

Oxymetallation. Part 10.¹ Synthesis of β -Mercurioalkyl Hydroperoxides and Bis- β -mercurioalkyl Peroxides from Hydrogen Peroxide

By A. J. Bloodworth* and M. E. Loveitt, The Christopher Ingold Laboratories, Chemistry Department, University College London, 20 Gordon Street, London WC1H 0AJ

Terminal alkenes react with mercury(II) trifluoroacetate and hydrogen peroxide in dichloromethane to provide mixtures of β -mercurioalkyl hydroperoxides ($\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CR}^1\text{R}^2\cdot\text{O}\cdot\text{OH}$) and bis- β -mercurioalkyl peroxides [$(\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CR}^1\text{R}^2\cdot\text{O})_2$]. Product ratios have been determined for reactions with amounts of hydrogen peroxide varying from 0.5 to 3 mol. equiv.

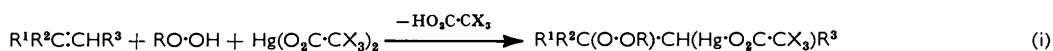
Representative peroxymercurials have been isolated, sometimes as the organomercury chloride, and characterised both spectroscopically and by their chemical reactivity. Under acidic conditions suitable hydroperoxides undergo a Criegee-type rearrangement to yield mercuriated ketones, whereas peroxides derived from monosubstituted ethenes undergo carbonyl-forming eliminations under basic conditions. Peroxides have also been characterised by bromodemercuration, and hydroperoxides by participation in further peroxymercuriations: the latter process has afforded the mixed peroxide $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{O}\cdot\text{OCHPh}\cdot\text{CH}_2\cdot\text{Hg}\cdot\text{O}_2\cdot\text{C}\cdot\text{CF}_3$.

¹³C N.m.r. spectroscopy has been shown to be particularly suitable for analysing mixtures of hydroperoxides and related peroxides, and has been used to distinguish diastereoisomeric peroxides in which the asymmetric centres are separated by the peroxide linkage.

PEROXYMERCURIATION [equation (i), X = H or F] provides the basis of a new method for preparing organic peroxides. We have utilised the reaction with t-butyl

would serve as a model for synthesising cyclic peroxides from dienes and hydrogen peroxide.

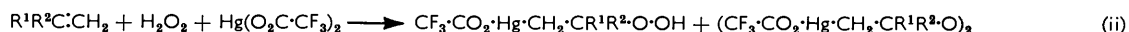
Mercury(II) trifluoroacetate (X = F) was found to be



hydroperoxide (R = Bu^t) and combined it with hydrogenodemercuration and halogenodemercuration to establish both routes to new types of peroxide^{2,3} and improved routes to known peroxides.^{1,2,4,5} As yet the generality of our preparative methods with respect to the peroxidic reagent RO·OH has not been investigated. Indeed even the scope of peroxymercuriation itself remains largely unexplored in this context.

The reaction with hydrogen peroxide [equation (i), R = H] commands greatest interest since hydrogen peroxide is one of the two prime sources of the dioxygen unit. Two previous reports^{6,7} of hydroperoxymercuriation [equation (i), R = X = H] describe the preparation of β -mercurioalkyl hydroperoxides from phenylethene, cyclohexene, norbornene, 1,1-diphenylethene, 1-phenylcyclohexene, and dihydropyran; a large excess of concentrated (55–90%) aqueous hydrogen peroxide was used, which is both wasteful and potentially hazardous.

The present investigation was initiated with two



objectives in mind: first to discover conditions under which β -mercurioalkyl hydroperoxides could be prepared by using only small amounts of hydrogen peroxide, and secondly to exploit the potential bifunctionality of hydrogen peroxide by utilising these β -mercurioalkyl hydroperoxides in further peroxymercuriations to afford bis- β -mercurioalkyl peroxides [equation (i), R = CR¹R²·CHR³·Hg·O₂·C·CX₃]. We hoped that the latter reaction

the best reagent in t-butylperoxymercuriation of simple alkenes⁸ and it has been employed in the present study. By varying the amount of hydrogen peroxide from 3 to 0.5 mol. equiv., both β -mercurioalkyl hydroperoxides and symmetrical bis- β -mercurioalkyl peroxides have been isolated from reactions with mono- and 1,1-di-substituted ethenes (R³ = H). Furthermore the mixed bis- β -mercurioalkyl peroxide $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{O}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{Hg}\cdot\text{O}_2\cdot\text{C}\cdot\text{CF}_3$ has been prepared by carrying out the peroxymercuriations in a stepwise fashion. The details of this investigation are now presented; the extension to dienes will be described in a subsequent publication.

RESULTS

Analysis of Crude Product Mixtures.—Ethene, propene, phenylethene, 2-methylpropene, and 2-phenylpropene each react with mercury(II) trifluoroacetate and 78–87% hydrogen peroxide in dichloromethane to give a mixture of β -mercurioalkyl hydroperoxide and bis- β -mercurioalkyl peroxide [equation (ii)]. After a maximum reaction time

of 5 min (see later), the solution was washed with an equal volume of water and dried, and the dichloromethane removed under reduced pressure. The resultant mixture of organomercury trifluoroacetates was dissolved in deuteriochloroform and immediately analysed by ¹³C n.m.r. spectroscopy.

Proton-decoupled ¹³C n.m.r. spectroscopy is the simplest and best technique available for analysing mixtures of

¹ Part 9, A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin I*, 1975, 695.

² A. J. Bloodworth and R. J. Bunce, *J.C.S. Perkin I*, 1972, 2787.

³ A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin I*, 1974, 688.

⁴ D. H. Ballard and A. J. Bloodworth, *J. Chem. Soc. (C)*, 1971, 945.

⁵ A. J. Bloodworth and G. S. Bylina, *J.C.S. Perkin I*, 1972, 2433.

⁶ E. Schmitz, A. Rieche, and O. Brede, *J. prakt. Chem.*, 1970, 312, 30.

⁷ V. I. Sokolov, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1972, 1089.

⁸ A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin I*, 1975, 195.

hydroperoxides (RO·OH) and related peroxides (RO·OR).[†] In particular the $\geq\text{C}\cdot\text{O}\cdot\text{O}$ resonance occurs at lower field in the hydroperoxide than in the peroxide; in our compounds the difference is 1—2 p.p.m.

