Oxymetallation. Part 14.[1] Modified Procedures for t-Butyl Peroxymercuriation and Bromodemercuriation that Lead to an Improved, Stereoselective, Conversion of Non-terminal Alkenes into β-Bromoalkyl Peroxides

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Stereospecific *trans*-peroxymercuriation of non-terminal alkenes with little or no accompanying acyloxymercuriation has been accomplished by using mercury(II) acetate under conditions of equilibrium control induced by the presence of 20 mol% of perchloric acid. Bromodemercuriation of the derived peroxymercurials, using bromine in methanol with added sodium bromide, stereoselectively affords β-bromoalkyl peroxides with predominant retention of configuration. Neither of the modified procedures is effective in improving the preparation of peroxides derived from norbornene. Ten diastereoisomerically pure bromoperoxides have been isolated by silica chromatography and characterised by ^{13}C n.m.r. spectroscopy. Configurations have been assigned to the cyclohexene and norbornene derivatives on the basis of their 200 MHz ^1H n.m.r. spectra.

β-BROMOALKYL t-BUTYL PEROXIDES have been prepared from alkenes by peroxymercuriation [equation (1); $X = O_2CCF_3$], anion exchange [equation (2)], and brominolysis [equation (3)].[2] Excellent yields were

$$R^1CH{=}CHR^2 + Bu^tOOH + HgX_2 \longrightarrow R^1CH(OOBu^t)CH(HgX)R^2 + HX \quad (1)$$

$$R^1CH(OOBu^t)CH(HgX)R^2 + KBr \longrightarrow R^1CH(OOBu^t)CH(HgBr)R^2 + KX \quad (2)$$

$$R^1CH(OOBu^t)CH(HgBr)R^2 + Br_2 \longrightarrow R^1CH(OOBu^t)CHBrR^2 + HgBr_2 \quad (3)$$

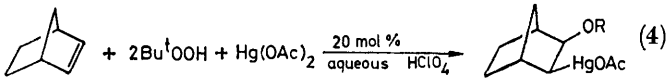
obtained, but the method suffers from two drawbacks. First, the use of mercury(II) trifluoroacetate, chosen to avoid the extensive acyloxymercuriation that accompanies peroxymercuriation if the acetate is used,[3,4] involves the inconvenience and expense of its preparation. Second, the stereospecificity of the initial peroxymercuriation[4,5] is wasted synthetically since the brominolysis, which was carried out in dichloromethane, proceeds by a free-radical-chain mechanism and *ca.* 1 : 1 mixtures of diastereoisomeric bromoperoxides are obtained from non-terminal alkenes. We now report modified procedures whereby mercury(II) acetate can be used in peroxymercuriation with little or no competing acetoxymercuriation and whereby bromodemercuriation can be carried out with a high degree of retention of configuration. Diastereoisomerically pure bromoperoxides have been isolated and characterised by 200 MHz ^1H and 20 MHz ^{13}C n.m.r. spectra.

RESULTS AND DISCUSSION

Peroxymercuriation.—In seeking an alternative to the use of mercury(II) trifluoroacetate to suppress acyloxymercuriation, our earlier observation[6] that acetoxymercurials were not detected in $HClO_4$-catalysed reactions of mercury(II) acetate and t-butyl hydroperoxide with styrenes appeared to merit further investigation.

We have analysed the mercurials obtained by the reaction of ten representative alkenes with mercury(II) acetate and a one-fold excess of t-butyl hydroperoxide in the presence of 20 mol% of $HClO_4$. Our results confirm the earlier finding for styrene and α-methylstyrene and show that products free from acetoxymercurials are also obtained with *cis*- and *trans*-but-2-ene, cyclopentene, and cyclohexene. The derived peroxymercurials were isolated in yields (>80%) similar to those obtained[4] by the trifluoroacetate route and stereospecific *trans*-addition was again observed for the non-terminal alkenes. Thus the $Hg(OAc)_2$–$HClO_4$ procedure becomes the method of choice for the preparation of these compounds.

However, the elimination of acyloxymercuriation is not as general as with mercury(II) trifluoroacetate. Thus, the mercurials from hex-1-ene and *cis*- and *trans*-hex-3-ene contained small amounts (7, <2, and 10 mol%, respectively) of acetoxymercurial, and the method failed spectacularly with norbornene [equation (4)]. All four



(4)

R	mol %
OBu^t	49
Ac	32
H	19

alkenes afforded only peroxymercurials when mercury(II) trifluoroacetate was used. Clearly, mercury(II) trifluoroacetate still has a valuable role to play in peroxymercuriation, but the simplicity and degree of success of the $Hg(OAc)_2$–$HClO_4$ procedure recommends it strongly as an alternative that should be tried first.

