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OXYMETALLATION

V*. THE METHOXYMERCURATION AND TERT-BUTYL PEROXYMERCURATION OF REPRESENTATIVE α,β-UNSATURATED ALDEHYDES AND THE TERT-BUTYL PEROXYMERCURATION OF α,β-UNSATURATED PERACETALS

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SUMMARY

The position of mercuration in the products RCH(OMe)CH(HgOAc)CHO, obtained from the methoxymercuration of cinnamaldehyde and crotonaldehyde, and in the products $AcOHgCH_2CMe(OR)CHO$, from the methoxymercuration and tert-butyl peroxymercuration of methacrolein, is as expected by analogy with related reactions of α,β-unsaturated ketones and esters. Oxymercurations of methacrolein also give the compounds $AcOHgCH_2CMe(OMe)CH(OMe)_2$ and $AcOHgCH_2$-CMe(OOBu-t)CH(OOBu-t)OH, formed by subsequent reaction at the aldehyde group. The tert-butyl peroxymercuration of cinnamaldehyde gives only the compound $PhCH(OOBu\text{-}t)CH(HgOAc)CH(OOBu\text{-}t)_2$, but here formation of the $\alpha\beta$-unsaturated peracetal, $PhCH{=}CHCH(OOBu\text{-}t)_2$, probably precedes oxymercuration. The compound $PhCH{=}CHCH(OOBu\text{-}t)_2$ and its analogue from methacrolein, $CH_2{=}CMeCH(OOBu\text{-}t)_2$, have been isolated and tert-butyl peroxymercuration of them yields the novel triperoxides $PhCH(OOBu\text{-}t)CH(HgOAc)CH(OOBu\text{-}t)_2$ and $BrHgCH_2CMe(OOBu\text{-}t)CH(OOBu\text{-}t)_2$ respectively.

INTRODUCTION

As part of our investigation into the application of oxymercuration to the synthesis of organic peroxides[1–4], we recently studied the tert-butyl peroxymercuration and methoxymercuration of α,β-unsaturated ketones and esters[3]. These are positionally specific additions in which the mercury becomes attached to the carbon β to the carbonyl group (β-mercuration) for ketones and esters alkylated solely at the α-carbon (eqn. 1), and to the α-carbon (α-mercuration) for all other compounds (eqn. 2).

$$\underset{(I)}{CH_2{=}CR^1{-}COY} + Hg(OAc)_2 + ROH \xrightarrow[-HOAc]{H^+} AcOHgCH_2{-}CR^1(OR){-}COY \qquad (1)$$

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* For Part IV see ref. 1.

TABLE 1

PRODUCTS FROM THE OXYMERCURATION OF α,β-UNSATURATED ALDEHYDES

α,β-Unsaturated aldehyde					
PhCH=CHCHO	*n*	*MeCH=CHCHO*	*n*	*CH$_2$=CMeCHO*	*n*
Methoxymercuration products					
PhCH(OMe)CH(HgOAc)CHO (III)	2.5	MeCH(OMe)CH(HgOAc)CHO (IV) (70%) MeCH(OMe)CH(HgOAc)CH(OMe)$_2$ (V) (30%)	3	AcOHgCH$_2$CMe(OMe)CHO (VI) (70%) AcOHgCH$_2$CMe(OMe)CH(OMe)$_2$ (VII) (30%)	3
t-Butyl peroxymercuration products					
PhCH(OOBu-t)CH(HgOAc)CH(OOBu-t)$_2$ (VIII) (33%)[a] PhCH=CHCH(OOBu-t)$_2$ (IX) (33%)[a]	2	[b]	4	AcOHgCH$_2$CMe(OOBu-t)CHO (X) (25%) AcOHgCH$_2$CMe(OOBu-t)CH(OOBu-t)OH (XI) (75%)	4

[a] The reaction mixture also contained an equimolar quantity of unchanged cinnamaldehyde. [b] Broad signals in the ^{1}H NMR spectrum precluded identification of the products; TLC indicated that at least three mercurials are present.

