

Oxymetallation. Part VI.¹ Halogenodemercuration of Peroxymercurials derived from $\alpha\beta$ -Unsaturated Esters and Ketones

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Conditions are described for the halogenolysis of the β - and α -carbonyl- β -mercurio-peroxides $RCH(OOBu^t)\cdot CH(HgX)\cdot COR'$ and $XHgCH_2\cdot CMe(OOBu^t)\cdot COR'$, formed by peroxymercuration of $\alpha\beta$ -unsaturated esters and ketones, to afford the previously unknown β - and α -carbonyl- β -halogeno-peroxides, respectively; eleven compounds have been characterised by elemental analysis and 1H n.m.r. spectroscopy.

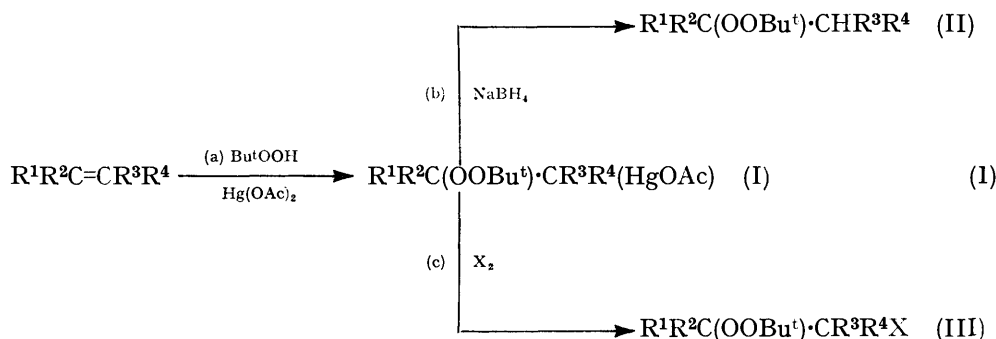
The peroxymercuration of methyl *cis*- and *trans*-cinnamate is shown to be stereospecific whereas both *cis*- and *trans*-chalcone give a mixture of diastereoisomers of the compound $PhCH(OOBu^t)\cdot CH(HgOAc)\cdot COPh$ in the same proportions (1:4). In methanol, halogenodemercuration of the methyl cinnamate peroxymercurial, and probably also of the chalcone derivative, involves extensive racemisation, suggesting a radical or an S_N1 mechanism as the major pathway.

A correlation is suggested between $J_{\alpha\beta}$ (and hence configuration) and the chemical shifts of *t*-butyl or methyl groups in the diastereoisomers of compounds of the type $RCH^\beta(OOBu^t)\cdot CH^\alpha Z\cdot COR'$ or $RCH^\beta(OMe)\cdot CH^\alpha Z\cdot COR'$. On the basis of this it is tentatively concluded that the greater stereoselectivity found for bromodemercuration of the compound $PhCH(OOBu^t)\cdot CH(HgBr)\cdot CO_2Me$ in dichloromethane as opposed to methanol is unexpectedly due to predominant inversion of configuration.

PEROXYMERCURATION [equation (Ia)], coupled with hydridodemercuration [equation (Ib)] and halogenodemercuration [equation (Ic)], has provided both routes to new organic peroxides and improved routes to known peroxides. Thus mercurated peroxides (I) have been prepared from mono- and 1,1-di-substituted ethylenes,^{2,4} vinyl ether and acetate,⁵ $\alpha\beta$ -unsaturated ketones and esters,⁶ and $\alpha\beta$ -unsaturated aldehydes and peroxyacetals.¹ The combination of peroxymercuration and hydridodemercuration has enabled the development of

followed by hydridodemercuration,⁷ and peroxymercuration of simple alkenes followed by halogenodemercuration.^{2,3} The main aim of the present work has been to extend halogenodemercuration to the functionally substituted peroxymercurials derived from $\alpha\beta$ -unsaturated ketones and esters, thereby providing a route to novel organic peroxides containing *two* other functional groups.

The peroxymercuration of $\alpha\beta$ -unsaturated ketones and esters is a regiospecific process in which mercury becomes attached to the α -carbon atom [α -mercuration;



high-yield syntheses of secondary alkyl peroxides (II; $R^2 = R^3 = R^4 = H$)³ and methoxycarbonyl-substituted peroxides (II; $R^3 = H$, $R^4 = CO_2Me$)⁷ which are a considerable improvement upon non-organometallic routes, and has led to the synthesis of previously unknown α -carbonyl peroxides (II; $R^3 = R^4 = H$, $R^1 = Me$, $R^2 = COMe$ or CO_2Me).⁷ Halogenodemercuration has been limited to bromo- and iodo-demercuration of peroxymercurials derived from simple terminal alkenes which provide β -halogeno-peroxides (III; $R^3 = R^4 = H$, $X = Br$ or I).^{2,3}

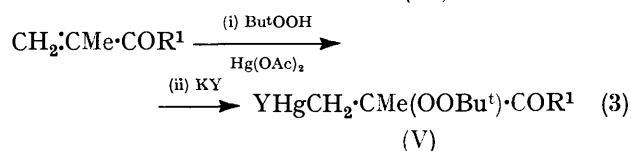
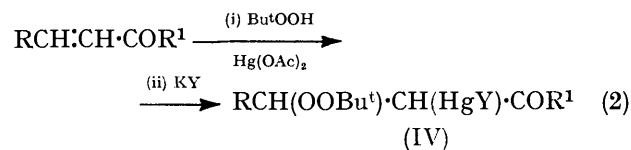
Two methods have thus been used to prepare mercury-free peroxides which contain functional substituents: peroxymercuration of functionally substituted alkenes

¹ Part V, A. J. Bloodworth and R. J. Bunce, *J. Organometallic Chem.*, 1973, **60**, 11.

² E. Schmitz, A. Rieche, and O. Brede, *J. prakt. Chem.*, 1970, **312**, 30.

³ D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. (C)*, 1971, 945.

e.g. equation (2)] except for compounds alkylated *solely* at the α -carbon atom, for which β -mercuration takes



⁴ A. J. Bloodworth and G. S. Bylina, *J.C.S. Perkin I*, 1972, 2433.

⁵ E. Schmitz and O. Brede, *J. prakt. Chem.*, 1970, **312**, 43.

⁶ A. J. Bloodworth and R. J. Bunce, *J. Chem. Soc. (C)*, 1971, 1453.