The success of mercury(II) trifluoroacetate in eliminating acyloxymercuriation was attributed to the nucleophilicities of trifluoroacetic acid and its anion being markedly lower than those of acetic acid and acetate.[4] In contrast, we believe that the suppression of acetoxymercuriation engendered by the presence of perchloric acid is the consequence of thermodynamic rather than kinetic factors. It is known that β-oxy-exchange in oxymercurials is catalysed by strong acids[7] and we envisage that the perchloric acid adopts this role to convert first-formed acetoxymercurials into t-butyl peroxymercurials [equation (5)].

$$AcO\cdot CHR\cdot CHR\cdot HgOAc + Bu^tOOH \overset{H^+}{\rightleftharpoons} Bu^tO\cdot OCHR\cdot CHR\cdot HgOAc + AcOH \quad (5)$$

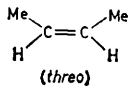
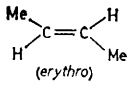
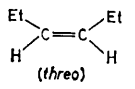
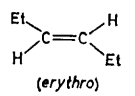
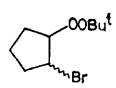
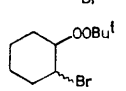
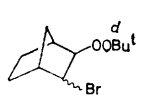
We obtained evidence to support this suggestion by preparing three acetoxymercurials and studying their reaction with t-butyl hydroperoxide. Thus, 2-acetoxycyclohexylmercury(II) acetate failed to react with t-butyl hydroperoxide (2 mol) during 20 h, but was converted *completely* into the peroxymercurial within 10 min of 20 mol% of $HClO_4$ being added. A similar result was obtained with 2-acetoxyhexylmercury(II) acetate except that the $HClO_4$-catalysed exchange afforded a mixture of peroxymercurial (93 mol%) and acetoxymercurial. This is identical with the mixture obtained in the t-butyl peroxymercuriation of hex-1-ene, and thus supports the hypothesis that the product distribution is equilibrium-controlled. Finally, it was shown that the norbornene acetoxymercurial was inert to t-butyl hydroperoxide plus perchloric acid over a period (1 h) six times greater than that during which the cyclohexene and hex-1-ene compounds had reached equilibrium. This agrees with earlier observations [7] that β-oxy-exchange is sluggish in norbornene oxymercurials and explains the dramatic failure of the $Hg(OAc)_2$–$HClO_4$ procedure to provide a pure peroxymercurial with this alkene.

Bromodemercuriation.—We previously attempted to carry out the brominolysis of peroxymercurials stereoselectively by using polar solvents with donor properties to encourage the reaction [equation (3)] to proceed by a configuration-preserving S_E2 mechanism.[2] For but-2-ene derivatives, isomer ratios of between 65 : 35 and 95 : 5 were obtained in pyridine under various conditions, but isolation proved difficult, and yields were only *ca.* 50%. Thus a recent report [8] that brominolysis of organomercurials in methanol containing sodium bromide proceeds with a high degree of retention of configuration prompted us to apply these conditions to our peroxymercurials.

With the aid of ^{13}C n.m.r. spectroscopy, we have analysed the distribution of diastereoisomeric bromoperoxides obtained from seven non-terminal alkenes *via* peroxymercuriation using the $Hg(OAc)_2$–$HClO_4$ procedure and brominolysis in dichloromethane or in methanol with added sodium bromide. The results are summarized in Table 1. The isomer ratios for four *cis* alkenes change from *ca.* 1 : 1 in dichloromethane to *ca.* 9 : 1 in MeOH–Br^-. The change is less pronounced for the *trans*-alkenes and no effect is observed for norbornene. The ratios for the but-2-enes are very similar to those obtained previously [2] for brominolyses in pyri-

TABLE 1

Yields and isomer distribution for β-bromoalkyl t-butyl peroxides obtained by brominolysis of peroxymercurials

Alkene (peroxymercurial configuration)	Bromoperoxide	Brominolysis in CH_2Cl_2		Brominolysis in MeOH with added NaBr	
		Yield [a,b] (%)	Degree of retention (%)	Yield [a] (%)	Degree of retention (%)
 (*threo*)	MeCHBrCH(OOBu^t)Me	78	48—51	93	90—92
 (*erythro*)	MeCHBrCH(OOBu^t)Me	86	49—54	93	74—77
 (*threo*)	EtCHBrCH(OOBu^t)Et	99	52—56	80	95—96
 (*erythro*)	EtCHBrCH(OOBu^t)Et	67	44—48	74	61—65
 (*trans*)		80	56—60	78	84—87
 (*trans*)		93	50—52	82	89—91
 (*cis-exo*)		87	56—60	100 [e]	56—60

[a] Of crude product; based on $Hg(OAc)_2$. [b] After allowing for the presence of Bu^t-OOH, the amount of which was calculated from the OH integral in the ^1H n.m.r. spectrum. [c] After allowing for the presence of the corresponding β-bromoalkyl acetate (10%). [d] From organomercury bromide prepared and isolated as described in ref. 2. [e] Contains appreciable amounts of other (methoxy-containing?) products.

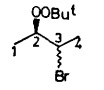
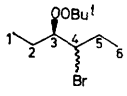
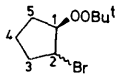
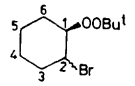
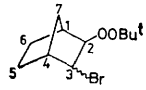
dine in the dark, but the present yields of over 90% compare very favourably with the 52 and 43% achieved in pyridine.

Bromodemercuriation was markedly faster in MeOH–Br^- than in dichloromethane and, except for the norbornene peroxymercurial, afforded bromoperoxides of comparable purity. The extensive formation of methoxy-containing products that was observed previously [2] in the brominolysis of *threo*-3-bromomercurio-2-t-butylperoxybutane in methanol *without added bromide* was almost completely suppressed. Some 10—20% of alkene bromination adducts were present in the products derived from *cis*- and *trans*-hex-3-ene, but no impurities were detected in the crude bromoperoxides obtained from *trans*-but-2-ene, cyclopentene, and cyclohexene.

Ten isomerically pure bromoperoxides were isolated by silica chromatography and were characterised by ^{13}C n.m.r. spectroscopy (Table 2). The 200 MHz ^1H n.m.r. spectrum of each separated diastereoisomer was recorded (Experimental section) and these data were used to assign configurations to the cyclohexene and norbornene derivatives.

