

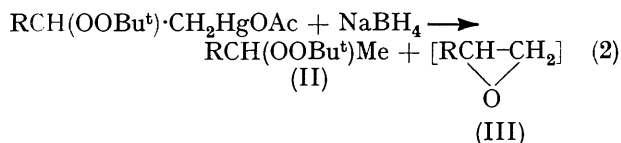
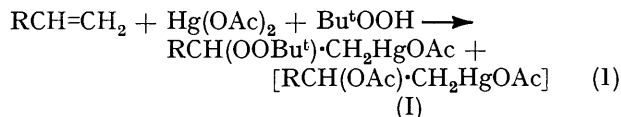
Oxymetallation. Part VII.^{1,2} Peroxymercuration of Terminal, Medial, and Cyclic Alkenes without Accompanying Acyloxymercuration

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Ethylene, propene, styrene, *cis*- and *trans*-but-2-ene, *trans*-hex-3-ene, *cis*- and *trans*-stilbene, *trans*-prop-1-enylbenzene, cyclohexene, norbornene, and 2-methylpropene each react with mercury(II) trifluoroacetate and *t*-butyl hydroperoxide in dichloromethane to provide the peroxymercurials $R^1R^3C(OOBu^t)\cdot CH(HgO_2C\cdot CF_3)R^2$. Unlike the corresponding reactions with mercury(II) acetate, competitive acyloxymercuration does not occur. The products are obtained in high yield (*ca.* 85%) and require little or no purification; they have been characterized by elemental analysis and ¹H n.m.r. spectroscopy.

A mixture of positional isomers is obtained from prop-1-enylbenzene but the compound $PhCH(OOBu^t)\cdot CH(HgO_2C\cdot CF_3)Me$ (84%) predominates. Diastereoisomeric products are obtained from the *cis/trans*-pairs and the spectra of the crude materials show that the reactions are stereospecific. When treated with mercury(II) trifluoroacetate and *t*-butyl hydroperoxide or methanol, the peroxy- and methoxy-mercurials from both *cis*- and *trans*-stilbene undergo oxidative demercuration with rearrangement to give the compounds $Ph_2CH\cdot CH(OR)_2$ where R = OBu^t or Me.

A NEW synthesis of secondary alkyl peroxides (II) was recently developed³ by combining the peroxymercuration of monosubstituted ethylenes [equation (1)] with subsequent hydridodemercuration [equation (2)]. Although this represents a considerable improvement



upon non-organometallic routes, both stages of the synthesis are marred by side reactions which account for about 20% of the products in each step. Acetoxymercurials (I) are formed in the peroxymercuration stage³ and epoxides (III) during reduction.⁴ We have extended reaction (1) to 1,2-disubstituted ethylenes such as but-2-ene and cyclohexene and here competitive acetoxymercuration consumes an even higher proportion (25–35%) of alkene.

Whereas the epoxides are easily separated from the peroxides (II) by distillation, the secondary alkyl acetates $[RCH(OAc)Me]$ formed by reduction of compounds (I) are not. Hence the acetoxymercurials have to be removed before the demercuration is carried out. This is time-consuming and leads to a further reduction in the overall yields of compounds (II).

It is believed that acetoxymercuration arises because the acetic acid which is generated during peroxymercuration successfully competes with the *t*-butyl hydroperoxide for capture of the cationic intermediate, but intervention of the acetate ion cannot be ruled out.

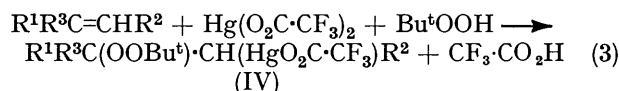
In either case the corresponding species derived from mercury(II) trifluoroacetate is a much weaker nucleophile, and the replacement of mercury(II) acetate by trifluoroacetate should thus lead to a decrease in the amount of accompanying acyloxymercuration.

Mercury(II) trifluoroacetate has been used previously in alkoxymercuration. Early work⁵ indicated that a maximum yield of only 60% of the methoxymercurial from cyclohexene could be obtained, but virtually quantitative yields in the methoxy-, ethoxy-, isopropoxy-, and *t*-butoxy-mercuration of a variety of alkenes were subsequently reported.⁶

We now describe how the problem of competing acyloxymercuration in peroxymercuration can be completely eliminated by using mercury(II) trifluoroacetate. We also report the extension of peroxymercuration to medial alkenes, including cyclohexene and norbornene. These developments considerably enhance the value of peroxymercuration in peroxide synthesis.

RESULTS AND DISCUSSION

Preparation and Characterization of β-Mercurioperoxides.—Ethylene, propene, styrene, *cis*- and *trans*-but-2-ene, *trans*-hex-3-ene, *cis*- and *trans*-stilbene, *trans*-prop-1-enylbenzene, cyclohexene, norbornene, and 2-methylpropene each react with mercury(II) trifluoroacetate and a one-fold excess of *t*-butyl hydroperoxide in dichloromethane to give the peroxymercurials (IV) [equation (3)]. Work-up after 5–10 min affords the



products in high yield. Some decomposition occurs if the solutions are kept longer, but reaction times of 20–70 min do not markedly affect the yields except

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

⁵ A. Rodgman, D. A. Shearer, and G. F. Wright, *Canad. J. Chem.*, 1957, **35**, 1377.