⁷ A. J. Bloodworth and R. J. Bunce, *J.C.S. Perkin I*, 1972, 2787.

place [e.g. equation (3)].⁶ Consequently for a representative study of the halogenodemercuration of these compounds, the reactions [equations (4) and (5)] of the peroxymercurials derived from methyl cinnamate (IV; R = Ph, R¹ = OMe), chalcone (IV; R = R¹ = Ph), methyl methacrylate (V; R¹ = OMe), and methyl isopropenyl ketone (V; R¹ = Me) with chlorine, bromine,

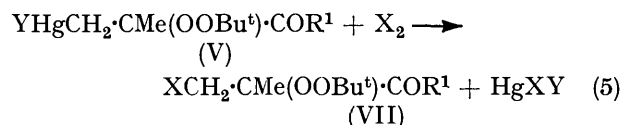
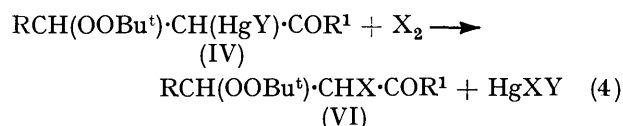
The products were characterised by ¹H n.m.r. spectroscopy (Tables 3 and 4). Compounds 1—7 were obtained as mixtures of diastereoisomers and, except for compound 7, the spectra of the components were clearly separated at 60 MHz. Hence the spectrum of each diastereoisomer is reported together with the diastereoisomeric ratio for each compound as calculated from

TABLE 1
β-Carbonyl-β-halogeno-peroxides RCH(OOBu^t)-CH(HgY)-COR' $\xrightarrow[\text{solvent}]{X_2}$ RCH(OOBu^t)-CHX-COR'

Compd.	R	R'	Y	X	Solvent	Yield (%)		M.p. (°C)	Found (%)			Reqd. (%)		
						Crude	Pure		C	H	X	C	H	X
1	Ph	OMe	Cl	Cl	CH ₂ Cl ₂		32 ^a	<i>b</i>	58.95	6.4		58.6	6.7	
2	Ph	OMe	Br	Br	MeOH		78	<i>b</i>	50.65	5.85	24.35	50.75	5.8	24.15
3	Ph	OMe	Br	I	MeOH		73	<i>b</i>	44.85	5.0		44.45	5.05	
4	Ph	Ph	Cl	Cl	CHCl ₃	78 ^e	55 ^d	76—78 ^d	68.6	6.55	10.85	68.55	6.35	10.65
5	Ph	Ph	Br	Br	MeOH	82 ^e	54 ^f	70—72 ^f	60.2	5.3	21.05	60.5	5.6	21.2
6	Ph	Ph	Br	I	MeOH		84	86—88 ^g	54.65	5.05		53.75	5.0	
7	Me	OMe	Br	Br	MeOH		80	<i>b</i>	40.1	6.3	29.7	40.15	6.35	29.75

^a Purified by column chromatography; low yield attributed to difficulty in removing HgCl₂. ^b Liquid. ^c Diastereoisomeric ratio 77 : 23 (Found: C, 68.4; H, 6.2; X, 11.8%). ^d Recrystallised from methanol; diastereoisomeric ratio 96 : 4. ^e Diastereoisomeric ratio 52 : 48; contained 20 mole % of PhCH(OMe)-CHBr-COPh. ^f Recrystallised from methanol; diastereoisomeric ratio 61 : 39. This was the second crop of crystals; the ¹H n.m.r. spectrum of the first crop (10%; m.p. 107—109°) indicated that it was pure isomer with the lower-field Bu^t signal, but elemental analysis was unsatisfactory (Found: C, 57.85; H, 5.5; X, 20.55%). ^g Diastereoisomeric ratio 64 : 36.

and iodine have been carried out; the reactions of the methyl crotonate derivative (IV; R = Me, R¹ = OMe) with chlorine and bromine have also been studied.



The peroxymercurials (IV) and the corresponding halogeno-peroxides (VI) contain two asymmetric carbon atoms, so that two diastereoisomeric pairs of enantiomers can exist in each case. The stereochemistry of halogenodemercuration of compounds (IV) has been studied by comparing the diastereoisomeric ratios in reactants and products.

RESULTS

Characterisation of Carbonyl-β-halogeno-peroxides.—Seven out of an expected eight β-carbonyl-β-halogeno-peroxides (Table 1) and four out of an expected six α-carbonyl-β-halogeno-peroxides (Table 2) were isolated; all are new compounds. They are colourless liquids except for the three chalcone derivatives (compounds 4—6) which are white crystalline solids. The bromoperoxides derived from methyl methacrylate and methyl isopropenyl ketone (compounds 8 and 10) and all the iodoperoxides (compounds 3, 6, 9, and 11) began to decompose at room temperature with the liberation of free halogen within hours of their isolation, and elemental analyses had to be carried out on the day of preparation.

integrals of suitable pairs of signals. The spectra of the diastereoisomers of compound 7 were resolved at 220 MHz, and at 60 MHz when a europium shift reagent was added. The methylene protons in compounds 8—11, like those in the parent peroxymercurials,⁶ are magnetically non-equivalent by virtue of the presence of

TABLE 2
α-Carbonyl-β-halogeno-peroxides
BrHgCH₂-CMe(OOBu^t)-COR $\xrightarrow[\text{MeOH}]{X_2}$ XCH₂-CMe(OOBu^t)-COR

Compd.	R	X	Yield (%)		Found (%)		Reqd. (%)	
			Crude	Pure	C	H	C	H
8	OMe	Br	79	<i>a</i>	41.0	6.4	40.15	6.35
9	OMe	I		54	33.9	5.25	34.2	5.4
10	Me	Br	71	<i>a</i>	41.9	6.35	42.65	6.75
11	Me	I		45	36.5	5.35	36.0	5.7

^a Purified by column chromatography; yield not recorded. The ¹H n.m.r. spectra of the crude and pure products were identical.

an adjacent asymmetric carbon and in each spectrum gave rise to an AB pattern.

Compounds 1, 2, and 9 were further characterised by mass spectrometry. Each spectrum showed parent ion peaks and intense peaks corresponding to loss of 89 mass units (OOBu^t), both sets having the isotope pattern appropriate to the halogen concerned. Similar mass spectra were reported for 2-phenyl-2-t-butylidioxyethyl bromide and iodide.³

Spectroscopic evidence suggested that chloro-peroxides were formed from methyl methacrylate, methyl isopropenyl ketone, and methyl crotonate peroxymercurials, but yields were low and we were unable to isolate analytically pure samples. In general the chalcone

peroxymercurial was more reactive in halogenodemercuration than the derivative from methyl cinnamate, both having markedly shorter reaction times than the methyl methacrylate and methyl isopropenyl ketone compounds. Failure to isolate pure chloro-peroxides from the methyl methacrylate and methyl isopropenyl ketone peroxymercurials can be attributed to difficulties

methanol than in dichloromethane and since methoxy-for-t-butylperoxy exchange was not a general problem, methanol was the solvent preferred. It was shown that the diastereoisomeric ratios obtained in compounds 1 and 2 are affected by the choice of solvent (see Table 5).