The results of the product analysis are presented in Table 1. In calculating the molar ratios it has been assumed that, under the standard conditions employed to accumulate the spectra, signal responses for a bis- β -mercurioalkyl peroxide will be twice as strong as the corresponding ones for an equimolar amount of the related β -mercurioalkyl hydroperoxide. The validity of this, to an accuracy of better

period. For the 2-phenylpropene products it was possible to get an 'instantaneous' value by ^1H n.m.r. spectroscopy a few minutes after the solution was prepared; atypically, this hydroperoxide and peroxide are distinguishable by their ^1H n.m.r. spectra.

^{13}C n.m.r. spectroscopy is also suitable for detecting the presence of any other oxymercurials in the crude products. Trifluoroacetoxymethylmercurials, hydroxymethylmercurials (arising independently from the aqueous content of the hydrogen peroxide or during work-up by the hydrolysis of trifluoroacetoxymethylmercurials⁸), and bis- β -mercurioalkyl ethers (arising

TABLE 1

Product analysis for dichloromethane-soluble fraction of crude peroxymercurials

$$R^1R^2C:CH_2 + H_2O_2 + Hg(O_2C:CF_3)_2 \longrightarrow CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CR^1R^2\cdot O\cdot OH + (CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CR^1R^2\cdot O)_2$$

Alkene	R ¹	R ²	x	y	Molar proportions ^a		Yield (%) ^b	
					RO·OH	RO·OR	RO·OH	RO·OR
Ethene	H	H	> 10 ^c	5	17	83	6 ^d	30 ^d
	H	H	10	30	43	57	6 ^e	17 ^e
Propene	Me	H	> 10 ^c	10	13	87	f	f
	Me	H	> 10 ^c	30	48	52	19	41
	Me	H	10	30	0	100	0	68
Phenylethene	Ph	H	10	5	37	63	39	66
	Ph	H	10	30	76	24	58	37
2-Methylpropene	Me	Me	> 10 ^c	5	29	71 ^g	33	80
	Me	Me	> 10 ^c	10	62	38 ^g	26	32
	Me	Me	> 10 ^c	30	79	21 ^g	62	33
2-Phenylpropene	Me	Ph	10	10	90	10 ^h	64	14

^a Calculated from ^{13}C n.m.r. spectra (C·O·O signal strengths). ^b Based on H_2O_2 when $y = 5$ and on $Hg(O_2C:CF_3)_2$ when $y = 10$ or 30. ^c Excess of alkene bubbled through reaction mixture. ^d Jointly 38% of product which also contained $CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CH_2\cdot O_2C:CF_3$ (43%) and $CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CH_2\cdot OH$ plus $(CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CH_2)_2O$ (19%). ^e Jointly 51% of product which also contained $CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CH_2\cdot O_2C:CF_3$ (27%) and $CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CH_2\cdot OH$ plus $(CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CH_2)_2O$ (22%). ^f Yield not determined; product contained 41% of $CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CHMe\cdot O_2C:CF_3$. ^g By using $^{13}\text{CH}_3$ signal strengths. ^h Calculated from peak heights in ^1H n.m.r. spectrum.

TABLE 2

β -Mercurioalkyl hydroperoxides and bis- β -mercurioalkyl peroxides (XHg·CH₂·CR¹R²·O·OR)

Compd. Parent alkene(s)	X	R ¹	R ²	R	M.p. (°C)	Found (%)		Calc. (%)		Yield (%)
						C	H	C	H	
(1) Phenylethene	OAc	Ph	H	H	115—116 ^a	30.3	3.1	30.3	3.3	68
(2) 2-Methylpropene	CF ₃ ·CO ₂	Me	Me	H	83	18.2	2.25	17.9	2.25	50
(3) 2-Phenylpropene	CF ₃ ·CO ₂	Ph	Me	H	90—91	28.35	2.65	28.45	2.4	50
(4) Ethene	Cl	H	H	CH ₂ ·CH ₂ ·HgCl	149—150	8.7	1.4	8.6	1.45	52
(5) Propene	CF ₃ ·CO ₂	Me	H	CHMe·CH ₂ ·Hg·O ₂ C·CF ₃ ^b	109—110.5	16.5	1.65	16.15	1.65	49
(6) Phenylethene	Cl	Ph	H	CHPh·CH ₂ ·HgCl ^b	148—150	26.85	2.3	27.0	2.25	31
(7) 2-Methylpropene	CF ₃ ·CO ₂	Me	Me	CMe ₂ ·CH ₂ ·Hg·O ₂ C·CF ₃	122.5—124	18.7	2.1	18.7	2.05	70
(8) 2-Methylpropene and phenylethene	CF ₃ ·CO ₂	Me	Me	CHPh·CH ₂ ·Hg·O ₂ C·CF ₃	96—97	23.3	1.35	23.45	1.95	50

^a Lit.,⁷ 114—115 °C; lit.,⁶ 118—119 °C. ^b Mixture of diastereoisomers.

than 95%, has been confirmed in the 2-methylpropene system by calibrating the spectrometer with a mixture of known weights of the two pure compounds.

The β -mercurioalkyl hydroperoxides from 2-methylpropene and 2-phenylpropene, in solution in deuteriochloroform, were gradually converted into the respective bis- β -mercurioalkyl peroxides. Thus after 3 days a solution originally containing 79 mol % of $CF_3\cdot CO_2\cdot Hg\cdot CH_2\cdot CMe_2\cdot O\cdot OH$ contained only 48% of hydroperoxide, but no new organic products were detected. The conversion took place more rapidly in the 2-phenylpropene system and was essentially complete after 3 days. Since each ^{13}C n.m.r. spectrum was accumulated for *ca* 1 h, the molar ratios quoted in Table 1 are necessarily determinations averaged over this

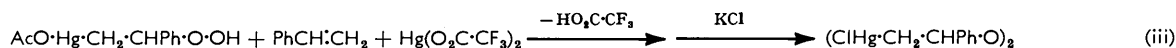
[†] Olah *et al.* (G. A. Olah, D. G. Parker, N. Yoneda, and F. Pelizza, *J. Amer. Chem. Soc.*, 1976, **98**, 2245) have reached the same conclusion independently.

from hydroxymethylmercurials) are all possible by-products and each will have a characteristic $\geq\text{C}\cdot\text{O}$ n.m.r. signal. The spectra clearly showed the absence of these nonperoxidic compounds in all products except those derived from ethene and one derived from propene (see footnotes to Table 1).