⁶ H. C. Brown and M.-H. Rei, *J. Amer. Chem. Soc.*, 1969, **91**, 5646.

¹ Part VI, A. J. Bloodworth and I. M. Griffin, *J.C.S. Perkin I*, 1974, 688.

² Preliminary account, A. J. Bloodworth and I. M. Griffin, *J. Organometallic Chem.*, 1974, **66**, C1.

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

with *trans*-stilbene. Unlike the reactions with mercury(II) acetate,⁴ the addition of a catalytic amount of perchloric acid is not advantageous, and appears to enhance the subsequent decomposition of the products, particularly those derived from *cis*- and *trans*-stilbene and *trans*-prop-1-enylbenzene.


Treatment of compounds (IV) with aqueous potassium bromide gives the corresponding organomercury bromides, $R^1R^3C(OOBu^t)\cdot CH(HgBr)R^2$. All 24 compounds are new except the bromide derived from styrene.³

Six organomercury trifluoroacetates were isolated pure from the reaction mixtures and single recrystallizations were sufficient to purify two others. Only the

derivatives closely resemble those previously reported⁷ for the corresponding organomercury chlorides, $R^1R^3C(OOBu^t)\cdot CH(HgCl)R^2$, except for the chemical shifts of the $CHOOBu^t$ resonance in the cyclohexene compounds. Our values are *ca.* 0.8 p.p.m. upfield of that reported⁷ for 2-chloromercuriocyclohexyl *t*-butyl peroxide; we feel that a resonance at τ 5.1 is more likely to be that of $CHOAc$ in 2-chloromercuriocyclohexyl acetate, the product of competitive acetoxymercuriation.

Absence of Acyloxymercuriation.—The trifluoroacetoxymercurials (V) of *cis*-but-2-ene, *cis*-stilbene, and norbornene were prepared by treating the alkenes with

TABLE I
 β -Mercurioperoxides $R^1CH(OOBu^t)\cdot CH(HgX)R^2$ *

Compound	Parent alkene	R ¹	R ²	X	Yield (%)		Found (%)		Calc. (%)		M.p. (°C)
					Crude	Pure	C	H	C	H	
(1a)	Ethylene	H	H	TFA ^a	<i>b</i>	86	22.7	3.1	22.3	3.0	Oil
(2a)	Propene	Me	H	TFA	88	69	24.4	3.5	24.2	3.6	36–38
(3)	Styrene	Ph	H	TFA	<i>b</i>	91	33.3	3.3	33.15	3.4	98
(4a)	<i>cis</i> -But-2-ene	Me	Me	TFA	<i>b</i>	86	26.5	3.6	26.2	3.7	40–43
(5a)	<i>trans</i> -But-2-ene	Me	Me	TFA	<i>b</i>	80	26.5	3.8	26.2	3.7	Oil
(5c)				Cl	77 ^c	29 ^d	25.4	4.55	25.2	4.5	Oil
(6a)				TFA	88 ^e	<i>d</i>	29.9	4.45	29.6	4.35	Oil
(7b)	<i>cis</i> -Stilbene	Ph	Ph	Br	70	34	39.3	3.8	39.3	3.85	118–120
(8b)	<i>trans</i> -Stilbene	Ph	Ph	Br	65	27	39.1	3.8	39.3	3.85	138
(9b)	<i>trans</i> -Prop-1-enylbenzene	Ph	Me	Br	83 ^f	47	32.1	3.9	32.0	3.9	92–94
(10a)	Cyclohexene	[CH ₂] ₄		TFA	<i>b</i>	85	30.0	3.9	29.7	3.95	99–101
(10b)				Br	89	31	26.7	4.25	26.6	4.2	90
(11a)	Norbornene			TFA	89	32	32.0	3.9	31.4	3.85	60–62
(11b)				Br	80	52	28.3	4.1	28.5	4.1	92

^a TFA=O·CO·CF₃. ^b Product required no further purification. ^c *via* RHgOAc; contained 25 mol % β -mercurioacetate. ^d Purified by column chromatography. ^e Found: C, 30.2; H, 4.5%. ^f Contained 16% MeCH(OOBu^t)·CH(HgBr)Ph. Found: C, 33.1; H, 4.0%.

* In addition, the compound Me₂C(OOBu^t)·CH₂HgO₂C·CF₃ (82%; m.p. 38°) was prepared from 2-methylpropene (Found: C, 26.6; H, 3.9. C₁₀H₁₇F₃HgO₄ requires C, 26.2; H, 3.7%).

peroxymercurials from *cis*- and *trans*-stilbene and *trans*-prop-1-enylbenzene, which could not be separated completely from the excess of *t*-butyl hydroperoxide, needed to be converted into the organomercury bromides to effect purification. Analytical data, yields, and m.p.s are given in Table I; compound (5c) was obtained from the mercury(II) acetate route but is included for completion. The following organomercury bromides (m.p.s in parentheses) were not analysed because they were prepared from pure trifluoroacetates: (1b) (50°), (2b) (oil), (4b) (oil), (5b) (oil), (6b) (oil), and (12b) (30°).

