Journal of Organometallic Chemistry, 386 (1990) 299–304
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20539

Oxymetallation

XXII *. Hydroperoxymercuriation using 30% hydrogen peroxide

A.J. Bloodworth * and Michael D. Spencer
Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ (U.K.)

(Received October 11th, 1989)

Abstract

Each of eleven representative alkenes, $R^1R^2C{=}CHR^3$, has been found to react with an equimolar amount of mercury(II) acetate in about an eightfold excess of 30% aqueous hydrogen peroxide to afford the hydroperoxymercurial, $R^1R^2C(OOH)CH(HgOAc)R^3$, or a mixture of the hydroperoxymercurial and the corresponding hydroxymercurial, $R^1R^2C(OH)CH(HgOAc)R^3$, which can be separated by column chromatography (SiO_2, CH_2Cl_2). Eight new hydroperoxymercurials have been characterized.

Introduction

Alkyl peroxymercuriation of alkenes (eq. 1, R^4 = alkyl) provides a very versatile method of preparing dialkyl peroxides, particularly when coupled with demercuriation [2]. The method tolerates a variety of functional groups in the alkene and can be extended to the synthesis of cyclic and bicyclic peroxides.

$$R^1R^2C{=}CHR^3 + R^4OOH + Hg(O_2CCX_3)_2 \rightarrow R^1R^2C(OOR^4)CH(HgO_2CCX_3)R^3 + HO_2CCX_3 \quad (1)$$

Hydroperoxymercuriation (eq. 1, $R^4 = H$) has been little studied by comparison. Only seven hydroperoxymercurials have been fully characterised, and all the preparations involved the use of concentrated aqueous (55–87%) or anhydrous hydrogen peroxide [3–5]. We now report that hydroperoxymercurials can be prepared using the commercially available and less hazardous 30% hydrogen peroxide.

---

* For part XXI see ref. 1.

0022-328X/90/$03.50

Results and discussion

When the alkene (10 mmol) was stirred for 45 min with a suspension of mercury(II) acetate (10 mmol) in 30% aqueous hydrogen peroxide (10 cm^3; ca. 90 mmol) and the mixture then extracted with dichloromethane, a product was obtained which, after anion exchange with aqueous potassium bromide consisted of either a mixture of hydroperoxymercurial (**1**) and hydroxymercurial (**2**) or the hydroperoxymercurial alone, depending upon the alkene (eq. 2: Table 1).

$$R^1R^2C{=}CHR^3 \xrightarrow[30\%\ H_2O_2]{Hg(OAc)_2} \xrightarrow[KBr]{aq.} \underset{(\mathbf{1})}{R^1R^2C(OOH)CH(HgBr)R^3} + \underset{(\mathbf{2})}{R^1R^2C(OH)CH(HgBr)R^3} \qquad (2)$$

Authentic samples of hydroxymercurials (**2**) were prepared, by using water in place of the 30% hydrogen peroxide, to provide comparative data. It is noteworthy that in the ^{13}C NMR spectra, the *C*OOH is consistently less shielded (δ larger by 11.3 to 13.8 ppm) that the corresponding *C*OH, whereas the *C*HgCOOH is consistently more shielded (δ smaller by 6.3 to 9.0 ppm) than the corresponding *C*HgCOH. Where the formation of hydroperoxymercurials alone is reported (Table 1), hydroxymercurials were undetected by both ^{13}C NMR spectroscopy and TLC. Analytically pure hydroperoxymercurials were obtained by gravity column chromatography (SiO_2, CH_2Cl_2).

An examination of the results in Table 1 reveals that hydroperoxymercurials were obtained exclusively and in yields exceeding 90% for all alkenes bearing either a single aryl substituent or geminal substituents, whereas mixtures in markedly lower

Table 1

Products, $R^1R^2C(OOH)CH(HgBr)R^3$ (**1**) and $R^1R^2C(OH)CH(HgBr)R^3$ (**2**), from hydroperoxymercuriation of alkenes, $R^1R^2C{=}CHR^3$, with 30% aqueous hydrogen peroxide

Alkene	Product distribution (mol%) [a]		Yield (%) of crude **1**+**2**	Yield (%) of pure **1**
	1	**2**		
Hex-1-ene	50	50	74	24
Styrene	100	0	94	– [b]
4-Methylstyrene	100	0	99	79
2-Methylpent-1-ene	100	0	92	86
α-Methylstyrene	100	0	92	– [b]
(*Z*)-But-2-ene	70	30	31 [c]	15
(*E*)-But-2-ene	70	30	15 [d]	10
Cyclopentene	100	0	41	13
Cyclohexene	45	55	44	– [b]
(*E*)-Hex-3-ene	55	45	58	11
1-Methylcyclohexene	100	0	96	82