Isolation of Pure Peroxides.—Four of the ten peroxymercurials were isolated by recrystallisation of suitable crude products and two others were obtained by precipitation as the organomercury chlorides upon treating appropriate crude products with aqueous potassium chloride. All six compounds are white solids, the trifluoroacetates being more highly crystalline than the chlorides. Details of the new products are provided in Table 2, which also includes our data for 1-acetoxymethylmercurio-2-hydroperoxy-2-phenylethane (1) prepared by Schmitz's method.⁶ Compound (1) was used to synthesise 1,6-bis(chloromercurio)-3,4-dioxo-2,5-diphenylhexane (6) independently by the route summar-

used in equation (iii). That this product and the one from the direct reaction with hydrogen peroxide are identical supports the assigned structure.

Although the compounds are analytically pure, the micro-analytical data for C and H are insufficiently sensitive for



the presence of hydroperoxide to be detected in samples of peroxide and *vice versa* [for example, compare the figures for compounds (2) and (7)]. The criterion of purity which we applied to each hydroperoxide and peroxide was the absence in its proton-decoupled ^{13}C n.m.r. spectrum of signals corresponding to its counterpart. This appears to be the *only* satisfactory method for determining the degree of purity of the β -mercurioalkyl hydroperoxides. We rejected the use of iodimetric titrations on the grounds of possible complications from consumption of the liberated iodine by reaction with mercury-carbon bonds. Preliminary attempts to assess purity by t.l.c. were unsuccessful. I.r. spectroscopy permits the detection of hydroperoxides (ν_{OH})

and absent in the spectra of bis- β -mercurioalkyl peroxides; all organomercury trifluoroacetates exhibited intense bands at 1 670, 1 200, and 1 150 cm^{-1} . In the ^1H n.m.r. spectra (Table 3) the chemical shifts, multiplicities, and coupling constants (^1H , ^1H and ^1H , ^{199}Hg) are consistent with the proposed structures and closely resemble the values for the related products of *t*-butylperoxymercuriation.⁸ The spectrum of compound (8), $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{O}\cdot\text{O}\cdot\text{CHPh}\cdot\text{CH}_2\cdot\text{Hg}\cdot\text{O}_2\text{C}\cdot\text{CF}_3$, is interesting because both the methylene protons and the methyl groups originating from 2-methylpropene are rendered magnetically non-equivalent by the asymmetric centre (C) generated on the far side of the peroxide linkage. This accounts for the methyl signal being broad and showing two ^1H , ^{199}Hg coupling constants. The non-equivalence of the methyl groups is seen more clearly in the proton-decoupled ^{13}C n.m.r. spectrum (Table 4) where the chemical shifts differ by 0.4 p.p.m.

TABLE 3

^1H N.m.r. spectra of β -mercurioalkyl hydroperoxides and bis- β -mercurioalkyl peroxides ($\text{XHg}\cdot\text{CH}_2\cdot\text{CR}^1\text{R}^2\cdot\text{O}\cdot\text{OR}$) in deuteriochloroform

Compd.	X	R ¹	R ²	R	τ			J ^1H - $^{199}\text{Hg}/\text{Hz}$		
					CH ₂	R ¹	R ²	CH ₂	R ¹	R ²
(1)	OAc ^a	Ph	H	H	7.58 (m) ^b	<i>c</i>	4.35 (m) ^d			
(2)	CF ₃ ·CO ₂	Me	Me	H	7.58	8.60	8.60	232	27	27
(3)	CF ₃ ·CO ₂	Ph	Me	H	7.30 (m) ^e	2.49	8.23	232		28
(4)	Cl ^f	H	H	CH ₂ CH ₂ HgCl	7.75 (t) ^g		5.49 (t) ^g	237		175
(5)	CF ₃ ·CO ₂	Me	H	CHMeCH ₂ Hg·O ₂ C·CF ₃ ^h	7.51 (m)	8.65 (d) ⁱ	5.40 (m)			
						8.68 (d) ⁱ				
(6)	Cl ^j	Ph	H	CHPhCH ₂ HgCl ^h	7.61 (d)	<i>c</i>	4.41 (t)			
(7)	CF ₃ ·CO ₂	Me	Me	CMe ₂ CH ₂ Hg·O ₂ C·CF ₃	7.58	8.60	8.60	232	27	27
(8)	CF ₃ ·CO ₂	Me	Me	CHPhCH ₂ Hg·O ₂ C·CF ₃ ^k	7.60	8.65br	8.65br	230	19	35

^a In pyridine; τ_{OAc} 7.85. For CCl_4 solution, Schmitz⁶ quotes τ 2.63 (Ph), 4.87 (CH), 7.95 (CH₂), and 8.15 (OAc). ^b AB of ABX. ^c Obscured by solvent resonance. ^d X of ABX, ΣJ 13.5 Hz. ^e Central two lines of AB, separated by 3 Hz (at 60 MHz). ^f In pyridine, spectrum recorded within 15 min of preparing solution. ^g Triplets distorted due to A_2B_2 character. ^h Mixture of diastereoisomers. ⁱ J 6 Hz. ^j In pyridine, spectrum recorded immediately after solution prepared but appreciable decomposition has taken place. Spectrum of crude organomercury trifluoroacetate: τ 2.55 (Ph), 4.72 (m, CH), and 7.57 (m, CH₂). ^k R resonances: 2.55 (Ph), 4.71 (X of ABX, ΣJ 13 Hz, CH), 7.50 (AB of ABX, CH₂).

but cannot be used to determine their purity, and in general the ^1H n.m.r. spectra of β -mercurioalkyl hydroperoxides and bis- β -mercurioalkyl peroxides are virtually indistinguishable.

The molecular weights of the two types of product are considerably different, and we measured the molecular weight of compound (2) in benzene by vapour pressure osmometry. The sample was pure by the ^{13}C n.m.r. criterion and yet the values found were intermediate between that required for the compound $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{O}\cdot\text{OH}$ (402) and that needed for the compound $(\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CMe}_2\cdot\text{O})_2$ (771). We believe that this is due to association of the hydroperoxide; in agreement with this the molecular weight increased appreciably with increasing concentration (570 at 10, 610 at 20, and 650 at 30 g dm^{-3}).

