# SOME ANOMALOUS OXYMERCURATION-DEMERCURATION REACTIONS

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Abstract—Vinylmercury acetates are anomalous products from the oxymercuration of 2-phenylbornylene and  $\beta$ -pinene. In contrast, oxymercuration proceeds normally for 1,1-diphenylethylene, bornylene and camphene.

THE rapid oxymercuration of an olefin, and the reductive cleavage of the carbonmercury bond *in situ* by NaBH<sub>4</sub>, provides a very rapid and convenient method for the Markownikov hydration of an olefin.<sup>1-3</sup> Recently we have reported<sup>4</sup> the attempted hydration of 2-phenylbornylene (1). Reaction of 2-phenylbornylene (1) with Hg(OAc)<sub>2</sub> in aqueous THF gave the vinylmercury acetate (2), which on demercuration *in situ* afforded regenerated 2-phenylbornylene (1) and the divinylmercury compound 3. In aqueous MeOH the formation of 1 was suppressed, the yield of 3 being virtually quantitative.

The vinylmercury acetate (2) is considered to arise by loss of the  $C^3-\underline{H}$  from 4 which process can compete favourably with nucleophilic attack by  $H_2O$  at the hindered  $C^2$ -position. The contrast of this reaction with the normal products found for the reactions of norbornylene (5),<sup>3</sup> apobornylene (6),<sup>3</sup> 1-methylnorbornylene (7),<sup>3</sup> 4-methylbornylene (8),<sup>5</sup> and 2-phenylnorbornylene (9),<sup>6</sup> led us to examine the mercuration of the series of compounds, 1,1-diphenylethylene, bornylene (10), camphene (11) and  $\beta$ -pinene (12), as part of an attempt to determine the required structural features for vinylmercury acetate formation.

1,1-Diphenylethylene reacted normally to give the hydroxymercury acetate (13), which was identified by its IR and NMR spectra and its conversion on reaction with NaBH<sub>4</sub> into the known 1,1-diphenylethanol.

Oxymercuration of bornylene (10) gave a crude product, the NMR spectrum of which exhibited no resonance characteristic of vinylic protons. Demercuration of this material gave a mixture of seven components (GLC), four of which were separated and identified as isoborneol (14a; 36%), isobornyl acetate (14; 10%), epiisoborneol (15a: 27%) and the acetate (15b, 9%). The isolation of significant quantities of the acetates (14b and 15b) from an oxymercuration reaction in aqueous THF is unusual, but may be rationalised in terms of the internal collapse of a mercuronium ion-acetate ion-pair which competes favourably with nucleophilic attack by water at the hindered C-2 and C-3 position.

Oxymercuration of camphene (11) followed by  $NaBH_4$  reduction gave a mixture in which the normal product, camphene hydrate (16), was a major component. Two further compounds were isolated. Preferential sublimation of camphene hydrate



from the above mixture afforded a residue from which di-(2-exohydroxycamphanyl)mercury (17) was isolated by crystallization. The assigned structure followed from an accurate mass measurement, IR and NMR data and by the LiAlH<sub>4</sub> reduction of 17 to camphene hydrate (16). It seems probably that this abnormal product (17) arises during the NaBH<sub>4</sub> reduction of the "normal" hydroxymercury acetate (18).

In an attempted chromatographic separation on alumina of the crude reaction product di-(2-exohydroxycamphanyl)-mercury (17) could not be eluted, but instead, in addition to camphene hydrate (16), a low yield of the four isomeric divinylmercury compounds (19) was obtained. The structure (19) is consistent with an accurate mass measurement and IR, UV and NMR data. In particular the presence of signals (integral total 2H/molecule) due to vinylic protons in the NMR spectrum support the divinyl mercury structure. Since no trace of (19) could be detected in the NMR spectrum of the crude reaction product, it is considered to arise from (17) by dehydration during chromatography.

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Reaction of  $\beta$ -pinene (12) with Hg(OAc)<sub>2</sub> in aqueous THF gave a crude product shown (NMR spectrum) to be a mixture (7:2) of the alkenylmercury acetates (20) and (21). In situ NaBH<sub>4</sub> reduction of this mixture afforded a complex mixture, the major components of which were  $\beta$ -pinene (12) and dimeric compounds (ratio ca. 1:2.7; GLC).

