Ozonolysis of Tetra-alkyl- and Unsymmetrically Dialkyl-substituted Olefins in an Alcoholic Medium

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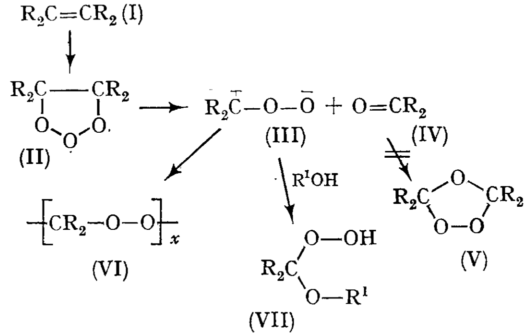
UNLIKE mono-, di-, and tri-substituted olefins, tetra-alkyl-substituted olefins (I) do not give normal ozonides (V) when subjected to classical ozonolysis procedures (those with an electron-withdrawing group in the α-position of an alkyl substituent are exceptions[1]). This result is usually explained by postulating that the Criegee zwitterion (III)[2,3] formed from the molozonide (II) does not react with the co-formed ketone (IV) to give the normal ozonide (V) as in the case of simpler olefins; instead it forms a polymeric peroxide (VI) which cannot be reduced to a ketone:



Criegee and Lohaus[4] have shown that the zwitterion (III) can add alcohols to give α-hydroperoxy-ethers, $R_2C(OR^1)OOH$ (VII), which are thermally stable and can be distilled in high vacuum.

It has now been found that addition of water to the products of ozonation of a tetra-alkyl-substituted olefin in alcohol medium at low temperature furnishes the corresponding ketones in very high yields. The intermediate α-hydroperoxy-ether (VII) is presumably readily hydrolyzed to give a ketone, an alcohol, and hydrogen peroxide:

$$R_2C(OR')OOH + H_2O \rightarrow R_2C{=}O + R'OH + H_2O_2$$

No reducing agents are required (*cf.* ref. **3**, **5**). The

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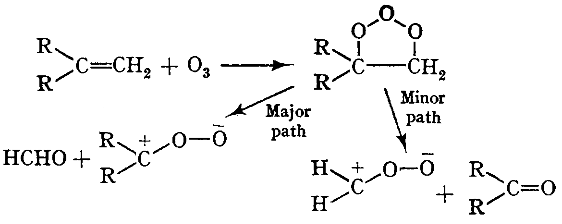
yields are not affected by adding the water before the treatment with ozone, but since the olefins are more soluble (at $-20°$) in water-free alcohol it is preferable to add it afterwards. Olefin concentration over the range 5—25% is not critical. A large excess of ozone should be avoided as it oxidizes ethanol to acetaldehyde.

In a typical experiment, an olefin (0·005—0·020 mole) in methanol or ethanol (10 ml.) is treated with a slight excess of ozonized oxygen at $-25°$ to $-18°$. The excess of ozone and oxygen is removed by a current of nitrogen at 0° for 30 min., water (1 ml.) is added, and the solution is stored at room temperature overnight before being analysed for ketone by g.l.c. and as 2,4-dinitrophenylhydrazone. Results are summarised below.

Unsymmetrical dialkyl-substituted olefins also give good yields of ketones by this procedure. Although two routes are available for decomposition of the unsymmetrical primary ozonide, Bailey,[6] Meinwald,[7] and Ledaal[8] have shown that the preferred path is to formaldehyde and $R_2\overset{+}{C}\text{–O–}\overset{-}{O}\text{–}$, under the present conditions the dialkyl zwitterion apparently then reacts preferentially with the alcohol rather than with the formaldehyde. The resulting dialkyl α-hydroperoxy-ether is then hydrolysed to its corresponding ketone.



Symmetrical dialkyl-substituted olefins do not give good yields of aldehydes by the present procedure: the zwitterion must be more reactive towards the intermediate aldehyde than towards alcohol and the predominant reaction is normal ozonide formation; a possible alternative explanation is that the α-hydroperoxy-ether is formed but is stable to hydrolysis by water (*cf.* Pappas[9]). Monoalkyl-substituted zwitterions have been found by Murry, Story, and Loan[10] to be more reactive towards a carbonyl function than the dialkyl-substituted zwitterion.

The main results obtained were as follows [olefin, ketone(s), yield (%) of ketone(s) (i) as 2,4-dinitrophenylhydrazone and (ii) by g.l.c., are given]:

2,3-dimethylbut-2-ene, acetone 84, 84;

2,3,4-trimethylpent-2-ene, acetone + isopropyl methyl ketone, 96, acetone 97 and isopropyl methyl ketone 99;

bicyclohexylidene, cyclohexanone, 86, 84;

1,2-dimethylcyclohexene, octane-2,7-dione, 98, —;

2,3-dimethylbicyclo[2,2,1]hept-2-ene, 1,3-diacetylcyclopentane, 99, —;

1,2-dimethylcyclopentene, heptane-2,6-dione, 97, —;

methylenecyclohexane, cyclohexanone, 80, 79;

2-methylenebicyclo[2,2,1]heptane, bicyclo[2,2,1]-heptan-2-one, 89, —;

2,4-dimethyl-3-methylenepentane, 2,4-dimethylpentan-3-one, 77, 75;

mesityl oxide, acetone, —, 85.

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