Deuterium Isotope Effects in the Oxidation of 2,3-Dimethyl-2-butene via the Bromohydroperoxide, by Singlet Oxygen and by Triphenyl Phosphite Ozonide[1,2]

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The partially deuterated alkenes $(CH_3)_2C{=}C(CD_3)_2$ (**1***b*) and $CH_3CD_3C{=}CCH_3CD_3$ (**1***c*) were prepared and converted to the corresponding allylic hydroperoxides by the routes shown in the title. Two bromohydroperoxides were formed from **1***b* in a 1.6:1 ratio with the major isomer having the OOH group on the carbon bearing the CH_3's. On treatment with base at 0° this mixture formed two allylic hydroperoxides in a 2.2:1 ratio with the major isomer having the OOH group on the carbon bearing the CD_3's, showing migration of the OOH group. This isomer predominated in a 1.4:1 ratio when **1***b* was oxidized with singlet oxygen at 15 or −52° and in a 1.6:1 ratio when **1***b* was oxidized with triphenyl phosphite ozonide at −70°. Under the same conditions C—H bond breaking also predominated in the oxidation of **1***c*, by 2.1:1 via the bromohydroperoxide, by 1.4:1 with singlet oxygen, and by 1.3:1 with triphenyl phosphite ozonide. Migration of the OOH group in the reaction of the bromohydroperoxide of **1***b* does not occur by way of a 1,2-dioxetane. A perepoxide may be the intermediate. Neither perepoxides nor 1,2-dioxetanes are involved in the singlet oxygen oxidation of **1***b* and *c*. At −70° the triphenyl phosphite ozonide oxidations do not proceed by way of these intermediates, either, or by way of singlet oxygen. The intermolecular deuterium isotope effect in the singlet oxygen oxidation of both *cis*- and *trans*-2,3-diphenyl-2-butene was found to be 1.1.

Les alcènes partiellement deutériés $(CH_3)_2C{=}C(CD_3)_2$ (**1***b*) et $CH_3CD_3C{=}CCH_3CD_3$ (**1***c*) ont été préparés puis convertis en hydropéroxydes allyliques correspondants, selon le schéma exposé dans le titre de ce mémoire. Deux hydropéroxydes bromés sont obtenus à partir de **1***b* dans le rapport 1.6:1, l'isomère prépondérant ayant le groupe OOH sur le carbone portent du CH_3. Par traitement basique à 0°, ce mélange conduit à deux hydropéroxydes allyliques, dans le rapport 2.2:1; avec l'isomère possédant le groupe OOH sur le carbone du CD_3, en majorité, montrant ainsi la migration du groupe OOH. Cet isomère prédomine dans le rapport 1.4:1 lorsque **1***b* est oxydé par l'oxygène singulet à 15 ou −52° et dans le rapport 1.6:1 lorsque cette oxydation est effectuée par l'oxyde de la triphénylphosphite à −70°. Dans les mêmes conditions, la cassure de la liaison C—H prédomine aussi dans l'oxydation de **1***c*, dans le rapport 2.1:1 via le bromohydropéroxyde, 1.4:1 dans le cas de l'oxygène singulet, et 1.3:1 avec l'ozonide de la triphénylphosphite. La migration du groupe OOH dans la réaction du bromohydropéroxyde de **1***b* ne se produit pas par l'intermédiaire du dioxétane-1,2. Une perépoxyde serait l'intermédiaire. Ni les perépoxydes, ni les dioxétanes-1,2 n'interviennent dans l'oxydation par l'oxygène singulet de **1***b* et *c*. A −70° les oxydations par l'ozonide de la triphénylphosphite ne passent pas par ces intermédiaires, ni par oxygène singulet. L'effet isotopique intermoléculaire de deutérium dans l'oxydation par l'oxygène singulet des *cis* et *trans* diphényl-2,3 butène-2 a été trouvé égal à 1.1.

[Traduit par le journal]

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Introduction

β-Halohydroperoxides derived from a variety of tetrasubstituted ethylenes are converted rapidly at 0° by base to allylic hydroperoxides in good to excellent yields (1, 2). The reaction sequence shown in Scheme 1 represents an alternate synthesis of allylic hydroperoxides which are usually prepared by the oxidation of alkenes with singlet oxygen (3). Indeed, essentially the same distributions of products are formed from the β-halohydroperoxides of 1,2-dimethylcyclohexene (1) and 2-methyl-3-(4-methoxyphenyl)-2-butene (2*b*) as are formed by the oxidation of these alkenes by singlet oxygen.