#### DISCUSSION

Reaction of alkene with Hg(OAc)<sub>2</sub> gives rise to a mercuronium ion which may either react with a nucleophile, H<sub>2</sub>O, AcOH, AcO<sup>-</sup>, to give a "normal" oxymercuration product, or lose a proton to give isomeric alkenylmercury acetates. Such alkenyl mercury acetates have been isolated as primary products from the attempted oxymercuration only of 2-phenylbornylene (1) and  $\beta$ -pinene (12). Other compounds, closely related structurally, have yielded normal oxymercuration products. These results lead to the suggestion that alkenylmercuryacetate formation occurs in those substrates where a tertiary carbonium ion could be formed and because of its abnormally hindered environment, be protected from external nucleophilic attack.

### EXPERIMENTAL

Rotations were measured for CHCl<sub>3</sub> solns (unless otherwise stated) at room temp. IR spectra were recorded on a Perkin-Elmer 337 spectrometer. UV spectra, on a Shimadzu MPS-50L Spectrophotometer, were recorded for cyclohexane solns. Alumina used for chromatography was P Spence, Grade H, deactivated by the addition of 5% or 10% of 10% AcOH. Light petroleum refers to the fraction b.p. 50-70°. NMR spectra were determined at 60Mc in CDCl<sub>3</sub> with CHCl<sub>4</sub> and TMS as internal standards.

#### D-(-)-2-Phenylborn-2-en-3-yl mercury acetate (2)

Hg(OAc)<sub>2</sub> (6·38 g) was added to a soln of D-( – )-2-phenylborn-2-ene (1;2·15 g) in aqueous THF (20 ml; 1:1) and the mixture stirred at 20° for 7 days. Isolation by means of ether gave the vinyl mercury acetate<sup>4</sup> (2; 4·22 g) as a gum  $[\alpha]_D - 14^\circ$  (c 1·10),  $n_D^{24}$  1·5928,  $\nu_{max}$  (liq. film) 1601, 1300, 764 and 700 cm<sup>-1</sup>,  $\lambda_{max}$  265 nm ( $\epsilon$  7710), M<sup>+</sup> (for Hg<sup>202</sup>) 470·130321 (C<sub>18</sub>H<sub>22</sub>HgO<sub>2</sub> requires: 470·130297), NMR (CDCl<sub>3</sub>)  $\delta$  7·29 (2phenyl); 2·49 ( $J_{4H,3exoH}$  3 c/s; C<sup>4</sup>H), 1·98 (OAc), 1·02 (Me), 0·94 (Me), 0·83 ppm (Me).

#### NaBH<sub>4</sub> Reduction of D-(-)-2-Phenylborn-2-en-3-yl mercury acetate (2)

(a) In aqueous THF. A soln (0-5M) of NaBH<sub>4</sub> in NaOH aq (10ml; 3M) was added to 2 (2.14 g) in THF (10 ml) and NaOH aq (10 ml; 1-5M) and the mixture stirred at 20° for 10 min. Isolation by means of ether gave a mixture (1·2 g) shown (GLC, NMR) to consist of 1 (24%) and 3 (69%).<sup>4</sup> (3) isolated from the mixture by crystallization from pentane had m.p. 132–133° and 136-5–138°,  $[\alpha]_D - 64^\circ$  (c 1-04),  $v_{max}$  (CS<sub>2</sub>) 764, 701 cm<sup>-1</sup>,  $\lambda_{max}$  280 nm ( $\varepsilon$  4140), 255 nm ( $\varepsilon$  4160), 246 nm ( $\varepsilon$  4140), NMR  $\delta$  7·20 (2-phenyl), 2·38 ( $J_{4H}$ , 5 and 3 c/s; C<sup>4</sup>H), 0·99 (Me), 0·84(Me), 0·78 ppm (Me).

(b) In aqueous McOH. As for (a) except replacing THF by McOH gave 1 (4%) and 3 (90%).

#### LAH Reduction of the divinylmercury compound (3)

LAH (1 g) was added to a soln of 3 (500 mg) in THF (100 ml) and the mixture heated under reflux for 4 hr. Isolation of the terpenoid material by means of ether gave pure (GLC, NMR) 1 (319 mg).