$$\underset{\text{(II)}}{R^2R^3C{=}CR^1{-}COY}+Hg(OAc)_2+ROH \xrightarrow[-HOAc]{H^+} ROCR^2R^3{-}CR^1(HgOAc){-}COY \quad (2)$$

We describe here the extension of this study to representative α,β-unsaturated aldehydes, namely methacrolein (I, $R^1 = Me, Y = H$), and cinnamaldehyde and crotonaldehyde (II, $R^3 = R^1 = Y = H$, $R^2 = Ph$, Me) for which opposite orientations of addition might again be expected. The only previous reports concerning oxymercuration of these compounds both deal with the kinetics of the methoxymercuration of cinnamaldehyde where no attempt was made to identify the product[5,6].

RESULTS

The products which were obtained when equimolar mixtures of α,β-unsaturated aldehydes and mercuric acetate were treated with n (where $2 < n < 4$) molar equivalents of methanol or tert-butyl hydroperoxide in the presence of perchloric acid are summarised in Table 1. None of the reactions occurred in the absence of perchloric acid.

The organomercury acetates were converted into the corresponding bromides which were identified on the basis of their ^1H NMR spectra using similar reasoning to that put forward for the oxymercurials derived from α,β-unsaturated esters and ketones[3]; the spectral data are presented in Table 3. The number of products from each reaction was determined by TLC but preparative separation of the components of mixtures was not generally achieved. Compounds (III) and (VIII′) were isolated and characterised satisfactorily.

The previously unknown organic peroxides, $CH_2{=}CMeCH(OOBu\text{-}t)_2$ and $PhCH{=}CHCH(OOBu\text{-}t)_2$, were prepared by acid-catalysed condensation of tert-butyl hydroperoxide with methacrolein and cinnamaldehyde respectively, and were isolated by chromatography on silica gel. The tert-butyl peroxymercuration of these α,β-unsaturated peracetals afforded single organomercurials which were purified chromatographically and identified by ^1H NMR spectroscopy as $BrHgCH_2CMe(OOBu\text{-}t)CH(OOBu\text{-}t)_2$ and compound (VIII) respectively.

DISCUSSION

In general the oxymercuration of α,β-unsaturated aldehydes is complicated by the formation of additional products arising from reaction of the aldehyde group. The conditions for oxymercuration, which involve an acid catalyst and an excess of the hydroxylic reagent, are just those suitable for promoting (per)acetal formation (eqns. 3 and 4).

$$R'CHO+ROH \overset{H^+}{\rightleftharpoons} R'CH(OR)OH \quad (3)$$

$$R'CH(OR)OH+ROH \overset{H^+}{\rightleftharpoons} R'CH(OR)_2+H_2O \quad (4)$$

No (per)ketals were obtained under similar conditions during the oxymercuration of the related α,β-unsaturated ketones[3], but (per)acetal formation is a much more favourable process.

In all products the site of mercuration is that predicted from the pattern obtained with the corresponding esters and ketones[3]. This, together with the fact that oxymercurials containing the aldehyde group are usually amongst the products, suggests that (per)acetal formation occurs *after* oxymercuration. The evidence below supports this view except in the tert-butyl peroxymercuration of cinnamaldehyde where the sequence is probably reversed.

Both cinnamaldehyde and methacrolein failed to react with methanol in the absence of mercuric acetate but under conditions otherwise identical with those of the oxymercurations. Thus compound (VII) must be formed from compound (VI) which is consistent with the reported lower reactivity of unsaturated aldehydes compared to saturated aldehydes towards acetal formation[7]. Methacrolein did react with tert-butyl hydroperoxide (eqn. 5) to yield the peracetal (XII), but the slowness of this reaction suggested that it would not compete favourably with the peroxymercuration.

$$\mathrm{CH_2{=}CMe{-}CHO + 2\ t\text{-}BuOOH \overset{HClO_4}{\rightleftharpoons} \underset{(XII)}{CH_2{=}CMe{-}CH(OOBu\text{-}t)_2} + H_2O} \qquad (5)$$

Furthermore although the peroxymercuration of the isolated α,β-unsaturated peracetal (eqn. 6) proceeded rapidly, the resultant adduct (XIII) was not one of the products obtained directly from methacrolein.

$$\mathrm{CH_2{=}CMe{-}CH(OOBu\text{-}t)_2 + t\text{-}BuOOH + Hg(OAc)_2 \xrightarrow[-HOAc]{H^+}}$$

$$\mathrm{\underset{(XIII)}{AcOHgCH_2{-}CMe(OOBu\text{-}t){-}CH(OOBu\text{-}t)_2}} \qquad (6)$$

The second product from methacrolein is thought to be the hemiperacetal (XI); presumably the reaction of compound (X) with tert-butyl hydroperoxide prefers to stop at the first stage (eqn. 3).