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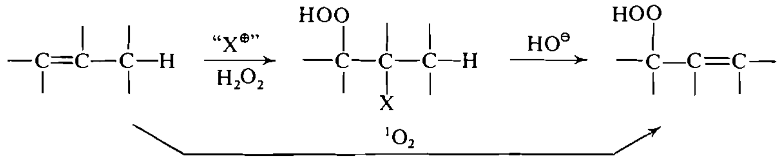
[1] Presented in part at the 51st Canadian Chemical Conference of the Chemical Institute of Canada, Vancouver, B.C., June, 1968, Abstracts p. 41; at the Symposium on Cyclic Peroxides at the Regional Meeting of the New York, New Jersey, and Puerto Rico Sections of the American Chemical Society, San Juan, Puerto Rico, April 30, 1971; and at the Symposium on Oxidations by Singlet Oxygen sponsored by the Division of Petroleum Chemistry Inc., 162nd National Meeting of the American Chemical Society, Washington, D.C., September, 1971, Petroleum Preprints **16**, No. 4, A65 (1971).

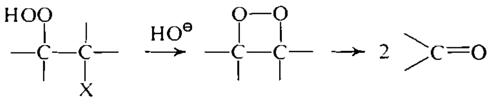
[2] Based on a dissertation submitted by J. H. van de Sande to the Faculty of Graduate Studies of the University of Alberta, Edmonton, Alberta, in partial fulfillment of the requirements of the Ph.D. degree, 1968.

[3] Holder of an NRCC Studentship, 1964–1967, and a University of Alberta Dissertation Fellowship, 1967–1968.



SCHEME 1

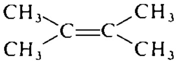
However, the formation of allylic hydroperoxides from β-halohydroperoxides is not a general reaction. In sharp contrast to the results outlined above no trace of allylic hydroperoxides could be found among the products of reaction, under similar conditions, between base and a number of less highly substituted ethylenes. A variety of products is formed (1). Carbon–carbon bond cleavage occurs in some cases (1, 4) which indicates that cyclic peroxides may be formed as intermediates, eq. 1. Trimethyl-

[1] 

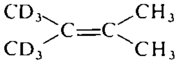
$$\mathrm{HOO{-}\overset{|}{\underset{X}{C}}{-}\overset{|}{\underset{|}{C}}{-}} \xrightarrow{HO^{\ominus}} \mathrm{\overset{O-O}{C{-}C}} \longrightarrow 2\ \mathrm{>C{=}O}$$

1,2-dioxetane (5, 6) and 3-methyl-3-phenyl-1,2-dioxetane (6) have been isolated recently from such reactions and are cleaved to carbonyl compounds on heating. No such cleavage products have yet been observed in the reactions between the β-halohydroperoxides of tetrasubstituted ethylenes and base.

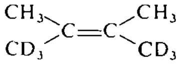
The present study was made in an attempt to distinguish between the several possible mechanisms that could be envisaged for the transformation of β-halohydroperoxides to allylic hydroperoxides and, in particular, to determine if the transformation also involves 1,2-dioxetanes as intermediates. In addition, it was of interest to determine whether this reaction and the reaction between singlet oxygen and tetrasubstituted ethylenes have common intermediates as well as common products. Two partially deuterated 2,3-dimethyl-2-butenes, 1,1,1-trideuterio-2-methyl-3-trideuteriomethyl-2-butene (**1***b*) and 2,3-bis(trideuteriomethyl)-2-butene (**1***c*) were prepared. The intramolecular deuterium isotope effects were determined for the conversion of these alkenes to allylic hydroperoxides by the routes (*1*) reaction between their β-bromohydroperoxides and base, (*2*) by oxidation with singlet oxygen generated by a variety of sensitizers and from the hydrogen peroxide–



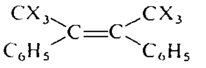
1*a*



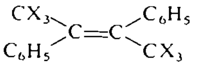
1*b*



1*c*



cis-**2**



trans-**2**

a X = H
b X = D

a X = H
b X = D

sodium hypochlorite reactions (3*b*), and (*3*) by oxidation with triphenyl phosphite ozonide (7). Also, *cis*- and *trans*-1,1,1,4,4,4-hexadeuterio-2,3-diphenyl-2-butene (*cis*- and *trans*-**2***b*) were prepared and the intermolecular deuterium isotope effects in the singlet oxygen oxidation of *cis*- and *trans*-2,3-diphenyl-2-butene (*cis*- and *trans*-**2***a*) were determined.

Results

Preparation of the Deuterated Alkenes

The syntheses of the deuterated alkenes **1***b*, **1***c*,[4] and *cis*- and *trans*-**2***b* are outlined in Schemes 2, 3, and 4, respectively.[5] The deuterated methyl hydroxyisobutyrate (Scheme 2) was prepared by addition of deuterium cyanide to hexadeuterioacetone followed by hydrolysis of the resulting product and then treatment of the hydroxy acid so obtained with diazomethane.