Choice of the Peroxymercurial Anion Y.—Bromo- and iodo-peroxides were prepared from organomercury

TABLE 3

¹H N.m.r. spectra (τ values; 60 MHz) of β-carbonyl-β-halogeno-peroxides, RCH_β(OOBu^t)·CH_αX·COR', in carbon tetrachloride

Compd.	R	R'	X	Concn. ^a (% w/v)	H _β ^b	H _α ^b	J _{αβ} /Hz ^c	R	R'	But ^t	Mole fraction ^a (%)
1	Ph	OMe	Cl	12	4.69	5.41	8.4	2.65	6.24	8.82	58
					4.65	5.55	6.6		6.43	8.79	42
2	Ph	OMe	Br	20	4.76	5.74	9.6	2.69	6.25	8.85	55
					4.82	5.66	8.7		6.50	8.78	45
3	Ph	OMe	I	30	4.73	5.51	9.9	2.68	6.25	8.87	45
					4.93	5.53	9.6		6.51	8.78	55
4	Ph	Ph	Cl	16	4.23	4.93	8.7	2.57	<i>d</i>	8.96	77
						4.60				8.77	23
5	Ph	Ph	Br	20	4.07	4.81	9.0	2.50	<i>d</i>	8.97	61
						4.48				8.74	39
6	Ph	Ph	I	17	4.39	4.55	9.9	2.60	<i>d</i>	8.98	64
					4.51	4.65	9.9			8.74	36
7	Me	OMe	Br	<i>f</i>	<i>g</i>	5.48	5.6 ^h	8.69	6.28	8.82	56
						5.57	5.2	8.68 ⁱ		8.81	44

^a Of the mixture of diastereoisomers. ^b Doublet. Chemical shift calculated from analysis of the AB pattern. ^c ±0.3 Hz. ^d For both diastereoisomers: broad multiplets at τ 1.8—2.0 and 2.3—2.8. ^e In CDCl₃. ^f Spectrum recorded at 220 MHz; concn. not recorded. ^g Overlapping multiplets at τ 5.65—5.82. ^h Measured from a 100 Hz sweep; ±0.1 Hz. ⁱ Doublet, J_{Me-CH_β} 6 Hz.

TABLE 4

¹H N.m.r. spectra (τ values; 60 MHz) of α-carbonyl-β-halogeno-peroxides, XCH_AH_B·CMe(OOBu^t)·COR, in carbon tetrachloride

Compd.	R	X	Concn. (% w/v)	H _A ^a	H _B ^a	Δν(H _B - H _A)/Hz ^b	J _{AB} /Hz ^c	Me	R	But ^t
8	OMe	Br	20	6.17	6.35	10.8	10.5	8.55	6.27	8.78
9	OMe	I	16	6.28	6.48	12.0	10.5	8.53	6.24	8.75
10	Me	Br	23	6.15	6.33	10.8	11.7	8.68	7.75	8.70
11	Me	I	27	6.33	6.49	9.6	11.1	8.70	7.75	8.70

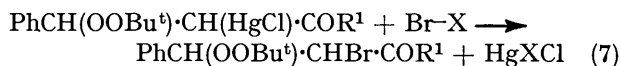
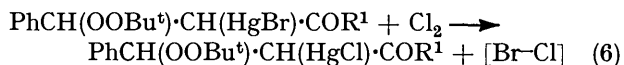
^a Doublet. Chemical shift calculated from analysis of the AB pattern. ^b ±0.6 Hz. ^c ±0.3 Hz.

in separating the products from considerable amounts of unchanged starting materials. In contrast the methyl crotonate peroxymercurial was completely consumed, but the principal product (58 mole %) in methanol was that of reductive demercuration⁷ rather than that of chlorodemercuration.

Influence of the Solvent.—Compound 1 [PhCH(OOBu^t)·CHCl·CO₂Me] was obtained in much higher yield (89%) by carrying out the reaction in methanol, but the product then contained 21 mole % of the compound PhCH(OMe)·CHCl·CO₂Me, which could not be removed by chromatography. The synthesis of compound 4 [PhCH(OOBu^t)·CHCl·COPh] was not carried out in methanol because the corresponding bromodemercuration (to give compound 5) afforded a product containing 20 mole % of the compound PhCH(OMe)·CHBr·COPh. Here the methoxy-compound could be removed by recrystallisation, but pure compound 5 (diastereoisomeric ratio 55:45) was also obtained (84% yield) by carrying out bromodemercuration of the organomercury acetate in dichloromethane.

Halogenodemercurations proceeded more rapidly in

bromides (*i.e.* Y = Br), but chlorine effected anion exchange [equation (6)] which led to competitive bromodemercuration [equation (7; X = Cl or Br)]. For both

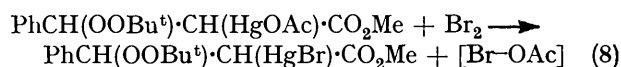


methyl cinnamate (R¹ = OMe) and chalcone (R¹ = Ph) derivatives, mixtures of alkyl bromide and chloride were obtained from reactions carried out in dichloromethane, but in methanol *only* alkyl bromides were detected. It was recently reported that chlorine reacts with phenylmercury bromide in tetrahydrofuran or carbon tetrachloride to give a mixture of phenyl bromide and chloride.⁸

The chloro-peroxides (1 and 4) were therefore prepared from the corresponding organomercury chlorides.

⁸ V. I. Stanko, O. Yu. Okhlobystin, G. A. Anorova, and I. P. Beletskaya, *Zhur. obschhei Khim.*, 1970, **40**, 2767.

It would be convenient if halogenodemercuration could be carried out on the organomercury acetates ($Y = \text{OAc}$) which are initially formed in peroxymercuration. This proved satisfactory in the synthesis of the bromoperoxide derived from chalcone (compound 5), but in the corresponding reaction with the methyl cinnamate peroxymercurial, an equimolar quantity of bromine afforded mixtures of alkyl bromide and organomercury bromide, both in dichloromethane and in methanol. It appears that anion exchange (equation 8) is again the first step and this is in agreement with an early report⁹ describing the bromodemercuration of the compound $\text{PhCH}(\text{OMe})\cdot\text{CH}_2\cdot\text{HgOAc}$. Although the bromoperoxides could presumably be obtained by using 2 equiv.



of bromine, it is easier and cheaper to bring about the initial bromide-for-acetate exchange with aqueous potassium bromide.⁶

methyl 4-methoxycinnamate to give the compound $4\text{-MeO}\cdot\text{C}_6\text{H}_4\cdot\text{CH}(\text{OMe})\cdot\text{CH}(\text{HgOAc})\cdot\text{CO}_2\text{Me}$ (VIII) is stereospecific.¹⁰ The configurations of the pair of diastereoisomers of compound (VIII) were assigned on the basis of the coupling constants between the protons attached to α - and β -carbon atoms, and this led to the conclusion that the methoxymercuration is a stereospecific *trans*-addition. Unfortunately the coupling constants of the peroxymercurials derived from methyl *cis*-cinnamate (9.3 Hz) and methyl *trans*-cinnamate (9.8 Hz) are too similar to permit a reliable configurational assignment.