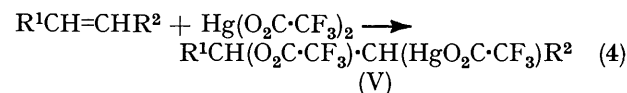
The structures of the β -mercurioperoxides were confirmed by their ¹H n.m.r. spectra. Chemical shifts and ¹H–¹H coupling constants of both trifluoroacetates and bromides are given in Tables 2 and 3, and further characterization is provided by the ¹⁹⁹Hg–¹H coupling constants reported in Table 4.

The ¹H n.m.r. spectroscopic data for the ethylene, propene, styrene, cyclohexene, and 2-methylpropene

* In contrast the norbornene trifluoroacetoxymercurial was unaffected by washing.

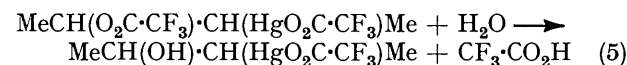
⁷ E. Schmitz, A. Rieche, and O. Brede, *J. prakt. Chem.*, 1970, **312**, 30.

mercury(II) trifluoroacetate in dichloromethane [equation (4)].⁸ The chemical shift of the $CH\cdot O_2C\cdot CF_3$ proton in



these compounds is *ca.* 1 p.p.m. downfield from that of the $CH\cdot OOBu^t$ proton of the corresponding peroxymercurials (IV). The absence of signals in this region in the high-gain ¹H n.m.r. spectra of all the crude peroxymercurials thus showed the absence of trifluoroacetoxymercurials.

However, the trifluoroacetoxymercurial from *cis*-but-2-ene was converted into the corresponding hydroxymercurial [equation (5)] under the conditions of aqueous



washing used during work-up of the peroxymercurials.* The $CH\cdot OH$ resonance of hydroxymercurials appears

⁸ Cf. (a) H. C. Brown and M.-H. Rei, *Chem. Comm.*, 1969, 1296; (b) H. C. Brown, M.-H. Rei, and K.-T. Liu, *J. Amer. Chem. Soc.*, 1970, **92**, 1760.

TABLE 2


¹H N.m.r. spectra (τ values; 60 MHz) of β-mercurioperoxides R¹R³C(OOBu^t)·CH^AH^BHgX in deuteriochloroform

Compound	Parent alkene	R ¹	R ³	X	Concn. (% w/v)	R ¹	R ³	H ^A	H ^B	Bu ^t	J/Hz			
											H ^A H ^B	H ^A R ³	H ^B R ³	R ¹ R ³
(1a)	Ethylene	H	H	TFA ^a	48				7.70t	8.72	6.3			
(1b)				Br	28	5.72t	5.68t			7.84t	8.73	6.7		
(2a)	Propene	Me	H	TFA	38	8.72d	5.6m	7.90dd	7.57dd	8.73	12.0	7.2	4.5	6.0
(2b)				Br	54	8.72d	5.5m	8.03dd	7.77dd	8.72	12.0	7.1	4.0	4.0
(3)	Styrene ^b	Ph	H	TFA	43	2.57s	4.79dd	7.65dd	7.50dd	8.72	12.0	7.9	4.9	
(12a)	2-Methylpropene	Me	Me	TFA	37				7.71s	8.74				
(12b)				Br	55	8.65s	8.65s			7.85s	8.72			

^a TFA = O·CO·CF₃. ^b Chemical shifts and coupling constants calculated by analysis of the ABX system (J. W. Emsley, J. Feeney, and L. H. Sutcliffe, 'High Resolution Nuclear Magnetic Resonance Spectroscopy,' Pergamon, Oxford, 1966, p. 375).

TABLE 3


¹H N.m.r. spectra (τ values; 60 MHz) of β-mercurioperoxides R¹CH^A(OOBu^t)·CH^B(HgX)R² in deuteriochloroform

