Preparation and base-catalyzed reactions of some β-halohydroperoxides

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The reaction between olefins, *N*-chloroacetamide or 1,3-dibromo-5,5-dimethylhydantoin, and hydrogen peroxide affords β-halohydroperoxides in good yields. These compounds react extremely rapidly in basic solution to give products which depend upon their structure. The 3-halo-2,3-dimethyl-2-butyl hydroperoxides form 2,3-dimethyl-3-hydroperoxy-1-butene and from the 2-halo-1,2-dimethylcyclohexyl hydroperoxides 1-methyl-2-methylene-cyclohexyl hydroperoxide is obtained. No allylic hydroperoxide can be detected from the reaction between base and 3-bromo-2-methyl-2-butyl hydroperoxide. Mainly cleavage products, acetone and acetaldehyde, are formed together with some 2,3-epoxy-2-methylbutane. The reaction between base and 2-bromo-1-phenylethyl hydroperoxide gives styrene oxide, benzoic acid, and some benzaldehyde. From *trans*-2-bromocyclohexyl hydroperoxide, *trans*-2-bromocyclohexanol, cyclohexene oxide, and some *trans*-1,2-cyclohexanediol are obtained upon reaction with base. No evidence for the formation of the allylic hydroperoxide was obtained.

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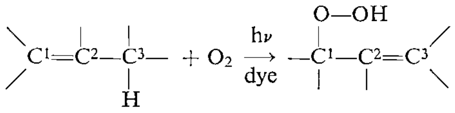
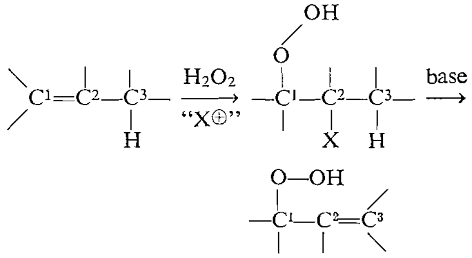
Introduction

The dye-photosensitized oxidation of olefins affords a unique route to allylic hydroperoxides of definite structure (1, 2). The hydroperoxy group is always introduced at one of the originally olefinic carbon atoms and a shift of the double bond always occurs, eq. [1], so that the reaction is very useful from a synthetic point of view.

[1] 

$$\mathrm{{>}C^1{=}C^2{-}\underset{H}{C^3}{-}} + O_2 \xrightarrow[\text{dye}]{h\nu} \mathrm{{-}\overset{O{-}OH}{C^1}{-}C^2{=}C^3{<}}$$

While the reaction proceeds well with tetrasubstituted olefins and somewhat less so with trisubstituted olefins, disubstituted and monosubstituted olefins are oxidized very slowly (3). The latter require very long irradiation times for significant yields of products so that other reactions of the olefins and further reactions of the product become important. This led to a consideration of other routes which would be as specific and more generally useful for the conversion of olefins to allylic hydroperoxides. It appeared that a reaction between base and β-halohydroperoxides could yield allylic hydroperoxides. Thus, conversion of an olefin to the β-halohydroperoxide and then the elimination of the elements of halogen acid would constitute a simple, two step, chemical transformation of the olefin to an allylic hydroperoxide. This transformation could introduce the hydroperoxy group and relocate the double bond of an olefin into the same positions as is observed in the photosensitized oxidation, eq. [2].

[2] 

$$\mathrm{{>}C^1{=}C^2{-}\underset{H}{C^3}{-}} \xrightarrow[\text{“X}^{\oplus}\text{”}]{H_2O_2} \mathrm{{-}\overset{O{-}OH}{C^1}{-}\underset{X}{C^2}{-}\underset{H}{C^3}{-}} \xrightarrow{\text{base}} \mathrm{{-}\overset{O{-}OH}{C^1}{-}C^2{=}C^3{<}}$$

This paper reports some of the results obtained in the study of this approach. After work had begun there appeared several reports on the reactions of β-halo- and β-cyanohydroperoxides with base (4–6). It is reported that 1-chloro-2-methyl-2-propyl hydroperoxide is rapidly decomposed by base to acetone and formaldehyde (4), while other workers report that upon treatment with base the bromo analogue, 1-bromo-2-methyl-2-propyl hydroperoxide is converted partly to isobutylene oxide as well as to acetone and formaldehyde (5). A similar cleavage reaction was observed when 2-methyl-2-hydroperoxypropionitrile was treated with base (6). Acetone and cyanate ion are produced. The above β-halohydroperoxides have halogen on the terminal carbon atom and a simple elimination route is not available to these materials.

Results and Discussion

Preparation of β-Halohydroperoxides

β-Halohydroperoxides have been prepared by

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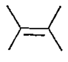
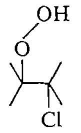
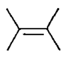
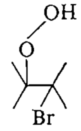
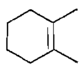
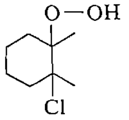
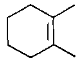
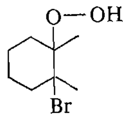
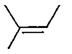
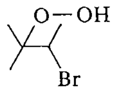
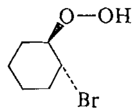
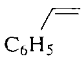
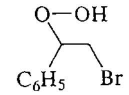
autoxidation of halogenated hydrocarbons (7, 8), by the acid-catalyzed addition of hydrogen peroxide to allylic halides (4), by the reaction between olefins, hydrogen peroxide, and *t*-butyl hypochlorite (9), and by the addition of bromine or chlorine to olefins in the presence of hydrogen peroxide (5, 10). In the present study it has been found that β-halohydroperoxides can be prepared conveniently and in good yield by the reaction between olefins, *N*-haloamides, and excess 98% hydrogen peroxide in ether solution. The reaction appears to be general and gives essentially no dihalogenated adducts, which are major by-products in Rieche's method (5, 10).