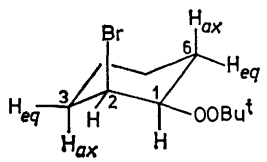
TABLE 2

^{13}C N.m.r. spectra of β-bromoalkyl t-butyl peroxides (δ) [a]

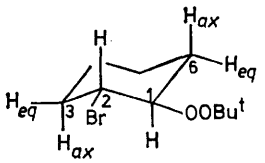
Compound	Isomer	C-1	C-2	C-3	C-4	C-5	C-6	C-7	CMe_3	CMe_3
	*threo*	12.31	82.05	48.64	18.74				80.32	26.23
	erythro	14.30	82.16	51.87	22.23				80.27	26.54
	*threo*	11.28	21.13	87.45	58.52	25.63	12.94		80.28	26.50
	erythro	10.57	22.73	86.61	60.10	28.24	12.68		80.20	26.64
	*cis*	85.07	54.81	33.35	19.36	25.71			80.54	26.55
	trans	91.22	53.90	34.13	21.88	27.48			80.21	26.38
	*cis*	81.71	55.37	32.72	21.12	23.62	25.53		80.28	26.60
	trans	83.63	51.37	33.79	22.27	23.97	28.43		80.46	26.50
	*cis*	39.97	84.33	54.93	46.69	27.83	24.42	33.02	80.66	26.57
	trans	40.66	94.14	56.29	43.02	24.57 [b]	23.93 [b]	34.55	80.56	26.41

[a] Solution in $CDCl_3$. [b] Assignments uncertain.

For the cyclohexene bromoperoxides, configurational assignments follow from a first-order analysis of the signals for protons (1- and 2-H) geminal to the peroxide and bromine substituents, assuming that conformations with equatorial $OOBu^t$ groups are preferred and that the apparent coupling constants follow the normal pattern for cyclohexanes.[9]



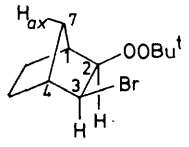
cis



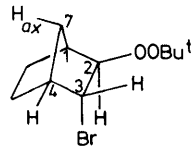
trans

Thus, in the *cis*-isomer, 1-H (δ 3.82), which is coupled to the protons 6-H_{ax}, 6-H_{eq}, and 2-H, shows splittings of J 9.5, 4.5, and 3.0 Hz indicating that 1-H is axially disposed, while 2-H (δ 4.82) is a narrow multiplet ($W_{\frac{1}{2}}$ 11.0 Hz) consistent with an equatorial orientation. In the *trans*-isomer, on the other hand, both 1-H (δ 4.01) and 2-H (δ 4.23) exhibit two large splittings (J 7.1 Hz) and one small splitting (J 3.5 Hz for 1-H and 4.5 Hz for 2-H), indicating that both have an axial disposition.

For the norbornene bromoperoxides, configurational assignments again follow from inspection of the signals for the protons (2- and 3-H) geminal to the peroxide and bromine substituents, by comparison with the known coupling patterns for norbornanes.[9] Thus, in the *cis*-isomer, 2-H (δ 4.00) and 3-H (δ 3.94) were coupled to each other with a value of J 7.0 Hz and to the 7-*anti*-proton with values of J 2.0 and 1.4 Hz, respectively, clearly showing that both protons are orientated *endo*. In the *trans*-isomer, on the other hand, 2-H (δ 4.01) and 3-H (δ 3.96) were coupled together with a value of J 2.5 Hz indicating an *endo-exo* arrangement. The *endo*-disposition of 2-H was confirmed by the observation of



cis



trans

w-plan coupling (J 2.5 Hz) to the 7-*anti*-proton, and double irradiation experiments confirmed that 3-H was coupled to the bridgehead proton (4-H) and is therefore orientated *exo*.

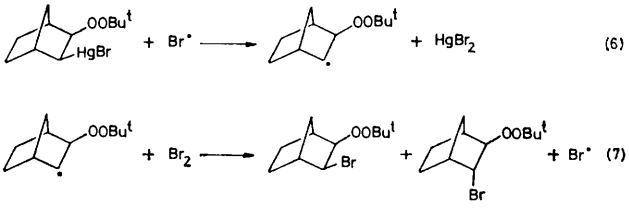
The spectroscopically-based configurational assignments for the cyclohexene bromoperoxides show that the *trans*-isomer is the major product of brominolysis in

$MeOH–Br^-$ and this indicates that, as expected, the stereoselectivity involves predominant retention of configuration. It has been assumed that this holds also for the bromoperoxides derived from but-2-ene, hex-3-ene, and cyclopentene and configurations have been assigned on this basis.

The stereochemical stability of reactants and products under brominolysis conditions was indicated by the data obtained with the isomeric pairs derived from but-2-ene and hex-3-ene, and was confirmed by the following results. Cyclopentene peroxymercurial was recovered unchanged after bromodemercuriation in dichloromethane had proceeded to an extent of 75%, and a 3 : 1 distribution of but-2-ene bromoperoxides was unaltered upon prolonged exposure to a mixture of bromine, sodium bromide, and mercury(II) bromide in methanol. It seems reasonable to conclude, therefore, that the predominant retention in $MeOH–Br^-$ is mechanistically significant and indicates that a substantial part of the brominolysis under these conditions proceeds by an S_E2 process.

