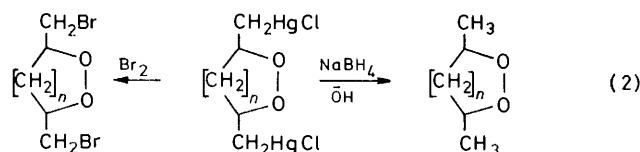
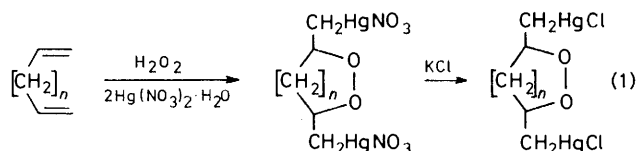


Oxymetallation. Part 12.¹ Further Syntheses of Monocyclic Peroxides via Peroxymercuriation

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The scope of cycloperoxymercuriation as a route to monocyclic peroxides has been investigated by studying the reaction of mercury(II) nitrate with ten representative dienes plus hydrogen peroxide, and with two alkenyl hydroperoxides. By hydrogeno- and bromo-demercuration of the resultant products, seven new methyl- and bromomethyl-substituted 1,2-dioxacyclo-pentanes and -hexanes have been prepared. The geometrical isomers of three of the 1,2-dioxacyclopentanes (4), (8), and (9) have been separated and assigned *cis* and *trans* configurations, and each of the four diastereoisomers of 4-bromo-3-bromomethyl-5-methyl-1,2-dioxacyclopentane (11) has been isolated. Two diastereoisomers of 4-bromo-6-bromomethyl-3-methyl-1,2-dioxacyclohexane (13) are formed and have been separated; their ¹H n.m.r. spectra indicate that each has a chair conformation with equatorial methyl and bromomethyl groups, the stereoisomerism arising from the disposition of the bromine substituent. The by-products of peroxymercuriation-reduction have been shown to be unsaturated alcohols whose formation is strongly favoured where the cycloperoxymercurial contains an endocyclic mercurio-substituent.

RECENTLY we described a new method for synthesising cyclic secondary alkyl peroxides.¹ Six new 1,2-dioxacycloalkanes were prepared in high yield by the reaction of penta-1,4-diene or hexa-1,5-diene with hydrogen peroxide and mercury(II) nitrate followed by treatment with chloride ion, reduction, or brominolysis [equations (1) and (2); *n* = 1 or 2]. To establish further



the scope of cycloperoxymercuriation as a preparative route to monocyclic peroxides, we have investigated similar reactions with several other non-conjugated dienes, with penta-1,3-diene and 2,5-dimethylhexa-2,4-diene, and with two alkenyl hydroperoxides, and we now report our findings.

RESULTS AND DISCUSSION

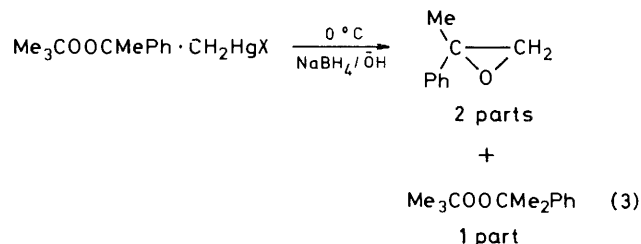
In general no attempt was made to purify the peroxymercurials and the cyclic peroxides characterised were those obtained after demercuration by reduction (Table 1) or brominolysis (Table 2). The structures shown are based primarily on the ¹H and ¹³C n.m.r. data provided in the Tables with supporting evidence coming from mass spectra and elemental analysis (Experimental section). For comparison the peroxides derived from penta-1,4-diene and hexa-1,5-diene are included in the Tables.

With two preparatively unimportant exceptions (see later), peroxymercuriation-reduction gave high yields of

products that contained 70–80% (g.l.c.) of cyclic peroxide. Usually there was only one major by-product (see later) and the peroxides were readily isolated by preparative g.l.c., which also enabled the *cis* and *trans* isomers of compound (4) to be separated. In general no organic impurities were detected in the crude products from peroxymercuriation-brominolysis, but the complete removal of inorganic mercury(II) salts sometimes proved troublesome. H.p.l.c. provided a convenient method of purification for the bromoperoxides and permitted the diastereoisomers of compounds (8), (9), (11), and (13) to be separated.

Methylated Penta-1,4-dienes and Hexa-1,5-diene.—By slightly modifying the procedure used for penta-1,4-diene and hexa-1,5-diene,¹ namely by carrying out the peroxymercuriations at 0 °C using Hg(NO₃)₂·1/2H₂O rather than at room temperature with Hg(NO₃)₂·H₂O, good yields of dioxacycloalkanes were obtained from 2-methylpenta-1,4-diene, 2,4-dimethylpenta-1,4-diene, 3,3-dimethylpenta-1,4-diene, and 2,5-dimethylhexa-1,5-diene.