β-Chlorohydroperoxides were prepared by the reaction between equivalent amounts of *N*-chloroacetamide and olefin and a 10-fold excess of 98% hydrogen peroxide in ether solution. The reaction was very slow at room temperature; however, a very vigorous, exothermic reaction occurred when a trace of *p*-toluenesulfonic acid was added to the reaction mixture at 0°. The β-bromohydroperoxides were prepared by the reaction between equivalent amounts of 1,3-dibromo-5,5-dimethylhydantoin and olefin and a 5-fold excess of hydrogen peroxide in ether. This reaction proceeded very rapidly at 0°, but some coloring occurred and some dibromide was produced. Dibromide formation could be entirely eliminated by adding the brominating agent to a solution of olefin and hydrogen peroxide in ether at −40°. Excess hydrogen peroxide and amide were removed by washing the reaction mixtures with water.

The β-halohydroperoxides prepared are listed in Table I. The 3-halo-2,3-dimethyl-2-butyl hydroperoxides, **1***a* and **1***b* (10), could be isolated as crystalline solids. This was done by concentration of the ether solution and crystallization from pentane. Several attempts at isolation of 2-chloro-1,2-dimethylcyclohexyl hydroperoxide, **2***a*, resulted in explosions, so that neither **2***a* nor 2-bromo-1,2-dimethylcyclohexyl hydroperoxide, **2***b*, were isolated or characterized. The remaining compounds, 3-bromo-2-methyl-2-butyl hydroperoxide (**3**), *trans*-2-bromocyclohexyl hydroperoxide (**4**), and 2-bromo-1-phenylethyl hydroperoxide (**5**), were isolated as liquids which gave clean nuclear magnetic resonance (n.m.r.) spectra and had 80–90% of the theoretical active oxygen content. These materials were isolated by removing the ether under 0.5 mm pressure at

TABLE I

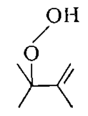
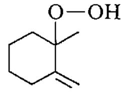
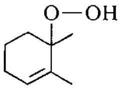
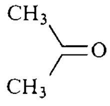
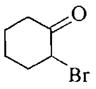
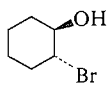
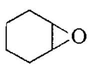
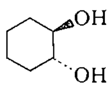
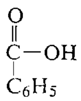
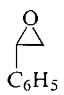
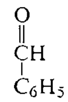
Yield of β-halohydroperoxides from olefins

Olefin	Halogen source*	β-Halo-hydroperoxide	% yield†
	A	 **1***a*	60‡
	B	 **1***b*	76§
	A	 **2***a*	57‖
	B	 **2***b*	86
	B	 **3**	80
	B	 **4**	73
	B	 **5**	55

*A, *N*-chloroacetamide; B, 1,3-dibromo-5,5-dimethylhydantoin.
†Yields based on starting olefin and determined by iodometric titration unless otherwise indicated.
‡Also isolated as a solid in 30% yield.
§Isolated yield of crystalline product.
‖By difference from unreacted starting material as determined by gas chromatography.

TABLE II

Products from reaction between β-halohydroperoxides and base

β-Halohydroperoxide	Total % yield	Product composition	% yield*
1*a*	70	 **6**	70†
1*b*	77	**6**	77†
2*a*	33	 **7**‡ +  **8**	33†, 1
2*b*	66	**7**‡ **8**	66(42†), 2
3	87	 $(CH_3)_2C{=}O$ + CH_3CHO + 	76, 77 10
4	58	 +   + 	trace, 27 29, 2
5	94	 C_6H_5COOH +  +  C_6H_5CHO	45†, 45, 4

*As determined by gas chromatographic analysis unless otherwise indicated.
†Yield of isolated product.
‡Characterized as the alcohol 9 after reduction.

30°. β-Bromohydroperoxides are formed in higher yields than β-chlorohydroperoxides.

All of the β-halohydroperoxides isolated were characterized by iodometric titration and by their nuclear magnetic resonance spectra. All showed broad singlet absorption of relative peak area ca. 1 in the range τ 1 to 2 in the n.m.r. spectrum. This is the characteristic region for the absorption of the hydroperoxy proton (11). Other features of the n.m.r. spectra of these compounds are straightforward and will not be discussed. In addition **1***a*, **4**, and **5** were further characterized by reduction to the corresponding halohydrins which proved in each case to be identical with authentic material.

Reaction of β-Halohydroperoxides with Base

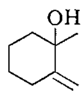
It was found that all the β-halohydroperoxides reacted extremely rapidly with base. The products formed are listed in Table II. The reactions were carried out by mixing the β-halohydroperoxide in methanol or ether solution with a methanolic solution of base at temperatures ranging from 0° to 30°. After about 1 to 2 h the reaction mixtures were poured into water and extracted with ether, except in the reaction of **2***a*. In this reaction sodium borohydride was added to the reaction mixture prior to workup to reduce the allylic hydroperoxide. The yields of products obtained from **1***a*, **1***b*, **2***a*, and **2***b* are yields of products actually isolated by distillation. The yields of products from the other reactions were determined by gas–liquid chromatography (g.l.c.) using internal standards.

The product from **1***a* and **1***b* was identical in every respect with authentic 2,3-dimethyl-2-hydroperoxy-1-butene (**6**), prepared by photosensitized oxidation of 2,3-dimethyl-2-butene (12).

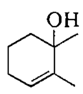
The allylic hydroperoxides, 2-methylene-1-methylcyclohexyl hydroperoxide (**7**) and 1,2-dimethyl-2-cylohexenyl hydroperoxide (**8**) were reduced to the corresponding alcohols, 2-methylene-1-methylcyclohexanol (**9**) and 1,2-dimethyl-2-cyclohexen-1-ol (**10**), and characterized as such. Essentially the same ca. 97–3 mixture of alcohols was produced in 80% yield by the photosensitized oxidation of 1,2-dimethylcyclohexene followed by reduction of the hydroperoxides formed. The product (**9**), always the major one, was identified by its n.m.r. spectrum and by comparison with authentic material (13) which was prepared by the Grignard reaction between methyl magnesium iodide and 2-methylenecyclohexanone. The n.m.r. spectrum showed two one proton absorptions at τ 5.15 and 5.39 characteristic of a terminal olefin.

Compound **10** was present in such a small amount in every case that it appeared not to affect the spectral properties of **9** and was only detectable by gas chromatography. It was identified in the reaction mixtures only by comparison of its gas chromatographic retention time with that of an authentic sample of **10** (14) prepared by reaction of methyllithium with 2-methyl-2-cyclohexenone. It is estimated that only ca. 3% to 5% of **10** was present in any of the product mixtures from **2***a* or **2***b* or from the photooxidation–reduction sequence.