Compound	Parent alkene	R ¹	R ²	X	Concn. (% w/v)	H ^A	H ^B	J _{AB} / Hz	R ¹	R ²	J _{H^AR¹} / Hz	J _{H^BR²} / Hz	Bu ^t
(4b)	Br	36	5.67quin	7.46dq	5.6	8.69d	8.51d	5.6	7.6	8.72			
(5a)	<i>trans</i> -But-2-ene	Me	Me	TFA	45	5.72dq	6.72dq	3.4	8.71d	8.60d	6.3	7.9	8.73
(5b)				Br	48	5.54dq	6.96dq	3.6	8.73d	8.60d	6.1	7.6	8.72
(6a)	<i>trans</i> -Hex-3-ene	Et	Et	TFA	60	8.89ddd ^b	6.73dt	2.9	8.2—8.55m ^c				8.72
(6b)				Br	60	5.74ddd	6.97ddd ^b	3.3	8.7—9.1m ^d				
(7a)	<i>cis</i> -Stilbene	Ph	Ph	TFA	45	4.58d	6.07d	6.7	2.67s				8.74
(7b)				Br	37	4.43d	6.26d	5.7	2.74s				8.73
(8a)	<i>trans</i> -Stilbene	Ph	Ph	TFA	38	4.55d	5.84d	6.0	2.73s				8.76
(8b)				Br	33	4.47d	6.05d	7.1	2.80s				8.82
(9a)	<i>trans</i> -Prop-1-enylbenzene	Ph	Me	TFA	39	4.86d	6.62dq	4.7	2.60s	8.73d		7.4	8.74
(9b)				Br	46	4.71d	6.93dq	5.9	2.60s	8.68d		7.5	8.74
(10a)	Cyclohexene	[CH ₂] ₄		TFA	24	5.94dt	<i>f</i>	10.5 ^g	7.3—9.2m				8.73
(10b)				Br	43	5.90dt	<i>f</i>	10.0 ^g	7.5—9.0m				8.71
(11a)	Norbornene			TFA	34	5.87d	7.22dd	6.7	7.1—7.4m ^h			2.4	8.74
(11b)				Br	29	5.84d	7.46dd	6.7	8.1—9.0m ⁱ				2.7
(13a)	<i>trans</i> -Prop-1-enylbenzene	Me	Ph	TFA	7 ^e	5.84dq	6.04d	3.5	8.90d	2.69s	6.0		8.69
(13b)				Br	37 ^j	5.39dq	6.30d	3.7	8.89d	2.69s	6.3		8.68

^a TFA = O·CO·CF₃. ^b Central two peaks overlap. ^c CH₂CH₃. ^d CH₂CH₃. ^e Mixture of (9a) and (13a). ^f Overlaps with R¹ and R² resonances. ^g Assigned by analogy with the hydroxymercurial (S. Wolfe and P. G. Campbell, *Canad. J. Chem.*, 1965, **43**, 1184); the other coupling constant is 4.4 Hz. ^h Bridgehead protons. ⁱ Methylene protons. ^j Mixed with (9b) (18% w/v).

TABLE 4

¹⁹⁹Hg-¹H Coupling constants of β-mercurioperoxides R¹R³C(OOBu^t)·CH(HgX)R² in deuteriochloroform

Compound	Parent alkene	R ¹	R ²	R ³	X	Concn. (% w/v)	J/Hz (±3 Hz)				
							R ¹	R ³	R ²	H	
(1a)	Ethylene	H	H	H	TFA ^a	48		286		231	
(1b)					Br	28	245		207		
(2a)	Propene	Me	H	H	TFA	38	23 ^b	236		220	
(2b)					Br	54	21 ^b	210		204	
(3)	Styrene	Ph	H	H	TFA	43		232		225	
(4a)	<i>cis</i> -But-2-ene	Me	Me	H	TFA	46		272	302		232
(4b)					Br	36		278			
(5a)	<i>trans</i> -But-2-ene	Me	Me	H	TFA	46		344	306		224
(5b)					Br	48		281			
(7a)	<i>cis</i> -Stilbene	Ph	Ph	H	TFA	52		273			282
(9a)	<i>trans</i> -Prop-1-enylbenzene	Ph	Me	H	TFA	47		303	307		
(9b)					Br	46		275			
(10a)	Cyclohexene	[CH ₂] ₄		H	TFA	43		104			
(11a)	Norbornene			H	TFA	37		108			230
(12a)	2-Methylpropene	Me	H	Me	TFA	37		25 ^b		225	
(12b)					Br	55		22 ^b		201	

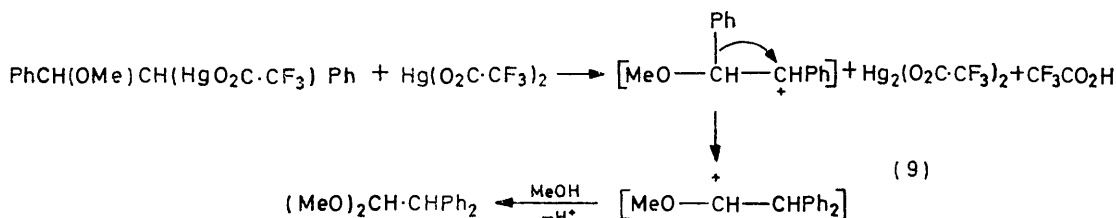
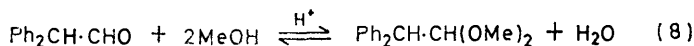
^a TFA = O·CO·CF₃. ^b ±1 Hz.

ca. 0.5 p.p.m. upfield from the $CH\cdot OOBu^t$ signal of the corresponding peroxymercurials, but again such signals are absent in the spectra of crude peroxymercurials.