It is tempting to suggest that in $MeOH–Br^-$ residual inversion arises from incomplete suppression of the free-radical-chain process,[2] particularly as the peroxide moiety represents a potential initiator. If this is so, then it appears that activation of the S_E2 pathway is less effective for the *erythro*-peroxymercurials than for the *threo*-compounds. The results for the norbornene peroxymercurial, which has an *erythro*-configuration, could then be accommodated within a general picture of concurrent S_E2 and free-radical-chain mechanisms by assuming that the radical pathway dominates completely. However, preliminary studies of the brominolysis of other norbornene oxymercurials and the formation of substantial amounts of methoxy-containing side products from the peroxymercurial suggest that the mechanism may be more complicated, and that it may be necessary to consider, additionally, processes such as electron transfer[8] between Br_2 and $RHgBr_2^-$.

There is nothing in the latest results to question our earlier suggestion[2] that brominolysis of the norbornene peroxymercurial in dichloromethane proceeds by a free-radical chain mechanism with the propagation stage shown in equations (6) and (7). By assigning configurations to the bromoperoxides, we have been able to establish that in the reaction of the *exo*-2-t-butylperoxynorborn-3-yl radical with bromine [equation (7)], *exo*-attack (56—60%) is slightly preferred to *endo*-attack.



Although our main interest has been in the stereoselective synthesis of bromoperoxides from non-terminal alkenes, we have also investigated briefly the brominolysis of the hex-1-ene peroxymercurial in $MeOH–Br^-$. In carbon tetrachloride, the brominolysis of peroxymercurials derived from terminal alkenes was complicated by the additional formation of α-bromoketones.[3] We have found that this also takes place in dichloromethane with the hex-1-ene derivative [equation (8)]. The formation

$$Br_2 + BuCH(OOBu^t)CH_2HgBr \xrightarrow{CH_2Cl_2} BuCH(OOBu^t)CH_2Br + BuCOCH_2Br \quad (8)$$

of this by-product has been attributed to a free-radical process[2] and so we felt that it might be suppressed if the brominolysis were carried out in $MeOH–Br^-$. This proved to be the case, but, unexpectedly, the bromodemercuriation was slower than with non-terminal alkene peroxymercurials, and it had proceeded to only 66% after 1 h.

EXPERIMENTAL

A commercial mixture (100 g) of Bu^tOOH (70%) and water was added to dichloromethane (50 cm^3) and shaken with saturated NaCl (25 cm^3). The organic layer was separated, dried ($MgSO_4$), and the solvent removed at a rotary evaporator. Vacuum distillation afforded Bu^tOOH, b.p. 28—32 °C/13.5—14 mmHg, which assayed iodometrically[10] as 93—94%. Hydroboration of hex-3-yne and reaction with acetic acid according to Brown and Zweifel's method[11] gave *cis*-hex-3-ene; δ_H (neat) 5.3 (m, 1 H), 2.05 (m, 2 H), and 0.95 (t, 3 H); δ_C 131.1, 20.61, and 14.50 p.p.m. The absence of *trans*-hex-3-ene was confirmed by i.r. spectroscopy. β-Bromomercurioalkyl t-butyl peroxides were prepared from norbornene and hex-1-ene *via* peroxymercuriation with mercury(II) trifluoroacetate as previously described.[4] All other materials were standard laboratory reagents which were used without further purification.

^1H N.m.r. spectra were recorded for solutions in $CDCl_3$ at 60 MHz using a Perkin-Elmer R12 and at 200 MHz using a Varian XL200, and ^{13}C n.m.r. spectra were recorded at 20 MHz using a Varian CFT20. Assignments of the ^{13}C n.m.r. signals (Tables 2—4) were based on comparisons with spectra of appropriate alkyl t-butyl peroxides[12] and the known substituent effects of mercurio-groups[13] and bromine.[14] I.r. spectra were obtained with a Perkin-Elmer 457 (KBr optics).

t-Butylperoxymercuriation by the $Hg(OAc)_2$–$HClO_4$ *Procedure.*—The alkene (10 mmol, or >10 mmol if a gas) was added to a magnetically stirred suspension of mercury(II) acetate (10 mmol) in dichloromethane (20 cm^3) which contained t-butyl hydroperoxide (20 mmol) and aqueous 60% perchloric acid (2 mmol; *ca.* 0.3 cm^3 added as 20 drops from a commercial Pasteur pipette). Gaseous alkenes were bubbled through the mixture, liquids were delivered by graduated pipette, and norbornene was added dissolved in dichloromethane (the total volume of dichloromethane used was kept at 20 cm^3). The mercury salt dissolved rapidly and after 10 min the solution gave a negative test (aqueous NaOH) for Hg^{2+} ions. The solution was decanted to remove any small amount of insoluble material, washed with water (3 × 10 cm^3), and vigorously stirred with aqueous potassium bromide (11 mmol, 10 cm^3) for 30 min. The organic phase was separated and the aqueous layer extracted with dichloromethane (2 × 10 cm^3). The extracts were combined, dried ($MgSO_4$), and the solvent was

removed at a water pump to afford the crude organomercury(II) bromide (mixed with t-butyl hydroperoxide), which was analysed spectroscopically. Some product distributions were assessed alternatively or additionally at the organomercury acetate stage; where both bromide and acetate were investigated, the conclusions concerning extent of acetoxymercuriation were identical.