The peroxymercuriation-reduction products (2), (3), and (6) each contain tertiary carbon atoms adjacent to the peroxide linkage and the demonstration that these compounds are formed in yields of about 70% with little side product is important in view of our earlier discovery² that related acyclic peroxymercurials afford mainly epoxide upon reduction [*e.g.* equation (3)]. Thus the



yields of peroxides (3) and (6) from peroxymercuriation-reduction [equation (4a)] are about double those obtained

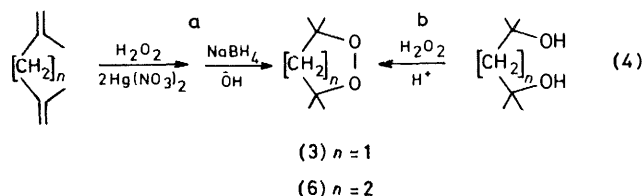
TABLE I

¹³C and ¹H N.m.r. spectra of methyl-substituted 1,2-dioxacycloalkanes prepared by cycloperoxymercuration and reduction of dienes

Parent diene	Cyclic peroxide	Isomer	δ Values					
			1	2	3	4	5	6
		δ_C <i>cis</i>	77.30	49.34	19.25			
		δ_C <i>trans</i>	77.04	48.61	18.40			
		δ_H <i>cis</i>	4.25(ddq)	{ 1.71 (dt) ^c 2.77 (dt) ^d	1.26 (d) ^e			
		δ_H <i>trans</i>	4.30 (tq)	2.19 (t) ^f	1.22 (d) ^e			
		δ_C	77.94	48.32	83.47	18.75	27.02	25.90
		δ_H	4.29 (ddq)	{ 1.85 (dd) ^g 2.39 (dd) ^h		1.24 (d) ^e	1.31 (s)	1.27 (s)
		δ_C	83.64	58.56	26.47			
		δ_H		2.08 (s)	1.25 (s)			
		δ_C <i>cis</i>	84.49	50.87	12.00	21.77	14.44	
		δ_C <i>trans</i>	85.38	50.80	12.92	21.53	21.53	
		δ_H <i>cis</i>	3.98 (q)		1.10 (d) ^e	0.98 (s)	0.85(s)	
		δ_H <i>trans</i>	3.93 (q)		1.13 (d) ^k	0.97 (s)	0.97 (s)	
		δ_C <i>cis</i>	76.30	27.04	18.18			
		δ_C <i>trans</i>	77.08	31.58	18.79			
		δ_H <i>cis</i>	} 4.06 (m)	1.56 (m)	1.16 (d) ^e			
		δ_H <i>trans</i>			0.98 (d) ⁿ			
		δ_C	77.00	31.10	27.18 } ^p			
		δ_H		1.65 (s)	22.40 } 1.25 (s) ^r			

^a Ref. 1. ^b Data for mixture containing 50% of *cis* isomer. ^c ²J 11.5, ³J 6.5 Hz. ^d ³J 7.2 Hz. ^e ³J 6.0 Hz. ^f ³J 6.7 Hz. ^g ²J 11.5, ³J 6.75 Hz. ^h ³J 7.25 Hz. ⁱ Previously known; see ref. 3. ^j Isomers separated from mixture containing 60% of *cis* which had the longer retention time. ^k ³J 6.5 Hz. ^l Data for mixture containing 20% of *cis* isomer. ^m *Trans* isomer also obtained from hexa-1,4-diene. ⁿ ³J 7.0 Hz. ^o Also prepared from 2,5-dimethylhexa-2,4-diene. ^p At 0 °C; broad singlet (width of half height \approx 70 Hz) at δ 24 obtained at normal probe temperature. ^r Lit. (G. Clacson, G. Androes, and M. Calvin, *J. Amer. Chem. Soc.*, 1961, **83**, 4357), δ 1.35 (CS₂).

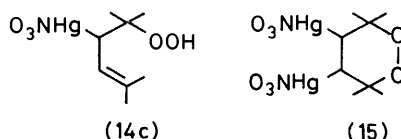
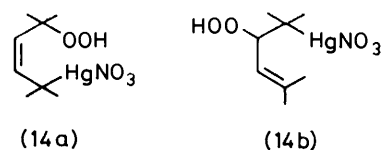
by the conventional acid-catalysed reaction of diols with concentrated hydrogen peroxide [equation (4b)].³



It is interesting to note that compound (6) was also obtained from the conjugated diene 2,5-dimethylhexa-2,4-diene. Three initial hydroperoxymercuration products can be envisaged, arising from 1,4-addition⁴ (14a), and the two possible orientations of 1,2-addition (14b and c). Of these only (14c) can cyclise by the favoured⁵ 5-*exo* or 6-*endo* modes. Since the mercury salt of a strong acid is involved, thermodynamic control of the product distribution can be expected and apparently favours formation of the dioxacyclohexane (15), in which addition at both

double bonds has taken place in the Markovnikov orientation.

As with the parent non-conjugated dienes¹ the four



methylated substrates studied here afford diastereoisomeric cycloperoxymercuration products. Of course, except for peroxide (4), this is not detectable from the reduction products, but it is revealed by brominolysis. The

presence of the methyl groups in the dienes has little or no effect upon the ratio of diastereoisomeric 1,2-dioxacyclopentanes formed and nearly equal amounts of each isomer are obtained.

Hexa-1,4-diene.—Only one isomer, thought to have the *trans* configuration, was detected in commercial '*cis/trans*' hexa-1,4-diene by ^{13}C n.m.r. spectroscopy.

Peroxymercuration–reduction of this material gave three major products as judged by g.l.c. analysis of the reaction mixture. The third fraction proved to be *trans*-3,6-dimethyl-1,2-dioxacyclohexane,¹ but the other two components were non-peroxidic (see later). Thus neither *cis*-3,6-dimethyl-1,2-dioxacyclohexane nor 3-ethyl-5-methyl-1,2-dioxacyclopentane were detected.

