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OXYMETALLATION

XIX *. PREPARATION OF THE FIRST OXYMERCURIALS DERIVED FROM CYCLOPROPANE

A.J. BLOODWORTH* and CHRISTOPHER J. COOKSEY

Christopher Ingold Laboratories, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ (Great Britain)

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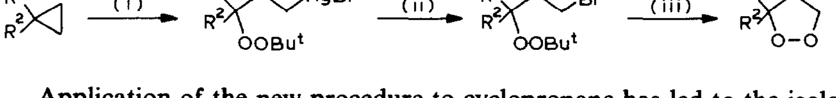
Summary

Three oxymercurials, $RO(CH_2)_3HgBr$ where $R = Bu^tO$, $BrHg(CH_2)_3$, and Ac, have been isolated from the reaction of cyclopropane with mercury(II) acetate, t-butyl hydroperoxide, and 60% aqueous perchloric acid (20 mol%) in dichloromethane for 5 d, followed by anion exchange with aqueous potassium bromide.

Introduction

The oxymercuration of substituted cyclopropanes has been extensively investigated [2], but as far as we are aware there are no reports of such reactions with cyclopropane itself. In the course of developing a new synthetic route for the conversion of cyclopropanes into 1,2-dioxolanes (eq. 1) [3], we discovered that t-butyl peroxymercuration of substituted cyclopropanes (step (i)) could be achieved more conveniently with mercury(II) acetate and 20 mol% of aqueous perchloric acid than with the previously used [4] mercury(II) trifluoroacetate.



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Application of the new procedure to cyclopropane has led to the isolation of the first 3-oxypropylmercury(II) salts, including the first example of a di(γ-mercurioalkyl) ether.

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* For part XVIII see ref. 1.

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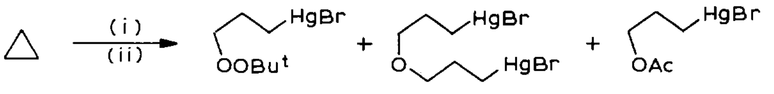
Results and discussion

The reaction was carried out in dichloromethane at room temperature and was monitored by ^1H NMR spectroscopy. It was complete after 4–5 d and TLC then showed the presence of three major organomercury products. These were separated by chromatography on silica to provide three white crystalline solids, which were identified as, in order of elution, 3-bromomercuriopropyl t-butyl peroxide (**1**), di(3-bromomercuriopropyl) ether (**2**), and 3-bromomercuriopropyl acetate (**3**) (eq. 2).



(1) (2) (3) (2)

Reagents: (i) 2 Bu^{t}OOH, $Hg(OAc)_2$, 0.2 $HClO_4$ (60%) + H_2O,
(ii) KBr/H_2O

The peroxymercurial **1** and acetoxymercurial **3** were unambiguously identified by their elemental analyses and ^1H and ^{13}C NMR spectra, additional evidence for **3** coming from the presence of a strong carbonyl band in the infrared spectrum. The elemental analysis and NMR data for **2** could conceivably be compatible also with the corresponding hydroxymercurial $HO(CH_2)_3HgBr$. However, this structure is unlikely in view of the chromatographic characteristics of the compound, and was ruled out by the absence of an OH band in the infrared spectrum. Further confirmation of the structure of **2** was obtained from a determination of its relative molecular mass by vapour pressure osmometry.

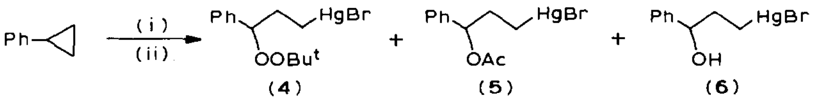
The isolated yields of pure **1**, **2**, and **3**, were 10, 14, and 15% respectively, but several chromatographic fractions still contained mixtures. Each product has a characteristic ^1H NMR chemical shift for the methylene groups attached to oxygen [δ 3.96 (**1**), 3.55 (**2**), and 4.11 (**3**)], so that integration in this region of the spectrum provided the molar ratio of **1**/**2**/**3** in the crude product. This was found to be 22/31/47, which together with the weight of the crude product, corresponds to a combined yield of the oxymercurials of 62%.