Thus, the addition–elimination sequence outlined in eq. [2] can, in fact, be used to transform 2,3-dimethyl-2-butene and 1,2-dimethylcyclohexene to the corresponding allylic hydroperoxides in good yield. The products are the same as those obtained from the photosensitized reaction, and in the case of 1,2-dimethylcyclohexene even the selectivities of the two processes are similar. The photosensitized reaction of 1,2-dimethylcyclohexene is rather selective when compared with other examples in which more than one product is possible (1, 2).

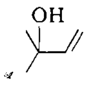


9

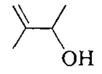


10

However, the situation in the case of 2-methyl-2-butene and cyclohexene is quite different. Although a rapid reaction took place, no evidence was found for the formation of any allylic hydroperoxide from the base-catalyzed reactions of **3** and **4**. Portions of the reaction mixture were reduced with sodium borohydride and analyzed by gas chromatography for the products of reduction of the allylic hydroperoxides, 3-methyl-1-butene-3-ol (**11**) and 2-methyl-1-butene-3-ol (**12**) in the case of the reaction mixture from **3**, and cyclohexene-3-ol (**13**) in the case of the reaction mixture from **4**. In neither case was any of the allylic alcohol detectable. Less than 0.5% of any of these compounds could have been detected.



11



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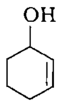

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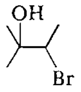
14



15

Instead, the products from **3**, found in the unreduced reaction mixture, consisted mainly of acetone and acetaldehyde, together with 2,3-epoxy-2-methylbutane (**14**). Thus, cleavage of the 2,3-carbon – carbon bond was the predominant reaction. This is the same type of reaction previously reported for the 1-bromo- and 1-chloro-2-methyl-2-propyl hydroperoxides (4, 5). It has been suggested (4, 5) that the cleavage proceeds via a four-atom cyclic peroxide. The oxide (**14**), must have resulted from ring closure of the intermediate bromohydrin, **15**. The bromohydrin could have resulted from a base-catalyzed reduction of the bromohydroperoxide, a reaction which is known to occur with tertiary hydroperoxides (15). Another, more likely, mode of formation of **15** is discussed below.

The predominant reaction of *trans*-2-bromocyclohexyl hydroperoxide (**4**) in the presence of base appears to be reduction to the bromohydrin which, in turn, is partly converted to cyclohexene oxide. A small amount of the latter is further converted to *trans*-1,2-cyclohexanediol. A search was made for adipaldehyde which might result from ring cleavage, and possible products derived from it, but no such material could be identified. Also, a search was made for 2-bromocyclohexanone, which would be expected to be formed by base-catalyzed elimination of hydroxide ion from the secondary hydroperoxide, **4**, (16). Again, although traces of a strongly lachrymatory substance were produced, no further evidence of it or products derived from it was obtained. The material balance in this reaction is not satisfactory, however, and some of the latter reactions may have occurred (see below).

Both reduction and carbon–carbon bond cleavage reactions were observed in the reaction between 2-bromo-1-phenylethyl hydroperoxide, (**5**), and base. An elimination pathway is not available to **5**. Products identified were styrene oxide, 2-bromo-1-phenylethanol, and benzoic acid. The latter may have resulted from a Cannizzaro reaction between formaldehyde and benzaldehyde which would be the primary products of carbon–carbon bond cleavage.

However, the benzoic acid may also be formed from oxidation of benzaldehyde by unreacted bromohydroperoxide, **5**. The other product of this reaction would be the bromohydrin, 2-bromo-1-phenylethanol, which, in turn, could be converted to styrene oxide under the reaction conditions. Such a sequence also seems to be a more plausible route to the oxides formed in the base-catalyzed reactions of **3** and **4** rather than the base-catalyzed reduction (15) of the hydroperoxy group mentioned in discussing the products formed from **3**. Such reactions, in the case of tertiary hydroperoxides without other functional groups (15), seem to require much higher temperatures than those used here, and it is not obvious that halogen substitution should speed the reaction.

The reactions between β-halohydroperoxides and base may take a variety of paths and the products of these reactions depend upon structure. Although it is probably too early to generalize, it appears that β-halohydroperoxides formed from tetrasubstituted olefins give almost exclusively elimination products, allylic hydroperoxides, when treated with base. Only trace amounts of cleavage product, acetone, were detected from reaction of the tetrasubstituted β-halohydroperoxides, **1***a* and **1***b*. Nor could the yield of any cleavage products from **2***b* have been significant, since a 66% yield (by analysis) of elimination product was formed. Also, β-halohydroperoxides of tetrasubstituted olefins suffer little, if any, reduction with base. No evidence for the formation of any halohydrin or epoxide from **1***a*, **1***b*, **2***a*, or **2***b* was found.

In contrast, neither **3** or **4**, which have, in principle, elimination pathways available to them, gave any trace of elimination product with base. The difference in behavior toward base between **1***a* or **1***b* and **3** is striking since the only difference between these materials is a methyl group.

The addition–elimination sequence outlined in eq. [2] is thus seen to lead to the desired allylic hydroperoxide only with tetrasubstituted olefins where it works very well.

The conversion of a trisubstituted or a *gem*-disubstituted olefin to the β-halohydroperoxide followed by the reaction of the latter with base may be a useful process for the cleavage of olefinic bonds.

Experimental

Melting points and boiling points are uncorrected. Infrared spectra were recorded on Perkin–Elmer model 421 and model 337 spectrophotometers. Nuclear magnetic resonance (n.m.r.) spectra were determined with a Varian A-60 analytical spectrometer with tetramethylsilane as internal standard. Gas–liquid chromatography (g.l.c.) was carried out on Aerograph 202 and A-90-P3 gas chromatographs. Quantitative g.l.c. analyses were made with calibrated internal standards. Microanalyses were determined by Mrs. D. Mahlow of these laboratories. Solutions were dried using anhydrous magnesium sulfate.

All preparations of β-haloperoxides were carried out behind shields. Apparatus containing these compounds was manipulated with the aid of tongs and hands were protected with heavy canvas gloves.