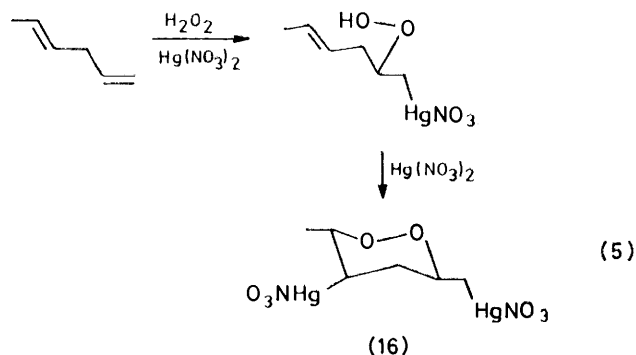
TABLE 2

^{13}C and ^1H N.m.r. spectra of bromomethyl-substituted 1,2-dioxacycloalkanes prepared by cycloperoxymercuration and brominolysis of dienes

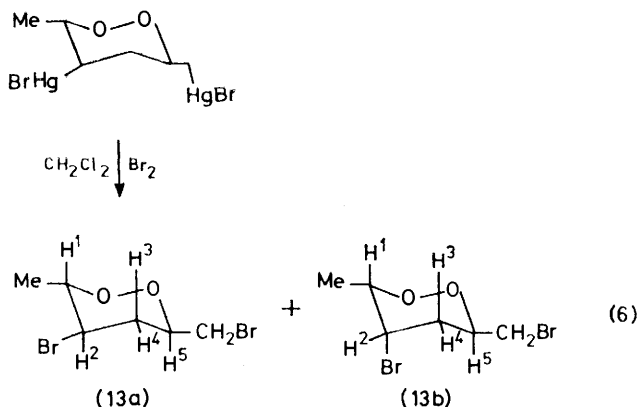
Parent diene	Cyclic peroxide	Isomer	δ Values						
			1	2	3	4	5	6	
		(7) ^{a,b}	δ_{C} <i>cis</i>	79.68	43.59	32.51			
			δ_{C} <i>trans</i>	80.35	43.49	31.34			
			δ_{H} <i>cis</i>	4.65 (m)	2.63 (m)	3.56 (m)			
			δ_{H} <i>trans</i>						
		(8) ^c	δ_{C} A ^d	80.90	48.04	84.99	32.99	37.97	21.57
			δ_{C} B	80.90	48.04	85.40	30.82	37.54	22.79
			δ_{H} A ^d	4.56 (m)	{ 2.34 (dd) ^e				
			δ_{H} B	4.60 (m)	{ 3.04 (dd) ^f		3.45 ^g	3.45 (s)	1.50 (s)
							3.48 (d) ^t	3.50 (s)	1.50 (s)
		(9) ^j	δ_{C} <i>cis</i>	85.75	52.39	37.20	23.47		
			δ_{C} <i>trans</i>	85.98	52.13	38.58	21.84		
			δ_{H} <i>cis</i>		2.20 ^k	3.49 ⁱ	1.52 (s)		
			δ_{H} <i>trans</i>		2.92 ^j	3.52 ⁱ	3.50 (s)	1.47 (s)	
		(10) ^m	δ_{C} <i>cis</i>	89.17	53.50	27.16	25.86	15.46	
			δ_{C} <i>trans</i>	89.17	52.61	28.14	22.12	22.12	
			δ_{H} <i>cis</i>	4.27 (t) ⁿ		3.35 (d)	1.08 (s)	1.33 (s)	
			δ_{H} <i>trans</i>	4.17 (t) ⁿ		3.41 (d)	1.23 (s)	1.23 (s)	
		(11) ^p	δ_{C} A	87.95	56.34	86.15	30.54	14.10	
			δ_{C} B	86.48	58.26	81.84	28.97	15.60	
			δ_{C} C	88.64	58.26	79.73	28.64	15.74	
			δ_{C} D	82.94	61.15	79.64	30.46	15.60	
			δ_{H} A	4.66 (ddd)	4.05 (dd) ^q	4.52 (dq)	3.51 ^r	1.39 (d) ^t	
			δ_{H} B	4.56 (m)	4.34 (t) ^t	4.56 (m)	3.55 ^s	1.40 (d) ^t	
		(12) ^{a,v}	δ_{C} <i>cis</i>	79.57	30.61	23.48			
			δ_{C} <i>trans</i>	80.19	30.61	27.30			
			δ_{H} <i>cis</i>	4.31 (m)	1.98 (m)	3.60 ^w			
			δ_{H} <i>trans</i>				3.39 (d) ^t		
		(13) ^x	δ_{C} A	82.28	39.84	48.57	81.36	29.54	16.19
			δ_{C} B	78.51	37.93	52.37	75.48	30.37	18.04
			δ_{H} A	4.46 (ddt)	{ 2.10 (dt) ^y	3.86 (ddd)	4.30 (dq) ^{aa}	3.30 (d) ^{bb}	1.34 (d) ^t
			δ_{H} B	4.77 (dq)	{ 2.56 (ddd) ^z	4.33 (dt)	4.19 (dq) ^{aa}	3.35 (d) ^{bb}	1.23 (d) ^u
					{ 2.33 (dd) ^{cc}				
					{ 2.35 (dd) ^{dd}				