#### 1-Hydroxy-1,1-diphenylethan-2-yl mercury acetate (13)

Hg(OAc)<sub>2</sub> (3·19 g) was added to a soln of 1,1-diphenyl ethylene (1·8 g) in aqueous THF (20 ml; 1:1) and the mixture stirred at 20° for 1 day. Isolation of the crude product by means of ether gave a mixture (3·61 g) of composition (GLC, NMR), 1,1-diphenylethylene (21%), 13 (79%), from which 13 was obtained by crystallization (CH<sub>2</sub>Cl<sub>2</sub>-ether) as an amorphous solid (3·1 g; pure by NMR), m.p. 116·5–117·5°,  $v_{max}$  (KBr) 3370 (broad), 753, 698 cm<sup>-1</sup>  $\lambda_{max}$  270 nm (shoulder,  $\varepsilon$  560), 266 nm (shoulder,  $\varepsilon$  790), 260 nm ( $\varepsilon$  1050), 254 nm (e 1080), 250 nm (e 1020); NMR (CDCl<sub>3</sub>)  $\delta$  7·27 (W<sub>h/2</sub> 16 c/s; phenyi), 3·76 (W<sub>h/2</sub> 13 c/s; OH), 2·85 (J<sub>Hg</sub> 199, 2-H<sup>2</sup>O4 c/s<sup>7</sup>; C<sup>2</sup>H), 1·84 ppm (OAc).

The acetate 13 was converted (cf. Ref. 5) into the corresponding chloride, m.p. 142–143·5° (dec),  $v_{max}$  (KBr) 3478 (sharp), 750, 695 cm<sup>-1</sup>,  $\lambda_{max}$  270 nm (shoulder,  $\varepsilon$  480), 266 nm (shoulder,  $\varepsilon$  650), 260 nm ( $\varepsilon$  860), 254 nm ( $\varepsilon$  850), 250 nm ( $\varepsilon$  800), M<sup>+</sup> (for Hg<sup>202</sup>, Cl<sup>35</sup>) Found: 434·035727 (C<sub>14</sub>H<sub>13</sub>ClHgO requires: 434·036113), NMR(CDCl<sub>3</sub>)  $\delta$  7·27 (W<sub>h/2</sub> 4·5 c/s; phenyl), 2·93 (J<sub>Hg</sub> 199,<sub>2-H</sub> 194 c/s<sup>7</sup>; C<sup>2</sup>H), 2·63 ppm (W<sub>h/2</sub> 8 c/s; OH).

#### NaBH<sub>4</sub> Reduction of 1-hydroxy-1,1-diphenylethan-2-yl mercury acetate (13)

A soln (0.5M) of NaBH<sub>4</sub> in NaOH aq (20 ml; 3M) was added to a soln of 13 (1 g) in THF (10 ml) and NaOH aq (10 ml; 3M) and the mixture stirred at 20° for 1 day. Isolation of the crude product by means of ether gave 1,1-diphenylethanol (433 mg), m.p. and m.m.p.  $80-81^{\circ}$ ,  $v_{max}$  (CS<sub>2</sub>) 3602, 698 cm<sup>-1</sup>, NMR (CDCl<sub>3</sub>)  $\delta$  7.37 (W<sub>b/2</sub> 5 c/s; phenyl), 2.19 (OH), 1.93 ppm (Me).

#### Oxymercuration-demercuration of bornylene (10)

Hg(OAc)<sub>2</sub> (7.05 g) was added to a soln of 10 (3 g.  $[\alpha]_D - 19^\circ$ ) in aqueous THF (45 ml) and the mixture stirred at 20° for 2.5 hr. A sample, isolated by means of ether, gave an NMR spectrum which did not exhibit signals characteristic of vinylic protons.

Aqueous NaOH (12ml; 3M) was added, followed by a soln (0.5M) of NaBH<sub>4</sub> in NaOH aq (12ml; 3M), and the resulting mixture stirred at 20° for 20 min. Isolation of the terpenoid material by means of ether gave a semi-solid product (3.01 g). Adsorption of this material (1.85 g) onto 10% deactivated alumina (100 g) and elution with pentane gave a mixture (GLC; 300 mg) of 14b and 15b. 14b, prepared from 14a  $([\alpha]_D - 1^\circ)$ , was an oil  $n_D^{24}$  1.4633,  $[\alpha]_D - 2^\circ$  (c 1.00),  $v_{max}$  (CS<sub>2</sub>) 1730, 1243 cm<sup>-1</sup>, NMR (CDCl<sub>3</sub>)  $\delta$  4.66  $(J_{2^{PP}ende, 3-ende}^{-5.7} c/s, J_{2^{PP}ende, 3-exe}^{-5.7} c/s; C^{2-ende}H)^8$  2.00 (OAc), 0.98 (Me), 0.84 ppm (Me; 6H). Subtraction of the NMR spectrum of 14b from that of the mixture gave a spectrum consistent with 15b, NMR (CDCl<sub>3</sub>)  $\delta$  4.49 ( $J_{2^{PP}ende, 3-ende}^{-7}$  c/s,  $J_{2^{PP}exe, 3-ende}^{-5}$  5 c/s; C<sup>3</sup>H), 1.98 (OAc), 1.02 (Me), 0.90, (Me), 0.88 (Me).