In the reactions of α,β-unsaturated aldehydes discussed so far it appears that no other olefinic species are involved in oxymercuration. The situation is less clear

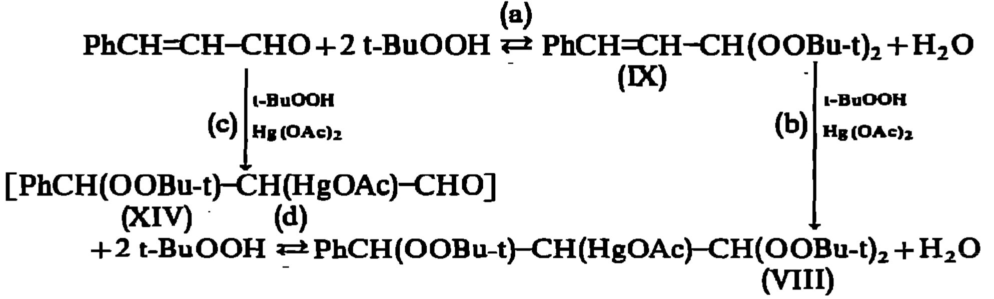
TABLE 2

DETAILS OF INDIVIDUAL OXYMERCURATIONS

α,β-Unsaturated aldehyde	*R*[a]	*Reaction time*[b] *(min)*	*Yield of crude R'HgOAc(%)*	*Yield of crude R'HgBr(%)*	*R_f of R'HgBr*
Cinnamaldehyde	Me	30	70		0.75[c]
Cinnamaldehyde	OBu-t	240	60	50	0.61
Crotonaldehyde	Me	30[d]	95	75	
Crotonaldehyde	OBu-t	120[e]	40	25	0.5, 0.4, 0.3
Methacrolein	Me	60[d]	90	84	0.5, 0.3
Methacrolein	OBu-t	30	92	50	0.58, 0.47

[a] Me = methoxymercuration; OBu-t = tert-butyl peroxymercuration. [b] Time before filtration from unreacted mercuric acetate. [c] For the organomercury(II) acetate using an eluant of ethanol (2 vol.) and water (1 vol.). [d] 100% Uptake of mercuric acetate. [e] 100% Uptake of mercuric acetate after 5 min followed by gradual reprecipitation.

cut in the tert-butyl peroxymercuration of cinnamaldehyde since both formation (eqn. 7a) and peroxymercuration (eqn. 7b) of the peracetal (IX) are rapid processes which together afford the same peroxymercurial (VIII) as is formed in the normal experiment. The absence of peroxymercurated aldehyde (XIV) and the presence of peracetal (IX) in the products from reaction with a deficiency of tert-butyl hydroperoxide (see Table 1) suggest that the peroxymercurial (VIII) is formed via reactions (7a) and (7b) rather than (7c) and (7d).



$$\begin{tikzcd}[column sep=small] PhCH{=}CH{-}CHO + 2\ t\text{-}BuOOH \arrow[r, leftrightharpoons, "(a)"] \arrow[d, "(c)"', "\begin{smallmatrix} t\text{-}BuOOH \\ Hg(OAc)_2 \end{smallmatrix}"] & PhCH{=}CH{-}CH(OOBu\text{-}t)_2 + H_2O \; \text{(IX)} \arrow[d, "(b)"', "\begin{smallmatrix} t\text{-}BuOOH \\ Hg(OAc)_2 \end{smallmatrix}"] \\ {[PhCH(OOBu\text{-}t){-}CH(HgOAc){-}CHO]} \; \text{(XIV)} + 2\ t\text{-}BuOOH \arrow[r, leftrightharpoons, "(d)"] & PhCH(OOBu\text{-}t){-}CH(HgOAc){-}CH(OOBu\text{-}t)_2 + H_2O \; \text{(VIII)} \end{tikzcd} \tag{7}$$