In contrast the peroxymercuration of chalcone gave a 20 : 80 mixture of diastereoisomers and an identical product was obtained from either pure *trans*-chalcone or a mixture containing 65% of *cis*-chalcone. Similar behaviour has been reported^{10,11} in the methoxymercuration of chalcone. We were able to confirm this, although under our conditions⁶ the diastereoisomeric ratio was 13 : 87 rather than 25 : 75¹⁰ or 19 : 81.¹¹ The formation of the

TABLE 5

RCH:CH:COR'		Ratios of diastereoisomeric β -carbonyl- β -halogeno-peroxides		RCH(OOBu ^t)CH(HgY)COR'		RCH(OOBu ^t)·CHX·COR'			
<i>cis</i> or <i>trans</i>		(i) $\text{Hg}(\text{OAc})_2\text{-HOObu}^t$	(ii) KY	(iii) X ₂	Solvent				
R	R'	<i>cis</i> - or <i>trans</i> -alkene ^a	Y	<i>threo</i> - or <i>erythro</i> - (IV) ^b	X	Solvent	Compd.	Yield (%)	Ratio of diastereoisomers of (VI) ^c
Ph	OMe	<i>t</i>	Cl	E	Cl	MeOH	1	89	39 : 61
Ph	OMe	<i>t</i>	Cl	E	Cl	CH ₂ Cl ₂	1	32	58 : 42
Ph	OMe	<i>t</i>	Br	E	Br	MeOH	2	85	55 : 45 ^d
Ph	OMe	<i>t</i>	Br	E	Br	CH ₂ Cl ₂	2	97	35 : 65 ^e
Ph	OMe	<i>t</i>	Br	E	Br	Pyridine	2	95	48 : 52
Ph	OMe	<i>c</i>	Br	T	Br	MeOH	2	83	56 : 44
Ph	OMe	<i>c</i>	Br	T	Br	CH ₂ Cl ₂	2	65	60 : 40 ^f
Ph	OMe	<i>t</i>	Br	E	I	MeOH	3	73	45 : 55
Ph	Ph	<i>t</i>	Cl	<i>h</i>	Cl	CHCl ₃	4	78	77 : 23
Ph	Ph	<i>t</i>	Br	<i>h</i>	Br	MeOH	5	92	52 : 48 ^g
Ph	Ph	<i>t</i>	OAc	<i>h</i>	Br	CH ₂ Cl ₂	5	84	55 : 45
Ph	Ph	<i>t</i>	Br	<i>h</i>	I	MeOH	6	84	64 : 36
Me	OMe	<i>t</i>	Br	E	Br	MeOH	7	83	56 : 44 ^h

^a *c* = *cis*, *t* = *trans*. ^b Assignment assuming *trans*-addition; E = *erythro*, T = *threo*. ^c Diastereoisomer with the upfield Bu^t signal is quoted first; where different $J_{\alpha\beta}$ values are known, this is also the diastereoisomer with the larger $J_{\alpha\beta}$ (see Table 3). ^d Reproduced in five experiments (yields 69–85%) including one carried out in the dark under oxygen. ^e Reproduced in three experiments (yields 66–97%). ^f In the dark. ^g In another experiment (yield 82%) the ratio was 48 : 52. ^h Mixture of diastereoisomers (ratio 20 : 80; isomer with upfield Bu^t signal the minor component). ⁱ In other experiments the ratios were 59 : 41 (yield 98%) and 56 : 44 (70%). ^j Reproduced in two experiments, one carried out in the dark under oxygen.

Stereochemistry of Peroxymercuration.—We have shown here that the peroxymercuration of methyl cinnamate is stereospecific. The crude organomercury bromide from methyl *cis*-cinnamate has a ¹H n.m.r. spectrum different from that of methyl *trans*-cinnamate. Each product contained less than 5% of the other: separate t-butyl signals were clearly visible in the ¹H n.m.r. spectrum of a 95 : 5 mixture of products. Hence each product must be essentially a single diastereoisomer. Similarly, other workers have shown that the methoxymercuration of

mixture of diastereoisomeric methoxymercurials has been attributed to equilibration *via* enolisation–reketonisation after the oxymercuration reaction;¹⁰ presumably a similar mechanism applies to the peroxymercurials.

Stereochemistry of Halogenodemercuration.—Unlike the peroxymercurials (IV) the β -halogeno-peroxides (VI) were invariably obtained as mixtures of diastereoisomers, the isomer ratios usually being close to 55 : 45 (see Table 5). Bromodemercuration of the methoxymercurials derived from methyl crotonate (a single diastereoisomer) and chalcone (a 13 : 87 mixture of diastereoisomers)

⁹ G. F. Wright, *J. Amer. Chem. Soc.*, 1935, **57**, 1993.

¹⁰ M. C. Cabaleiro, A. D. Ayala, and M. D. Johnson, *J.C.S. Perkin II*, 1973, 1207.

¹¹ R. G. Smith, H. E. Ensley, and H. E. Smith, *J. Org. Chem.*, 1972, **37**, 4430.

similarly gave mixtures of diastereoisomeric β -halogenoethers with isomer ratios of 80 : 20 and 58 : 42, respectively.

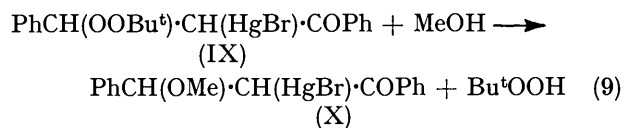
We are aware of only two previous reports dealing with the stereochemistry of halogenodemercuration of oxymercurials derived from $\alpha\beta$ -unsaturated carbonyl compounds, and both contain data similar to ours. Thus diastereoisomers were isolated in the ratio 56 : 44 from the bromodemercuration of the compound $\text{PhCH(OMe)\cdot CH(HgBr)\cdot CO}_2\text{H}$ in boiling ethyl acetate,¹² and the iododemercuration of a 15 : 85 mixture of the diastereoisomers of $\text{PhCH(OMe)\cdot CH(HgOAc)\cdot COMe}$ gave, in methanol, a 60 : 40 mixture of diastereoisomeric β -iodoethers.¹¹

Interruption of the reaction giving compound 2 in dichloromethane showed that no isomerisation of the reactant had taken place; the ratio of diastereoisomers in the product changed from 22 : 78 at 52% conversion to 35 : 65 when the reaction was allowed to go to completion. An independent check showed that methyl 2-bromomercurio-3-phenyl-3-*t*-butyldioxypropionate and compound 2 are stereochemically stable in the presence of mercury(II) bromide, which is the byproduct of the halogenodemercuration. It is therefore concluded that the halogenodemercuration of the peroxymercurial derived from methyl cinnamate (and presumably of that derived from methyl crotonate) proceeds with a considerable degree of racemisation.