N-Chloroacetamide was prepared according to the method of Orton (17), m.p. 111°. Reported (18) m.p. 110°. Iodometric analysis showed 38.18% Cl; required 37.97% Cl.

The 1,3-dibromo-5,5-dimethylhydantoin used was obtained from Matheson, Coleman, and Bell and contained 98% of the theoretical amount of active bromine by iodometric analysis.

3-Chloro-2,3-dimethyl-2-butyl Hydroperoxide, 1a

The 2,3-dimethyl-2-butene was prepared from 2,3-dimethyl-2-butanol by dehydration over 85% phosphoric acid. The crude product was fractionally distilled through a Nestor–Faust annular teflon spinning band distillation column. The product had b.p. 70–71° (700 mm), n_D^{25}

1.4075. Reported (19) b.p. 73°, n_{D}^{25} 1.4094. Analysis by g.c. using a 5 ft × 1/4 in. FFAP column indicated that the material was > 99% pure.

To a solution of 9.0 g (107 mmole) of 2,3-dimethyl-2-butene, 9.45 g (101 mmole) *N*-chloroacetamide and 50 ml ether in a three-necked flask, fitted with a thermometer and reflux condenser and cooled in an ice bath, was added 15 g (400 mmole) of 98% hydrogen peroxide (FMC Corp.) at a rate to keep the temperature from rising above 10°. After the resulting solution had cooled to 0° ca. 1 g of *p*-toluenesulfonic acid was added. The temperature rose rapidly and the solution began to boil. It was stirred in the ice bath for 1 h. (Usually, the solution ceased boiling after a few minutes. However, in some reactions the reaction was so exothermic that all the ether was driven out and temperatures of up to 150° were observed in the reaction flask.) The reaction mixture was then washed with several portions of water and with 10% sodium bicarbonate solution. In separate exeriments it was determined that four washings with water were sufficient to remove all the hydrogen peroxide and 5,5-dimethylhydantoin or acetamide from ether.

Twenty per cent of the dried ethereal solution was concentrated on a bath at 40° and the residue taken up in 15 ml pentane. The pentane solution was cooled to −65°. The precipitate, which formed over several hours, was filtered in a low-temperature filtration apparatus. This material, (1.0 g, 30%), m.p. 72–73° (decomposition), appeared to be hygroscopic. The n.m.r. spectrum (CCl_4) showed absorption at τ 1.9–2.1 (broad singlet) for the hydroperoxy proton and at τ 8.38 (singlet) and 8.60 (singlet) for the protons of the two *gem*-dimethyl groups with relative peak areas 0.9:6.4:6.0, required 1:6:6. A satisfactory elemental analysis could not be obtained on this material, but it had 99% of the theoretical active oxygen content as determined by iodometric titration. The *p*-nitrobenzoate ester was prepared, m.p. 104.5–105°. The n.m.r. spectrum (benzene) showed absorption at τ 2.40 (singlet) for the aromatic protons and at τ 8.43 (singlet) and 8.68 (singlet) for the protons of the two *gem*-dimethyl groups with relative peak areas 4.28:6.0:5.65, required, 4:6:6.

Anal. Calcd. for $C_{13}H_{16}NO_5Cl$: C, 51.75; H, 5.35. Found: C, 51.25; H, 5.56.

Ten per cent of the ether solution of **1***a* was added to a stirred slurry of 0.3 g of lithium aluminium hydride in 20 ml ether at 0°. The mixture was hydrolyzed after 10 min with 15% potassium hydroxide. Gas–liquid chromatographic analysis using a 5 ft × 1/4 in. column of 10% DEGS on Chromosorb W at 70° showed the presence of only one product in addition to some 2,3-dimethyl-2-butene. The product, 3-chloro-2,3-dimethyl-2-butanol, was collected from the effluent stream of the g.l.c. and had n.m.r. and infrared spectra identical with those of an authentic (20) sample.

2,3-Dimethyl-3-hydroperoxy-1-butene (6) from 1a

Sixty per cent of the solution of **1***a* prepared above was added to a solution of 4.0 g sodium hydroxide in 100 ml methanol at 0° and the resulting mixture was stirred for 1 h. The reaction mixture was then poured into ice-water. This mixture was extracted twice with ether. The combined ether layers were washed several times with water and dried. After careful distillation of the ether through a 4 ft Podbielniak column the residual oil was distilled to yield 3.6 g (48%) of **6**, b.p. 56–57° (16 mm), n_{D}^{25} 1.4390. Reported (12) b.p. 55° (12 mm), n_{D}^{20} 1.4428. The n.m.r. spectrum (CCl_4) showed absorption at τ 1.6–1.8 (broad singlet) for the hydroperoxy proton, τ 5.1–5.2 (multiplet) for the vinyl protons, τ 8.22 (multiplet) for the protons of the allylic methyl group, and τ 8.70 (singlet) for the protons of the *gem*-dimethyl groups with relative peak areas 1.05:1.88:3.0:5.8, required, 1:2:3:6. This material was identical (n.m.r. and infrared spectra) with a sample of **6** prepared by the photosensitized oxidation (12) of 2,3-dimethyl-2-butene.

Another solution of **1***a* prepared as described above from 5.0 g of 2,3-dimethyl-2-butene was shown by iodometric titration to contain a 60% yield of chlorohydroperoxide, **1***a*. Four-fifths of this solution was reacted with methanolic base and the product isolated as described above. There was obtained 2.3 g (42% overall, 70% based on **1***a* formed) of **6**, n_{D}^{25} 1.4385, identical (n.m.r. and infrared spectra) with authentic **6**.

Gas–liquid chromatographic analysis of the reaction mixtures containing **6** before distillation indicated only traces of material with the retention-time of acetone. No evidence for the formation of any chlorohydrin or oxide was obtained.