The peroxymercurations of α,β-unsaturated peracetals (eqns. 6 and 7b) are the most attractive reactions described here from a preparative point of view. They proceed with positional specificity and cleanly provide novel triperoxides in high yield. The orientation of addition to methacrolein peracetal (XII) is in line with what has been found in the tert-butyl peroxymercuration of simple 1,1-disubstituted ethylenes[4,8]. No similar model exists for the peroxymercuration of cinnamaldehyde peracetal (IX), but the methoxymercuration of 1-phenylpropene is reported to give a mixture of positional isomers[9].

EXPERIMENTAL

α,β-Unsaturated aldehydes were commercial samples which were redistilled; tert-butyl hydroperoxide, methanol, mercuric acetate, potassium bromide, and silica gel for chromatography were treated as previously described[2,3]. TLC was carried out with Eastman silica gel sheet 6060 using benzene as eluant and a spray of dithizone (2%) in chloroform to detect the organomercurials. 60 MHz NMR spectra were recorded with a Perkin–Elmer R12 instrument and IR spectra were obtained with a Unicam SP 1000 spectrometer. Molecular weights were determined for solutions in AR chloroform using a Mechrolab vapour pressure osmometer (model 301A) calibrated with benzil; concentrations are expressed in g/l.

Oxymercuration of α,β-unsaturated aldehydes

(*a*). *Method.* α,β-Unsaturated aldehyde (20 mmol) was added to a solution of methanol or tert-butyl hydroperoxide (40 to 80 mmol; the molar ratios for individual reactions are given in Table 1) in dichloromethane (30 ml) containing mercuric acetate (20 mmol) and aqueous 60% perchloric acid (ca. 0.4 mmol), and the mixture was stirred magnetically. When no more solid dissolved, the mixture was filtered and the filtrate washed with water (2 × equal volume), dried ($MgSO_4$), and evacuated at 15 and then 0.01 mmHg to yield the crude organomercury(II) acetate(s). The ^1H NMR spectrum of this material was recorded, then it was converted into the corresponding organomercury(II) bromide(s) by redissolving it in dichloromethane (50 ml) and stirring vigorously with an aqueous solution of potassium bromide (1 molar equiv.) for 20 min. The organic layer was separated, dried ($MgSO_4$), and the dichloromethane removed under reduced pressure. This conversion was carried out to simplify the ^1H NMR spectra and to provide less polar materials for chromatographic separation. The details of individual reactions are given in Table 2; the products were oils except for that from the methoxymercuration of cinnamaldehyde.

(*b*). *Identification of the products.* ^1H NMR spectroscopy was used extensively to identify the products; assigned resonances for individual compounds are presented in Table 3. Where mixtures were obtained, integration of appropriate peaks provided an estimate of the molar fractions of the components (see Table 1). This was best carried out using the simpler spectra of the organomercury(II) bromides, but comparison of these with the spectra of their acetate precursors indicated that no alteration to the balance of products occurred during the anion exchange.

Assignments of resonances for compounds (VI′) and (VII′) and (VIII′) were helped by a comparison with spectra of the products obtained from corresponding reactions in which the molar ratio of methanol or hydroperoxide to aldehyde was 6/1. Two compounds were isolated, and characterised by other means. Thus 2-(acetoxymercuri)-3-methoxy-3-phenylpropanal (nc) (compound III) was purified by recrystallisation from CH_2Cl_2/CCl_4; ν_{max} 1665 (CHO) and 1585 (OAc) cm^{-1}. (Found: C, 33.95; H, 3.5. $C_{12}H_{14}HgO_4$ calcd.: C, 34.1; H, 3.35%.) 1,1,3-Tris(tert-butylperoxy)-2-(bromomercuri)-3-phenylpropane (nc) (compound VIII′) was isolated chromatographically [30 cm × 2 cm diam. column; benzene eluant; 1st fraction (0–120 ml)]. It is a waxy solid which begins to melt at 55°, decomposes above 75°, and explodes above 100°. [Found: C, 38.6; H, 5.45, Br, 13.55; Hg, 31.5; mol.wt.,