Elution with pentane-benzene (19:1) gave 14a (604 mg), m.p. and m.m.p.  $207-208^{\circ}$ ,  $[\alpha]_D - 19^{\circ}$  (c 1-02; toluene)  $\nu_{max}$  3616 cm<sup>-1</sup>, NMR (CDCl<sub>3</sub>)  $\delta$  3-62 ( $J_{2-endo}^{opp}$ ,  $_{3-endo}^{o}$  6-7 c/s,  $J_{2-endo}^{app}$ ,  $_{3-exo}^{o}$  4-2 c/s; C<sup>2</sup>H), 1-02 (Me), 0-90 (Me), 0-82 ppm (Me).

Elution with pentane-benzene (3:1) gave 15a (277 mg), m.p. 190–191°,  $[\alpha]_D + 12^\circ$  (c 1.03; toluene),  $\nu_{max}$  (CS<sub>2</sub>) 3613 cm<sup>-1</sup>, NMR(CDCl<sub>3</sub>)  $\delta$  3.83 ( $J_{2^-endo, 3-endo}^{app}$  6.8 c/s,  $J_{2^-exo, 3-endo}^{app}$  4.9 c/s; C<sup>3</sup>H), 1.35 (OH), 1.08 (Me), 0.88 (Me), 0.83 ppm (Me).

The composition of the product mixture was estimated by GLC as 14b (10%), 15b (9%) 14a (36%) and 15a (27%).

#### Oxymercuration-demercuration of camphene (11)

Hg(OAc)<sub>2</sub> (30 g) was added to a soln of 11 (10 g.  $[\alpha]_D + 17^\circ$  (c 1.02)) in aqueous THF (100 ml; 1.1) and the mixture stirred at 20° for 5 hr. NaOH aq (100 ml; 3M) was added followed by a soln (0.5 M) of NaBH<sub>4</sub> in NaOH aq (100 ml; 3M) and stirring continued at 20° for 30 min. Isolation by means of ether gave a solid (12.13 g). This material was treated as follows:

(a) Adsorption of the crude product (5.8 g) onto 5% deactivated alumina (300 g) and elution with pentane gave material (269 mg), tentatively assigned structure 19, m.p. 117-118°,  $[\alpha]_D + 6°$  (c 1.06),  $v_{max}$  (CS<sub>2</sub>) 2876, 1300, 1255, 1197, 1102, 1053, 953, 819, 761, 698 cm<sup>-1</sup>,  $\lambda_{max}$  237 nm ( $\epsilon$  15,400), M<sup>+</sup> (for Hg<sup>202</sup>) 472.204286 (C<sub>20</sub>H<sub>30</sub>Hg requires: 472.205365), NMR (CDCl<sub>3</sub>)  $\delta$  6.26 (W<sub>b/2</sub> 2.5 c/s), 5.78, 5.50 (integral ratio respectively 15:6:2; vinylic protons), 2.62 (W<sub>b/2</sub> 6.5 c/s; C<sup>1</sup>H), 1.25 (Me), 1.18 ppm (Me).

Elution with benzene gave 16 (2.44 g), m.p. and m.m.p. 150–151°,  $[\alpha]_D - 5^\circ$  (c 1.06),  $v_{max}$  (CS<sub>2</sub>), 3608 cm<sup>-1</sup>, NMR (CDCl<sub>3</sub>) $\delta$  1.37 (OH), 1.17 (C<sup>2</sup>H<sub>3</sub>), 0.99 (C<sup>3-exo</sup>H<sub>3</sub>), 0.90 ppm (C<sup>3-exo</sup>H<sub>3</sub>).