3-Bromo-2,3-dimethyl-2-butyl Hydroperoxide, 1b

To a solution of 4.8 g (57 mmole) of 2,3-dimethyl-2-butene and 9.0 g (260 mmole) of 98% hydrogen peroxide in 50 ml ether stirred at −40° was added 8.1 g (57 mmole) of 1,3-dibromo-5,5-dimethylhydantoin in small portions over a 10 min period. The reaction mixture, protected with a calcium chloride tube, was allowed to warm to room temperature, washed with 25 ml cold, saturated sodium bicarbonate solution and several times with water. Ether was distilled from the dried organic layer through a 2 ft Podbielniak column using a 40° water bath. The residual oil crystallized when the remainder of the ether was removed under vacuum. Two recrystallizations from pentane gave 8.5 g (76%) of constant melting product, m.p. 93–94°. Reported (5) m.p. 93°. Two iodometric titrations indicated 96.77% and 96.75% of the theoretical amount of active oxygen. The n.m.r. (CCl_4) spectrum showed absorption at τ 1.8–2.3 (broad singlet) for the hydroperoxy proton and at τ 8.19 (singlet) and 8.55 (singlet) for the protons of the two *gem*-dimethyl groups with relative peak areas of 0.7:6.0:6.1, required 1:6:6.

The reaction as carried out above gave colorless solutions. No dibromide and no gas evolution could be detected. Addition of the brominating agent at 0° resulted in a vigorous reaction with the evolution of gas and the generation of a bromine color. Considerable amounts of dibromide were also produced.

2,3-Dimethyl-3-hydroperoxy-1-butene from 1b

Four grams of **1***b* gave 1.8 g (77%) of the allylic hydroperoxide **6**, n_{D}^{25} 1.4385, when treated with base in the manner described for **1***a*. The product was identical (n.m.r. and infrared spectra) with authentic **6**.

1-Methyl-2-methylenecyclohexanol, 9

(a) From 2-Bromo-1,2-dimethylcyclohexyl Hydroperoxide, 2b

The method due to Hammond (21) was used to prepare 1,2-dimethylcyclohexene. The product was fractionally distilled through the annular teflon spinning band distillation column and had b.p. 133° (700 mm), n_{D}^{24} 1.4573.

Reported (21) b.p. 136.2° (745 mm), n_D^{25} 1.4587. Gas chromatographic analysis using a 5 ft × 1/4 in. column of dinonylphthalate on Chromosorb P at 110° showed that less than 1% of the isomeric olefins were present in the fraction collected.

A solution of **2***b* in ether was prepared from 2.0 g (18.2 mmole) 1,2-dimethylcyclohexene, 2 ml (82 mmole) of 98% hydrogen peroxide and 2.6 g (9.1 mmole) of 1,3-dibromo-5,5-dimethylhydantoin in 20 ml ether using the procedure described above for the preparation of **1***b*. Iodometric titration of an aliquot of the solution showed that 86% of hydroperoxide had formed. The solution was added to a solution of 2 g sodium hydroxide in 100 ml methanol at 0°. After stirring for 90 min at 0° the reaction mixture was poured into 200 ml ice-water. The resulting mixture was extracted twice with 100 ml ether and the combined organic layers were washed three times with 100 ml water. The dried solution was added slowly to a stirred slurry of 1.5 g lithium aluminium hydride in 35 ml ether. This mixture was heated under reflux for 1 h and then a solution of 15% potassium hydroxide was added dropwise until the organic layer became clear. The organic layer was decanted and the precipitate slurried several times with ether and the combined organic solutions were dried. An aliquot of the solution was analyzed by g.l.c. on a 5 ft × 1/4 in. column of 10% FFAP on Chromosorb W at 120°. There were present 12% 1,2-dimethylcyclohexene and 66% of product, **9**, based on the hydroperoxide yield. Also present was ca. 2% of a material with the same g.c. retention time as the isomeric alcohol, 1,2-dimethyl-2-cyclohexenol (**10**).

Ether was distilled from the solution and the residual oil was distilled to give 0.85 g (42% based on the hydroperoxide content of the starting solution) of **9**, b.p. 58–61° (15 mm), n_D^{25} 1.4799. Reported (13) b.p. 58° (10 mm). The n.m.r. spectrum (CCl_4) showed absorption at τ 5.15 (multiplet) and 5.39 (multiplet) for the olefinic protons, τ 7.6 to 8.6 (broad) for the ring and hydroxyl protons and τ 8.72 (singlet) for the protons of the methyl group with relative peak areas of 1.0:0.92:9.2:2.84, required: 1:1:9:3. The infrared spectrum (neat) showed hydroxyl absorption at 3660 (sharp) and 3550 to 3200 (broad) cm^{-1} and absorption characteristic of a terminal olefin at 1640 (strong) and 990 (strong) cm^{-1}. There was no absorption at τ 4.68 in the n.m.r. spectrum where the olefinic proton of the isomeric alcohol **10** absorbs.

This product was identical (g.l.c. retention time, n.m.r. and infrared spectra) with authentic **9** (13) prepared by the addition of methylmagnesium iodide to 2-methylenecyclohexanone as described below.

(*b*) *From 2-Chloro-1,2-dimethylcyclohexyl Hydroperoxide,* 2*a*

The procedure described for the preparation of **1***a* was used to prepare a solution of **2***a* from 9.6 g (86 mmole) of 1,2-dimethylcyclohexene, 11 g (500 mmole) of 98% hydrogen peroxide, and 8.4 g (86 mmole) of *N*-chloroacetamide. An aliquot of the dried solution, after removal of hydrogen peroxide and acetamide, was analyzed by g.c. on the FFAP column using chlorobenzene as an internal standard. It was found that 43% of the original 1,2-dimethylcyclohexene had not reacted. The solution containing **2***a* was then added to 4 g sodium hydroxide in 100 ml methanol at 0° and the resulting mixture was stirred at 0° for 1 h. To this mixture was added 0.25 g sodium borohydride dissolved in a little methanol. After 1 h at room temperature the reaction mixture was poured into ice-water. The resulting mixture was extracted twice with ether. The combined ether extracts were washed several times with water and dried. The ether was distilled and the residual oil adsorbed on a 2.5 × 30 cm column of basic alumina. The column was washed with 200 ml pentane to remove the unreacted 1,2-dimethylcyclohexene and then the product was eluted with 200 ml ether. The ether was removed and the residual oil distilled to give 1.1 g (19% based on reacted olefin) of **9**, n_D^{25} 1.4813. This material was identical (n.m.r. and infrared spectra) with authentic **9**. The n.m.r. spectrum showed no absorption at τ 4.68 where the olefinic proton of the isomeric alcohol **10** absorbs. Gas-chromatographic analysis indicated the presence of *ca.* 1% of a material with the same retention time as the isomeric alcohol **10**. Several attempts to isolate **2***a* resulted in explosions.