Since the chalcone peroxymercurial is a mixture of diastereoisomers at equilibrium, the observed product isomer ratios are a less reliable indication of the stereochemistry of halogenodemercuration. If the rates of halogenodemercuration of the two diastereoisomers are approximately the same, or are considerably greater than, the rate of equilibration, then stereochemical retention would lead to the same distribution in the products as that in the reactants (*i.e.* 20 : 80). Since no dramatic difference was found in the reactivity of the diastereoisomers of the methyl cinnamate peroxymercurial, it seems likely that the observations again indicate considerable racemisation in bromo- and iodo-demercuration of the chalcone derivative.

DISCUSSION

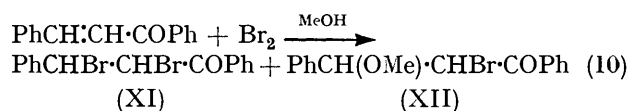
In general methanol proved a satisfactory medium for the halogenodemercurations (see Tables 1 and 2) but partial replacement of *t*-butylperoxy by methoxy was observed in the reactions of $\text{PhCH(OOBu}^t\text{)\cdot CH(HgCl)\cdot CO}_2\text{Me}$ with Cl_2 and of $\text{PhCH(OOBu}^t\text{)\cdot CH(HgBr)\cdot COPh}$ with Br_2 . Such β -oxy exchanges seem more likely to occur in the parent peroxymercurials [*e.g.* equation (9)] than in the product halogeno-peroxides. Thus



¹² E. J. Van Loon and H. E. Carter, *J. Amer. Chem. Soc.*, 1937, **59**, 2555.

solvolytic of the acetoxymethyl of cyclohexene to give the corresponding methoxymethyl¹³ and the similar transformation of methoxymethyls into ethoxymethyls¹⁴ have been reported previously; these transoxymethylations probably proceed by a mercurinium ion mechanism without the formation of free alkene.

However our evidence indicates that transoxymethylation-bromodemercuration is *not* the pathway by which the contaminant $\text{PhCH(OMe)\cdot CHBr}\cdot\text{COPh}$ is produced. The peroxymercurial (IX) underwent no exchange with methanol either in the absence or in the presence of mercury(II) bromide during a period equivalent to that required for completion of bromodemercuration. Furthermore the bromodemercuration of compound (X) in an independent experiment afforded a 58 : 42 mixture of diastereoisomers of the alkyl bromide, whereas only the more abundant diastereoisomer was detected as the contaminant of compound 5. The latter observation also appears to rule out an alternative pathway of deoxymethylation-methoxybromination, since the reaction of free chalcone with bromine in methanol [equation (10)] yielded a mixture of compounds (XI) (27 mole %) and (XII) (73 mole %; ratio of diastereoisomers, 74 : 26).



The formation of methoxy by-products thus remains unexplained. It depends upon the halogen as well as upon the structure of the peroxymercurial, for it occurred during the chloro- but not the bromo- or iodo-demercuration of the methyl cinnamate peroxymercurial, and during the bromo- but not the iodo-demercuration of the chalcone derivative. The associated preparative problems are readily circumvented by carrying out the halogenodemercurations in dichloromethane, although reaction times are then longer.

Although this work has been primarily preparative, some tentative mechanistic conclusions can be drawn from the stereochemical results. The demonstration that the peroxymercurial of methyl cinnamate is stereospecific is the first stereochemical information pertaining to peroxymercurial. Because the configurations of the diastereoisomeric peroxymercurials cannot be assigned reliably, the observed stereospecificity is consistent with either *cis*- or *trans*-addition, but by analogy with the corresponding methoxymethylation,¹⁰ it seems probable that the addition is *trans* and that the specificity indicates a mercurinium ion mechanism.

Our stereochemical results for the halogenodemercurations are unusual. Halogenolysis of other organomercurials generally occurs with racemisation in non-polar solvents such as CCl_4 or CS_2 but with a high degree of retention in the presence of even small amounts of polar additives such as methanol; complete retention is

¹³ A. G. Brook and G. F. Wright, *Canad. J. Res.*, 1950, **28B**, 623.

¹⁴ R. E. Bach, R. N. Brummel, and R. F. Richter, *Tetrahedron Letters*, 1971, 2879.

generally found in pyridine.¹⁵ These observations together with kinetic data have been taken to indicate that halogenodemercuration is a non-stereospecific free radical process in non-polar solvents, with an S_E2 mechanism becoming effective in more polar media. In contrast we have found extensive racemisation in methanol and in pyridine. Furthermore the bromodemercuration of the diastereoisomeric peroxymercurials obtained from methyl *cis*- and *trans*-cinnamate gave identical mixtures (ratio 55 : 45) of diastereoisomeric alkyl bromides, indicating the involvement of a common intermediate.

This could mean that stabilisation of the intermediate alkyl radicals by the α -carbonyl groups favours a homolytic process even in polar media. However this same structural feature will stabilise the corresponding carbanions, and the possibility of an S_E1 mechanism must be considered, especially since one of the few authentic examples of an S_E1 process involves the structurally similar compound $\text{PhCH}(\text{HgBr})\cdot\dot{\text{C}}\text{O}_2\text{Et}$.^{15,16}

Thus the stereochemical results point to a radical or an S_E1 mechanism as the major pathway for halogenodemercuration. We have no evidence sufficiently compelling to allow a choice between these mechanisms, but some of our observations are mildly disfavoured to a radical process. The halogenodemercurations were carried out in the air, which usually inhibits the free-radical mechanism.¹⁵ The ratio of diastereoisomeric alkyl bromides from the methyl cinnamate peroxymercurial was unaffected by carrying out the reaction in the dark and under oxygen, conditions intended to suppress the radical process even more strongly. Formation of the compound $\text{MeCH}(\text{OOBu}^t)\cdot\text{CH}_2\cdot\text{CO}_2\text{Me}$ from the corresponding peroxymercurial and chlorine in methanol has not been explained, but it is unlikely that it occurs *via* the radical $\text{MeCH}(\text{OOBu}^t)\cdot\dot{\text{C}}\text{H}\cdot\text{CO}_2\text{Me}$, since the reaction of alkyl radicals with chlorine is generally much faster than hydrogen abstraction from methanol.* The bromodemercuration of the methyl *trans*-cinnamate peroxymercurial exhibited a greater stereoselectivity in dichloromethane (ratio 35 : 65) than in methanol (ratio 55 : 45). This implies the incursion of a stereospecific mechanism and the simplest explanation would seem to be the introduction of an S_E2 (or S_Ei) component. Since this occurs in the less polar medium, it in turn suggests that the racemisation in methanol derives from an S_E1 mechanism. The two ratios quoted above were reproducible, but it is disconcerting that the related result (ratio 60 : 40) from the methyl *cis*-cinnamate derivative was not reproduced in a second run.