All peroxymercurials, except compound (6) (see later), were characterised by ^1H and ^{13}C n.m.r. and i.r. spectroscopy and, for some, further structural proof was provided by their chemical reactions.

Spectroscopic Characterisation.—A broad absorption of medium intensity at 3 350 cm^{-1} (ν_{OH}) was present in the i.r. spectra (Nujol mulls) of β -mercurioalkyl hydroperoxides

⁹ A. J. Bloodworth, P. G. Cookson, and A. G. Davies, unpublished work.

The complexity of the ^1H n.m.r. spectra of compounds (5) and (6) (as the trifluoroacetate) arises not only because of the non-equivalence of methylene protons adjacent to asymmetric centres, but also because the generation of *two* such centres during the reaction results in these compounds being obtained as mixtures of diastereoisomers. For derivatives of monosubstituted alkenes, the unambiguous detection of diastereoisomerism elegantly diagnoses the presence of a bis- β -mercurioalkyl peroxide and was achieved in the ^1H n.m.r. spectrum of compound (5) by the presence of two equally intense methyl doublets; interestingly it is the signals for CH and CH₂ which are resolved in the ^{13}C n.m.r. spectrum (Table 4).

Full details of the proton-decoupled ^{13}C n.m.r. spectra are provided in Table 4; this includes data for organomercury trifluoroacetates which were not isolated, since these data provide the basis for the product analysis presented in Table 1. The chemical shifts and ^{13}C , ^{199}Hg coupling constants (where observed) are again consistent with the proposed structures. In particular the $\geq\text{C}\cdot\text{O}\cdot\text{O}$ resonance falls in a characteristic region which we have defined by studying a representative series of simple alkyl hydroperoxides and dialkyl peroxides,⁹ and the magnitudes of one-

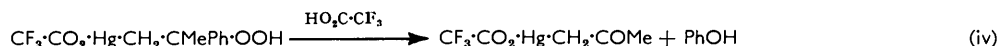
TABLE 4
Proton-decoupled ^{13}C n.m.r. spectra of β -mercurioalkyl hydroperoxides and bis- β -mercurioalkyl peroxides ($\text{XHg}\cdot\text{CH}_2\cdot\text{CR}^1\text{R}^2\cdot\text{O}\cdot\text{OR}$) in deuteriochloroform

Compd. ^a	X	R ¹	R ²	R	Chemical shift ^b				$J(^{13}\text{C},^{199}\text{Hg})/\text{Hz}$		
					COO	CH ₂	R ¹	R ²	¹ J	² J	³ J(R ¹)
(4)	CF ₃ ·CO ₂	H	H	H	74.8	23.7			1 710	43	
	CF ₃ ·CO ₂	H	H	CH ₂ CH ₂ Hg·O ₂ C·CF ₃	72.8	23.9					
	Cl ^c	H	H	CH ₂ CH ₂ HgCl	73.6	25.2					
	CF ₃ ·CO ₂	Me	H	H	80.1	31.3	21.7				
(5)	CF ₃ ·CO ₂	Me	H	CHMeCH ₂ Hg·O ₂ C·CF ₃ ^d	78.78	31.3	21.9		1 699	137	197
					78.73	31.6			1 699		185
(1)	OAc ^e	Ph	H	H	85.9	29.2	<i>f</i>		1 780	90	
	CF ₃ ·CO ₂	Ph	H	H	85.6	30.7					
	Cl ^f	Ph	H	H	86.1	34.4					
	CF ₃ ·CO ₂	Ph	H	CHPhCH ₂ Hg·O ₂ C·CF ₃ ^d	84.2	30.7					
(2)	CF ₃ ·CO ₂	Me	Me	H	83.5	37.6	27.6	27.6	1 692	127	154
	CF ₃ ·CO ₂	Me	Me	CMe ₂ CH ₂ Hg·O ₂ C·CF ₃	82.5	38.2	28.1	28.1			152
(7)	CF ₃ ·CO ₂	Me	Me	CMe ₂ CH ₂ Hg·O ₂ C·CF ₃	82.5	38.2	28.1	28.1	1 731	121	156
	CF ₃ ·CO ₂	Me	Ph	H	86.4	38.0	28.2	<i>g</i>			
(3)	CF ₃ ·CO ₂	Me	Ph	H	86.4	38.0	28.2	<i>g</i>			
	CF ₃ ·CO ₂	Me	Ph	CMePhCH ₂ Hg·O ₂ C·CF ₃ ^d	85.4	39.4	28.5				
(8)						39.1					
	CF ₃ ·CO ₂	Me	Me	CHPhCH ₂ Hg·O ₂ C·CF ₃ ^h	83.6	38.5	28.0	28.4			

^a Absence of a number indicates that the data refer to a crude product. ^b In p.p.m. downfield from internal Me₄Si. ^c In pyridine (1 cm³)—C₆D₆ (0.2 cm³). ^d Mixture of diastereoisomers. ^e In pyridine (0.8 cm³)—CDCl₃ (0.2 cm³); for compound (1) δ (CH₃CO₂) 23.4. ^f δ (Ph) 126.4, 127.7, 128.5, and 144.1. ^g δ (Ph) 125.1, 128.1, 129.1, and 144.9. ^h R resonances: δ (C—O—O) 84.4; δ (CH₂) 31.1; δ (Ph) 126.3, 128.8, 129.0, and 141.2.

two-, and three-bond couplings to mercury resemble those reported previously for other alkylmercury salts.¹⁰

Reactions of β -Mercurioalkyl Hydroperoxides.—Compounds (2) and (3) were characterised chemically by their ability to participate in reactions of the type shown by related mercury-free hydroperoxides. Thus when treated with trifluoroacetic acid compound (3) was converted into a mixture of phenol and mercuriated acetone [equation (iv)]

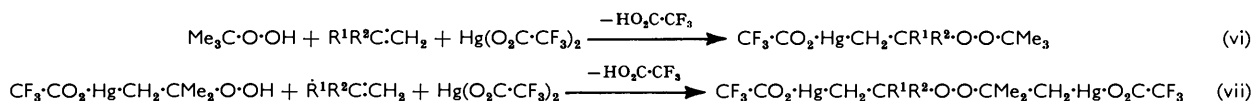


thereby paralleling the behaviour of 1-methyl-1-phenylethyl hydroperoxide¹¹ [equation (v)]. Under similar



conditions no analogous decomposition takes place with either compound (2) or *t*-butyl hydroperoxide.