The absence of both trifluoroacetoxy- and hydroxymercurials thus establishes that acyloxymercuration does not accompany peroxymercuration when mercury(II) trifluoroacetate and a one-fold excess of *t*-butyl hydroperoxide are used. This holds for *cis*-but-2-ene even when the excess of *t*-butyl hydroperoxide is reduced to 10%. However a reaction with norbornene using 1.05 equiv. of *t*-butyl hydroperoxide afforded a product containing 27% of the trifluoroacetoxymercurial. The ratio of peroxymercurial to trifluoroacetoxymercurial was the same whether the mixture was worked up after 5 or 60 min. This differs from the *t*-butoxymercuration of norbornene where short reaction times give rise to a higher proportion of trifluoroacetoxymercurial.⁶

Stereospecificity.—The 1H n.m.r. spectra of the peroxymercurials derived from *cis*-but-2-ene and *cis*-stilbene are quite distinct from those of the compounds from the corresponding *trans*-alkenes (see Table 3). None of the *trans*-derived peroxymercurials can be detected in the spectra of the crude products from the *cis*-alkenes and *vice versa*. Therefore it is concluded that the peroxymercuration of these simple alkenes, like that of methyl cinnamate,¹ is stereospecific. The spectra of the crude peroxymercurials from *trans*-hex-3-ene, cyclohexene, and norbornene similarly indicate stereospecificity, but our lack of the alternative diastereoisomers for comparison renders these observations less conclusive.

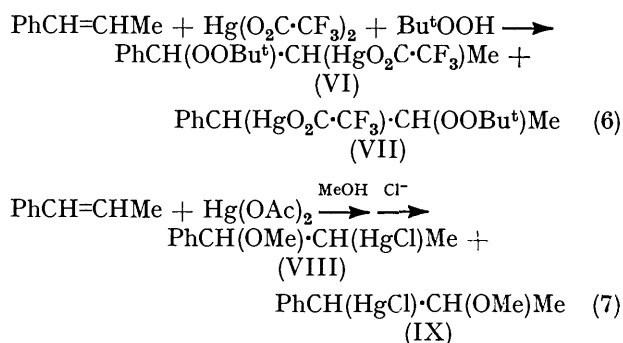
Positional Isomerism.—A mixture of positional isomers (VI) and (VII) is obtained from *trans*-prop-1-enylbenzene, but compound (VI) (84%) predominates [equation (6)]. These isomers were identified in the 1H n.m.r. spectrum of the crude product by using the peroxymercurials derived from *trans*-stilbene and *trans*-but-2-ene as model compounds. The relative yields were determined by integration.



This may be compared with the methoxymercuration of *trans*-prop-1-enylbenzene [equation (7)] which is reported to give isomers (VIII) and (IX) in the ratio 60:40.⁹ Here the relative yields were determined by converting the isomeric methoxymercurials into ketones by sequential bromodemercuration, dehydrobromin-

⁹ W. R. R. Park and G. F. Wright, *J. Org. Chem.*, 1954, **19**, 1435.

ation, and acidic hydrolysis, and then estimating the ketones as the corresponding 2,4-dinitrophenylhydrazones. The ratio was reported to be unaffected if



mercury(II) benzoate replaced mercury(II) acetate. For the reaction with mercury(II) trifluoroacetate we obtain a ratio of 65:35, again by 1H n.m.r. spectroscopy. Our ratio is probably the more reliable being obtained directly by a non-chemical process, but there is good agreement with the earlier work.

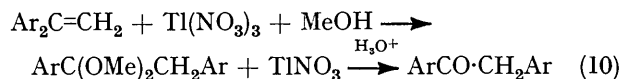
Oxidative Demercuration of Stilbene Derivatives.—Both stilbenes rapidly afford peroxymercurials in high yield [equation (3); $R^1 = R^2 = Ph$, $R^3 = H$]. This contrasts with the reported difficulty with which the *trans*-isomer undergoes methoxymercuration; with mercury(II) acetate in methanol, the presence of 0.1 mol. equiv. of benzoyl peroxide (no satisfactory explanation has been given for the function of this additive) and a long reaction time were required and then the yield was only 24%.¹⁰ Hence we attempted to carry out the methoxymercuration of *trans*-stilbene using mercury(II) trifluoroacetate under conditions analogous to those for peroxymercuration.

The 1H n.m.r. spectrum of the crude reaction mixture contained signals attributable to the required compound, $PhCH(OMe)\cdot CH(HgO_2C\cdot CF_3)Ph$, but a second and similar set of resonances was also present. The

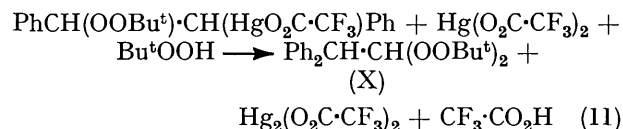
same extra signals, though much less intense, were apparent in the spectrum of the crude methoxymercurial from *cis*-stilbene. It was shown that the second set of resonances arises from the product of oxidative demercuration. Thus treatment of the initial products from both *cis*- and *trans*-stilbene with a second equivalent