^a Ref. 1. ^b Data for mixture containing 40% of *cis* isomer. ^c Isomers separated from mixture containing 55% of A which had the shorter retention time. ^d Probably *cis* bromomethyl groups. ^e ²J 13.25, ³J 4.0 Hz. ^f ³J 8.0 Hz. ^g AB of ABX: δ_{AB} 20.9 Hz, J_{AB} 10.5, ³J 7.75, 6.0 Hz. ^h AB of ABX: δ_{AB} 9.6 Hz, J_{Ad} 12.5, ³J 7.7, 6.8 Hz. ⁱ ³J 6.0 Hz. ^j Isomers separated from mixture containing 55% of *cis* isomer which had the longer retention time. ^k J_{AB} 13 Hz. ^l J_{AB} 11 Hz. ^m Data for mixture containing 60% of *cis* isomer. ⁿ ³J 6.5 Hz. ^o Effectively contains 17% *cis*; see ref. 4. ^p Isomers separated from mixture containing 50% A, 20% B, 20% C, and 10% D; retention times: A < B < C < D. ^q ³J_{1,2} 4.0, ³J_{2,3} 7.0 Hz. ^r AB of ABX: δ_{AB} 14.2 Hz, J_{AB} 10.8, ³J 8.6, 5.5 Hz. ^s AB of ABX: δ_{AB} 9.7 Hz, J_{AB} 11, ³J 7.6, 5.4 Hz. ^t ³J_{1,2} 5.5, ³J_{2,3} 4.0 Hz. ^u AB of ABX: δ_{AB} 8.1 Hz, J_{AB} 10.5, ³J 7.15, 6.35 Hz. ^v Data for mixture containing 25% of *cis* isomer. ^w AB of ABX. ^x Isomers separated from mixture containing 50% of A which had the shorter retention time. ^y Axial H; ^z ³J 13, ³J 11.25 Hz. ^{aa} Equatorial H; ³J_{1,2} 2.0 Hz, ³J_{2,3} 5.0 Hz. ^{ab} ³J_{3,4} 9.5 Hz. ^{bb} ³J_{1,5} 5.5 Hz. ^{cc} Axial H; ³J_{1,2} 7.5, ³J_{2,3} 3.25 Hz. ^{dd} Equatorial H; ³J_{1,2} 5.5, ³J_{2,3} 3.25 Hz. ^{ee} ³J_{3,4} 1.75 Hz.

This result is consistent with thermodynamic control favouring 6-*endo* cyclisation (*cf.* the result with 2,5-dimethylhexa-2,4-diene) to afford the diastereoisomer (16) with all three substituents disposed equatorially [equation (5)].



In support of this the ^{13}C n.m.r. spectrum (in D_2O) of the crude peroxymercurial showed only six strong lines, with chemical shifts (δ 82.10, 81.98, 47.92, 39.97, 25.57, and 20.43) in keeping with structure (16). Conclusive evidence for the structure of the peroxymercurial was provided by brominolysis [equation (6)] under free-radical chain conditions,⁶ which afforded two diastereoisomeric peroxides (13A and B).^{*} These were separated

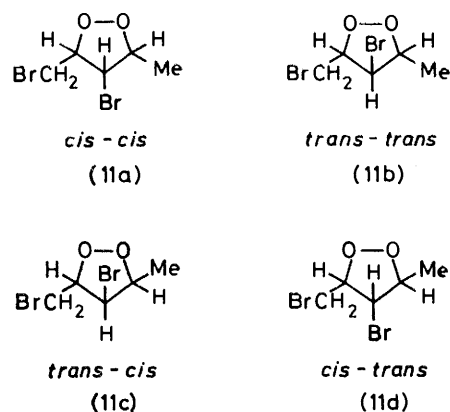


by h.p.l.c. and identified by ^1H n.m.r. spectroscopy as (13a) and (13b) respectively. The structures were diagnosed from vicinal ^1H - ^1H coupling constants obtained by first-order analysis of the 100 MHz spectra. Thus compound (13A) had large values for the coupling constants $J_{1,2}$ (9.5 Hz), $J_{2,3}$ (11.25 Hz), and $J_{3,5}$ (11.25 Hz) but small values for the coupling constants $J_{2,4}$ (5.0 Hz) and $J_{4,5}$ (2.0 Hz), while compound (13B) showed small values of $J_{1,2}$ (1.75 Hz), $J_{2,3}$ (3.25 Hz), $J_{2,4}$ (3.25 Hz), and $J_{4,5}$ (5.5 Hz), but a larger value for $J_{3,5}$ (7.5 Hz). These data also indicate that the fraction of molecules in the inverted chair conformations with axial methyl and bromomethyl substituents is small.

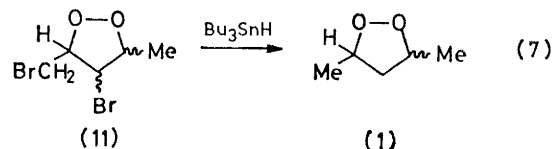
Penta-1,3-diene.—Some reactions were carried out using 100% *trans*-penta-1,3-diene but the same results were obtained using a mixture containing 74% of the *trans* isomer. Since it is known⁴ that in the presence of $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ there is rapid isomerisation of penta-1,3-

diene to a mixture containing 83% of the *trans* isomer, this is considered to be the effective reagent.

Peroxymercuriation of penta-1,3-diene appeared to proceed similarly to that of the non-conjugated dienes, but subsequent reduction gave only a very poor yield ($\leq 5\%$) of cyclic peroxide. However, brominolysis proved more successful. Crude products from several bromodemercuriations in dichloromethane were isolated, and analysed by ^{13}C n.m.r. spectroscopy. The spectra were essentially unchanged for brominolyses of organomercury bromide, chloride, and nitrate (*in situ*), and were insensitive to yield which ranged from 43 to 73%. All lines in the spectrum of the crude product were accounted for by the spectra of the four fractions (11A—D, in order of elution) isolated by h.p.l.c. Each fraction was peroxidic and had a mass spectrum consistent with the molecular formula $\text{C}_5\text{H}_8\text{Br}_2\text{O}_2$. The ^1H and ^{13}C n.m.r. spectra (Table 2) indicate that these fractions are the four diastereoisomers of 4-bromo-3-bromomethyl-5-



methyl-1,2-dioxacyclopentane (11a—d). This conclusion is supported by the fact that reduction [equation (7)] of the crude bromoperoxide with tributyltin hydride¹ afforded a *cis*-*trans* mixture of 3,5-dimethyl-1,2-dioxacyclopentane (1), albeit in low yield.