However just as *t*-butyl hydroperoxide participates in

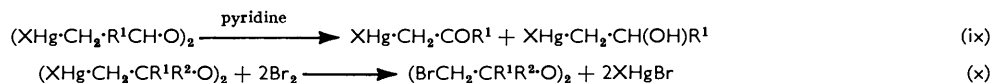


peroxymercuriation⁸ [equation (vi)], so too does compound (2) [equation (vii)]. Reaction with 2-methylpropene



afforded compound (7), whereas with phenylethene the mixed bis- β -mercurioalkyl peroxide (8) was obtained

Reactions of Bis- β -mercurioalkyl Peroxides.—It is well



known that primary and secondary alkyl peroxides undergo carbonyl-forming elimination under basic conditions¹² [equation (viii)]. With compounds (4)–(6), which fall into this category, the reaction took place in pyridine solution [equation (ix)]. As with simple peroxides,¹² the presence

¹⁰ W. Kitching, D. Praeger, D. Doddrell, F. A. L. Anet, and J. Krane, *Tetrahedron Letters*, 1975, 759.

of an α -phenyl group ($\text{R}^1 = \text{Ph}$) accelerates the decomposition, and the phenylethene derivative decomposed much more rapidly than the ethene- or propene-derived compounds. [This is why we were unable to obtain ^{13}C n.m.r. data for compound (6): it is insufficiently soluble in solvents in which it does not decompose.]

The mercuriated carbonyl compounds formed here [equation (ix)] and in the acid-induced decomposition of

compound (3) [equation (iv)] were identified by comparison with authentic materials; their presence was further demonstrated by their slow (adventitious) protolysis to give the compounds MeCOR.

Compounds (5) and (6) were further characterised by bromodemercuration (*cf.* ref. 1), a reaction [equation (x)] also applied to compound (7). Of the resultant di- β -bromoalkyl peroxides, only the one derived from compound (7)

was isolated in an analytically pure state, but the ^1H and ^{13}C n.m.r. spectra of all three crude products were fully consistent with the proposed formulations. Furthermore the mass spectra of the propene and 2-methylpropene derivatives showed parent ion peaks with the correct isotope pattern for a compound containing two bromine atoms; the propene derivative also exhibited intense peaks corresponding to loss of CH_2Br .

DISCUSSION

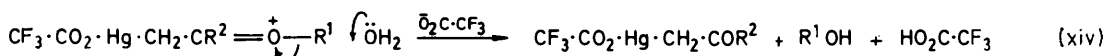
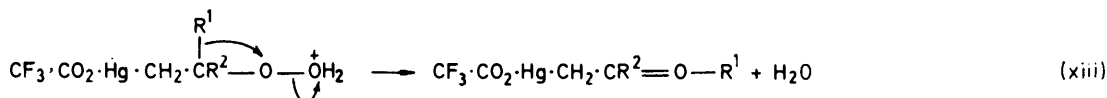
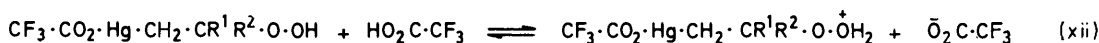
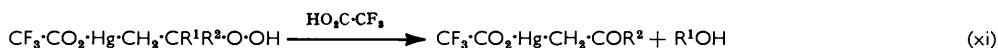
Some difficulties are encountered in preparing β -mercurioalkyl hydroperoxides by this method. A

¹¹ A. W. Van Stevenick and E. C. Kooyman, *Rec. Trav. chim.*, 1960, **79**, 413.

¹² R. Hiatt in 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1972, vol. 3, p. 23.

general problem is one of separating the hydroperoxides from the bis- β -mercurioalkyl peroxides formed concurrently. The proportion of hydroperoxide rises as the amount of hydrogen peroxide used is increased, but appreciable quantities of bis- β -mercurioalkyl peroxides are produced even when 3 equiv. of hydrogen peroxide are employed (Table 1). Although we were able to isolate the hydroperoxides from 2-methylpropene and 2-phenylpropene by fractional crystallisation, compounds

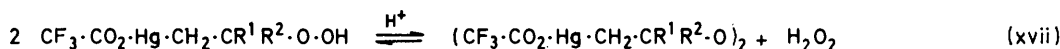
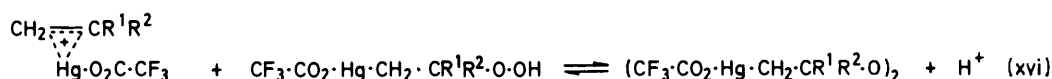
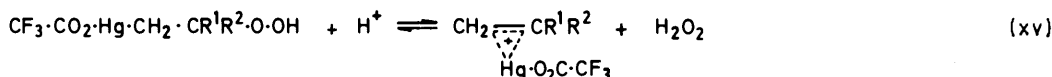
explains why it occurs with compound (3) ($R^1 = \text{Ph}$) but not with compound (2) ($R^1 = \text{Me}$). It was possible to avoid any appreciable decomposition of compound (3) by working up the reaction mixture from 2-phenylpropene within 5 min. However the corresponding decomposition in products from 1,1-diphenylethene ($R^1 = \text{Ph}$) and 2,3,3-trimethylbut-1-ene ($R^1 = \text{Bu}^t$) was more rapid and the β -mercurioalkyl hydroperoxides could not be isolated.



pure by ^{13}C n.m.r. spectroscopy could not be obtained from ethene, propene, or phenylethene. For reactions with ethene (and to a lesser extent with propene) the isolation problem is exacerbated by the lower recovery of crude products. This may arise from an appreciable solubility of the derived peroxymercurials, particularly the hydroperoxides, in the acidic aqueous layer produced during work-up, and some evidence for this came from the ^1H n.m.r. spectra of the appropriate solutions. We were also unable to isolate 1-acetoxymercuro-2-hydroperoxyethane from a reaction with ethene carried out under the conditions employed to prepare compound (1).