[a] Calculated to the nearest 5% from ^{13}C NMR peak intensities. [b] Not purified; $R^1R^2C(OOH)CH(HgX)R^3$ is known (see experimental section). [c] Organomercury(II) acetates (ratio 80/20) isolated in 92% yield by liquid–liquid extraction with refluxing CH_2Cl_2. [d] Organomercury(II) acetates (ratio 75/25) isolated in 44% yield by liquid–liquid extraction with refluxing CH_2Cl_2.

yields were generally obtained for monoalkyl- and 1,2-dialkyl-ethenes; no reaction occurred with (*Z*)- or (*E*)-stilbene. The very low yields obtained from (*Z*)- and (*E*)-but-2-ene were shown to be due largely to water solubility of the products. Thus, when the organomercury(II) acetates were isolated by liquid–liquid extraction of the reaction mixtures with refluxing dichloromethane, the yields were increased to 44 and 92% for (*E*)- and (*Z*)-but-2-ene respectively, each product mixture being slightly enriched in hydroperoxymercurial.

We believe that the product distributions observed arise from equilibrium control. In support of this, the hydroxymercurial derived from 4-methylstyrene was completely transformed into the corresponding hydroperoxymercurial when stirred for 45 min with 30% hydrogen peroxide and an equimolar amount of acetic acid (eq. 3).

$$\text{4-MeC}_6\text{H}_4\text{CH(OH)CH}_2\text{HgOAc} \xrightarrow[\text{AcOH}]{30\%\text{H}_2\text{O}_2} \text{4-MeC}_6\text{H}_4\text{CH(OOH)CH}_2\text{HgOAc} \quad (3)$$

A single hydroperoxymercurial was obtained from each alkene, indicating that the regio- and stereo-specificity normally observed for (per)oxymercuriations is preserved. Thus, this simple procedure using commercially available reagents affords fair to excellent yields of hydroperoxymercurials from a representative range of alkenes.

Experimental

Unless otherwise stated, NMR spectra were recorded with a Varian XL 200 spectrometer for solutions in $CDCl_3$, and chemical shifts are downfield from tetramethylsilane. 60 and 400 MHz ^1H NMR spectra were recorded with a Jeol PMX60 and Varian VXR 400 spectrometer respectively, and 20 MHz ^{13}C NMR spectra with a Varian CFT20 spectrometer. All reagents were commercial samples which were used as received.

Hydroperoxymercuriation

The alkene (10 mmol) was added to a magnetically stirred suspension of mercury(II) acetate (3.19 g; 10 mmol) in 30% aqueous hydrogen peroxide (10 cm^3; ca. 90 mmol). The mixture was stirred for 45 min and then extracted with dichloromethane (3×10 cm^3). The combined extracts were stirred vigorously with aqueous potassium bromide (1.31 g; 11 mmol, 10 cm^3) for 30 min. The organic phase was separated and the aqueous layer extracted with more dichloromethane (2×10 cm^3). The combined dichloromethane solutions were dried ($MgSO_4$) and the solvent was removed with a rotary evaporator to afford the crude product.

The only variations on this procedure were as follows. (i) The reactions with (*Z*)- and (*E*)-but-2-ene were carried out at $-15\,^\circ C$, with addition of the alkene as the neat liquid; the anion exchange was carried out at room temperature in the normal way. (ii) The reaction mixture containing 4-methylstyrene was placed in an ultrasound bath for 30 min before being stirred as usual.

Pure hydroperoxymercurial (**1**) was isolated by column chromatography on Merck Kieselgel (70–230 mesh) with dichloromethane as eluant. The eluted fractions were analysed by TLC (Merck aluminium-backed Kieselgel 60 F_{254}; CH_2Cl_2), a solution of dithizone in chloroform being used to reveal the organomercurials.

Each hydroxymercurial **2** was eluted ahead of the corresponding hydroperoxymercurial **1**. Yields are given in Table 1; spectroscopic and analytical data are given below.

1-Bromomercurio-2-hydroperoxyhexane (from hex-1-ene): oil; δ(H) 0.92 t (3H), 1.2–1.6 m (5H), 1.6–1.9 m (1H), 2.14 dd (J 12, 6.4 Hz; 1H), 2.41 dd (J 12, 4.6 Hz; 1H), 4.43 m (1H), and 8.77 s (1H); δ(C) 14.19, 22.67, 28.01, 35.88, 38.98, and 84.64. (Found: C, 17.92; H, 3.31. $C_6H_{13}BrHgO_2$ calcd.: C, 18.12; H, 3.29%).

1-Bromomercurio-2-hydroperoxy-2-phenylethane (from styrene): oil (not purified); δ(H) 2.11, 2.22 *AB*X (J 12, 7, 7 Hz; 2H), 5.23 t (1H), 7.20–7.35 m (5H), and 8.1 br s (1H); δ(C) 39.39, 86.09. 126.14, 128.41, 128.91, and 141.90.