The products **1**–**3** are clearly derived from the three oxygen nucleophiles present in solution, namely t-butyl hydroperoxide, water from the aqueous perchloric acid, and acetate or acetic acid from the mercury(II) acetate. However, the product distribution does not reflect the relative concentrations of these, let alone their anticipated nucleophilicities. Thus, mercury(II) acetate is only partially soluble, so that the concentration of derived acetate or acetic acid should be low, yet the acetoxymercurial **3** is the major product. The 20 mol% of 60% aqueous perchloric acid is calculated to provide 14.5 mmol of water to compete with the 38 mmol of t-butyl hydroperoxide, yet the ether **2** is also preferred to the peroxymercurial **1**.

The low yield of peroxymercurial **1** is in marked contrast to the results obtained when the same reagents were used with alkenes [5]. Here, high proportions of peroxymercurials result from equilibrium control, whereby first-formed acetoxymercurials undergo β-oxy exchange catalysed by perchloric acid (eq. 3) [5].

$$BuCH(OAc)CH_2HgOAc + Bu^tOOH \overset{H^+}{\rightleftharpoons} BuCH(OOBu^t)CH_2HgOAc + AcOH \quad (3)$$

Peroxymercurials are also the major products in similar reactions with substituted cyclopropanes [3]. For example, phenylcyclopropane affords 65 mol% of peroxymercurial **4**, 21 mol% of acetoxymercurial **5**, and 14 mol% of hydroxymercurial **6** (eq. 4).



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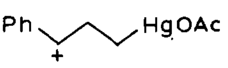
Reagents: (i) 2 Bu^{t}OOH, Hg(OAc)$_2$, 0.2 HClO$_4$ (60%) + H$_2$O,
(ii) KBr/H$_2$O

However, we have shown that this product distribution is kinetically controlled, since γ-oxy exchange analogous to eq. 3 does not take place. By implication, then, the products obtained from cyclopropane also result from kinetic control.

Any attempt to account for the observed difference in behaviour between cyclopropane and phenylcyclopropane requires a consideration of the nature of the cationic intermediates involved in the two reactions. Presumably there is, in each case, an initial complexation of the cyclopropane ring to a suitable mercury(II) electrophile. Evidence suggests that with phenylcyclopropane this interaction develops further to generate an intermediate which is essentially the benzylic carbocation **7** [3].



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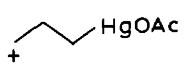

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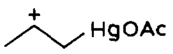

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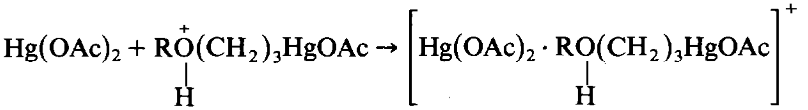
However, with cyclopropane the analogous carbocation **8** is unlikely to be formed, and if it were it would be expected to rearrange to **9**, yet no propene-derived oxymercurials were detected. Thus, it seems likely that with unsubstituted cyclopropane the mercury atom remains intimately associated with the positive charge, giving an intermediate of composition $[(CH_2)_3HgOAc]^+$ which is best described as a homomercurinium ion by analogy with the bridged mercurinium ions generally believed to be involved in the oxymercuration of symmetrical alkenes [2].

The catalysis of oxymercuration by perchloric acid has been ascribed to protonation of the mercury(II) acetate [6], so that the active mercury(II) electrophile here is possibly of the composition $[Hg(OAc)_2 \cdot H_3O]^+ \ ClO_4^-$. Reaction of such a species with cyclopropane can be envisaged to afford the homomercurinium ion in intimate contact with a molecule of acetic acid and a molecule of water. The proximity of these nucleophiles then accounts for the preferential formation of acetoxy- and hydroxymercurials.

The mechanism of catalysis requires that several molecules of mercury(II) acetate are activated by each molecule of perchloric acid. This can be achieved by reaction of mercury(II) acetate with the protonated oxymercurials, which then fulfil the role initially played by H_3O^+ (eq. 5). With the product from water (R = H), the reaction of the resultant electrophile with cyclopropane (eq. 6) then generates the homomercurinium ion in intimate contact with a molecule of hydroxymercurial, which can itself function as the nucleophile to afford the ether (eq. 7).



