

THE ATTEMPTED OXYMERCURATION-DEMERCURATION OF 2-PHENYLBORNYLENE

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During other studies we required a stereospecific route to the exo-alcohol (1). A convenient procedure¹ for the Markovnikov hydration of olefins involves oxymercuration of the olefin followed by in situ demercuration using NaBH_4 . Since such reaction of apobornylene(2) gives² the exo-alcohol(3), it was anticipated that similar treatment of 2-phenylbornylene(4a) would give the required alcohol(1).

We now report that oxymercuration-demercuration of 2-phenylbornylene(4a) gives the divinylmercury compound (5; 61%) in addition to some starting material (4a; 21%).

The assignment of the divinylmercury structure(5) to the major product, m.p. 132-133° and m.p. 136.5-138°, $[\alpha]_D - 64^\circ$; ν_{max} 764, 701 cm^{-1} ; λ_{max} 280 nm (ϵ 4140), 246 nm (4140), 225 nm (4160) (Found: C, 61.7; H, 6.2. $\text{C}_{32}\text{H}_{38}\text{Hg}$ requires C, 62.1; H, 6.3%) NMR δ 7.20 ppm (2-phenyl), 2.38 ($\text{C}^4\text{-H}$; $J_{4,5\text{-exo}}$ 3 cps), 0.99 (CH_3), 0.84 (CH_3), 0.78 (CH_3), was based on the following evidence. The molecular formula for (5) was confirmed by accurate mass measurement and peak intensity ratios for the parent ion in the mass spectrum. Reduction of (5) with LiAlH_4 gave 2-phenylbornylene (4a; 94%).

In view of the abnormal reaction product the oxymercuration-demercuration sequence was examined as two discrete reactions. Oxymercuration of 2-phenylbornylene(4a) gave the vinylmercury acetate(4b) as a viscous gum, $[\alpha]_D - 14^\circ$, $n_D^{24} 1.5928$, ν_{max} 1601, 1300, 764, 700 cm^{-1} , λ_{max} 265 nm (ϵ 7710), M^+ (for Hg^{200}) 470.130321 ($\text{C}_{18}\text{H}_{22}\text{HgO}_2$ requires 470.130297), NMR δ 7.29 (2-phenyl), 2.49 ($\text{C}^4\text{-H}$; $J_{4,5\text{-exo}}$ 3.0 cps), 1.98 (OAc), 1.02 (CH_3), 0.94 (CH_3), 0.83 (CH_3). Reduction of the vinylmercury acetate(4b) with NaBH_4

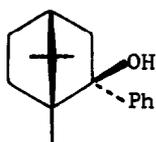
gave 2-phenylbornylene (4a; 24%) and the divinylmercury compound (5; 69%).

A full account of this and other related work will be published later.

References

* Determined at 60 Mc for CDCl_3 solutions.

1. H.B. Henbest and B. Nicholls, J. Chem. Soc., 227 (1959).
2. H.C. Brown, J.H. Kawakami and S. Ikegami, J. Amer. Chem. Soc., 89, 1525 (1967).



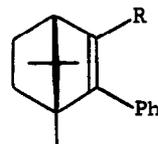
(1)



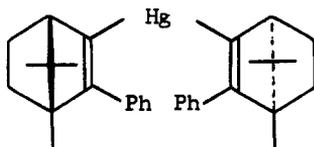
(2)



(3)



(4) (a) R = H
(b) R = HgOAc.



(5)