I.r. spectroscopy provided a sensitive probe for detecting β-mercurioalkyl acetates. The carbon-bound acetate group shows a strong absorption at ν 1 690—1 750 cm^{-1} whereas the mercury-bound acetate group absorbs at ν 1 580—1 610 cm^{-1}. Quantitative product analyses were carried out by integrating appropriate resonances in the ^1H n.m.r. spectra, the signals arising from the t-butyl peroxymercurials being identified from the data reported previously,[3,4,6] and those arising from the acetoxymercurials by comparison with the spectra of authentic samples prepared as described below. For some alkenes, the results were confirmed by ^{13}C n.m.r. spectroscopy, and the chemical shift data are presented in Tables 3 and 4. Details of previously unreported compounds are given below.

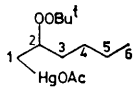
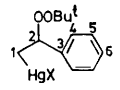
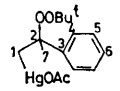
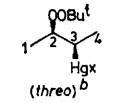
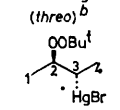
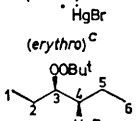
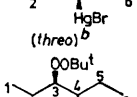
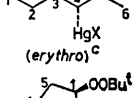
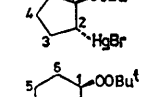
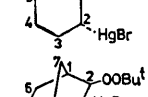
trans-2-*Bromomercurio*-1-*t-butylperoxycyclopentane* was obtained as a viscous oil by removal of the solvent and the excess of t-butyl hydroperoxide from the crude product at 0.01 mmHg in the dark (4 h). The product decomposed quite rapidly when stored and elemental analysis was carried out immediately after isolation; δ_H (200 MHz) 4.78 [dt, $J_{1.2}$ and $J_{1.5}$ 4.5, $J_{1.5'}$ 7.0, $^3J(^{199}Hg)$ 150 Hz, 1-H], 2.76 [dt, $J_{2.3}$, $J_{2.3'}$ 7.0, $^2J(^{199}Hg)$ 185 Hz, 2-H], 2.17 (sextet, $J_{3.3'}$ 14.0, $J_{3.4}$ 7.0 Hz, 3-H), 1.97 (ddt, $J_{5.5'}$ 13.6 Hz, 5'-H), 1.94 (sextet, 3'-H), 1.70 (quintet, $J_{4.5}$ 6.8 Hz, 4 and 4'-H), 1.56 (ddt, 5-H), and 1.25 (s, Bu^t) (Found: C, 24.65; H, 3.95. $C_9H_{17}BrHgO_2$ requires C, 24.69; H, 3.92%).

threo-4-*Bromomercurio*-3-*t-butylperoxyhexane* was obtained similarly; δ_H (200 MHz) 4.13 [q, $J_{2.3}$ and $J_{3.4}$ 5.6, $^3J(^{199}Hg)$ 273 Hz, CHOO], 2.65 [ddd, $J_{4.5}$ 6.5, $J_{4.5'}$ 8.5, $^2J(^{199}Hg)$ 218 Hz, CHHg], 2.1—1.2 (4 H, m), 1.28 (s, Bu^t), 1.09 (3 H, t, J 7.0 Hz), and 0.97 (3 H, t, J 7.6 Hz) (Found: C, 25.65; H, 4.6. $C_{10}H_{21}BrHgO_2$ requires C, 26.47; H, 4.67%).

Acetoxymercuriation.—The preparation of *trans*-1-acetoxy-2-acetoxymercuriocyclohexane is given below as a typical example. Cyclohexene (20 mmol) was added to a stirred suspension of mercury(II) acetate (20 mmol) in glacial acetic acid (AR; 40 cm^3) and, after 1 h, the bulk of the solvent was removed under reduced pressure at 35 °C. The resultant slurry was dissolved in dichloromethane

TABLE 3

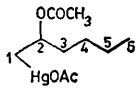
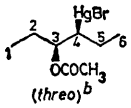
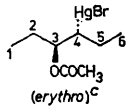
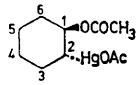
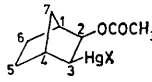
^{13}C N.m.r. spectra of t-butylperoxymercurials (δ) [a]

Compound		C-1	C-2	C-3	C-4	C-5	C-6	C-7	CMe_3	CMe_3
		36.54	82.33	28.51	28.08	22.43	13.96		80.42	26.51
	X = OAc X = TFA [g]	30.08 31.64	83.82 83.68	142.72 141.50	128.53 128.92	126.06 126.08	127.89 128.52		80.40 81.55	26.41 26.47
		37.43	84.03	146.58	128.23	124.97	127.03	28.85	79.57	26.62
	X = OAc X = Br	18.23 18.49	83.94 84.39	44.77 53.98	20.03 19.91				80.02 80.45	26.46 26.55
		18.87	83.12	53.95	15.67				80.54	26.56
		10.29	27.26	87.99	63.13	26.37	16.88		80.56	26.67
	X = OAc X = Br	10.78 10.54	26.01 25.56	87.54 87.40	55.19 63.08	22.88 22.33	16.87 16.64		80.55 79.91	26.54 26.54
		88.17	56.72	29.09	23.58	29.94			79.91	26.53
		85.74	57.39	32.75	28.26	24.59	31.63		80.98	26.55
		39.65	88.34 [d]	61.50 [e]	40.53	30.71	23.30	35.61	79.95	26.56

[a] Solution in $CDCl_3$; ^1J (^{199}Hg–^{13}C) in range 1 620—1 675 Hz, ^2J (^{199}Hg–^{13}C) for $COOBu^t$ in range 100—115 Hz; OAc resonances in range δ 176.75—177.4 (OCOMe) and 23.3—23.65 (OCO*Me*). [b] From *cis*-alkene. [c] From *trans*-alkene. [d] ^2J (^{199}Hg–^{13}C) 134 Hz. [e] ^1J (^{199}Hg–^{13}C) 1 564 Hz. [f] ^3J (^{199}Hg–^{13}C) 254 Hz. [g] TFA = trifluoroacetate.