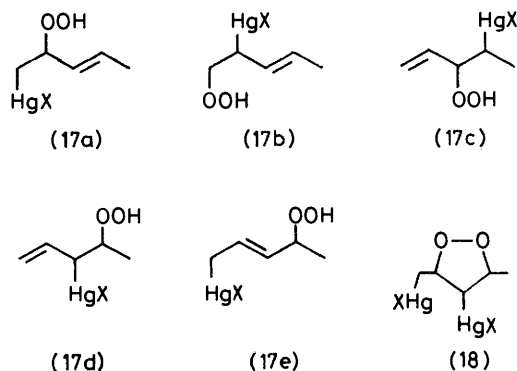


Several reaction pathways that lead to formation of compound (11) can be envisaged. To simplify the discussion only those reactions involving *trans*-penta-1,3-diene are considered. Of the five possible adducts (17a—e) that could arise in the initial hydroperoxymercuriation, two (17b and c) are unable to cyclise to the precursor (18) of compound (11). By analogy with the methoxymercuriation of penta-1,3-diene,⁴ both the product (17a) of Markovnikov 1,2-addition to the terminal double bond and the product (17e) of 1,4-

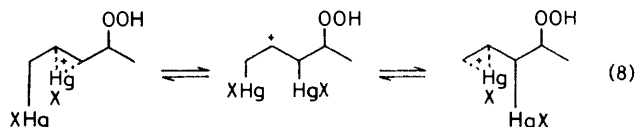
^{*} We use capital letters to identify stereoisomers on the basis of chromatography retention times (A is eluted before B, etc.), and small letters to identify molecular structures as defined in the text.

addition are expected to be formed, but little or no product (17d) of 1,2-addition to the medial double bond is anticipated.

Cyclisation of (17a) would have to proceed by a disfavoured ⁵ 5-*endo* mode and thus appears unlikely. At



first sight the conversion of (17e) into (18) also requires a 5-*endo* cyclisation, but it is possible to envisage a facile equilibration of the mercurinium ions derived from (17e) and (17d) [equation (8)], with cyclisation of the latter proceeding in the favoured 5-*exo* mode. A closely



related pathway involves the fully fledged rearrangement, catalysed by mercury(II) salt,⁷ of (17e) into (17d) prior to cycloperoxymercuration.

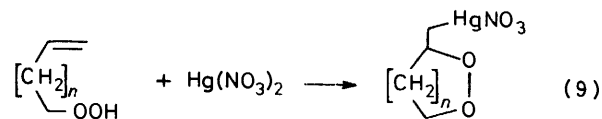
Since the prevailing conditions are conducive to the interconversion of the isomers of (17), the cyclisation can be completely channelled through a common intermediate, which in all probability is the mercurinium ion of (17d).

Although the diastereoisomers of (11) were separately isolated, we were unable to assign their configurations unambiguously. In any case, the formation of all four isomers is mechanistically uninformative since products (18) with both *cis* and *trans* arrangements of the methyl and mercuriomethyl groups are predicted for all mechanisms of cycloperoxymercuration, and scrambling of the stereochemistry at the C-4 position is expected⁶ in the bromodemercuration step.

Alkenyl Hydroperoxides.—Only secondary and tertiary cyclic peroxides can be prepared *via* the peroxymercuration of dienes because in each addition the mercury substituent is directed regiospecifically to any primary olefinic carbon atoms that are present. In an attempt to extend the method to the synthesis of rings with one primary carbon next to the peroxide bond, we began an investigation of the cycloperoxymercuration of but-3-enyl and pent-4-enyl hydroperoxides [equation (9); $n = 1$ or 2].

Owing to the very poor yields we obtained in the conventional preparation of the hydroperoxides from the

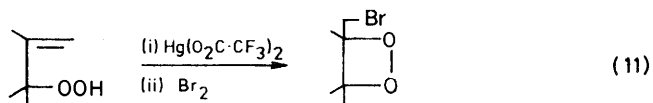
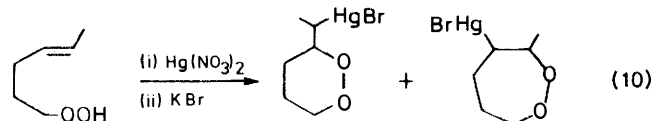
corresponding methanesulphonates, the reactions with mercury(II) nitrate could be run only on a small scale. Convincing evidence that the cyclisations take place was obtained, but analytically pure derivatives of the pro-



ducts were not isolated. Thus the crude organomercury nitrate from reaction with but-3-enyl hydroperoxide showed a clean four-line ¹³C n.m.r. spectrum with chemical shifts (δ 78.90, 70.53, 43.69, and 29.65) consistent with the proposed structure. Supporting evidence was provided by the ¹H n.m.r. spectrum of the corresponding organomercury bromide which showed multiplets at δ 4.15 (3 H) and 2.2 (4 H).

While our work was still in progress we became aware that Porter *et al.*^{8,9} had carried out a thorough study of the cycloperoxymercuration of four primary unsaturated hydroperoxides. In view of this and of our difficulties in preparing the starting hydroperoxides we did not pursue our studies further.

Porter⁹ reported the formation of a seven-membered peroxide ring [equation (10)] and Adam and Sakanishi¹⁰ have prepared a dioxetan [equation (11)] *via* cyclo-

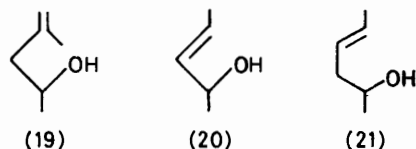


peroxymercuration. Although the yields were low these results show that cycloperoxymercuration is not limited to the synthesis of 1,2-dioxacyclo-pentanes and -hexanes. We carried out a preliminary investigation of the cycloperoxymercuration-reduction of $\alpha\omega$ -dienes with chains of more than six carbon atoms. No peroxide was detected in the product from hepta-1,6-diene, but ¹H n.m.r. and t.l.c. evidence suggested the presence of a cyclic peroxide, presumably an eight-membered ring, in the product from octa-1,7-diene. The yield was low and the compound was not isolated.