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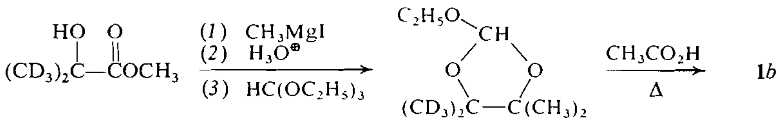
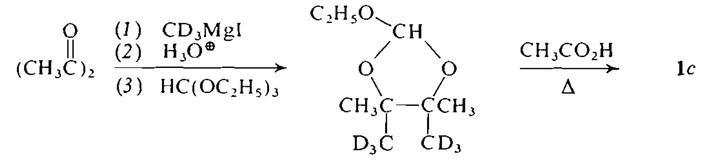
[4] Although only the *cis* isomer of **1***c* is shown as the product of the reaction sequence, nearly equimolar amounts of the *cis* and *trans* isomers undoubtedly are formed (8).

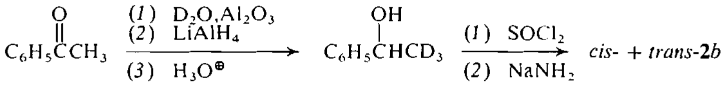
[5] In principle, a simpler route to **1***b* would involve addition of trideuteriomethylmagnesium iodide to an ester of isobutyric acid followed by dehydration of the resulting alcohol. However, in numerous exploratory experiments dehydration of 2,3-dimethyl-2-butanol by various methods in the absence of strong acid produced mainly 2,3-dimethyl-1-butene and only small amounts of the desired internal alkene. Acid-catalyzed dehydration of the alcohol gives predominantly the internal alkene, but extensive isotopic exchange would have occurred in the dehydration of the appropriate partially deuterated alcohol (9).



SCHEME 2



SCHEME 3



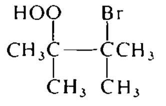
SCHEME 4

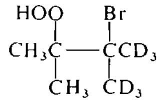
Only two points concerning the reactions will be made here. We found the preparation and subsequent decomposition (without isolation) of the orthoformate ester derivative of 2,3-dimethyl-2,3-butanediol to be a more convenient route (10) for the preparation of 2,3-dimethyl-2-butene (**1**a) than the preparation and decomposition of the thionocarbonate derivative (11). Also, 2,2,2-trideuterioacetophenone could be prepared quickly and on a large scale by passing a solution of acetophenone through a long column of alumina pretreated with deuterium oxide.

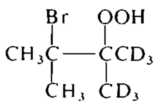
Mass spectral analysis (12) at low ionizing voltage (9.5–12 eV) showed that the trideuteriomethyl groups of **1**b are 99.4% deuterated, those of **1**c are 95.3% deuterated, and those of *cis*- and *trans*-**2**b are 92% deuterated. Analysis of the $M^{\oplus} - CX_3$ (X = H or D) region of the mass spectrum taken at 70 eV of **1**b and c showed that very little, if any, exchange of deuterium between the CD_3 and the CH_3 groups had occurred during the preparation of these materials.

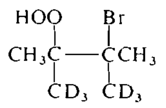
Isotope Effect in Elimination of Hydrogen Bromide from 3-Bromo-2,3-dimethyl-2-butyl Hydroperoxide

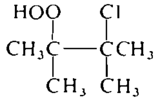
The alkenes **1**b and c were converted to the bromohydroperoxides, **3**b + c and **3**d, respectively, by adding 1,3-dibromo-5,5-dimethylhydantoin (dibromantin) to solutions of the alkenes and excess 98% hydrogen peroxide in ether at −40° and then allowing the temperature to rise to 0° (1). The two products from **1**b, 3-bromo-4,4,4-trideuterio-3-trideuteriomethyl-2-methyl-2-butyl hydroperoxide (**3**b) and 3-bromo-1,1,1-trideuterio-2-trideuteriomethyl-2-butyl hydroperoxide (**3**c) were formed in unequal amounts. The material containing the hydroperoxy group on the carbon bearing the CH_3 groups, **3**b, made up 61.5% of the product mixture. The product ratio was determined from the n.m.r. spectrum (CCl_4) of the product mixture by comparing the area of the signal at τ 8.57, due to the CH_3 groups of **3**b, with the area of the signal at τ 8.20, due to the CH_3 groups of **3**c. The assignments are made on the basis that a bromine atom causes a greater deshielding of β-protons than does a hydroxyl or an alkoxy group (13) and that the hydroperoxy group causes a deshielding similar in magnitude to that of the latter groups. For example, the n.m.r.