TABLE 4

^{13}C N.m.r. spectra of acetoxymercurials (δ) [a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	C-7	COC(:O)Me	COC(:O)*M* [e]
	37.98	73.99	29.95	27.78	21.41	13.97		170.83	22.44
 (*threo*) [b]	10.15	29.90	78.66	65.55	25.79	16.32		171.04	21.38
 (*erythro*) [c]	10.09	29.24	78.21	59.03 [d]	23.98	16.55		171.33	21.32
	75.81 [e]	49.70 [f]	33.78	27.60	21.48	30.84		170.61	23.60
 X = Br	42.70	80.62	65.48	40.54	30.27	23.68	36.49	169.62	21.69
X = OAc [g]	42.6	80.2	56.3	40.1	30.0	23.7	36.4	170.0	21.8
X = Cl [g,h]	43.3	80.0	61.7	40.8	30.9	24.6	36.9		22.4

[a] Solution in $CDCl_3$; HgOAc resonances at δ 177.2 and 23.6. [b] From *cis*-hex-3-ene. [c] From *trans*-hex-3-ene. [d] ^1J (^{199}Hg–^{13}C) 1 695 ± 2.5 Hz. [e] ^2J (^{199}Hg–^{13}C) 75 ± 2.5 Hz. [f] ^1J (^{199}Hg–^{13}C) 1 720 ± 2.5 Hz. [g] From ref. 13*b*. [h] In $(CD_3)_2SO$.

(250 cm³) and shaken with water (100 cm³). [To obtain organomercury bromides the water contained potassium bromide (22 mmol)]. The layers were separated, the aqueous layer extracted with dichloromethane (2 × 20 cm³), and the combined organic layer dried ($MgSO_4$). The solvent was removed under reduced pressure to afford a crude product (91%) which was recrystallised from hot light petroleum (b.p. 40—60 °C) to yield white crystals (76%), m.p. 86—88 °C (lit.,[15] m.p. 86—88 °C); δ_H 4.7—5.25 (m, C*H*OAc), 2.35—2.9 (m, CHHg), 2.05 and 2.0 (s, Ac), and 1.2—2.2 (8 H, m).

2-Acetoxy-1-mercuriohexane [δ_H 4.9—5.3 (m, C*H*OAc), 2.0—2.3 (AB of ABX, CH_2Hg), 2.05 and 2.0 (s, OAc), 1.1—1.8 (6 H, m), and 0.7—1.1 (3 H, m)], *threo*-3-acetoxy-4-bromomercuriohexane {δ_H (200 MHz) 5.33 [ddd, $J_{3,4}$ 2.9, $J_{2,3}$ 4.9, $J_{2,3'}$ 6.9, ^3J(^{199}Hg) 376 Hz, C*H*OAc], 2.87 [ddd, $J_{4,5}$ 6.8, $J_{4,5'}$ 9.2, ^2J(^{199}Hg) 228 Hz, CHHg], 2.10 (s, OAc), 1.87 (2 H, m, CH_2·CHHg), 1.69 (2 H, m, CH_2·CHOAc), 1.07 (3 H, t, *J* 7.23 Hz), and 0.94 (3 H, t, *J* 7.3 Hz)}, and *erythro*-3-acetoxy-4-bromomercuriohexane {δ_H (200 MHz) 5.22 [ddd, $J_{3,4}$ 5.0, $J_{2,3}$ 3.6, $J_{2,3'}$ 9.0, J(^{199}Hg) 276 Hz, C*H*OAc], 2.92 [quintet, *J* 5.1, ^2J(^{199}Hg) 217 Hz, C*H*Hg], 2.08 (s, OAc), 1.99—1.55 (4 H, m), 1.12 (3 H, t, *J* 7.1 Hz), and 0.96 (3 H, t, *J* 7.4 Hz)} were isolated as viscous oils; *exo*-2-acetoxy-*exo*-3-bromomercuriobicyclo[2.2.1]heptane was isolated as a white crystalline solid, m.p. 105—106 °C (from boiling glacial HOAc *); δ_H 4.85 (d, *J* 7 Hz, C*H*OAc), 2.35—2.8 (m, C*H*HgBr and bridgehead *H*), 2.0 (OAc), and 0.9—1.8 (6 H, m).

Reaction of Acetoxymercurials with t-Butyl Hydroperoxide.—A solution of the acetoxymercurial (10 mmol) and t-butyl hydroperoxide (20 mmol) in dichloromethane (20 cm³) was divided into two equal portions and 60% aqueous perchloric acid (10 drops) was added to one. After stirring for the appropriate time (see text), each mixture was washed with water (3 × 5 cm³), dried, and the solvent removed at 12 mmHg. The resultant oil was analysed spectroscopically (i.r., ^{1}H and ^{13}C n.m.r.) as described in the t-butylperoxymercuriation section (see above).

* Attempted recrystallisation from boiling MeOH led to some β-oxy-exchange.

No exchange occurred with the norbornene acetoxymercurial after 10 min, 1 h, and 4 d, but extensive decomposition took place in the last case.

Brominolysis of t-Butylperoxymercurials in Dichloromethane.—Solutions, in dichloromethane, of crude β-peroxyalkylmercury(II) bromides mixed with Bu^{t}OOH were prepared as described above and subjected to brominolysis and work-up by the procedure reported previously [2] for the pure compounds. It is important to use *freshly prepared* peroxymercurials since they slowly decompose with formation of a white mercury(I) precipitate. The rate of decomposition is minimised by storing the compounds under a stream of air and in the dark.