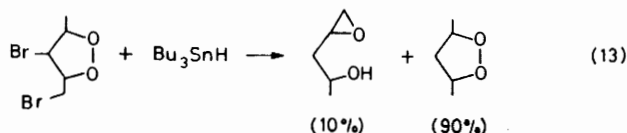
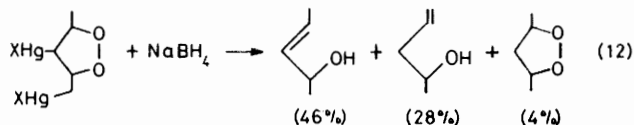
Thus our results and those of others have shown that cycloperoxymercuration is a versatile method for the synthesis of cyclic peroxides. Yields are excellent for 1,2-dioxacyclo-pentanes and -hexanes but other ring sizes can be obtained. Peroxides with secondary or tertiary carbon atoms adjacent to the O-O bond can be obtained from dienes and products with one such primary carbon atom are accessible from unsaturated hydroperoxides.

By-products of Reduction.—For some of the reductions we showed that, as with the cycloperoxymercuration

derived from penta-1,4-diene,¹ the main side product is *not* epoxy-alcohol as expected by analogy with the behaviour of acyclic systems,² but rather is unsaturated alcohol. Thus in the peroxymercuration-reduction of 3,3-dimethylpenta-1,4-diene, 2-methylpenta-1,4-diene, penta-1,3-diene, and hexa-1,4-diene, the by-products were isolated by g.l.c. and identified unambiguously from their ¹H n.m.r. spectra. In each of the last three of these reactions, the formation of *two* unsaturated alcohols can be envisaged, but the dominant by-product was always that isomer with the most substituted double bond, *i.e.* compounds (19), (20), and (21) respectively.



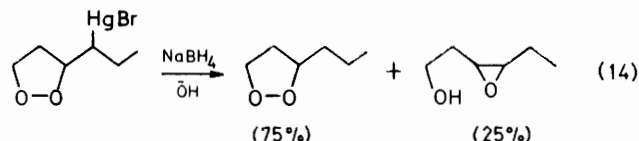
It appears that cycloperoxymercureals containing endocyclic mercurio-substituents (*i.e.* those from penta-1,3-diene and hexa-1,4-diene) have a very strong tendency to deoxymercuriate under reduction conditions, and yields of peroxides are drastically reduced. That the unsaturated alcohols are formed by polar deoxymercuriation rather than by β -scission of intermediate alkyl radicals is suggested by a comparison of the borohydride reduction [equation (12)] of the peroxymercureal derived from penta-1,3-diene with the tributyltin hydride reduction [equation (13)] of the corresponding bromo-



peroxide. This result is also synthetically significant in that it implies that poor peroxide yields may be overcome by replacing direct borohydride reduction with a sequence of bromodemercuration and tributyltin hydride reduction.

Two further points should be mentioned in connection with reactions (12) and (13). A small amount of 1,2-epoxypentan-4-ol was formed in the tributyltin hydride-bromoperoxide reaction but, significantly, no 2,3-epoxypentan-4-ol was detected. This is consistent with the idea¹¹ that an endocyclic radical is unable to undergo γ -scission of the O-O bond for reasons of unfavourable geometry. The second point is that under our g.l.c. conditions the retention times for pent-3-en-2-ol and 2,3-epoxypentan-4-ol were identical, and those for pent-1-en-4-ol and 1,2-epoxypentan-4-ol were very similar. Thus isolation and characterisation by n.m.r. spectroscopy are essential for correct identification of the by-products in these reductions.

Whereas we obtain unsaturated alcohols as the main by-products in the synthesis of 1,2-dioxacyclopentanes by peroxymercuration-reduction of dienes, Porter *et al.*⁹ found that epoxy-alcohols are the by-products when cycloperoxymercureals derived from alkenyl hydroperoxides are reduced [*e.g.* equation (14)]. We are



unable to explain why the two systems behave differently.

EXPERIMENTAL

3,3-Dimethylpenta-1,4-diene was prepared from a commercial sample of 3,3-dimethylglutaric acid by esterification,¹² reduction to the diol with lithium aluminium hydride,¹³ conversion into the dibromide with phosphorus tribromide,¹³ and dehydrobromination by treatment with sodium iodide and 2-methylquinoline.¹⁴ The product was purified by distillation, b.p. 69.0–70.8 °C at 754 mmHg (lit.,¹⁵ 69.5–70 °C), and had a ¹H n.m.r. spectrum in agreement with that previously reported;¹⁵ δ_C 146.88, 110.80, 39.86, and 26.60. 2,5-Dimethylhexa-1,5-diene and 2,5-dimethylhexa-2,4-diene were separated from a commercially available mixture by preparative g.l.c. using a silicone oil column (10 ft \times 3/8 in o.d.) with nitrogen carrier gas (10 lbf in⁻²) and an oven temperature of 60 °C; the non-conjugated diene had the shorter retention time. All other dienes were commercial samples which were used without further purification.

Alkenyl hydroperoxides were prepared from the corresponding alcohols according to Porter's procedure.¹⁶ But-3-enyl hydroperoxide showed δ 5.76 (m, 1 H), 5.2 (m, 2 H), 3.91 (t, ³J 7 Hz, 2 H), and 2.3 (m, 2 H); δ_C 134.82, 116.81, 76.01, and 32.53 p.p.m. Pent-4-enyl hydroperoxide had δ 5.75 (m, 1 H), 5.11 (m, 2 H), 4.01 (t, ³J 7 Hz, 2 H), and 1.96 (m, 4 H).