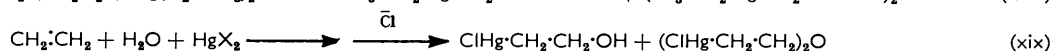
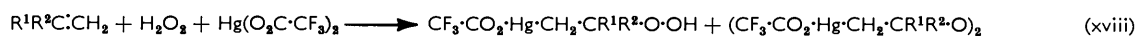
If the protonation of β -mercurioalkyl hydroperoxide takes place at the non-hydroxylic oxygen the onset of deoxymercuration will ensue. Once the mercurium ion has been generated [equation (xv)]; it may be captured by another molecule of β -mercurioalkyl hydroperoxide with the resultant formation of bis- β -mercurioalkyl peroxide [equation (xvi)]. Thus acid should catalyse the interconversion of β -mercurioalkyl hydroperoxide and bis- β -mercurioalkyl peroxide [equation (xvii)].

It seems likely, therefore, that the 'ageing' of crude samples of compounds (2) and (3) was induced by traces of trifluoroacetic acid not removed by the aqueous



A second, less general, problem is that certain types of hydroperoxide are acid-sensitive and decomposition to carbonyl compounds [equation (xi)] can be induced by the trifluoroacetic acid generated during peroxymercuriation. Presumably the reaction involves a Criegee-type rearrangement¹³ in which heterolytic fission of the O-O

washing. In support of this, solutions of a recrystallised sample of compound (2) did not produce any compound (7). Furthermore formation of bis- β -mercurioalkyl peroxide competed with decomposition *via* a Criegee-type rearrangement [equation (iv)] when compound (3) was treated with trifluoroacetic acid.



bond is induced by protonation of the hydroxylic oxygen [equation (xii)] accompanied by a 1,2-nucleophilic migration [equation (xiii)], the final products being formed by hydrolysis of the resultant oxonium ion [equation (xiv)]. The rearrangement will be favoured by a high migratory aptitude in the group R^1 , which

The similarity between our system [equation (xviii)] and the reaction of ethene with aqueous solutions of mercury(II) salts¹⁴ [equation (xix)] is striking even

¹³ R. Hiatt in 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1971, vol. 2, p. 65.

¹⁴ J. Chatt, *Chem. Rev.*, 1951, **48**, 1.

though the conditions for the latter reaction were very different to ours. In particular the conversion of β -mercurioethyl alcohol into bis- β -mercurioethyl ether is acid-catalysed.

Our conditions are best suited to the preparation of bis- β -mercurioalkyl peroxides. Highest yields are obtained when the stoichiometrically ideal ratio of reagents is used, but even here some hydroperoxide remains after short reaction times.* The 'ageing' phenomena suggest that the equilibrium between hydroperoxide and peroxide [equation (xvii)] lies well over to the right, but as yet no attempt has been made to exploit this synthetically.

Deoxymercuration provides a potential pathway whereby a mixed bis- β -mercurioalkyl peroxide could be converted into a mixture of the symmetrical compounds, but we found no evidence of this occurring in the preparation of compound (8).

The ability to distinguish the diastereoisomers of compound (5) (I; X = CF₃·CO₂Hg) by ¹H and ¹³C n.m.r. spectroscopy is interesting since neither technique is successful with di-*s*-butyl peroxide⁹ (I; X = Me). Presumably spectroscopic differences between diastereoisomers will be heightened if certain conformations in each are strongly preferred. By analogy with the organomercury trifluoroacetates formed by *t*-butylperoxymercuration of medial alkenes,¹⁵ such conformational preferences could arise in compound (5) through intra-



molecular O···Hg co-ordination. In the *t*-butylperoxymercurials the intramolecular co-ordination was destroyed by adding pyridine.¹⁵ When 2 equiv. of pyridine were added to the solution of compound (5) in deuteriochloroform the methyl signal in the ¹H n.m.r. spectrum collapsed to a *single* doublet, so that the diastereoisomers could no longer be distinguished by this technique.

However, the diastereoisomers of the dipyridine derivative of compound (5) (I; X = pyHg·O₂C·CF₃) remain distinguishable in the ¹³C n.m.r. spectrum. Similarly the diastereoisomers of the bis- β -bromoalkyl peroxide (I; X = Br) formed by brominolysis of compound (5) are distinguishable by ¹³C n.m.r. but not by ¹H n.m.r. spectroscopy. Presumably conformational preferences here have their origin in repulsive rather than attractive interactions and it appears that upon co-ordination with pyridine compound (5) exchanges one set of preferences for another.

Why are the diastereoisomers of di-*s*-butyl peroxide not distinguishable? The groups pyHg·O₂C·CF₃ and Br may induce greater conformational preferences in the diastereoisomers of (I) than does Me, or their electronic properties may give rise to greater chemical shift differences in the two conformationally averaged isomers; more likely both factors contribute.

* Exceptionally a reaction utilising the correct amount of propene and an excess of hydrogen peroxide afforded compound (5) alone in 68% yield, but the reason for this is not clear.

¹⁵ A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin II*, 1975, 531.

EXPERIMENTAL

Mercury(II) trifluoroacetate was prepared by Brown and Rei's method.¹⁶ Hydrogen peroxide was a gift from Laporte Industries Ltd., and was stored at 0 °C. Commercial alkenes (high-grade), dichloromethane and light petroleum (reagent grade), potassium chloride, bromine and pyridine (AnalaR), deuteriochloroform (99.8 atom %), and hexadeuteriobenzene (99.5 atom %) were used without further purification.

The hydrogen peroxide strength was determined iodometrically¹⁷ and checked at approximately 3-monthly intervals. Required amounts ($\pm 5\%$) were measured out by glass pipette, with the density assumed to be 1.33 g cm⁻³.¹⁸

I.r. spectra were recorded with a Perkin-Elmer 457 instrument (KBr optics) and mass spectra with an A.E.I. MS12 (inlet temperature 40–60 °C). ¹H N.m.r. spectra were recorded with a Perkin-Elmer R12 (60 MHz; 35 °C) or Varian HA 100 (100 MHz; 27 °C) instrument, and ¹³C (natural abundance) n.m.r. spectra by the pulse Fourier transform method with a Varian CFT 20 spectrometer.