(b) The crude product (3:86 g) was heated in a sublimation apparatus at 100° and 0.1 mm for 8 hr. The residue (1:89 g) on crystallization from pentane gave di(2-exo-hydroxycamphanyl)mercury (17; 209 mg) m.p. 166-167° (dec),  $[\alpha]_D - 20°$  (c 1:01)  $\nu_{max}$  (CS<sub>2</sub>) 3360 cm<sup>-1</sup> (broad), M<sup>+</sup> (for Hg<sup>202</sup>) 508:227186 (C<sub>20</sub>H<sub>34</sub>HgO<sub>2</sub> requires: 508:226491), NMR (CDCl<sub>3</sub>)  $\delta$  1:92 (OH), 1:29 (--CH<sub>2</sub>--Hg--CH<sub>2</sub>--), 1:00 (Me), 0:92 ppm (Me).

#### LAH Reduction of di(2-exohydroxycamphanyl)mercury (17)

To a soln of 17 (50 mg) in ether (5 ml) was added LAH (100 mg) and the mixture heated under reflux for 1 hr. Isolation of the terpenoid material by means of ether gave 16 (17 mg) and m.m.p. 150-151°.

#### Oxymercuration of $\beta$ -pinene (12)

Hg(OAc)<sub>2</sub> (31-9 g) was added to a soln of 12 (13-6 g),  $[\alpha]_D - 15^\circ$  (c 1.15), 98% pure by GLC), in aqueous THF (200 ml; 1:1), and the mixture stirred at 20° for 10 min.

Isolation of the terpenoid material by means of ether gave 20 and 21 (20:15 g) as a waxy solid,  $[\alpha]_D - 14^\circ$ (c 1.01),  $v_{max}$  (film) 2821, 1603, 1302, 798 cm<sup>-1</sup>,  $\lambda_{max}$  245 nm ( $\varepsilon$  8130), 203 ( $\varepsilon$  9390), NMR (CDCl<sub>3</sub>)  $\delta$  5.33, 4.99 (C<sup>3</sup>—H and C<sup>1.0</sup>H vinylic protons in 20 and 21 (7:2), 2.75 (CH<sub>2</sub>HgOAc in (20)), 2.01 (HgOAc), 1.29 (Me), 0.89 ppm (Me).

Reaction of 20 and 21 (7.79 g) with NaCl in  $H_2O$ —CH<sub>2</sub>Cl<sub>2</sub> gave the mixed alkenylmercury chlorides (7:2; 6.47 g) as needles, m.p. 87–89,  $[\alpha]_D - 24^{\circ}$  (c 1.09),  $\nu_{max}$  (CS<sub>2</sub>) 2836, 805 cm<sup>-1</sup>,  $\lambda_{max}$  249 nm ( $\epsilon$  8240), 203 nm ( $\epsilon$  9210), NMR (CDCl<sub>3</sub>)  $\delta$  5.32, 4.89 (C<sup>3</sup>—H and C<sup>10</sup>—H vinylic protons: 7:2), 2.76 (—<u>CH</u><sub>2</sub>HgCl), 1.30 (Me), 0.89 ppm (Me).

#### Demercuration of the alkenylmercury acetates (20 and 21) -

The acetates 20 and 21, prepared as above from  $\beta$ -pinene (34 g) were reduced in situ by the addition of NaOH aq (25 ml; 3M) followed by a soln (0.5M) of NaBH<sub>4</sub> in NaOH aq (25ml; 3M) and stirring at 20° for 10 min. Isolation by means of ether gave the crude product (3.31 g) shown by GLC to contain 12 and dimeric compounds (ca 1:2.7).

A major dimeric component, isolated by preparative GLC, was a mixture,  $n_0^{22}$  1.5111,  $[\alpha]_D - 19^\circ$  (c 1.08),  $\lambda_{max}$  215 nm (e 10,900), M<sup>+</sup>270. (Found : C, 88.9; H, 11.3. C<sub>20</sub>H<sub>30</sub> requires : C, 88.8, H, 11.2%), NMR (CDCl<sub>3</sub>)  $\delta$  5.20, 4.52 (vinylic protons, 1H; ca. 2:1) major peaks, 1.27 (Me), 0.83 ppm (Me); minor peaks, 1.24, 1.22, 1.08, 0.87 and 0.75 ppm.

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