TABLE 3

^1H NMR SPECTRA OF OXYMERCURIALS DERIVED FROM α,β-UNSATURATED ALDEHYDES

Compound formula (No.; solvent)	*Resonances (assignments)*
$PhCH^C(OMe)CH^B(HgO_2CMe)CH^AO$ (III; $CDCl_3$)	0.8d (H^A: J_{AB} 2.5 Hz), 2.85 (Ph) 5.1d (H^C; J_{BC} 6Hz), 6.2 2 × d (H^B), 6.8 (OMe), 8.0 (O_2CMe)
$MeCH^C(OMe)CH^B(HgBr)CH^AO$ (IV′; $CDCl_3$)	0.8d (H^A), 5.8 2 × q (H^C), 6.3 2 × d (H^B), 6.7 (OMe), 8.75d (CMe)
$MeCH^C(OMe)CH^B(HgBr)CH^A(OMe)_2$ (V′; $CDCl_3$)	5.4m (H^A and H^C), 6.65, 6.8 (OMe), 8.0m (H^B), 8.6d (CMe)
$BrHgCH_2CMe(OMe)CHO$ (VI′; $CDCl_3$)	0.3[CHO; $J(^{199}Hg)^a$ 6Hz], 6.65(OMe), 7.8 AB pattern[b], [CH_2; $J(^{199}Hg)$ 205Hz], 8.6 [CMe; $J(^{199}Hg)$ 10Hz]
$BrHgCH_2CMe(OMe)CH(OMe)_2$ (VII′; $CDCl_3$)	5.8 (CH), 6.4, 6.5, 6.75 (OMe), 8.0 (CH_2), 8.7 (CMe)
$PhCH^C(OOBu\text{-}t)CH^B(HgBr)CH^A(OOBu\text{-}t)_2$ (VIII′; $CDCl_3$)	2.9(Ph), 4.3d (H^A; J_{AB} 3Hz), 4.95d (H^C; J_{BC} 10Hz), 7.15 2 × d(H^B) 8.7, 8.8, 8.85 (t-Bu).
$BrHgCH_2CMe(OOBu\text{-}t)CHO$ (X′; CCl_4)	0.7(CHO), 8.1AB pattern[c] (CH_2), 8.7 (CMe), 8.8 (t-Bu)
$BrHgCH_2CMe(OOBu\text{-}t)CH(OOBu\text{-}t)OH$ (XI′; CCl_4)	4.9(CH), 8.1 AB pattern[c] (CH_2), 8.7 (CMe), 8.85 (t-Bu); the OH resonance was not identified.

[a] $J(^{199}Hg)$ = constant for coupling between the protons concerned and the naturally occurring 16.84% of ^{199}Hg nuclei. [b] J_{AB} 10Hz; δ_{AB} 6.6Hz. [c] Overlapping.

622 (20.1 g/l), 639 (29.0), 615 (37.8), 625 (48.3); mean 625. $C_{21}H_{35}BrHgO_6$ calcd.: C, 37.95; H, 5.3; Br, 12.15; Hg, 30.2%; mol.wt. 664.] No adequate separation of compounds (VI′) and (VII′) was achieved by chromatography (12 cm column) and compounds (X′) and (XI′) decomposed on the column (30 cm), only mercuric bromide being recovered.

Synthesis of α,β-unsaturated peracetals

(*a*). *From methacrolein.* A mixture of tert-butyl hydroperoxide (45 mmol) and methacrolein (15 mmol) in dichloromethane (25 ml) was treated with perchloric acid (0.5 mmol). The progress of the reaction was followed by ^{1}H NMR spectroscopy which showed the extent of peracetal formation to be 50, 60, 75 and 90% after ½, 2, 24, 48 h respectively. The solution was washed with water, dried ($MgSO_4$), and chromatographed (5 cm column; benzene) to yield pure 2-methyl-3,3-bis(tert-butylperoxy)-propene (nc) $CH_2{=}CMeCH(OOBu\text{-}t)_2$ (70%) as on oil; τ ($CDCl_3$): 4.4 (CH), 4.9d (CH_2), 8.2 (CMe), 8.7 (t-Bu). (Found: C, 61.7; H, 10.4. $C_{12}H_{24}O_4$ calcd.: C, 62.0; H, 10.45%.)