(*c*) *From Sensitized Oxidation of 1,2-Dimethylcyclohexene*

The photolysis cell consisted of a 2.5 cm × 25 cm water-jacketed test tube fitted with a ground glass stopper containing an outlet tube and an inlet tube with a fritted disk which reached to the bottom of the test tube. The inlet tube was connected to the exhaust port of a Dynaport air pump. The outlet tube was connected to a T-tube which was, in turn, connected to an oxygen buret and to the inlet port of the air pump.

A solution of 3.0 g 1,2-dimethylcyclohexene and 30 mg of methylene blue in 30 ml methanol was placed in the photolysis cell. The pump was turned on and after pressure equilibrium was reached the cell was illuminated with two 100 W frosted light bulbs placed against the cell on either side. Aluminium foil was placed around the apparatus. Oxygen uptake became very slow after 70 min when 610 ml (STP) had been consumed (theoretical 570 ml). This solution was poured into 100 ml ice-water and the resulting mixture extracted twice with 30 ml pentane. The combined pentane extracts were washed with water and with saturated sodium chloride. The dried solution was added slowly to a slurry of 1 g lithium aluminium hydride in 50 ml ether. The mixture was heated under reflux for 2 h and then worked up as described under A. The product was separated from olefin on alumina as described under B. The product was distilled to give 2.4 g (71%) of an oil, b.p. 88–90° (85 mm), n_D^{25} 1.4786. The product was identical (n.m.r. and infrared spectra) with authentic **9**. The n.m.r. spectrum showed no absorption at τ 4.68 where the vinylic proton of the isomeric alcohol **10** absorbs. Gas–liquid chromatographic analysis indicated the presence of ca. 5% of a material with the same retention time as **10**.

(*d*) *From 2-Methylenecyclohexanone*

The 2-methylenecyclohexanone was prepared according to the procedure of Mannich (22). A mixture of 9 g 37% formaldehyde solution, 9 g dimethylamine hydrochloride, and 48 g cyclohexanone was heated on the steam bath. Water (50 ml) was added to the cooled mixture and the aqueous layer extracted several times with ether. The aqueous layer was concentrated using a rotatory evaporator. The crystals which formed were recrystallized from acetone–alcohol to give 10 g (54%) of salt, m.p. 150–151° (reported (22) m.p. 152°).

This salt (5 g) was pyrolyzed under vacuum (0.15 mm). The pyrolysate was caught in a trap at −70°, redistilled and stored at −70° until a solution of methylmagnesium iodide made from 0.5 g magnesium and 3 g methyl iodide in 50 ml ether was added. The reaction mixture was allowed to warm to room temperature and then hydrolyzed with water. The ether layer was dried and the solvent removed. The small amount of residual oil had two high-boiling components in a 60:40 ratio which were isolated by trapping the effluent from g.l.c. (FFAP column). A sufficient quantity of each was isolated for spectral analysis. The major component had a g.l.c. retention time and n.m.r. and infrared spectra which were identical with **9** prepared by methods (*a*)–(*c*) above. The second component was not identified. It had hydroxyl but no olefinic absorption in the infrared spectrum and no absorption in the n.m.r. spectrum below τ 6.

1,2-Dimethyl-2-cyclohexene-1-ol, **10**

The procedure of Warnhoff and Johnson (23) was used for the preparation of 2-methylcyclohexenone, b.p. 95–100° (75 mm), n_{D}^{25} 1.4820. Reported (23) b.p. 98–101 (77 mm), n_{D}^{25} 1.4836.

2-Methylcyclohexenone (1 g) in 5 ml ether was added to 4 ml of 0.24 *M* methyllithium at −40° under a nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and was then hydrolyzed with 10% potassium hydroxide solution. The organic layer was dried, the ether was removed, and the residual oil was distilled to give 0.4 g material b.p. 82–85° (25 mm). Reported (14) for **10**, b.p. 132° (180 mm). Gas chromatographic analysis on the FFAP column at 120° showed two components in a *ca.* 60:40 ratio in addition to a small amount of starting material. The two products were collected from the effluent of the g.l.c. The major product, n_{D}^{26} 1.4764 (reported (14) for **10**, n_{D}^{20} 1.4844), had the same g.c. retention time as the minor product formed with **9** in the various oxidations of 1,2-dimethylcyclohexene described above. Its n.m.r. spectrum (CCl_4) showed absorption at τ 4.68 (multiplet) for the olefinic proton, τ 7.9–8.6 (b) for the ring, hydroxyl, and allylic methyl protons and τ 8.80 (singlet) for the protons of the other methyl group with relative peak areas of 1:11.3:3.5, required: 1:10:3, consistent with the structure of **10**. The infrared spectrum (CCl_4) showed hydroxyl absorptions at 3600 (sharp) and 3500–3300 (broad) cm^{-1} as well as olefinic CH stretching absorption at 3160–3120 cm^{-1}.

The minor product, n_{D}^{25} 1.4616, showed hydroxyl absorptions but no absorption characteristic of an olefin in the infrared spectrum and had no absorption in the n.m.r. spectrum below τ 6. It was not investigated further.

trans-2-Bromocyclohexyl Hydroperoxide, **4**

The procedure described for the preparation of **1***b* was used to prepare an ether solution of *trans*-2-bromocyclohexyl hydroperoxide from 8.2 g (100 mmole) of redistilled cyclohexene, 14.3 g (50 mmole) of 1,3-dibromo-5,5-dimethylhydantoin, and 17 g (500 mmole) of 98% hydrogen peroxide. The dried solution was concentrated under aspirator pressure using a rotary evaporator on a water bath at 30°. The crude product, 19.8 g, contained 72% of the theoretical amount of hydroperoxide by iodometric titration. It was taken up in 100 ml pentane and the resulting solution was cooled to −78°. The pentane was decanted from the crystals which formed. These melted at ca. −20°. The hydroperoxide content of this oil was 88% of the theoretical. The n.m.r. spectrum (CCl_4) showed absorption at τ 1.04 (broad singlet) for the hydroperoxy proton, τ 5.80 (multiplet) for the methine protons, and τ 7.4–9.0 (broad) for the methylene protons of the ring with relative peak areas 0.89:2.0:8.1, required 1:2:8.

