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INTERACTION OF OZONE WITH 3,7-DIMETHYLOCTYL ACETATE ON SOLID ADSORBENTS

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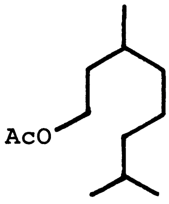
Oxidation with ozone of the acetate (1) adsorbed on silica-gel, alumina, or barium sulphate proceeds in good yield and gives mainly the alcohol (2) and the ketone (3). The high regioselectivity of the reaction when conducted at a suitable substrate loading is attributed to the mutual steric effect of one molecule upon the other in the adsorbed monolayer.

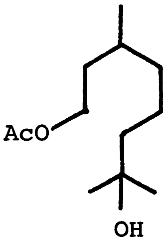
Recent publications[1] by Mazur and his co-workers have described a method for the selective hydroxylation of unactivated tertiary C-H positions by treatment with ozone of saturated compounds adsorbed on silica-gel. We now present the results of experiments conducted independently in this laboratory which demonstrate that the reaction when conducted at a suitable substrate loading is highly regiospecific, and indicate reasons why this should be so.

Treatment of a solution of 3,7-dimethyloctyl acetate (1) in ethyl acetate with ozone gave a complex mixture containing at least ten components (total yield, 53%). The four major products (total yield, 42%) were indentified by comparison with authentic samples as the mono-hydroxylated compounds (2) and (4), the ketone (3), and the diol (5). The ratio of yields of identified products formed by oxidation at C-7 and C-3 respectively was 8:1. The preference for reaction at C-7 probably reflects the deactivating influence of the electron-attracting acetate group on electrophilic attack by ozone.[2]

The reaction of ozone with samples of (1) adsorbed on silica-gel, alumina, or barium sulphate, was more selective. A stream of ozone in oxygen was passed through silica-gel bearing 1% by weight of adsorbed acetate (1) at -78°. When the silica-gel had become saturated with ozone the gas stream was stopped and the sample was allowed to warm slowly (15 h) to ambient temperature. G.l.c analysis of crude product (total yield, 98%) revealed the presence of only three major components: (2), (3) and (5) in yields of 65%, 27% and 9% respectively. The alcohol (4) was formed in small yield (0.6%) and there were also detected unidentified compounds (total yield, 5%), formed, presumably, by oxidation of (1) at primary and secondary positions.



(1)



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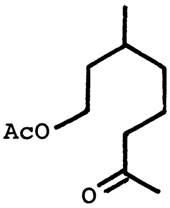

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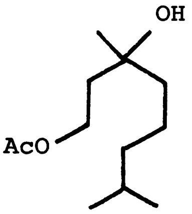

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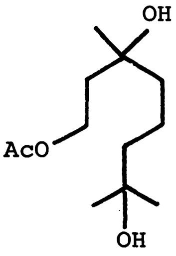

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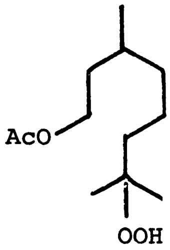
In this experiment and those previously described[1] the silica-gel acts both as the adsorbent for the organic substrate and the absorbent for ozone. These two functions may be separated. When ozone in relatively high partial pressure, generated by desorption from silica-gel, was passed at ambient temperature into a separate sample of silica-gel bearing adsorbed acetate (1) the combined yield of (2), (3), (4) and (5) was 58%. Good yields (*ca*90%) of the same products were obtained when ozone was passed at -78 into a mixture of pure silica-gel with a sample of acetate (1) adsorbed on either silica-gel or alumina, and the flask was then allowed to warm-up. When (1) adsorbed on barium sulphate was similarly treated the total yield of identified products, which included 2% of diol (5), was somewhat less (57%). No reaction occurred when a sample of (1) on silica-gel was treated with ozone at -78°, and the reaction vessel was then swept with a stream of oxygen during the warming-up period. On the basis of these results we conclude that the reaction involves attack of ozone in the gas phase on the organic substrate. There appears to be little direct interaction between absorbed ozone and adsorbed acetate (1).

A series of experiments conducted with samples of silica-gel bearing varying amounts (0.1-10%) of acetate (1) showed the regioselectivity of the reaction to be related to the concentration of adsorbed substrate. With a loading of 0.1% the conversion was high (*ca*90%) but a relatively large amount (*ca*20%) of unidentified products was formed and the ratio of yields of products formed by oxidation at C-7 and C-3 (9:1) was similar to that observed for the reaction in solution. When loadings of 0.5% and 1.0% were used this ratio improved only slightly but the yield of unidentified products fell to 5%. However, when silica-gel bearing 5% of the acetate (1) was exposed to ozone in the usual way neither the 3-alcohol (4) nor the diol (5) could be detected. The only products identified were those formed by oxidation at C-7, namely the alcohol (2) and the ketone (3) in yields of 58% and 29% respectively.

Adsorption experiments indicate that a substrate loading of 5% is approximately that required for the formation of a close-packed monolayer on the surface of the adsorbent. We suggest, therefore, that the above results support the hypothesis, first adumbrated by one of us,[3] and recently tested for chlorination reactions,[4] that molecules in close-packed ordered films are subject to mutual steric effects which direct chemical attack towards exposed terminal positions. Further experiments are in hand to test the utility of this method for the regioselective oxidation of suitable substrates.



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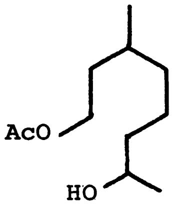

(7)

In the above experiments the ratio of yields of alcohol (2) and ketone (3) varied within the range 2:1 to 3:1. The ketone (3) does not appear to arise by decomposition of the possible hydroperoxide intermediate (6) during work-up, for when the crude ozonization product was extracted from the silica-gel with ethanol containing sodium borohydride the yield of the 7-alcohol (3) was unchanged, whilst the yield of the nor-alcohol (7) was the same as that of ketone (3) isolated by the normal extraction procedure.

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