The crude β-bromoalkyl t-butyl peroxides were identified by their ^{1}H n.m.r. spectra.[2] The previously unknown 1-*bromo*-2-*t*-*butylperoxycyclopentane* gave δ_H 5.0—4.0 (m, C*H*Br and C*H*OO), 2.8—1.55 (6 H), and 1.25 (s, Bu^t). The spectra were also used to estimate the amount of t-butyl hydroperoxide present in the samples (typically 10—15%) and thus permit the overall yields of bromoperoxides to be calculated (Table 1). The ratios of diastereoisomers were determined by ^{13}C n.m.r. spectroscopy. The grouping of the signals and the configurational assignments were made primarily on the basis of the data obtained from the stereoselective bromodemercuriations in methanol (below). A set of isomer ratios was calculated for each bromoperoxide from the peak integrals of the pairs of signals obtained for each carbon type and at least 75% of the values thus obtained fell within the ranges quoted in Table 1.

Brominolysis of t-Butylperoxymercurials in Methanol with added Sodium Bromide.—Crude β-peroxyalkylmercury(II) bromide, mixed with Bu^{t}OOH, was prepared as described above and dissolved or suspended in methanol (10 cm³). To this was added a mixture of bromine (10 mol% excess) and sodium bromide (3 g) in methanol (20 cm³), rinsed in with more methanol (10 cm³). The resulting mixture was stirred for 1 h in an open flask which was cooled in a bath of cold water. Water (20 cm³) and light petroleum (b.p. <35 °C; 20 cm³) were added, the mixture was shaken thoroughly, and the layers were separated. The aqueous

layer was extracted with more light petroleum (2 × 20 cm³) and the organic layers were combined, dried ($MgSO_4$), and the solvent was removed at a water pump to afford the crude bromoperoxide free from Bu^tOOH.

The ratios of diastereoisomers were determined by ^{13}C n.m.r. spectroscopy, as before, and are given, together with yields, in Table 1.

Chromatographic Separation of Diastereoisomeric Bromoperoxides.—Crude β-bromoalkyl t-butyl peroxides (10 mmol), obtained by brominolysis in dichloromethane, were chromatographed on Merck silica (70—230 mesh; *ca.* 100 g) with a 3 : 1 mixture of light petroleum (redistilled; b.p. <35 °C) and dichloromethane as eluant. The solvent was removed under reduced pressure from each fraction (25 cm³) and the residue, or if necessary the combined residue from successive fractions, was examined by n.m.r. spectroscopy. It should be noted that these bromoperoxides, unlike related bicyclic compounds,[1] do *not* oxidize acidified iron(II) thiocyanate.

For the product obtained from each parent alkene, the progress and efficiency of the chromatographic separation are indicated below by the yields and configurations of the bromoperoxides isolated from various fractions (*F*). cis-*But-2-ene*: *F* 13—15 *threo* (21%), *F* 16 mixture (2.5%), *F* 17—21 *erythro* (15%); trans-*hex-3-ene*: *F* 10 *threo* (23%), *F* 11 mixture (20%), *F* 12 + 13 *erythro* (11%); *cyclopentene*: *F* 16—20 *trans* (23%), *F* 21—25 mixture (7%), *F* 26 *cis* (16%); *cyclohexene*: *F* 16 + 17 *trans* (24%), *F* 18—24 mixture (34%), *F* 25—30 *cis* (9%); *norbornene* [brominolysis of product from $Hg(OAc)_2$–$HClO_4$ procedure which contained 49 mol% of peroxymercurial]: *F* 16—21 *trans* (*endo-Br*) (17%), *F* 22 no solute, *F* 23—26 *cis-exo* (10%).

2-*Bromo*-1-*t-butylperoxycyclopentane* is previously unreported; the mixture of *cis*- and *trans*-isomers obtained, as an oil, from chromatography [*F* 21—25 (above)] was analysed (Found: C, 45.7; H, 7.15. $C_9H_{17}BrO_2$ requires C, 45.57; H, 7.24%).

The previously unknown 1-*bromo*-2-*t-butylperoxyhexane*, mixed with some 1-bromohexan-2-one, was obtained in 87% yield from brominolysis of the corresponding organomercury bromide in dichloromethane. Purification by silica chromatography using a 1 : 1 mixture of dichloromethane and light petroleum as eluant afforded the pure *bromoperoxide* (77%); δ_H (200 MHz) 4.10—3.96 (m, CHOO), 3.62 (dd, ^2J 10.2 and ^3J 3.4 Hz; CH_AH_BBr), 3.49 (dd, ^3J 6.4 Hz, CH_AH_BBr), 1.7—1.4 (m, 3-H), 1.4—1.28 (4 H, m), 1.25 (s, Bu^t), and 0.92 (distorted, t, *J* 6.6 Hz, 6-H); δ_C 82.17 (C-2), 80.17 [CMe_3], 33.64 (C-1), 30.73 (C-3), 27.75 (C-4), 26.51 [CMe_3], 22.70 (C-5), and 13.92 (C-6) (Found: C, 47.0; H, 8.1; Br, 31.6. $C_{10}H_{21}BrO_2$ requires C, 47.43; H, 8.38; Br, 31.55%).