$$Hg(OAc)_2 + R\underset{\displaystyle H}{\overset{+}{O}}(CH_2)_3HgOAc \rightarrow \left[Hg(OAc)_2 \cdot R\underset{\displaystyle H}{O}(CH_2)_3HgOAc \right]^+ \quad (5)$$

$$[Hg(OAc)_2 \cdot H_2O(CH_2)_3HgOAc]^+ + (CH_2)_3 \rightarrow [(CH_2)_3HgOAc]^+ + HO(CH_2)_3HgOAc + HOAc \quad (6)$$

$$[(CH_2)_3HgOAc]^+ + HO(CH_2)_3HgOAc \rightarrow [AcOHg(CH_2)_3]_2\overset{+}{O}H \xrightarrow[\text{(cf. eqns 5, 6)}]{-H^+} [AcOHg(CH_2)_3]_2O \quad (7)$$

The difference between cyclopropane (eq. 2) and phenylcyclopropane (eq. 4) can therefore be rationalised if it is assumed that the homomercurinium ion is more reactive than the benzylic cation **7** and therefore shows a higher discrimination for proximate nucleophiles.

The hydroxymercuration of ethene affords, in addition to the hydroxymercurial, an ether **10** analogous to compound **2**; the proportion of **10** increases under strongly acidic conditions and with ageing of the reaction mixture [7]. This has been ascribed to an acid-catalysed disproportionation by a β-oxy exchange mechanism (eq. 8) [8].

$$HOCH_2CH_2HgX + HOCH_2CH_2HgX \overset{H^+}{\rightleftharpoons} \underset{\textbf{(10)}}{O(CH_2CH_2HgX)_2} + H_2O \quad (8)$$

However, a parallel pathway for the formation of our cyclopropane-derived ether is unlikely since β-oxy exchange does not appear to proceed readily (see earlier).

Experimental

NMR spectra were recorded with a Varian XL200 spectrometer for solutions in $CDCl_3$, and chemical shifts are downfield from internal tetramethylsilane (^1H and ^{13}C) or external dimethylmercury (^{199}Hg). Relative molecular mass determinations were carried out on solutions in chloroform using a Hewlett Packard 302 Vapour Pressure Osmometer calibrated with benzil. t-Butyl hydroperoxide was purified as described previously [5], except that light petroleum (b.p. 40–60°C) was used instead of dichloromethane. All other reagents were commercial samples which were used as received.

Cyclopropane (1.1 cm^3; 19 mmol) was condensed into a tube at −80°C and then added to a magnetically stirred mixture of mercury(II) acetate (6.4 g, 20 mmol), dichloromethane (40 cm^3), t-butyl hydroperoxide (3.8 cm^3, 38 mmol), and 60% aqueous perchloric acid (4 mmol; ca. 0.6 cm^3, added as 40 drops from a commercial Pasteur pipette) cooled at −40°C. The mixture was allowed to warm to −5°C over 30 min, maintained at this temperature for 2 h, and then allowed to warm to room temperature. The progress of the reaction was monitored by 60 MHz ^1H NMR spectroscopy.

After 5 d the mercury(II) acetate had nearly all dissolved and the concentration of cyclopropane had remained constant for 24 h. Water (100 cm^3) was added and after stirring for 30 min, the phases were separated and the aqueous layer was extracted with dichloromethane (50 cm^3). The combined organic phases were stirred for 1 h with a solution of potassium bromide (2.6 g, 23 mmol) in water (20 cm^3). The aqueous layer was removed and the dichloromethane solution was dried ($MgSO_4$). The dichloromethane was removed by roto-evaporation at water pump pressure and 25°C followed by evacuation at 0.01 mm, to give a cloudy oil (4.42 g).

TLC on silica (Kieselgel 60 F_{254}), eluting with a 1/1 mixture of dichloromethane and light petroleum (b.p. 60–80°C), showed three main organomercury products with R_f values of 0.37, 0.33, and 0.11, which were visualised by spraying with a solution of dithizone (2%) in chloroform. Chromatography on silica (Merck Kieselgel 80, 70–230 mesh), eluting with a 1/1 mixture of dichloromethane and light petroleum (b.p. 60–80°C), gave two fractions shown by NMR to be (a) mainly **1** plus some **2**, and (b) a mixture of **2** and **3**.

Flash chromatography of fraction (a) on silica (Merck Kieselgel 80, 230–400 mesh), eluting with a 1/1 mixture of dichloromethane and light petroleum (b.p. 60–80°C) afforded a pure sample of **1** (0.78 g, 10%). Flash chromatography of fraction (b) on the same type of silica and eluting with a 6/1/1 mixture of cyclohexane, dichloromethane, and ethyl acetate, gave pure samples of **2** (0.85 g, 14%) and **3** (1.10 g, 15%). The purity of all three products was confirmed by TLC.