Mercury(II) nitrate demihydrate was a commercial sample which was protected from moisture by storing the closed bottle over silica gel in a desiccator. Hydrogen peroxide was a gift from Laporte Industries Limited, and was stored at 0 °C; required amounts ($\pm 5\%$) were measured out by glass pipette assuming the density to be 1.33 g cm⁻³. Reagent grade solvents were redistilled for h.p.l.c. work but otherwise were used without purification.

I.r. spectra were recorded with a Unicam SP 1000 or Perkin-Elmer 457 instrument (KBr optics) and mass spectra with an A.E.I. MS12 spectrometer (inlet temperature 40–60 °C). ¹H N.m.r. spectra were recorded with a Perkin-Elmer R12 or Varian HA 100 instrument, and ¹³C n.m.r. spectra by the pulse Fourier transform method with a Varian CFT 20 spectrometer.

The general procedures described below for peroxymercuration, reduction, and brominolysis were followed with only minor variations. Details of individual compounds are reported after the appropriate general recipe or are given in Tables 1–3.

Peroxymercuration.—To a vigorously stirred suspension of mercury(II) nitrate demihydrate (10 mmol) in dichloromethane (15 cm³) cooled in an ice-bath was added 80%

hydrogen peroxide (0.16 cm³, 5 mmol) followed *immediately* by a solution of diene (5 mmol) in dichloromethane (5 cm³). The mixture was stirred for 15–30 min and the supernatant liquid was then decanted to leave a viscous oil containing the crude organomercury nitrate. The reaction was often run using double these quantities, and was scaled up by a factor of four without difficulty.

Conversion into organomercury halide was carried out as follows. The viscous oil was dissolved in water (5 cm³; plus a few drops of 4*M*-HNO₃ if necessary), aqueous potassium chloride or bromide (10 mmol in 10 cm³) was added, and the mixture was shaken or stirred vigorously. The resulting precipitate was isolated by filtration or by decanting the supernatant solution, washed with water (4 × 5 cm³), and dried *in vacuo*.

Reduction.—An ice-cold solution of sodium borohydride (1.51 g) in 3*M*-sodium hydroxide (40 cm³) was added slowly

gave (4) (69%), 3,3-dimethylpent-1-en-4-ol (24%), and unidentified material (7%); 2,5-dimethylhexa-1,5-diene gave (6) (77%), unidentified material (19%), and unidentified material (4%); penta-1,3-diene [peroxymercuriation using mercury(II) trifluoroacetate] gave (1) (4%), pent-1-en-4-ol (28%), pent-3-en-2-ol (46%), and unidentified material (22%); hexa-1,4-diene gave *trans*-(5) (53%), hex-4-en-2-ol (45%), and unidentified material (2%).

The major by-products were identified from their ¹H n.m.r. spectra either by comparison with commercial samples or, for the following compounds, from the data reported here. 2-Methylpent-1-en-4-ol had δ 4.8 d (CH₂=), 3.84 m (CHOH), 2.08 (d, CH₂), 1.74 (br s, CH₃C=), 1.40 (s, OH), 1.14 (d, CH₃); 3,3-dimethylpent-1-en-4-ol had δ 5.85 (m, CH=), 5.12 (m, CH₂=), 3.50 (q, CHOH), 1.11 (d, CH₃), and 0.98 (s, CH₃); hex-4-en-2-ol had δ 5.43 (m, CH=CH), 3.62 (m, CHOH), 2.1 (m, CH₂), 1.79 (dd, CH₃C=), and 1.1 (d, CH₃).

TABLE 3

Analytical data for methyl and bromomethyl 1,2-dioxacycloalkanes

Compound	Found (%)			Calc. (%)			Mass spectrum ^a
	C	H	Br	C	H	Br	
(2)	61.8	10.25		62.05	10.35		116
(3)	64.8	10.7		64.6	10.75		130
<i>cis</i> -(4)	64.0	11.2		64.6	10.75		130
<i>trans</i> -(4)	65.0	10.75		64.6	10.75		<i>b</i>
(6)	66.8	11.5		66.65	11.1		144 ^c
(8A)	26.5	4.05		26.25	3.65	58.4	272, 274, 276 ^d
(8B)	26.0	3.75		26.25	3.65	58.4	<i>e</i>
<i>cis</i> -(9)	29.2	4.2	55.65	29.15	4.15	55.55	286, 288, 290 ^d
<i>trans</i> -(9)	29.05	4.15	55.8	29.15	4.15	55.55	<i>f</i>
(10)	29.0	4.05		29.15	4.15	55.55	286, 288, 290 ^d
(11) ^g	22.15	3.0		23.1	3.05	61.5	
(11A)	23.1	2.95	61.2	23.1	3.05	61.5	258 260, 262 ^d
(11B/C)				23.1	3.05	61.5	<i>h</i>
(11D)	24.4	3.3	59.8	23.1	3.05	61.5	<i>h</i>
(13A)	26.05	3.5		26.25	3.65	58.4	272, 274, 276 ^d
(13B)	26.5	3.8	58.4	26.25	3.65	58.4	<i>i</i>

^a *m/e* of observed molecular ion. ^b Identical with that of *cis*-(4). ^c Weak; strong peaks at *m/e* 129 (*M* - CH₃), 116 (*M* - C₂H₄), and 86 (*M* - CH₃COCH₃). ^d Intensity ratio 1 : 2 : 1. ^e Identical with that of (8A). ^f Identical with that of *cis*-(9). ^g Crude. ^h Identical with that of (11A). ⁱ Identical with that of (13A).

over 30 min to a well stirred suspension of the crude organomercury nitrate or halide (*ca.* 5 mmol) in dichloromethane (40 cm³) cooled in an ice-salt-bath. The mixture was allowed to warm to room temperature, the phases were separated, and the aqueous layer was extracted with more dichloromethane (10 cm³). The combined dichloromethane solution was dried (MgSO₄) and the solvent was removed under reduced pressure to afford the crude peroxide (64–77%).