For the corresponding organomercury(II) acetate: white solid, m.p. 110–114 °C (lit. m.p. 114–115 °C [4], 118–119 °C [3]); δ(H) (60 MHz; 1/1 $CDCl_3$ & pyridine) 2.02 s (3H), 2.25 *AB*X (2H), 5.28 t (1H), other signals obscured by solvent; δ (C) (20 MHz; 1/1 $CDCl_3$ & pyridine) 23.41, 29.57, 85.77, 126.31, 128.36, 128.56, 143.86, and 176.62.

1-Bromomercurio-2-hydroperoxy-2-(4-methylphenyl)ethane (from 4-methylstyrene): oil; δ(H) 2.20, 2.28 *AB*X (J 12, 7.4, 6.3 Hz; 2H), 2.32 s (3H), 5.27 t (1H), 7.17, 7.24 AB (J 8.3 Hz, 4H), 8.62 s (1H): δ(C) 21.49, 39.88, 86.33, 126.44, 129.86, 138.38, and 139.14. (Found: C, 24.73; H, 2.60. $C_9H_{11}BrHgO_2$ calcd.: C, 25.04; H, 2.56%).

1-Bromomercurio-2-hydroperoxy-2-methylpentane (from 2-methylpent-1-ene): oil; δ(H) 0.89 t (3H), 1.27 s (3H), 1.33 m (2H), 1.53 m (2H), 2.19 s (2H), and 8.26 s (1H); δ(C) (20 MHz) 14.61, 17.67, 25.74, 42.63, 44.62, and 86.17. (Found: C, 18.11, H, 3.26. $C_6H_{13}BrHgO_2$ calcd.: C, 18.12; H, 3.29%).

1-Bromomercurio-2-hydroperoxy-2-phenylpropane (from α-methylstyrene): oil (not purified); δ(H) 1.67 s (3H), 2.34, 2.38 AB (J 12 Hz, 2H), 7.20–7.46 m (5H), and 8.25 br s (1H) (lit. 1.77 (3H), 2.70 AB (2H), and 7.51 (5H) for corresponding organomercury(II) trifluoroacetate [5]); δ(C) 28.09, 47.13, 86.98, 124.94, 127.67, 128.86, and 145.23 (lit. 28.2, 38.0, 86.4, 125.1, 128.1, 129.1 and 144.9 for corresponding organomercury(II) trifluoroacetate [5]).

threo-2-Bromomercurio-3-hydroperoxybutane (from (Z)-but-2-ene): white solid (unstable); δ(H) (400 MHz) 1.33 d (3H), 1.47 d (^3J(Hg–H) 134 Hz, 3H), 2.58 dq (^3J 7.5, 5.1 Hz, ^2J(Hg–H) 109 Hz, 1H), 4.35 dq (^3J 5.9, 5.1 Hz, ^3J(Hg–H) 136 Hz, 1H), and 8.16 s (1H); δ(C) 18.55, 19.81, 52.66, and 86.20.

For the corresponding organomercury(II) acetate: δ(C) 18.27, 19.64, 22.77, 45.05, 85.66, and 177.40.

erythro-2-Bromomercurio-3-hydroperoxybutane (from (E)-but-2-ene): oil, δ(H) 1.32 d (3H), 1.45 d (3H), 3.16 dq (^3J 8, 4 Hz, 1H), 4.49 dq (^3J 6, 4 Hz, 1H), and 7.28 s (1H); δ(C) 16.17, 19.11, 53.38, and 85.06. (Found: C, 12.91; H, 2.17. $C_4H_9BrHgO_2$ calcd.: C, 13.00; H, 2.45%).

For the corresponding organomercury(II) acetate: δ(C) 15.98, 18.98, 22.46, 46.62, 84.50, and 177.31.

trans-1-Bromomercurio-2-hydroperoxycyclopentane (from cyclopentene): oil; δ(H) 1.5–1.8 m (4H), 1.97 m (1H), 2.17 m (1H), 2.85 m (1H), 4.89 m (1H), and 8.2 br s (1H); δ(C) 24.14, 29.56, 30.17, 56.28, and 90.40. (Found: C, 16.08; H, 2.23. $C_5H_9BrHgO_2$ calcd.: C, 15.70; H, 2.37%).

trans-1-Bromomercurio-2-hydroperoxycyclohexane (from cyclohexene): white solid with very low solubility (not purified); δ(C) (mixed with corresponding hydroxymercurial; DMSO/DMSO-d_6) 23.55, 27.86, 30.33, 32.38, 55.44, and 85.19. The corresponding organomercury(II) acetate is known, m.p. 102–103° C [3], 95–102° C [4], but no NMR data have been reported.

erythro-3-Bromomercurio-4-hydroperoxyhexane (from (*E*)-hex-3-ene): oil; δ(H) 1.05 t (3H), 1.12 t (3H), 1.40–1.68 m (1H), 1.70–1.94 m (3H), 3.10–3.20 m (1H), 4.23–4.32 m (1H), and 8.51 br s (1H); δ(C) 10.60, 16.86, 23.44, 26.84, 63.52, and 89.75. (Found: C, 18.16; H, 3.33. $C_6H_{13}BrHgO_2$ calcd.: C, 18.12; H, 3.29%).

