

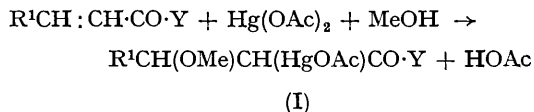
A New Orientation in the Oxymercuration of $\alpha\beta$ -Unsaturated Carbonyl Compounds

By A. J. BLOODWORTH* and R. J. BUNCE

(Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ)

Summary Novel β -mercuration is found in the oxymercuration of α -only substituted $\alpha\beta$ -unsaturated carbonyl compounds ($\text{CH}_2:\text{CR}\cdot\text{CO}\cdot\text{Y}$).

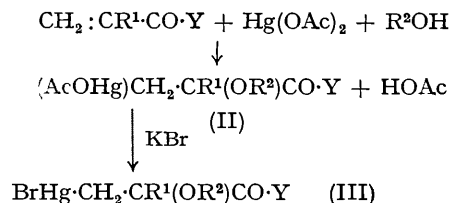
EXISTING literature¹ describing the oxymercuration of $\alpha\beta$ -unsaturated carbonyl compounds is limited to the methoxymercuration of (β -alkyl)acrylic acids and esters or β -phenylaldehydes or ketones. Although structural evidence was not always compelling and, at the time, inevitably of a chemical nature, these reactions are reported to provide exclusively products in which the mercury becomes attached to the α -carbon:



where $\text{R}^1 = \text{H}$, alkyl, Ph; $\text{Y} = \text{OH}$, OR^2 , H, Ph.

By using an n.m.r. technique we have been able to confirm that α -mercured structures (I) are obtained in both methoxy- and *t*-butylperoxy-²mercuration 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 oxymercurationals derived from $\alpha\beta$ -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:

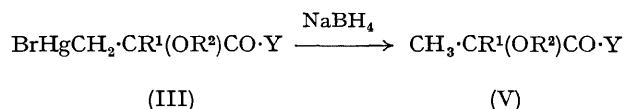


where $\text{R}^1 = \text{Me}$, Ph; $\text{Y} = \text{OMe}$, Me, H; $\text{R}^2 = \text{Me}$, O^tBu .

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.

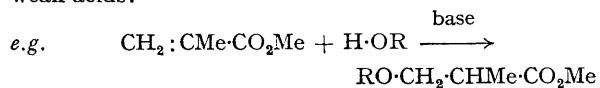
In all these products the β -methylene protons come into resonance in the region τ 7.6 to 8.1, and generally they appear as an AB pattern by virtue of the magnetic non-equivalence which results from the asymmetry generated at the α -carbon. By comparison with oxymercurationals derived from simple terminal alkenes,³ this is precisely the chemical shift which is anticipated for the structures given. However, in the alternative orientation, $\text{R}^2\text{O}\cdot\text{CH}_2\cdot\text{CR}^1(\text{HgBr})\cdot\text{CO}\cdot\text{Y}$ (IV), the methylene protons would be expected to appear at about τ 6.2 ($\text{R}^2 = \text{Me}$) or 5.6 ($\text{R}^1 = \text{O}^t\text{Bu}$), by analogy with model compounds. In the cases where $\text{R}^1 = \text{Me}$, confirmation of the assigned structure was obtained from measurements of the coupling between these α -methyl protons and the 16.84% of naturally-occurring ¹⁹⁹Hg nuclei. These were found to be in the range of 20 to 25 Hz, in agreement with previously measured⁴ coupling constants for $\text{Hg}-\text{C}-\text{C}-\text{CH}_3$ [as in structure (III)], but too small by a factor of ten^{3a,5} for the system $\text{Hg}-\text{C}-\text{CH}_3$ [as in structure (IV)].

A third piece of evidence relating to the orientation can be obtained by employing the borohydride reduction developed by Brown⁶ to replace mercury in the oxymercurationals by hydrogen:



Thus *t*-butyl 1-methoxycarbonyl-1-methylethyl peroxide (V; $\text{R}^1 = \text{Me}$, $\text{R}^2 = \text{O}^t\text{Bu}$, $\text{Y} = \text{OMe}$) 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:



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⁴ E. F. Kiefer and W. L. Waters, *J. Amer. Chem. Soc.*, 1965, **87**, 4401.

⁵ (a) S. Brownstein, *Discuss. Faraday Soc.*, 1962, **34**, 25; (b) M. M. Kreevoy and J. F. Schaefer, *J. Organometallic Chem.*, 1966, **6**, 589.

⁶ H. C. Brown and P. Geoghegan, *J. Amer. Chem. Soc.*, 1967, **89**, 1522.