General Procedure for Peroxymercuration.—To mercury(II) trifluoroacetate (10 mmol) in dichloromethane (25 cm³) was added, with vigorous stirring, hydrogen peroxide (5–30 mmol), followed immediately by a solution of alkene (10 mmol) in dichloromethane (5 cm³). Ethene, propene, and 2-methylpropene were usually bubbled through the reaction mixture and were present in excess. Alternatively the solution of mercury(II) trifluoroacetate and hydrogen peroxide was immediately introduced into a 250 cm³ flask filled with the gaseous alkene and rigged so that absorbed gas was replaced by nitrogen; the vessel was shaken vigorously for the period of the reaction. After 3–5 min the solution was washed with water (25 cm³), dried (MgSO₄), and evaporated at 12 then 0.05 mmHg to afford the crude mixture of organomercury trifluoroacetates.

The composition of individual mixtures as determined by ¹³C n.m.r. spectroscopy is given in Table 1. In the ¹³C n.m.r. spectra, the trifluoroacetate resonances appeared as quartets at δ 119 (¹J_{13C,19F} 288 Hz, CF₃) and 162 (²J_{13C,19F} 39 Hz, CO); other details for peroxides and hydroperoxides are given in Table 4. In crude mixtures from ethene, signals at δ 70.5, 68.5, 27.8, and 27.6 were assigned to CF₃·CO₂·Hg·CH₂·CH₂·OH and (CF₃·CO₂·Hg·CH₂·CH₂)₂O. Authentic trifluoroacetoxymethylmercurials of ethene and propene were prepared by passing each gas into a solution of mercury(II) trifluoroacetate in trifluoroacetic acid; ¹³C n.m.r. spectra were obtained with CDCl₃ as solvent. For CF₃·CO₂·Hg·C_AH₂·C_BH₂·O₂C·CF₃ δ _C 67.4 (¹J_{13C,199Hg} 1 734 Hz, C_A) and 23.4 (²J_{13C,199Hg} 43 Hz, C_B); for CF₃·CO₂·Hg·C_AH₂·C_BHMe·O₂C·CF₃ δ _C 76.1 (¹J_{13C,199Hg} 1 742 Hz, C_A), 31.4 (²J_{13C,199Hg} 75 Hz, C_B), and 23.4 (³J_{13C,199Hg} 145 Hz, Me).

Compounds (2), (3), and (5) were isolated by recrystallisation from dichloromethane–light petroleum (b.p. 40–60 °C) at 0 °C. Compound (4) was precipitated when the crude trifluoroacetate (obtained by using 9 mmol of H₂O₂, a perchloric acid catalyst, and a reaction time of 15 min) in dichloromethane (25 cm³) was shaken with aqueous potassium chloride (10 mmol; 25 cm³). Obtained similarly was compound (6), which showed strong i.r. absorptions at 1 485, 1 445, 1 350,

¹⁶ H. C. Brown and M-H. Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646.

¹⁷ C. D. Wagner, R. H. Smith, and E. D. Peters, *Analyt. Chem.*, 1947, **19**, 976.

¹⁸ W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, 'Hydrogen Peroxide,' Reinhold, New York, 1955, p. 199.

1 305, 1 205, 1 150, 1 040, 1 025, 980, 965, 940, 915, 830, 770, 735, 730, 700, and 590 cm^{-1} . Yields, m.p.s, and analytical data are given in Table 2 and n.m.r. spectral details in Tables 3 and 4.

Reactions of β -Mercurioalkyl Hydroperoxides.—(a) *Acid-catalysed decomposition.* An equimolar amount of trifluoroacetic acid was added to a solution of compound (3) in deuteriochloroform and the ensuing decomposition [equation (iv)] was monitored by ^1H n.m.r. spectroscopy; the extent of decomposition was considerable after 10 min and essentially complete after 1 h. The product $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{COMe}$ was identified by signals at τ 6.95 (q, 4J 0.7 Hz, CH_3) and 7.71 (t, CH_2), and the presence of phenol was indicated by changes in the Ph resonance; resonances at τ 7.33 (CH_2) and 8.20 (Me) were assigned to $(\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CMePh}\cdot\text{O})_2$ on the basis of the simultaneous spontaneous changes observed in the ^1H and ^{13}C n.m.r. spectra of a crude sample of compound (3). Acetone (peak enhancement) was a secondary product.

The ^1H n.m.r. spectrum of the crude peroxymercuriation product from 2,3,3-trimethylbut-1-ene showed the two peaks due to $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{COMe}$ (see above) plus a singlet arising from *t*-butyl alcohol (peak enhancement).

The ^1H n.m.r. spectrum of the crude peroxymercuriation product from 1,1-diphenylethene contained singlets at τ 7.02 and 6.57 (intensity ratio 4 : 3) assigned respectively to the CH_2 groups of $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CPh}_2\cdot\text{O}\cdot\text{OH}$ and $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{COPh}$; a smaller singlet at τ 6.86 may arise from the bis- β -mercurioalkyl peroxide. Acetophenone (peak enhancement) was a secondary product.

(b) *Peroxymercuriation.* (i) Phenylethene (1 mmol) in dichloromethane (5 cm^3) was added to a stirred solution of mercury(II) trifluoroacetate (1 mmol) and compound (2) (1 mmol) in dichloromethane (25 cm^3). After 30 min the mixture was filtered and volatile material removed from the filtrate at 12 mmHg to yield a white solid (94%). Recrystallisation from dichloromethane–light petroleum (b.p. 40–60 $^\circ\text{C}$) at -10°C afforded compound (8). The ^1H n.m.r. spectra of crude and recrystallised samples were identical.

(ii) 2-Methylpropene was bubbled through a stirred solution of mercury(II) trifluoroacetate (4 mmol) and compound (2) (4 mmol) in dichloromethane (20 cm^3) for 15 min. The volatile material was then removed under reduced pressure to yield an off-white solid, m.p. 115 $^\circ\text{C}$ (100%). Recrystallisation from dichloromethane–light petroleum (b.p. 40–60 $^\circ\text{C}$) afforded compound (7), m.p. 122.5–124 $^\circ\text{C}$; a second crop, m.p. 119–124 $^\circ\text{C}$, was also obtained.

(iii) Phenylethene (5 mmol) in dichloromethane (5 cm^3) was added to a stirred mixture of mercury(II) trifluoroacetate (5 mmol) and compound (1) (5 mmol) in dichloromethane (25 cm^3). After 1.5 h the solution was washed with water (25 cm^3) and then shaken with aqueous potassium chloride (10 mmol; 25 cm^3) to afford a white precipitate of compound (6) (32%).