At first sight, attempts to interpret the ratios of diastereoisomeric products in terms of predominant retention (expected for an S_E2 mechanism) or inversion of configuration during halogenodemercuration seem unjustified. Not only are the configurational assignments for the peroxymercurials open to doubt (as dis-

cussed earlier), but so too are any assignments to the alkyl halides since the coupling constants ($J_{\alpha\beta}$) between protons on α - and β -carbon atoms are again very similar and in some isomers unobtainable (see Table 3).

However we have noticed a correlation between $J_{\alpha\beta}$ and the chemical shift of the oxy-substituent which holds for a wide range of oxymmercurials and related alkyl halides of type $\text{RCH}(\text{OOBu}^t)\cdot\text{CHZ}\cdot\text{COR}'$ or $\text{RCH}(\text{OMe})\cdot\text{CHZ}\cdot\text{COR}'$. This is that the diastereoisomer with the

TABLE 6
Chemical shifts of OMe and $J_{\alpha\beta}$ values in diastereoisomers of compounds $\text{RCH}^\beta(\text{OMe})\cdot\text{CH}^\alpha\text{Z}\cdot\text{COR}'$

R	R'	Z	$J_{\alpha\beta}/\text{Hz}$	τ_{OMe}	Ref.
Ph	Me	HgOAc	9.8	6.82	10, 11
			6.5	6.76	
Ph	Ph	HgOAc	9.8	6.80	<i>a</i> , 10, 11
			6.8	6.72	
<i>p</i> -NO ₂ ·C ₆ H ₄	Me	HgOAc	10.2	6.74	10
			8.2	6.70	
<i>p</i> -NO ₂ ·C ₆ H ₄	Ph	HgOAc	10.4	6.75	10
			7.6	6.66	
<i>p</i> -MeO·C ₆ H ₄	Me	HgOAc	10.0	6.84	10
			6.8	6.80	
<i>p</i> -MeO·C ₆ H ₄	Ph	HgOAc	10.0	6.85	10
			7.8	6.75	
<i>p</i> -MeO·C ₆ H ₄	OMe	HgOAc	10.0	6.78	10
			6.8	6.76	
Me	OH	Cl	7.4	6.66	18
			5.0	6.57	
Me	OMe	Cl	8.0	6.66	18
			5.6	6.64	
Ph	Me	Cl	8.6	6.88	19
			5.4	6.80	
Ph	Me	Br	9.5	6.87	11
			8.0	6.73	
Ph	Me	I	10.5	6.81	11
			9.5	6.78	
Ph	Ph	Cl	9.8	6.90	19
			8.6	6.75	
<i>p</i> -NO ₂ ·C ₆ H ₄	Me	Cl	9.2	6.72	19
			7.2	6.68	
<i>p</i> -NO ₂ ·C ₆ H ₄	Ph	Cl	9.4	6.75	19
			7.2	6.62	
<i>p</i> -MeO·C ₆ H ₄	Me	Cl	9.0	6.90	19
			5.8	6.78	
<i>p</i> -MeO·C ₆ H ₄	Ph	Cl	9.6	6.88	19
			7.0	6.72	
Me	OH	Br	8.6	6.61	18
			6.5	6.56	
Me	OMe	Br	8.4	6.73	<i>a</i> , 18
			6.8	6.70	
Ph	Ph	Br	10.0	6.80	<i>a</i>
			9.4	6.67	

* This work.

larger $J_{\alpha\beta}$ value is also that with the upfield t-butyl or methyl signal. Six t-butyl peroxides [compounds 1, 2, 3, 7, $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$, and $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgCl})\cdot\text{COPh}$; see Table 3 and Experimental section] and twenty methyl ethers (see Table 6) fit this pattern, and no exceptions have been found to date.

¹⁵ (a) M. H. Abraham, 'Comprehensive Chemical Kinetics,' ed. C. H. Bamford, and C. F. H. Tipper, Elsevier, Amsterdam, 1973, vol. 12; (b) F. R. Jensen and B. Rickborn, 'Electrophilic Substitution of Organomercurials,' McGraw-Hill, New York, 1968; (c) O. A. Reutov and I. P. Beletskaya, 'Reaction Mechanisms of Organometallic Compounds,' North-Holland, Amsterdam, 1968.

¹⁶ I. P. Beletskaya, K. P. Butin, and O. A. Reutov, *Organometallic Chem. Rev. (A)*, 1971, 7, 51.

¹⁷ (a) J. A. Kerr, 'Free Radicals,' ed. J. K. Kochi, Wiley-Interscience, New York, 1973, ch. 1; (b) P. Gray and A. A. Herod, *Trans. Faraday Soc.*, 1968, 64, 2723.

* From gas phase data for the reactions, $\dot{\text{E}}\text{t} + \text{Cl}_2 \xrightarrow{k_1} \text{EtCl} + \dot{\text{C}}\text{l}$ (ref. 17a) and $\dot{\text{M}}\text{e} + \text{MeOH} \xrightarrow{k_2} \text{MeH} + \dot{\text{C}}\text{H}_2\text{OH}$ (ref. 17b), $k_1/k_2 = 10^{8.5}$ at 20°

For the diastereoisomers of many methyl ethers the differences in $J_{\alpha\beta}$ are sufficient to allow the isomer with the larger value to be confidently assigned the *erythro*-configuration (*e.g.* see refs. 18 and 19). Since the shielding experienced by the oxy-substituent will be dependent upon the configuration of the molecule, it seems reasonable to suggest that, in general, isomers with the upfield methyl or *t*-butyl signal have the *erythro*-configuration.

On the basis of this postulate it may be tentatively concluded that bromodemercuration of the compound $\text{PhCH}(\text{OObu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$ in dichloromethane (the fourth example in Table 5) involves predominant *inversion*. This unexpected conclusion suggests that the mechanism of reactions of this type warrants more thorough investigation.

