16 g) was separated and distilled under reduced pressure to give a colourless liquid (10 g) bp 102-110°/4 mm Glc analysis (cholesterol myristate packed column)[4] showed the liquid to contain only two products, which were identified as hexyl-2-acetate (54%) and hexyl-3-acetate (46%) by using authentic materials as references. The mixture was also hydrolyzed and gave only 2-hexanol and 3-hexanol in approximately equal amounts. The residue after distillation was a viscous liquid (∿ 6 g) which was a low m.w. polymer containing acetoxy groups. No hexyl-1-acetate was identified in this experiment, and a reasonable materials balance was obtained by recovery of unreacted hexane.

A similar result was obtained when the reaction was promoted photochemically, however the oxidation was then more rapid. n-Hexane (25 g) and lead tetraacetate (140 g) in acetic acid (200 ml), in a quartz flask, were exposed to strong sunlight for 6 days. A similar work up produced a volatile liquid (10 g), shown by glc analysis to contain hexyl-2-acetate (50%), hexyl-3-acetate (45%) and about 5% of a mixture of other substances, however there was no evidence for the presence of hexyl-1-acetate. About 5 g of polymer was also obtained and the remaining hexane made up the materials balance



$$CH_3CH_2CH_2CH_2CH_2CH_3 \xrightarrow[h\nu \text{ or } \Delta]{Pb(OCOCH_3)_4} CH_3\underset{OCOCH_3}{\underset{|}{C}}HCH_2CH_2CH_2CH_3 + CH_3CH_2\underset{OCOCH_3}{\underset{|}{C}}HCH_2CH_2CH_3$$

n-Heptane was oxidized with lead tetraacetate thermally (80°) for 18 days and gave a 50% yield of volatile liquid products identified by glc analysis as heptyl-2-acetate (40%), heptyl-3-acetate (40%) and heptyl-4-acetate (20%). Photochemical oxidation with lead tetraacetate (10 days sunlight) gave a very similar mixture of acetates, with the addition of a few percent of more complex substances. In both reactions some polymer (∿ 15%) was obtained but no heptyl-1-acetate was detected. Thermal oxidation of n-octane (31 days) provided a 50% yield of volatile products which were identified as octyl-2-acetate, -3-acetate and -4-acetate in approximately equal quantities, and about 10% of polymer.

The reactivity of the acetates towards further oxidation was tested in an experiment where authentic samples of hexyl-1-acetate, -2-acetate and -3-acetate were heated individually with lead tetraacetate in acetic acid for 40 days. No reaction products were detected; the acetates were recovered quantitatively and the oxidant was also found to be largely unreacted (∿ 80%).

The oxidation of n-hexane was repeated using trifluoroacetic acid as solvent and in this case the reaction was completed after 3 hrs stirring at room temperature. Careful work up gave a mixture shown to contain roughly equal amounts of hexyl-2-trifluoroacetate and hexyl-3-trifluoroacetate, however normal work up gave a mixture of 2-hexanol and 3-hexanol. Lead tetraacetate in trifluoroacetic acid has previously been reported to oxidize heptane to a mixture of heptanols, but the isomer composition was not determined.[5] Heptane in strong acid solution has also been oxidized by molecular oxygen catalyzed by cobalt III acetate[6] Under nitrogen this process gives heptanols, but with free access of air further oxidation to heptanones occurs.

The reactions now described represent a relatively mild and selective oxidative procedure for functionalizing the normally unreactive alkanes. Although the process is slow with acetic acid as solvent it is much faster in trifluoroacetic acid. The initial products, the secondary acetates are very unreactive and no further oxidation occurs.

The mechanism of the reaction is not at present clear, but it would appear to be a free radical process with a high degree of selectivity towards the secondary positions of the hydrocarbon chain. The lack of reactivity of the acetates compared to the original alkanes is surprizing and shows that they are not precursors of polymer formation An alternative process must lead to the formation of polymer, and the nature of the polymer is under investigation.

References

1. Lee, D.G. in "Oxidation" (Ed., Augustine, R.L.), Marcel Dekker Inc., New York, Vol 1, 1, 1969.
2. Butler, R.N. in "Synthetic Reagents" (Ed., Pizey, J.S.), Ellis Harwood, Chichester, England, Vol 3, 227, 1977.
3. Detilleux, E. and Jadot, J., Bull. Soc. Roy. Sci. Liege, 24, 366, 1955, C.A. 50, 16717h.
4. The usual types of packed glc columns were unable to resolve the isomeric acetates, a cholesterol myristate column, operating at 90°C with a N_2 flow rate of 30 ml/min gave adequate separation of the isomers.
5. Partch, R.E., J Amer. Chem. Soc., 89, 3662, 1967.
6. Hanotier, J., Camermam, Ph., Hanotier-Bridoux, M and de Radzitzky, P , J Chem. Soc., Perkin II, 2247, 1972.

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