Hydrogenation of 1.95 g (0.01 mole) of this oil in 25 ml ether over platinum oxide at 0° and one atmosphere resulted in the rapid uptake of 178 ml (STP), 80% (based on weight of starting material) of hydrogen. The reaction mixture was filtered, the filtrate dried, and the ether removed. Gas–liquid chromatographic analysis of the residual oil on a 5 ft × 1/4 in. column of 10% QF-1 on Chromosorb W at 150° showed the presence of a trace of dibromocyclohexane in addition to the major product which had a retention time identical with authentic *trans*-2-bromo-cyclohexanol (24). The *p*-bromobenzenesulfonyl ester was prepared, m.p. and mixture melting point with authentic material 90.0–90.5°; reported (24) m.p. 90–90.5°.

Reaction of trans-2-Bromocyclohexyl Hydroperoxide with Base

A solution of 5.6 g potassium hydroxide in 25 ml ethanol was added to a solution of 19.5 g *trans*-2-bromocyclohexyl hydroperoxide (80% hydroperoxide) in 100 ml ether at 25°. The resulting mixture began to boil and deposit a precipitate. Boiling continued for ca. 30 min, and the solution was allowed to stir overnight at 25°. Titration of an aliquot showed that 95% of the hydroperoxide had been consumed. The mixture was filtered and the filtrate stirred vigorously with 50 ml of 2 *M* sodium sulfite for 1 h. The organic layer was then washed twice with water, dried, and the ether was removed through a vigreaux column.

The residual oil had a pungent odor. The infrared spectrum (neat) showed broad, strong absorption in the region 3600–3200 cm^{-1} and a medium intensity absorption with several maxima at 1735–1715 cm^{-1}. The major volatile components were found by g.l.c. analysis to be cyclohexene oxide and *trans*-2-bromocyclohexanol. These compounds were identified by comparison of their retention times with authentic cyclohexene oxide (25) and *trans*-2-bromocyclohexanol (24) on the QF-1 column and on a 5 ft × 1/4 in. column of 20% DEGS on Chromosorb W. Quantitative g.l.c. analysis using the QF-1 column showed that 29% cyclohexene oxide and 27% *trans*-2-bromocyclohexanol had been formed (based on the hydroperoxide content of the starting material). No trace of any material with the retention time of authentic cyclohexen-3-ol could be found.

Attempted distillation of a portion of the oil resulted in decomposition soon after boiling began (pot temperature 100°, 10 mm). A small amount of material which had collected in the condenser was taken up in carbon tetrachloride. The infrared spectrum of this material was identical with that of authentic cyclohexene oxide.

The combined aqueous extracts were extracted several times with ether and the combined ether extracts were concentrated. The viscous oil, 0.3 g which remained crystallized on standing, and was recrystallized from benzene, m.p. 96.0–97.5°. The mass spectrum of this material showed a parent peak at *m*/*e* 116.0835 corresponding to a molecular formula of $C_6H_{12}O_2$ which requires 116.0837. It was identified as *trans*-1,2-cyclohexanediol by its melting point behavior, mixture melting point with authentic *trans*-1,2-cyclohexanediol (26) 96–101° and mixture melting point with authentic *cis*-1,2-cyclohexanediol[2] (27) 65–74°. The authentic diols had m.p. 98–101°, reported (26) m.p. 104°, and 96–98°, reported (28) m.p. 98°, respectively.

The precipitate obtained on filtering the initial reaction mixture was taken up in a small amount of water. The resulting solution was made acid with 6 *N* hydrochloric acid and extracted with chloroform. The organic layer was dried and the solvent was removed to leave 0.8 g of a viscous oil. A thin-layer chromatogram of this material using silica gel G.F. 254 as adsorbent and ether as eluent indicated that at least six components were present. The material was not investigated further.

Several other reactions between *trans*-2-bromocyclohexyl hydroperoxide and base were carried out. The reaction temperature and time, concentrations of reactants, and method of reduction (sodium borohydride, lithium aluminium hydride) of the crude reaction mixture were varied. In no case was any trace of cyclohexen-3-ol found.

Cyclohexen-3-ol

A solution of 8 g (0.05 mole) 3-bromocyclohexene (29) and 4.1 g (0.05 mole) of sodium acetate in 50 ml acetic acid was heated on the steam bath for 5 min. The resulting mixture was filtered and the filtrate was slowly poured into an aqueous slurry of sodium carbonate. The resulting mixture was extracted with 100 ml ether. The dried ether solution was added to a slurry of 1 g lithium aluminium hydride in 50 ml ether. The reaction mixture was hydrolyzed by dropwise addition of saturated potassium carbonate until the organic layer became clear. The solution was decanted, the precipitate washed with a little ether, and the combined ether solutions were concentrated. Distillation of the residue gave 2.0 g, 45%, of colorless oil, b.p. 53° (6 mm). Reported (30) b.p. 63–65° (12 mm). The n.m.r. spectrum (neat) showed absorption at τ 4.32 (multiplet) for the olefinic protons, τ 4.97 (singlet) for the hydroxyl proton, τ 5.89 (b) for the methine proton and τ 7.8–8.8 (b) for the ring methylene protons with relative peak areas 2.0:0.96:0.96:6.3, required 2:1:1:6.