EXPERIMENTAL

Materials and Spectra.—*t*-Butyl hydroperoxide, methanol, and $\alpha\beta$ -unsaturated esters and ketones were purified as described previously.^{3,6} Mercury(II) acetate, potassium chloride and bromide, chlorine, bromine, iodine and dichloromethane were high-grade commercial products which were used without further purification. A mixture of *cis*- and *trans*-chalcone, obtained by irradiating a solution of the *trans*-isomer (5 g) in iso-octane (800 ml) with a medium-pressure u.v. lamp for 2 h, was passed through an alumina column (1½ in × 1 in diam.) and then recrystallised from light petroleum (b.p. <40°) at -25°. Hand picking of the darker yellow crystals provided a sample (m.p. 35°) containing 85% of *cis*-chalcone. Methyl *cis*-cinnamate was obtained by g.l.c. (20 in Carbowax C20M) of the mixture (containing 20% of *cis*-isomer) prepared by irradiating a solution of the *trans*-isomer (50 g) in light petroleum (b.p. 80–100°; 750 ml) with a medium-pressure u.v. lamp for 36 h.

¹H N.m.r. spectra (60 MHz) were recorded at 35° on a Perkin-Elmer R12 instrument. Mass spectra were obtained with an inlet temperature of 55–60°.

Peroxymercuration.—Peroxymercurials were prepared as described previously;⁶ the following three new compounds were characterised.

threo-Methyl 2-bromomercurio-3-phenyl-3-*t*-butyldioxypropionate (from methyl *cis*-cinnamate) had m.p. 150–151°; τ (CDCl₃; 8%) 2.63 (s, Ph), 4.39 (d, $J_{\alpha\beta}$ 9.3 Hz, CH^βOO), 6.38 (s, Me) 6.55 (d, CH^αHg), and 8.71 (s, Bu^t) (Found: C, 31.2; H, 3.6. C₁₄H₁₉BrHgO₄ requires C, 31.6; H, 3.6%); for the *erythro*-isomer (from methyl *trans*-cinnamate),⁶ $J_{\alpha\beta}$ 9.8 Hz, τ_{Bu^t} 8.77 (s).

erythro-Methyl 2-chloromercurio-3-phenyl-3-*t*-butyldioxypropionate (from methyl *trans*-cinnamate) had m.p. 119°; τ (CDCl₃; 11%) 2.53 (s, Ph), 4.32 (d, $J_{\alpha\beta}$ 9.0 Hz, CH^βOO), 6.28 (s, Me), 6.30 (d, CH^αHg), and 8.77 (s, Bu^t) (Found: C, 34.4; H, 3.9. C₁₄H₁₉ClHgO₄ requires C, 34.5; H, 3.9%).

2-Chloromercurio-1,3-diphenyl-3-*t*-butyldioxypropanone (from chalcone) was obtained as a mixture of diastereoisomers (ratio 20:80) by treatment of the organomercury acetate⁶ with chlorotrimethylsilane in dichloromethane (see ref. 4). Recrystallisation from light petroleum-dichloromethane afforded the more abundant isomer, m.p. 158–159°; τ (CDCl₃; 10%) 1.9–2.1 (m) and 2.3–2.7 (m) (Ph), 4.06 (d, $J_{\alpha\beta}$ 9.7 Hz, CH^βOO), 5.36 (d, CH^αHg), and 8.67 (s, Bu^t) (Found: C, 42.7; H, 3.9. C₁₉H₂₁ClHgO₃ re-

quires C, 42.8; H, 4.0%). The less abundant isomer had τ (CDCl₃; 1.5%) 1.9–2.1 and 2.3–2.7 (Ph), 3.90 (d, $J_{\alpha\beta}$ 11.6 Hz, CH^βOO), 5.15 (d, CH^αHg), and 8.85 (s, Bu^t).

Synthesis of Carbonyl- β -halogeno-peroxides.—The following general procedure was adopted. A solution of the halogen (5.5 mmol) in methanol or dichloromethane (5 ml) was added dropwise during 5–10 min to a stirred suspension or solution of the peroxymercurial (5 mmol) in the same solvent (10 ml). Completion of the reaction was indicated when the colour due to halogen no longer faded and the solution was then filtered to remove any insoluble mercury(II) salt. The solvent was removed under reduced pressure to afford a mixture of the halogeno-peroxide and mercury(II) salt. This mixture was extracted with light petroleum (b.p. 40–60°; 3 × 7 ml) and the solvent removed under reduced pressure to yield the halogeno-peroxide. In synthesis of iodo-peroxides, the excess of iodine was removed by shaking the light petroleum extract with aqueous 0.1N-sodium thiosulphate (5 ml) followed by washing with water and drying (MgSO₄), before removal of solvent.

Many of the peroxides were obtained analytically pure at this stage and the ¹H n.m.r. spectra of all products indicated the absence of any appreciable amounts of other proton-containing material. If necessary the halogeno-peroxides were purified by elution from a column [1 in × 1 in diam.; activated silica gel (Hopkin and Williams)] with benzene; the benzene was then removed by evaporation at 12 mmHg and finally at 0.05 mmHg. Details for the individual peroxides are in Tables 1 and 2.

Typical reaction times were <10 min, 30 min, and 2–3 h for the synthesis in methanol of compounds 5, 2, and 10, respectively, and 30 min and 2–3 h for the preparation in dichloromethane of compounds 5 and 2, respectively.

Formation of Methoxy By-products during Halogenodemercurations in Methanol.—(a) $\text{PhCH}(\text{OObu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{COPh} + \text{Br}_2$. One diastereoisomer (τ_{OMe} 6.80) of $\text{PhCH}(\text{OMe})\cdot\text{CHBr}\cdot\text{COPh}$ (XII) was detected in the ¹H n.m.r. spectrum of the crude bromo-peroxide. Compound (XII) was identified by adding a sample of the mixture of diastereoisomers obtained by bromodemercuration of the chalcone methoxymercurial or by methoxybromination of chalcone [see (i) and (ii) below]; all the resonances due to the by-product increased in intensity relative to those of the peroxide.

(i) Methoxymercuration-bromodemercuration of chalcone. The methoxymercuration of *trans*-chalcone was carried out as described previously⁶ but the product was identified as a mixture (13:87) of diastereoisomeric methoxymercurials; an identical product was obtained from a mixture of *cis*- (85%) and *trans*-chalcone. The ¹H n.m.r. spectra of the diastereoisomers agreed well with those previously reported^{10,11} and the spectra of the corresponding organomercury bromides were very similar except that the H^β absorptions appeared at τ 4.62 and 4.63. Brominolysis of the organomercury bromides was carried out by the procedure described for the synthesis of carbonyl- β -halogeno-peroxides and afforded both diastereoisomers of compound (XII), τ (CDCl₃; 20%) 1.8–2.0 (m) and 2.3–2.7 (m) (Ph), 4.80 (d) and 4.56 (d) (CH^βOMe, $J_{\alpha\beta}$ 10.0 and 9.4 Hz, respectively), 5.13 (d) and 5.17 (d) (CH^αBr), and 6.80 (s) and 6.67 (s) (OMe).

¹⁸ H. Chartier and R. Vessière, *Ann. Chim. (France)*, 1969, 313.