(*b*). *From cinnamaldehyde.* A 4/1 molar ratio of tert-butyl hydroperoxide to cinnamaldehyde was treated as in (*a*); 50% and 85% of aldehyde was consumed after 5 and 90 min respectively. 1-Phenyl-3,3-bis(tert-butylperoxy)propene (nc) (IX) $PhCH^A{=}CH^BCH^C(OOBu\text{-}t)_2$ was a waxy solid, m.p. 50–55°; τ ($CDCl_3$): 2.6 (Ph), 3.04, 3.3 (H^A, J_{AB} 16 Hz), 3.58, 3.68, 3.84, 3.94 (H^B), 4.14, 4.24 (H^C; J_{BC} 6 Hz), 8.7 (t-Bu); integration 5/1/1/1/18 as calculated. (Found: C, 67.65; H, 8.55. $C_{17}H_{26}O_4$ calcd.: C, 69.0; H, 8.9%.)

In the ^{1}H NMR spectrum (CCl_4) of the products from peroxymercuration of cinnamaldehyde where the peracetal was mixed with equimolar quantities, of cinnamaldehyde and compound (VIII′), all peracetal resonances were shifted about 25 Hz to higher field.

tert-Butyl peroxymercuration of α,β-unsaturated peracetals

(*a*). *Methacrolein peracetal.* The reaction was carried out as described for α,β-unsaturated aldehydes using 2 molar equivalents of hydroperoxide; the crude organomercury bromide was chromatographed (8 cm column; benzene) to give a viscous oil (60%), 1,1,2-tris(tert-butylperoxy)-2-methyl-3-(bromomercuri)propane (nc) $BrHgCH_2CMe(OOBu\text{-}t)CH(OOBu\text{-}t)_2$. R_f 0.8; τ ($CDCl_3$): 4.45 (CH), 8.0 AB pattern (CH_2, J_{AB} 12 Hz, δ_{AB} 17.2 Hz), 8.6 [CMe, $J(^{199}Hg)$ 16 Hz], 8.7, 8.75, 8.8 (t-Bu). (Found: C, 32.45; H, 5.6. $C_{16}H_{33}BrHgO_6$ calcd.: C, 31.95; H, 5.5%.)

(*b*). *Cinnamaldehyde peracetal.* (*i*). *Using aldehyde-free peracetal.* The reaction was carried out as described for α,β-unsaturated aldehydes, using 2 molar equivalents of hydroperoxide, and was complete after 30 min. Compound (VIII), $PhCH^C(OOBu\text{-}t)\text{-}CH^B(HgO_2CMe)CH^A(OOBu\text{-}t)_2$ (72%), was isolated; τ ($CDCl_3$): 2.6 (Ph), 4.2d (H^A, J_{AB} 3 Hz), 4.6d (H^C, J_{BC} 10 Hz) 6.9 2 × d (H^B), 8.05 (O_2CMe), 8.65, 8.7, 8.8 (t-Bu); integration 5/1/1/1/3/27 as calculated.

(*ii*). *Using a mixture of peracetal* (85%) *and aldehyde* (15%). A solution of the mixture of peracetal (IX) and cinnamaldehyde, obtained as described above, was washed with water and dried ($MgSO_4$). Mercuric acetate (1 molar equiv.) was added and the mixture stirred for 4 h; the ^{1}H NMR spectrum showed that no reaction had occurred. Perchloric acid (2 mole %) was added and after 30 min the ^{1}H NMR spectrum showed the resonances due to compound (VIII) plus unchanged cinnamaldehyde, but those due to compound (IX) were absent. After 4 h the aldehyde doublet (τ 0.2) had disappeared.

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