¹⁰ A. M. Birks and G. F. Wright, *J. Amer. Chem. Soc.*, 1940, **62**, 2412.

of mercury(II) trifluoroacetate and 2 equiv. of methanol brought about precipitation of a mercury(I) salt and cleanly yielded the common product. This was identified as $\text{Ph}_2\text{CH}\cdot\text{CH}(\text{OMe})_2$ by its ^1H n.m.r. spectrum and independent synthesis from diphenylacetaldehyde [equation (8)]. Thus the oxidative demercuration takes place with complete 1,2-nucleophilic migration of the phenyl group [equation (9)]. This contrasts with the oxidation of stilbene by methanolic mercury(II) nitrate which affords a mixture of $\text{PhCH}(\text{OMe})\cdot\text{CH}(\text{ONO}_2)\text{Ph}$, $\text{PhCH}(\text{OMe})\cdot\text{CH}(\text{OMe})\text{Ph}$, and $\text{Ph}_2\text{CH}\cdot\text{CH}(\text{OMe})_2$ of which the latter only constitutes 26–29%.¹¹ However, it is similar to the oxidative rearrangements found in the reaction of monoarylethylenes and 1,1-diarylethylenes with methanolic thallium(III) nitrate [equation (10)].¹²



The stilbene-derived peroxymercurials underwent an analogous reaction with mercury(II) trifluoroacetate and t-butyl hydroperoxide [equation (11)] to give the product which is generated if the crude peroxymercuriation mixtures are not worked up immediately. This reaction is slower and appears to be less clean than that with the methoxymercurial. The ^1H n.m.r. spectrum



of the product contained signals tentatively assigned, on the basis of chemical shift and multiplicity, to $\text{PhCH}(\text{OOBu}^t)\cdot\text{CH}(\text{OOBu}^t)\text{Ph}$ (17%) and $\text{PhCH}(\text{O}_2\text{C}\cdot\text{CF}_3)\cdot\text{CH}(\text{OOBu}^t)\text{Ph}$ (19%) in addition to those of the peroxyacetal (X).

Presumably peroxymercuriation with mercury(II) trifluoroacetate proceeds to an equilibrium position which is appreciably displaced from completion (*cf.* ref. 5) so that free mercury(II) trifluoroacetate is present to bring about the subsequent oxidation. The relative ease of forming a carbonium ion at a secondary carbon bearing a phenyl substituent must account for the particular susceptibility of the stilbene derivatives towards oxidative demercuration.

EXPERIMENTAL

Materials and Spectra.—Mercury(II) trifluoroacetate was prepared by Brown and Rei's method.⁶ t-Butyl hydroperoxide was purified as described previously,³ methanol was dried by distillation from magnesium turnings, and norbornene was sublimed; all other materials were commercial products used without further purification.

^1H N.m.r. spectra were recorded on Perkin-Elmer R12 (60 MHz; 35°) or Varian HA100 (100 MHz; 27°) instruments.

Peroxymercuriation.—The following general procedure

¹¹ D. A. Shearer and G. F. Wright, *Canad. J. Chem.*, 1955, **33**, 1002.

was adopted, although the quantities were sometimes halved. Alkene (20 mmol) was added to a magnetically stirred solution of t-butyl hydroperoxide (40 mmol) and mercury(II) trifluoroacetate (20 mmol) in dichloromethane (30 ml). Gaseous alkenes were bubbled through the solution, liquids were delivered by syringe, and solids were added dissolved in dichloromethane, the volume of dichloromethane containing the peroxide and mercury(II) salt being proportionately reduced to maintain the overall amount used at 30 ml. After 5–10 min the solution was filtered, washed with water (20 ml), dried (MgSO_4), and the volatile material removed at 12 then 0.05 mmHg to give crude organomercury trifluoroacetate.

Conversion into organomercury bromide was carried out by vigorously stirring the washed dichloromethane solution with aqueous potassium bromide (22 mmol; 20 ml) for 1 h, drying (MgSO_4) the organic phase, and removing the solvent *in vacuo*. If the aqueous washing of the organomercury trifluoroacetate was omitted, a highly dispersed precipitate of mercury(II) bromide was sometimes formed which created difficulty in separating the phases.

Individual yields, m.p.s, and analytical data are given in Table 1, and ^1H n.m.r. spectral details in Tables 2–4. Compound (2a) was recrystallized from light petroleum (b.p. 40–60°) at –78°, compounds (7b–10b) from light petroleum (b.p. 60–80°) containing a little dichloromethane, compound (11a) from aqueous methanol at –20°, and compound (11b) from methanol. Compound (6a) was chromatographed on silica gel³ (1 × 1 in diam.); 60 ml of light petroleum (b.p. 60–80°) eluate was discarded and pure (6a) was eluted with chloroform (60 ml). The acetoxymercurial contaminating compound (5c) was removed by chromatography on silica gel (14 × 1 in diam.); light petroleum–benzene (400 ml; 1 : 1), benzene (100 ml), and chloroform (125 ml) eluates were discarded and pure (5c) was eluted in the 125–400 ml chloroform fraction.