¹⁹ M. C. Cabaleiro, M. D. Johnson, and A. B. Chopra, *J.C.S. Perkin II*, 1974, 452.

(ii) Methoxybromination of chalcone. A solution of bromine (1.76 g, 11 mmol) in methanol (10 ml) was added to a solution of chalcone (2.08 g, 10 mmol) in methanol (20 ml). After 20 min the solvent and the excess of bromine were removed *in vacuo* to leave a pale yellow solid which was identified by ^1H n.m.r. spectroscopy as a mixture of compound (XII) [spectrum identical with that of the product from (i) except that the ratio of diastereoisomers was 74:26 rather than 58:42] and the compound $\text{PhCHBr}\cdot\text{CHBr}\cdot\text{COPh}$ [spectrum identical with the product obtained after 10 min from chalcone (10 mmol) and bromine (11 mmol) in dichloromethane (30 ml); τ (CDCl_3 ; 10%) 1.8–2.0 (m) and 2.3–2.7 (m) (Ph), 4.09 (d) and 4.35 (d) ($J_{\alpha\beta}$ 11.3 Hz)].

(iii) Attempted transoxymercuration. A solution of 2-bromomercurio-1,3-diphenyl-3-t-butylidioxopropanone (0.58 g, 1 mmol) and mercury(II) bromide (0.36 g, 1 mmol) in methanol (2 ml) and dichloromethane (0.5 ml) (the latter added to solubilise the peroxymercurial) was stirred for 15 min. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (3×2 ml). The dichloromethane was removed at 12 mmHg; the ^1H n.m.r. spectrum of that fraction of the residue soluble in CDCl_3 showed no methoxy absorption.

(b) $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgCl})\cdot\text{CO}_2\text{Me} + \text{Cl}_2$. The ^1H n.m.r. spectrum of the crude chloro-peroxide contained a resonance at τ 6.80 which it was shown was not due to methanol. By analogy with (a) we assign this to the compound $\text{PhCH}(\text{OMe})\cdot\text{CHCl}\cdot\text{CO}_2\text{Me}$; the molar fraction was again calculated from the integrated spectrum.

Reactions Involving Anion Exchange—(a) *Chloride for bromide*. (i) In methanol. Chlorine and $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$ afforded compound 2 (85%), identified by mass spectrometry [m/e 330 and 332 (M^+) and intense peaks at 241 and 243 ($M - 89$)] and elemental analysis (Found: C, 50.9; H, 5.7; Br, 25.3. $\text{C}_{14}\text{H}_{19}\text{BrO}_4$ requires C, 50.8; H, 5.8; Br, 24.1%).

Chlorine and $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{COPh}$ gave a mixture of compound 5, identified by comparison of its ^1H n.m.r. spectrum with that of authentic material, and 36 mole % of methoxy byproduct.

(ii) In dichloromethane. Chlorine and $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$ afforded a mixture of compounds 1 and 2 (in the ratio 80:20), identified and estimated by ^1H n.m.r. spectroscopy. A mixture of compounds 4 and 5 was similarly identified as the product from chlorine and $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{COPh}$, but the relative proportions could not be estimated because the appropriate resonances overlap.

(b) *Bromide for acetate*. A solution of bromine (5.5 mmol) in methanol (5 ml) was added to $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgOAc})\cdot\text{CO}_2\text{Me}$ (2.68 g; 5 mmol) in methanol (12 ml). After 30 min the solvent was removed at 12 mmHg to give a white solid which was extracted with light petroleum (b.p. 40–60°; 2×10 ml). Recrystallisation (dichloro-

methane–light petroleum) of the residue afforded $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me}$ (0.93 g), identified by ^1H n.m.r. spectroscopy. Removal of the solvent from the mother liquor yielded more white solid (0.66 g) which contained 73% of the organomercury bromide.

Stereochemical Stability Studies.—(a) *Interruption of the reaction* $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me} + \text{Br}_2$. At suitable time intervals samples (1 ml) of a stirred solution of bromine (0.35 g, 2.2 mmol) and the peroxymercurial derived from methyl *trans*-cinnamate (1.06 g, 2 mmol) in dichloromethane (8 ml) were removed and the volatile material was rapidly pumped off. The residues were dissolved in CDCl_3 , the solutions filtered to remove mercury(II) bromide, and the ^1H n.m.r. spectra recorded. No isomerisation of the peroxymercurial was detected. The extent of reaction and the ratios of diastereoisomers in the alkyl bromide (compound 2) were estimated from the integrated spectra. The following results were obtained [time (h), % reaction, ratio of diastereoisomers]: 0.2, 52, 22:78; 0.5, 75, 24:76; 1.0, 84, 26:74; 72, 100, 35:65.

(b) $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{HgBr})\cdot\text{CO}_2\text{Me} + \text{HgBr}_2$. A mixture of *erythro*-methyl 2-bromomercurio-3-phenyl-3-t-butylidioxopropanoate [from methyl *trans*-cinnamate (0.83 mmol)] and mercury(II) bromide (0.83 mmol) in methanol (2 ml; containing a little dichloromethane to solubilise some of the peroxymercurial) was stirred for 1 h. The solvent was removed under reduced pressure and the product extracted with dichloromethane (3×3 ml). The dichloromethane was removed *in vacuo*; the ^1H n.m.r. spectrum of the residue (in CDCl_3) showed no signals due to the *threo*-isomer.

(c) $\text{PhCH}(\text{OOBu}^t)\cdot\text{CHBr}\cdot\text{CO}_2\text{Me} + \text{HgBr}_2$. A solution of compound 2 prepared *via* bromodemercuration in dichloromethane (0.66 g, 2 mmol; ratio of diastereoisomers 35:65) and mercury(II) bromide (0.72 g, 2 mmol) in methanol (10 ml) was stirred for 1 h and then worked up as in the synthesis of carbonyl- β -halogeno-peroxides; 66% of compound 2 was recovered. The ^1H n.m.r. spectrum indicated no change in the ratio of diastereoisomers.

(d) *cis*-Chalcone under oxymercuration conditions. The fraction of *cis*-chalcone [τ (CDCl_3) 1.8–2.0 (m) and 2.3–2.8 (m) (Ph), 2.90 (d, H^β , $J_{\alpha\beta}$ 13.1 Hz), and 3.35 (d, H^α)] in a mixture of *cis*- and *trans*-isomers was estimated from the ^1H n.m.r. spectrum by comparing the integral of the doublet at τ 3.35 with the total integral in the range τ 1.5–3.5. This fraction (85%) remained unchanged for a solution of the mixture in dichloromethane containing methanol or *t*-butyl hydroperoxide and perchloric acid in the same proportions as used in oxymercuration during 1–5 h; after 22 h the fraction of *cis*-isomer had fallen to 53%.

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