A New Orientation in the Oxymercuration of αβ-Unsaturated Carbonyl Compounds

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Summary Novel β-mercuration is found in the oxymercuration of α-only substituted αβ-unsaturated carbonyl compounds ($CH_2{:}CR{\cdot}CO{\cdot}Y$).

EXISTING literature[1] describing the oxymercuration of αβ-unsaturated carbonyl compounds is limited to the methoxymercuration of (β-alkyl)acrylic acids and esters or β-phenyl-aldehydes or ketones. Although structural evidence was not always compelling and, at the time, inevitably of a chemical nature, these reactions are reported to provide exclusively products in which the mercury becomes attached to the α-carbon:

$$R^1CH{:}CH{\cdot}CO{\cdot}Y + Hg(OAc)_2 + MeOH \rightarrow R^1CH(OMe)CH(HgOAc)CO{\cdot}Y + HOAc$$

(I)

where R^1 = H, alkyl, Ph; Y = OH, OR^2, H, Ph.

By using an n.m.r. technique we have been able to confirm that α-mercurated structures (I) are obtained in both methoxy- and t-butylperoxy-[2] mercuration of a wide range of such compounds in which there are (a) no other substituents, (b) β-only substituents, or (c) both α and β substituents.

We report now the first oxymercurials derived from αβ-unsaturated carbonyl compounds in which the mercury becomes attached to the β-carbon atom. This reversed orientation has been obtained only with molecules which are alkylated solely in the α-position, namely methyl methacrylate, methyl atropate, isopropenyl methyl ketone, and methacraldehyde:

$$\begin{tikzcd} CH_2{:}CR^1{\cdot}CO{\cdot}Y + Hg(OAc)_2 + R^2OH \arrow[d] \\ (AcOHg)CH_2{\cdot}CR^1(OR^2)CO{\cdot}Y + HOAc \quad (II) \arrow[d, "KBr"] \\ BrHg{\cdot}CH_2{\cdot}CR^1(OR^2)CO{\cdot}Y \quad (III) \end{tikzcd}$$

where R^1 = Me, Ph; Y = OMe, Me, H; R^2 = Me, OBu^t.

The reactions were carried out in dichloromethane using 2 mole % of perchloric acid as a catalyst, and the products (II) are viscous oils or low-melting crystalline solids for which correct elemental analyses have been obtained. The orientation was determined by analysis of the ^1H n.m.r. spectra of the corresponding bromomercurials (III), which are obtained from treatment with aqueous KBr.

In all these products the β-methylene protons come into resonance in the region τ 7·6 to 8·1, and generally they appear as an AB pattern by virtue of the magnetic non-equivalence which results from the asymmetry generated at the α-carbon. By comparison with oxymercurials derived from simple terminal alkenes,[3] this is precisely the chemical shift which is anticipated for the structures given. However, in the alternative orientation, $R^2O{\cdot}CH_2{\cdot}CR^1(HgBr){\cdot}CO{\cdot}Y$ (IV), the methylene protons would be expected to appear at about τ 6·2 (R^2 = Me) or 5·6 (R^1 = OBu^t), by analogy with model compounds. In the cases where R^1 = Me, confirmation of the assigned structure was obtained from measurements of the coupling between these α-methyl protons and the 16·84% of naturally-occurring ^{199}Hg nuclei. These were found to be in the range of 20 to 25 Hz, in agreement with previously measured[4] coupling constants for $Hg–C–C–CH_3$ [as in structure (III)], but too small by a factor of ten[3a,5] for the system $Hg–C–CH_3$ [as in structure (IV)].

A third piece of evidence relating to the orientation can be obtained by employing the borohydride reduction developed by Brown[6] to replace mercury in the oxymercurials by hydrogen:

$$BrHgCH_2{\cdot}CR^1(OR^2)CO{\cdot}Y \xrightarrow{NaBH_4} CH_3{\cdot}CR^1(OR^2)CO{\cdot}Y$$

(III) (V)

Thus t-butyl 1-methoxycarbonyl-1-methylethyl peroxide (V; R^1 = Me, R^2 = OBu^t, Y = OMe) was prepared in this way. This provides a convenient route to ethers or peroxides which have the inverse orientation to those obtainable by base-catalysed nucleophilic addition of the weak acids:

$$e.g. \quad CH_2{:}CMe{\cdot}CO_2Me + H{\cdot}OR \xrightarrow{\text{base}} RO{\cdot}CH_2{\cdot}CHMe{\cdot}CO_2Me$$

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