Reactions of Bis- β -mercurioalkyl Peroxides.—(a) *Base-catalysed decomposition.* (i) Compound (4) was dissolved in pyridine and the ensuing decomposition [equation (ix)] was monitored by ^1H n.m.r. spectroscopy; decomposition was appreciable after 3 days but incomplete after 42 days. The product $\text{ClHg}\cdot\text{CH}_2\cdot\text{CHO}$ was identified by comparison with authentic material, and distorted triplets at τ 5.79 and 7.61 were assigned to $\text{ClHg}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{OH}$. Acetaldehyde (peak enhancement) was a secondary product.

(ii) The ^1H n.m.r. spectrum of compound (5) was recorded

immediately after dissolution in pyridine: τ 5.17 (q, CH), 7.56 (d, 3J 6 Hz, CH_2), and 8.53 (d, 3J 7 Hz, Me) [*cf.* the more complex spectrum obtained in deuteriochloroform (Table 3)]. The subsequent decomposition [equation (ix)] was complete after 4 days. The product $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{COMe}$ was identified by comparison with the product of acid-catalysed decomposition of compound (3) (see above) and by its spectral similarity to authentic $\text{ClHg}\cdot\text{CH}_2\cdot\text{COMe}$; resonances at τ 5.45 (q, CH), 7.5 (m, CH_2), and 8.56 (d, 3J 7 Hz, Me) were assigned to $\text{CF}_3\cdot\text{CO}_2\cdot\text{Hg}\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{OH}$. Acetone (peak enhancement) was a secondary product.

The ^{13}C n.m.r. spectrum of a solution of compound (5) plus 2 equiv. of pyridine in deuteriochloroform showed δ_{C} 78.70, and 78.51 (C·O·O), 29.9br (CH_2), and 22.1 (Me) [*cf.* the spectrum of compound (5) alone (Table 4)].

(iii) ^1H N.m.r. spectroscopy indicated that about 50% of compound (6) had decomposed 5–10 min after dissolution in pyridine; a singlet at τ 6.3 (CH_2) was assigned to $\text{ClHg}\cdot\text{CH}_2\cdot\text{COPh}$ and resonances at τ 4.46 (t, CH) and 7.35 (AB of ABX, CH_2) to $\text{ClHg}\cdot\text{CH}_2\cdot\text{CHPh}\cdot\text{OH}$. Acetophenone (peak enhancement) was formed slowly as a secondary product.

(b) *Bromodemercuriation.* The method was that previously applied to *t*-butylperoxymercurials.¹

(i) Compound (5) afforded impure $(\text{BrCH}_2\cdot\text{CHMe}\cdot\text{O})_2$ (85%), τ (CDCl_3) 5.63 (sextet, CH), 6.41 (d, 3J 5 Hz, CH_2Br), and 8.70 (d, 3J 6 Hz, Me); δ_{C} (CDCl_3) 78.51 and 78.33 (C·O·O), 34.7 (CH_2), and 16.84 and 16.78 (Me); *m/e* 274 ($^{79}\text{Br}_2$), 276 (^{79}Br and ^{81}Br), and 278 ($^{81}\text{Br}_2$) (relative intensities 1 : 2 : 1) and 181 and 183 (base peaks, relative intensities 1 : 1) (Found: C, 24.5; H, 3.6. $\text{C}_6\text{H}_{12}\text{Br}_2\text{O}_2$ requires C, 26.1; H, 4.4%).

(ii) Compound (6) quantitatively afforded impure $(\text{BrCH}_2\cdot\text{CH}\cdot\text{PhO})_2$, τ (CDCl_3) 2.68 (Ph), 4.80 (2 t, CH), and 6.36 (m, CH_2); δ_{C} (CDCl_3) 137.0, 136.9, 128.9, 128.5, and 127.3 (Ph), 85.4 (COO), and 32.0 (CH_2) (Found: C, 46.35; H, 3.95; Br, 43.95. $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{O}_2$ requires C, 48.05; H, 4.05; Br, 39.95%).

(iii) Compound (7) afforded impure $(\text{BrCH}_2\cdot\text{CMe}_2\cdot\text{O})_2$ (85%). Chromatography [silica gel (2 cm \times 1.5 cm diam.) twice; CH_2Cl_2] gave *bis*-(1-bromomethyl-1-methylethyl)peroxide, τ (CDCl_3) 6.43 (CH_2Br) and 8.64 (Me); δ_{C} (CDCl_3) 79.8 (C·O·O), 39.5 (CMe_2), and 23.5 (Me); *m/e* 302 ($^{79}\text{Br}_2$), 304 (^{79}Br and ^{81}Br), and 306 ($^{81}\text{Br}_2$) (relative intensities 1 : 2 : 1) (Found: C, 31.9; H, 5.0. $\text{C}_8\text{H}_{16}\text{Br}_2\text{O}_2$ requires C, 31.6; H, 5.3%).

Independent Synthesis of Mercuriated Carbonyl Compounds.

—(a) 2-Chloromercurioethanal was prepared (60%) from ethyl vinyl ether by Nesmeyanov's method; $^{19}\text{m.p.}$ 129 $^\circ\text{C}$ (lit.,¹⁹ 130–131 $^\circ\text{C}$), τ (pyridine) 0.14 (t, 3J 4.7 Hz, CH) and 6.80 (d, $^2J_{\text{H},^{199}\text{Hg}}$ 324 Hz, CH_2).

(b) 1-Chloromercuriopropenone was prepared (32%) from isopropenyl methyl ether by Nesmeyanov's method; $^{19}\text{m.p.}$ 100–102 $^\circ\text{C}$ (lit.,¹⁹ 104 $^\circ\text{C}$), τ (pyridine) 6.90 (q, 4J 0.72 Hz, $^2J_{\text{H},^{199}\text{Hg}}$ 325 Hz, CH_2) and 7.84 (t, $^4J_{\text{H},^{199}\text{Hg}}$ 15 Hz, CH_3) (Found: C, 12.3; H, 1.8. Calc. for $\text{C}_3\text{H}_5\text{ClHgO}$: C, 12.3; H, 1.7%).

One of us (M. E. L.) thanks the S.R.C. for a maintenance grant.

[6/1853 Received, 4th October, 1976]

¹⁹ L. G. Makarova and A. N. Nesmeyanov, 'The Organic Compounds of Mercury,' North-Holland, Amsterdam, 1967, p. 181.