Characterisation of Separated Diastereoisomers.—The diastereoisomerically pure bromoperoxides were all liquids. Their ^{13}C n.m.r. spectra are reported in Table 2 and details of their 200 MHz ^1H n.m.r. spectra are given below. Where necessary, assignments and measurement of coupling constants were assisted by appropriate spin-decoupling experiments. In reporting assignments the numbers designate the carbon to which each proton is attached (see Table 2); in cyclohexene derivatives *ax* and *eq* refer to *axial* and *equatorial*, and in norbornene derivatives *x*, *n*, *a*, and *s* indicate *exo*, *endo*, *anti*, and *syn*, respectively. Chemical shifts are in p.p.m. and coupling constants in Hz.

threo-3-Bromo-2-t-butylperoxybutane δ 1.21 (d, $J_{1.2}$ 6.67, 1-H), 4.28 (dq, $J_{2.3}$ 3.95, 2-H), 4.50 (dq, 3-H), 1.62 (d, $J_{3.4}$ 6.87, 4-H), and 1.23 (s, Bu^t); *erythro*-3-bromo-2-t-butylperoxybutane δ 1.23 (d, $J_{1.2}$ 6.37, 1-H), 3.88 (dq, $J_{2.3}$ 3.80, 2-H), 4.51 (dq, 3-H), 1.65 (d, $J_{3.4}$ 6.87, 4-H), and 1.25 (s, Bu^t); *threo*-4-bromo-3-t-butylperoxyhexane δ 1.00 (t, $J_{1.2}$ and $J_{1.2'}$ 7.3, 1-H); 1.83 (d quintet, $J_{2.2'}$ 7.3 and $J_{2.3}$ 2.9, 2-H), 1.41 (d quintet, $J_{2'.3}$ 9.9, 2'-H), 4.05 (ddd, $J_{3.4}$ 3.0, 3-H), 4.31 (ddd, $J_{4.5}$ 2.9, $J_{4.5'}$ 10.6, 4-H), 1.9 (d quintet, $J_{5.5'}$ and $J_{5.6}$ 7.4, 5-H), 1.60 (d quintet, 5'-H), 1.07 (t, 6-H), and 1.23 (s, Bu^t); *erythro*-4-bromo-3-t-butylperoxyhexane δ 1.03 (t, $J_{1.2}$ and $J_{1.2'}$ 7.5, 1-H), 1.77—1.60 (m, 2- and 2'-H), 3.75 (dt, $J_{3.4}$ 4.0, $J_{2.3}$ and $J_{2'.3}$ 6.1, 3-H), 4.34 (dt, $J_{4.5}$ 4.0, $J_{4.5'}$ 9.5, 4-H), 2.05—1.77 (m, 5- and 5'-H), 1.09 (t, $J_{5.6}$ and $J_{5'.6}$ 7.4, 6-H), and 1.26 (s, Bu^t); *cis*-2-bromo-1-t-butylperoxycyclopentane δ 4.23 (dt, *J* 4.0 and 7.7, 1-H), 4.45 (q, *J* 4.0, 2-H), 2.25—1.44 (m, 3-, 4-, and 5-H), and 1.25 (s, Bu^t); *trans*-2-bromo-1-t-butylperoxycyclopentane δ 4.69—4.45 (m, 1- and 2-H), 2.35—1.43 (m, 3-, 4-, and 5-H), and 1.21 (s, Bu^t); *cis*-2-bromo-1-t-butylperoxycyclohexane: 3.82 (ddd, *J* 3.0, 4.5, and 9.5, 1-H), 4.82br (s, $w\frac{1}{2}$ 11.0, 2-H), 2.18 (1 H, m) and 2.0—1.2 (7 H, m) (both 3-H—6-H), and 1.28 (s, Bu^t); *trans*-2-bromo-1-t-butylperoxycyclohexane δ 4.01 (dt, *J* 7.1 and 3.5, 1-H), 4.23 (dt, *J* 7.1 and 4.5, 2-H), 2.26 (1 H, m), and 1.92—1.2 (6 H, m) (both 3-H—6-H), and 1.26 (s, Bu^t); *exo*-3-bromo-*exo*-2-t-butylperoxynorbornane δ 2.56br (s, $w\frac{1}{2}$ 8.4, 1- or 4-H), 4.00 (dd, $J_{2.3}$ 7.0, $J_{2.7ax}$ 2.0, 2-H), 3.94 (dd, $J_{3.7ax}$ 1.4, 3-H), 2.47br (s, $w\frac{1}{2}$ 8.1 1- or 4-H), 1.73—1.45 (m, 5- and 6-H), 1.94br (dt, $J_{7s.ax}$ 10.0, 7-H_s), 1.18br (dt, 7_{ax}-H), and 1.28 (s, Bu^t); and *endo*-3-bromo-*exo*-2-t-butylperoxynorbornane δ 2.43—2.35 (m, 1- and 4-H), 4.01 (t, $J_{2.3}$ 2.5, $J_{2.7ax}$ 2.5, 2-H), 3.96 (m, $w\frac{1}{2}$ 8.0, 3-H), 1.98—1.82 (m, 5-H_n), 1.49 (dddd, $J_{5x.n}$ 12.0, $J_{5x.6x}$ 8.0, $J_{5x.6n}$ 4.0, J_{5x3x} 2.0, 5-H_x), 1.6 (m, 6-H_x), 1.23 (m, 6-H_n), 1.70 (dm, 7-H_s), 1.36 (ddt, $J_{7ax.s}$ 10.0 $J_{7ax.1}$ and $J_{7ax,4}$ 2.0, 7-H_{ax}), and 1.25 (s, Bu^t).

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