The ability to detect a peroxymercurial in the presence of its diastereoisomer was demonstrated by preparing a mixture of the products from *cis*- and *trans*-stilbene in the ratio 95 : 5; in the ^1H n.m.r. spectrum, the t-butyl signal of the minor component was clearly visible.

Trifluoroacetoxymercuration.—(a) *cis*-But-2-ene gave $\text{CH}^A_3\text{CH}^B(\text{O}\cdot\text{CO}\cdot\text{CF}_3)\cdot\text{CH}^C(\text{HgO}\cdot\text{CO}\cdot\text{CF}_3)\text{CH}^D_3$; τ (CDCl_3 ; 60%) 4.59 (dq, J_{AB} 7.7, J_{BC} 3.3 Hz, H^B), 6.86 (dq, J_{CD} 7.7, H^C), and 8.47 [d, $J(^{199}\text{Hg}\text{--}\text{H}^D)$ 288 Hz, H^A and H^D]. By washing with water the product was converted into $\text{CH}^A_3\text{CH}^B(\text{OH})\cdot\text{CH}^C(\text{HgO}\cdot\text{CO}\cdot\text{CF}_3)\text{CH}^D_3$; τ (CDCl_3 ; 40%) 3.50br (s, OH), 6.28 (m, H^B), 7.05 (m, H^C), 8.47 [d, J_{CD} 7.5 Hz, $J(^{199}\text{Hg}\text{--}\text{H}^D)$ 307 Hz, H^D], and 8.70 (d, J_{AB} 5.3 Hz, H^A).

(b) *cis*-Stilbene gave $\text{PhCH}^A(\text{O}\cdot\text{CO}\cdot\text{CF}_3)\cdot\text{CH}^B(\text{HgO}\cdot\text{CO}\cdot\text{CF}_3)\text{Ph}$; τ (CDCl_3) 2.3–2.9 (m, Ph), 3.70 (d, J_{AB} 5.6 Hz, H^A), and 5.95 (d, H^B).

(c) Norbornene gave a product with τ (CDCl_3 ; 52%) 4.89 (d, J 6.7 Hz, $\text{CHO}\cdot\text{CO}\cdot\text{CF}_3$), 7.00 (dd, J 2.5 and 6.7 Hz, CHHg), 7.1–7.4br (bridgehead H), and 8.0–9.0 (m; methylene H). Brown^{8b} reports τ (C_6D_6) 5.55 (d, J 7 Hz, $\text{CHO}\cdot\text{CO}\cdot\text{CF}_3$) and 8.09 (dd, J 2.5 and 7 Hz, CHHg).

Methoxymercuration.—The method was analogous to that used for peroxymercuriation.

(a) *trans*-But-2-ene gave an oil (80%) identified as 2-methoxy-3-trifluoroacetoxymercurobutane, $\text{CH}^A_3\text{CH}^B(\text{OCH}_3)\text{CH}^C(\text{HgO}_2\text{C}\cdot\text{CF}_3)\text{CH}^D_3$; τ (CDCl_3 ; 40%) 6.35—

¹² A. McKillop, J. D. Hunt, F. Kienzle, E. Bigham, and E. C. Taylor, *J. Amer. Chem. Soc.*, 1973, **95**, 3635.

6.80 (m, H^B and H^C), 6.58 (s, OCH₃), 8.59 [d, *J* 7.3, *J*(¹⁹⁹Hg-H^D) 317 Hz, H^D], and 8.71 (d, *J* 5.9 Hz, H^A) (Found: C, 20.6; H, 2.8. C₇H₁₁F₃HgO₃ requires C, 21.0; H, 2.9%).

(b) *cis*-But-2-ene gave the diastereoisomer, also an oil, τ (CDCl₃; 40%) 6.57 (m, H^B), 6.57 (s, OCH₃), 7.05 (dq, *J*_{BC} 4.3 Hz, H^C), 8.50 [d, *J*_{CD} 7.3, *J*(¹⁹⁹Hg-H^D) 307 Hz, H^D], and 8.75 (d, *J*_{AB} 6.0 Hz, H^A).

(c) *cis*-Stilbene gave, after 3 min, PhCH^A(OMe)·CH^B(HgO₂C·CF₃)Ph, τ (CDCl₃) 2.58 and 2.65 (s, Ph), 5.28 (d, *J*_{AB} 3.9 Hz, H^A), 6.02 (d, H^B), and 6.63 (s, OMe), contaminated with unchanged *cis*-stilbene and Ph₂CH·CH(OMe)₂ (0.2 mol. equiv.). Treatment with aqueous potassium chloride and recrystallization from light petroleum-dichloromethane gave PhCH^A(OMe)·CH^B(HgCl)Ph, m.p. 144° (lit.¹³ 143°), τ (CDCl₃; 23%) 2.61 and 2.76 (s, Ph), 5.12 [d, *J*_{AB} 4.0, *J*(¹⁹⁹Hg-H^A) 311 Hz, H^A], 6.36 [d, *J*(¹⁹⁹Hg-H^B) 261 Hz, H^B], and 6.63 (s, OMe).