(a) *Preparative g.l.c.* The cyclic peroxides were isolated by g.l.c. using a Varian Aerograph 712 instrument fitted with a silicone oil column (10 ft or 20 ft × 3/8 in o.d.) with nitrogen carrier gas (10 lbf in⁻²) and an oven temperature of 70–80 °C; major by-products were also collected.

In a typical run 0.18 g (14%) of *trans*-(4) and 0.27 g (21%) of *cis*-(4) were isolated from multiple injections (*ca.* 100 μl each) of the crude product (0.89 g; 68%) obtained from 3,3-dimethylpenta-1,4-diene (10 mmol).

(b) *Analytical g.l.c.* The composition of each crude peroxymercuriation-reduction product was determined by cutting out and weighing the peaks of a chromatogram obtained in an analytical run. Thus 2-methylpenta-1,4-diene gave (2) (66%), 2-methylpent-1-en-4-ol (26%), and unidentified material (8%); 2,4-dimethylpenta-1,4-diene gave (3) (78%), 2,4-dimethylpent-1-en-4-ol (16%), and unidentified material (6%); 3,3-dimethylpenta-1,4-diene

The i.r. spectrum of each compound showed a strong band in the OH-stretching region.

Brominolysis.—Bromine (10 mmol) in dichloromethane (5 cm³) was added slowly to a well-stirred suspension of the crude organomercury nitrate or halide (*ca.* 5 mmol) in dichloromethane (40 cm³). The mixture was stirred overnight, filtered, and the filtrate dried (MgSO₄) and evaporated under reduced pressure. The resultant residue was extracted with a mixture of pentane (95 cm³) and dichloromethane (5 cm³) and the solvent removed from the extract (at 12 then 0.1 mmHg) to afford the crude bromoperoxide (65–78%).

This material was chromatographed on silica gel 60 (Merck; 70–230 mesh) using dichloromethane (10–20%) and pentane as eluant. The fractions that oxidised acidic ferrous thiocyanate were combined and the solvent was removed *in vacuo*. Final purification and separation of the diastereoisomers was effected by h.p.l.c. For compound (11), a Water Associates LC 500 instrument fitted with a column (30 cm × 5.7 cm o.d.) of silica gel was used and the eluant was 250 cm³ min⁻¹ of dichloromethane (25%) and pentane; this afforded (11A), a mixture of (11B) and (11C), and (11D). To separate (11B) from (11C) and for compounds (8), (9), (10), and (13), a Water Associates LC 100 instrument fitted with columns (3 × 25 cm × 4.5 mm i.d.) of Partisil 10 was used. The eluants (2 cm³ min⁻¹ unless

otherwise indicated) were dichloromethane-pentane (3 : 20) for (11B/C), dichloromethane-light petroleum (b.p. 30—40 °C) (1 : 5) for (8) and (13), dichloromethane-light petroleum (b.p. 30—40 °C) (1 : 4) for (9), and 1 cm³ min⁻¹ of ethyl acetate-light petroleum (b.p. 30—40 °C) (1 : 9) for (10); the diastereoisomers of (10) were not separated.

The preparation of (13) from hexa-1,4-diene (10 mmol) provides a representative example of the actual amounts of pure peroxide isolated. Column chromatography of the crude product (2.05 g, 75%) afforded 1.80 g (66%) of peroxidic material. Part of this (0.5 g) was purified by h.p.l.c.; multiple runs of ca. 20 mg load yielded 0.225 g of (13a) and 0.180 g of (13b).

Reduction of 4-Bromo-3-bromomethyl-5-methyl-1,2-dioxacyclopentane.—Crude (11) (5 mmol) was carefully added to a well stirred mixture of tributyltin hydride (15 mmol) and di-*t*-butyl hyponitrite¹⁷ (0.03 mmol) in benzene (25 cm³). After 1 h the product (contaminated with a little benzene) was isolated by trap-to-trap distillation at 0.1 mmHg. An analytically pure sample of (1) was isolated by preparative g.l.c. under conditions described above for other methyl-substituted 1,2-dioxacycloalkanes.

For comparison with by-products of peroxymercuration-reduction of penta-1,3-diene, 1,2-epoxypentan-4-ol and *trans*-2,3-epoxypentan-4-ol were prepared from the corresponding unsaturated alcohols by epoxidation with cumene hydroperoxide and V₂O₅, following List and Kuhnen's recipe.¹⁸ Pure samples were obtained by fractional distillation followed by preparative g.l.c. (silicone oil). 1,2-Epoxypentan-4-ol had δ 1.20 (d, ³J 6 Hz, CH₃), 1.62 (t, ³J 6 Hz, CH₂), 2.3—3.2 (m, -CH-CH₂O), 3.45 (s, OH), and 4.0 (sextet, CHOH); *trans*-2,3-epoxypentan-4-ol had δ 1.23 (d, ³J 6.5 Hz, CH₃), 1.25 (d, ³J 6.5 Hz, CH₃), 1.31 (d, ³J 5 Hz, CH₃), 2.50 (s, OH), 2.72 (m, 2-H), 3.02 (m, 3-H), 3.62 (dq, ³J 6.5 and 5.5 Hz, CHOH), and 3.90 (dq, ³J 6.5 and 3.5 Hz, CHOH).

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