2-Bromo-1-phenylethyl Hydroperoxide, 5

The procedure described for the preparation of **1***b* was used to prepare an ethereal solution of **5** from 10.4 g (0.1 mole) of purified styrene, 14.3 g (0.05 mole) of 1,3-dibromo-5,5-dimethylhydantoin, and 17 g (0.5 mole) of 98% hydrogen peroxide. The dried solution was concentrated to constant weight under 0.5 mm pressure on a water bath at 30° using a rotary evaporator. The residual oil, 14.1 g, and 86% of the theoretical hydroperoxide content. The n.m.r. spectrum (CCl_4) showed absorption at τ 1.00 (b) for the hydroperoxy proton, τ 2.80 (singlet) for the phenyl protons, τ 5.07 (triplet, $J = 6.5$ c.p.s.) for the methine proton, and τ 6.48 (doublet, $J = 6.5$ c.p.s.) and τ 6.53 (doublet, $J = 6.5$ c.p.s.) for the nonequivalent methylene protons. The relative peak areas were 0.57:5.0:0.85:1.8, required 1:5:1:2. A mixture of 13.0 g of this material in 100 ml ether and 31 g sodium bisulfite was stirred vigorously overnight. The organic layer was separated, dried, and concentrated. Distillation of the residual oil yielded 9.2 g, 87% (based on hydroperoxide content) of 2-bromo-1-phenylethanol, b.p. 78–79° (0.3 mm), n_D^{26} 1.5763. Reported (31) b.p. 120–123° (5 mm), $n_D^{19} = 1.5785$. The n.m.r. and infrared spectra were identical with those of an authentic sample (31).

Reaction of 2-Bromo-1-phenylethyl Hydroperoxide with Base

A solution of 4 g sodium hydroxide in 15 ml methanol was added to 20.6 g of **5**, 78% hydroperoxide content, in 100 ml methanol at 0°. A white precipitate soon began to form. The mixture was stirred at 0° for 2 h. Water (200 ml) was added and the mixture extracted four times with 100 ml pentane. The aqueous layer was concentrated to a small volume and made acidic with 6 *N* hydrochloric acid. An oil separated which began to crystallize. The mixture was extracted with 100 ml ether and the ether was dried. Evaporation of the ether left an oil which crystallized on standing, 4.3 g. The solid, recrystallized from methanol, had m.p. and mixture melting point with benzoic acid 119–120°. The yield was 45% based on the hydroperoxide content of the starting material.

The dried organic layer was concentrated to a small volume through a 4 ft Podbielniak column. The odor of benzaldehyde was detected in the concentrate. 1,2-Dianilinoethane (2 g) (32) in 20 ml methanol was added to 21% of the concentrate. The solution was left at 0° overnight. The crystals which separated were filtered to give 0.133 g, 2.9% (based on the hydroperoxide content of the starting material **5**), of 1,2,3-triphenyltetrahydroimidazole, melting point and mixture melting point with authentic (32) material 131–131.5°. Reported (32) m.p. 137°.

The remainder of the concentrate was adsorbed on a 1.5 × 30 cm column of neutral alumina. The column was washed with 100 ml pentane and with 200 ml ether. The eluents were analyzed by g.l.c. on a 9.5 ft × 1/4 in. column of 10% Ucon-50-HB-5100 on Chromosorb W at 158°. The pentane eluent contained only styrene and the ether eluent only benzaldehyde and styrene oxide. Further elution of the column with 200 ml ether gave no more product. Quantitative g.l.c. analysis showed that 4% benzaldehyde and 45% styrene oxide (based on the hydroperoxide content of the starting material) had been formed in the reaction.

Concentration of 63% of the ether eluent and distillation of the residual oil yielded 1.34 g, 33%, of styrene oxide, b.p. 53° (2.8 mm), n_D^{26} 1.5312. Reported (31) b.p. 65° (5 mm), n_D^{20} 1.5340. The n.m.r. spectrum of this product was identical with authentic (31) material as was the infrared spectrum except for a weak absorption at 1 700 cm^{-1}.

3-Bromo-2-methyl-2-butyl Hydroperoxide, 3

The procedure described for the preparation of **1***b* was used to prepare an ether solution of **2** from 7.0 g (0.1 mole) of 2-methyl-2-butene, 14.3 g (0.05 mole) of 1,3-dibromo-5,5-di-methylhydantoin, and 17 g (0.5 mole) of 98% hydrogen peroxide. The dried solution was concentrated to constant weight under 0.5 mm pressure on a water bath at 30° using a rotary evaporator. The residual oil, 16 g, had 92% of the theoretical hydroperoxide content. The n.m.r. spectrum (CCl_4) showed absorption at τ 1.40 (b) for the hydroperoxy proton, τ 5.56 (quartet, $J = 7$ c.p.s.) for the methine proton τ 8.32 (doublet, $J = 7$ c.p.s.) for the terminal methyl protons, and τ 8.63

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[2] Kindly donated by Mr. S. Evani.

and 8.72 for the protons of the non-equivalent *gem*-dimethyl groups. The relative peak areas were 0.77: 1.0:3.3:5.9, required 1:1:3:6.

Reaction of 3-Bromo-2-methyl-2-butyl Hydroperoxide with Base

A solution of 4.4 g sodium hydroxide in 16 ml methanol was added slowly to a well-stirred solution of 18 g of **3** in 100 ml ether kept at 0°. The solution was stirred at 0° for 1½ h after addition was complete. Gas–liquid chromatographic analysis of an aliquot on a 5 ft × 1/4 in. column of 10% Carbowax 1500 on Chromosorb W at 50° indicated that 76% acetone and 77% acetaldehyde had been formed. Acetaldehyde and acetone were identified by comparison of their retention times on the Carbowax column and on a 5 ft × 1/4 in. column of 10% glycerol on Chromosorb W. Thin-layer chromatography on silica gel GF-254 using benzene as eluent of a mixture of 2,4-dinitrophenylhydrazones obtained from an aliquot of the reaction mixture gave two partially resolved spots. The R_f values were equal to those of the 2,4-dinitrophenylhydrazones of acetone and acetaldehyde.

The reaction mixture was poured into 200 ml water and the mixture was extracted with ether. An aliquot of the dried organic layer analyzed by g.l.c. on the Carbowax column at 50° showed that 10% of 2,3-epoxy-2-methylbutane had been formed.

The organic layer was carefully concentrated through a 4 ft Podbielniak column. From the residual oil 2,3-epoxy-2-methylbutene was isolated by trapping it from the effluent of the g.l.c. column. Its n.m.r. and infrared spectra were identical with those of authentic (33) material.

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