(d) *trans*-Stilbene gave, after 2 min, the diastereoisomeric PhCH^A(OMe)·CH^B(HgO₂C·CF₃)Ph, τ (CDCl₃) 2.3—2.8 (Ph), 5.31 (d, *J*_{AB} 7.3 Hz, H^A), 5.75 (d, H^B), and 6.81 (s, OMe), contaminated with unchanged *trans*-stilbene and Ph₂CH·CH(OMe)₂ (0.37 mol. equiv.).

(e) *trans*-Prop-1-enylbenzene afforded an oil (76%) consisting of PhCH^A(OMe)·CH^B(HgO₂C·CF₃)CH^C₃ (65%), τ (CDCl₃) 2.55 (s, Ph), 5.67 (d, *J*_{AB} 5.3 Hz, H^A), 6.6 (m, H^B), 6.73 (s, OMe), and 8.76 [d, *J*_{BC} 7.3 *J*(¹⁹⁹Hg-H^C) 312 Hz, H^C], and PhCH^A(HgO₂C·CF₃)·CH^B(OMe)CH^C₃, τ (CDCl₃) 2.65 (s, Ph), 5.74 (d, *J*_{AB} 5.3 Hz, H^A), 6.3 (m, H^B), 6.60 (s, OMe), and 8.81 (d, *J*_{BC} 5.8 Hz, H^C).

Oxidative Demercuration of Stilbene Derivatives.—(a) *Methoxymercurials.* The crude organomercury trifluoroacetate (3.6 mmol) from *cis*-stilbene was mixed with methanol (7.2 mmol) and mercury(II) trifluoroacetate (3.94 mmol) in dichloromethane (5 ml). After 30 min a white precipitate was filtered off; this turned black when treated with dilute sodium hydroxide. The filtrate was washed with water and dried (MgSO₄); removal of the solvent *in vacuo* gave 1,1-dimethoxy-2,2-diphenylethane (88%) as an oil, τ (CDCl₃; 35%) 2.5—2.9 (m, Ph), 4.99

[d, *J* 7.7 Hz, CH(OMe)₂], 5.74 (d, CHPh₂), and 6.72 (s, OMe).

An identical product (peak enhancement in n.m.r.) was obtained from *trans*-stilbene and by treating diphenylacetaldehyde with methanol (2 equiv.) in the presence of a catalytic amount of trifluoroacetic acid.

(b) *Peroxymercurials.* A solution of *cis*-stilbene (5 mmol), mercury(II) trifluoroacetate (10 mmol), and *t*-butyl hydroperoxide (20 mmol) in dichloromethane (15 ml) was stirred for 2 h and filtered. The filtrate was washed with water and dried (MgSO₄). Removal of the solvent *in vacuo* gave an oil which contained the peroxymercurial (7a) (25%) and 1,1-diphenyl-2,2-di-*t*-butylperoxyethane (48%), τ (CDCl₃) 2.4—2.8 (m, Ph), 4.06 [d, *J* 7.6 Hz, CH(OOBu^t)₂], 5.43 (d, CHPh₂), and 8.91 (s, Bu^t); the ¹H n.m.r. spectrum also contained doublets (*J* 8.3 Hz) at τ 3.78 and 4.73 [possibly PhCH(O₂C·CF₃)·CH(OOBu^t)Ph; 14%] and singlets at τ 4.77 and 4.82 [possibly *meso*- and *DL*-PhCH(OOBu^t)·CH(OOBu^t)Ph; 13%]. The peroxymercurial was removed by chromatography on silica gel (2.5 × 1 in diam.; 1:1 benzene-cyclohexane) to afford an oil which slowly crystallized [Found: C, 71.2; H, 7.85%. Calc. for a mixture (n.m.r.) of Ph₂CH·CH(OOBu^t)₂ (64%), PhCH(OOBu^t)·CH(OOBu^t)Ph (17%), and PhCH(O₂C·CF₃)·CH(OOBu^t)Ph (19%): C, 71.5; H, 7.85%].

A similar product (peak enhancement in n.m.r.) was obtained by treating the peroxymercurial from *trans*-stilbene (8a) with mercury(II) trifluoroacetate and *t*-butyl hydroperoxide.

Under conditions analogous to those which afford the dimethylacetal, diphenylacetaldehyde gave the hemiperoxyacetal Ph₂CH^A·CH^B(OOBu^t)OH, τ (CDCl₃) 2.4—2.8 (m, Ph), 4.16 (d, *J* 6.4 Hz, H^B), 5.70 (d, H^A), and 8.90 (s, Bu^t). Azeotropic dehydration of the mixture in benzene under reduced pressure (60° for 30 min; H₂SO₄ catalyst) effected partial conversion (35%) into a product identical (peak enhancement in n.m.r.) with the major component from the stilbene oxidations.

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¹³ G. F. Wright, *J. Amer. Chem. Soc.*, 1935, **57**, 1993.