For the corresponding organomercury(II) acetate: δ(C) 10.55, 16.71, 23.15, 23.48, 26.72, 62.93, 88.80, and 177.78.

1-Bromomercurio-2-hydroperoxy-2-methylcyclohexane (from 1-methylcyclohexene): white solid, decomposes at ca. 110° C; δ (H; 400 MHz) 1.32–1.46 m (2H), 1.41 s (3H), 1.63–1.76 m (4H), 1.78–1.88 m (1H), 2.16–2.21 m (1H), 2.90 dd (*J* 11.3, 3.8; 1H), and 7.56 s (1H); δ(C) 22.82, 25.36, 28.65, 30.28, 37.14, 64.07, and 85.66. (Found: C, 20.55; H, 3.08. $C_7H_{13}BrHgO_2$ calcd.: C, 20.52; H, 3.20%).

Hydroxymercuriation

The method was identical to hydroperoxymercuriation except that water was used in place of 30% hydrogen peroxide.

1-Bromomercurio-2-hydroxyhexane (from hex-1-ene): white solid (87%); δ(C) 14.13, 22.66, 28.30, 41.47, and 45.37, and 71.42.

1-Bromomercurio-2-hydroxy-2-phenylethane (from styrene): white solid, m.p. 108–110° C (97%); δ(C) 46.34, 73.29, 124.78, 128.03, 129.06, and 146.64.

1-Bromomercurio-2-hydroxy-2-(4-methylphenyl)ethane (from 4-methylstyrene): white solid, m.p. 82–85° C (85%); δ(C) 21.15, 46.97, 73.19, 124.77, 129.69, 137.73, and 143.74.

1-Bromomercurio-2-hydroxy-2-methylpentane (from 2-methylpent-1-ene): white solid (83%); δ(C) 14.74, 18.23, 31.29, 48.56, 51.88, and 74.84.

1-Bromomercurio-2-hydroxy-2-phenylpropane (from α-methylstyrene): white solid, m.p. 64–67° C (94%); δ(C) 33.70, 53.40, 75.65, 123.90, 126.86, 128.45, and 149.62.

threo-2-Bromomercurio-3-hydroxybutane (from (*Z*)-but-2-ene): δ(C) 18.79, 25.19, 60.96, and 73.25.

erythro-2-Bromomercurio-3-hydroxybutane (from (*E*)-but-2-ene): δ(C) 17.03, 24.76, 60.80, and 72.57.

trans-1-Bromomercurio-2-hydroxycyclopentane (from cyclopentene): oil (11%); δ(C) 23.56, 29.20, 33.90, 57.40, and 77.28.

trans-1-Bromomercurio-2-hydroxycyclohexane (from cyclohexene): white solid (80%); δ(C) (DMSO/DMSO-d_6) 23.87, 27.40, 31.11, 37.76, 63.70, and 72.46.

erythro-3-Bromomercurio-4-hydroxyhexane (from (*E*)-hex-3-ene): white solid (5%); δ(C) 10.30, 16.58, 24.12, 32.02, 70.91, and 75.94.

1-Bromomercurio-2-hydroxy-2-methylcyclohexane (from 1-methylcyclohexene): white solid (71%); δ(C) 23.33, 28.35, 30.47, 31.12, 42.90, 70.71, and 74.33.

Acknowledgements

We thank J.L. Courtneidge for carrying out preliminary studies with styrene. MDS thanks the SERC for financial support.

References

1 Part XXI: A.J. Bloodworth and G.M. Lampman, J. Org. Chem., 53 (1988) 2668.

2 A.J. Bloodworth and J.L. Courtneidge, J. Chem. Soc., Perkin Trans. 1, (1982) 1797, and earlier parts of the series.

3 E. Schmitz, A. Rieche, and O. Brede, J. Prakt. Chem., 312 (1970) 30.

4 V.I. Sokolov, Izv. Acad. Nauk USSR Ser. Khim., (1972) 1089.

5 A.J. Bloodworth and M.E. Loveitt, J. Chem. Soc., Perkin Trans. 1, (1977) 1031.