3-Bromomercuriopropyl t-butyl peroxide (1) was a white crystalline solid, m.p. 24–25°C; δ(H) 1.27 s (9H), 1.92 ca. t [$^2J(^{199}Hg-^1H)$ 193 Hz; 2H], 2.05 m [$^3J(^{199}Hg-^1H)$ 311; 2H], and 3.96 ca. t (2H); δ(C) 26.48 q (3C), 26.98 t [$^2J(^{199}Hg-^{13}C)$ 97 Hz], 30.14 t [$^1J(^{199}Hg-^{13}C)$ 1504 Hz], 76.33 t [$^3J(^{199}Hg-^{13}C)$ 113 Hz], and 80.95 s; δ(Hg) 1319 tt [$J(^{199}Hg-^1H)$ 195 and 316 Hz]. (Found: C, 20.62; H, 3.64. $C_7H_{15}BrHgO_2$ calcd.: C, 20.42, H, 3.67%).

Di-(3-bromomercuriopropyl) ether (2) was recrystallised from chloroform and cyclohexane to give white crystals, m.p. 93–94°C; δ(H) 1.89 ca. t [$^2J(^{199}Hg-^1H)$ 195 Hz; 2H], 2.21 m [$^2J(^{199}Hg-^1H)$ 336 Hz; 2H], and 3.55 ca. t (2H); δ(C) 28.56 t [$^2J(^{199}Hg-^{13}C)$ 109 Hz], 30.29 t [$^1J(^{199}Hg-^{13}C)$ 1545 Hz], and 72.31 t [$^3J(^{199}Hg-^{13}C)$ 96 Hz]; δ(Hg) 1258 tt [$J(^{199}Hg-^1H)$ 202 and 345 Hz]; IR shows no band in the OH region; Rel. mol. mass (c/g cm^{-3}) 715 (0.012), 657 (0.024), 700 (0.033), and 716 (0.050) $C_6H_{12}Br_2Hg_2O$ calcd.: 661. (Found: C, 11.06; H, 1.66. $C_6H_{12}Br_2Hg_2O$ calcd.: C, 10.89; H, 1.82%).

3-Bromomercuriopropyl acetate (3) was recrystallised from chloroform and cyclohexane to give white crystals, m.p. 40–41°C; δ(H) 2.00 ca. t [$^2J(^{199}Hg-^1H)$ 196 Hz; 2H], 2.14 m [$^3J(^{199}Hg-^1H)$ 296 Hz; 2H], 2.14 s (3H), and 4.11 ca. t (2H); δ(C) 21.22 q, 27.65 t [$^2J(^{199}Hg-^{13}C)$ 91 Hz], 31.16 t [$^1J(^{199}Hg-^1H)$ 1521 Hz], 66.00 t [$^3J(^{199}Hg-^1H)$ 154 Hz], and 170.89 s; δ(Hg) 1297 tt [$J(^{199}Hg-^1H)$ 202 and 296 Hz]; IR shows δ(C=O) 1740 cm^{-1} vs; Rel. mol. mass (c/g cm^{-3}) = 393 (0.011) and 399 (0.013). $C_5H_9BrHgO_2$ calcd.: 382. (Found: C, 15.66; H, 2.30. $C_5H_9BrHgO_2$ calcd.: C, 15.73; H, 2.37%).

References

1 Part XVIII: A.J. Bloodworth and H.J. Eggelte, J. Chem. Soc., Perkin Trans. I, (1984) 1009.

2 A.J. Bloodworth, in C.A. McAullife (Ed.), The Chemistry of Mercury, Macmillan, London, 1977, p. 182.

3 Part XX: A.J. Bloodworth, K.H. Chan, and C.J. Cooksey, J. Chem. Soc., Perkin Trans., in preparation.

4 A.J. Bloodworth and J.L. Courtneidge, J. Chem. Soc., Perkin Trans. I, (1982) 1807.

5 A.J. Bloodworth and J.L. Courtneidge, J. Chem. Soc., Perkin Trans. I, (1981) 3258.

6 M.C. Cabaleiro, A.D. Ayala, and M.D. Johnson, J. Chem. Soc., Perkin Trans. II, (1973) 1207.

7 J. Chatt, Chem. Rev., 48 (1951) 13.

8 W. Kitching, Organomet. Chem. Rev., 3 (1968) 86.