3a

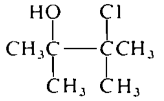

3b


3c

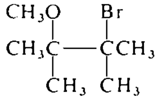

3d


$\mathrm{CH_3C(OOH)(CH_3)-CCl(CH_3)CH_3}$

4


$\mathrm{CH_3C(OH)(CH_3)-CCl(CH_3)CH_3}$

5


$\mathrm{CH_3C(OCH_3)(CH_3)-CBr(CH_3)CH_3}$

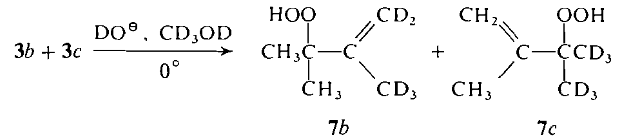
6

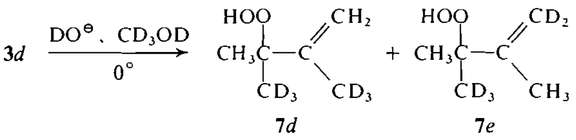
spectra (CCl_4) of 3-chloro-2,3-dimethyl-2-butyl hydroperoxide (**4**) and 3-chloro-2,3-dimethyl-2-butanol (**5**) show signals for the methyl groups at τ 8.38 and 8.60, and at τ 8.36 and 8.69, respectively (1), and the *gem*-dimethyl groups of 3-bromo-2-methoxy-2,3-dimethylbutane (**6**), prepared by the addition of dibromantin to **1***a* in methanol, absorb at τ 8.26 and 8.67.

Freshly prepared samples of the bromohydroperoxides **3***b* + *c* and **3***d* were converted to allylic hydroperoxides by allowing them to react at 0° for 6 h with a five-fold excess of sodium deuteroxide in methanol-d_4, eqs. 2 and 3. Benzene was added as an internal standard so as to be able to obtain material balances for the reactions. A material balance was also obtained in this way for the conversion of the undeuterated bromohydroperoxide **3***a* to 2,3-dimethyl-3-hydroperoxy-1-butene (**7***a*) under similar conditions, eq. 4. The reaction mixtures were analyzed directly by n.m.r. spectroscopy. The relative intensities of the signals at τ 8.70, due to the CH_3 groups attached to the carbon bearing the hydroperoxy group, and at τ 8.22, due to the allylic CH_3 group, of the allylic hydroperoxides were measured by careful integration and the ratios **7***c*/**7***b* and **7***d*/**7***e* were determined as described in the Experimental. Integration of methanolic solutions of **7***a* made from freshly prepared samples of **3***a* gave area ratios for the peaks at τ 8.70 and 8.22 of 2.02 ± 0.06 to 1.00, so no corrections were applied to the area ratios obtained from the runs using the deuterated bromohydroperoxides. However, this area ratio was somewhat larger than 2.0 to 1.0 when samples of **3***a* which had been stored for several weeks at 5° were used to prepare solutions of **7***a*. It was found that this was due to the formation of some 2,3-epoxy-2,3-dimethylbutane whose n.m.r. absorption in methanol solution is almost superimposable upon that of the *gem*-dimethyl group of **7***a*, see below.

The results in Table 1 show that in each case conversion to allylic hydroperoxide is essentially quantitative. Furthermore, it is clear that in the case of the bromohydroperoxides **3***b* and *c* a shift of the hydroperoxy group occurs during the reaction. The compound with the hydroperoxy group on the carbon bearing the CH_3 groups, **3***b*, predominates in the starting mixture while in the product mixture the compound with the hydroperoxy group on the carbon bearing the CD_3 groups, **7***c*, predominates. Clearly, the reaction does not proceed by a direct elimination of the elements of HBr or DBr. In this case the product ratio, **7***c*/**7***b* would have been the same as the ratio, **3***c*/**3***b*, of the starting materials, namely, 0.63. The actual product ratio, **7***c*/**7***b*, is about 2.2.

Further evidence that a C—H or C—D bond is not broken in the rate-determining step of the elimination was obtained by carrying out the elimination reactions on the mixture of **3***b* and *c* with less than one equivalent of base. The relative amounts of **3***b* and *c* remaining at various conversions were determined by n.m.r.

[2] 

[3] 

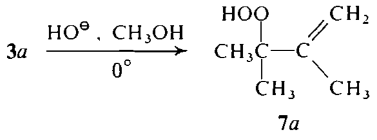
[4] 

TABLE 1. Yield and product distribution in the reaction between the β-bromohydroperoxides 3*a*–*d* and base in methanol*

Starting material	Temperature (°C)	% Yield	7*c*/7*b*	7*d*/7*e*†
3*a*‡	25	100		
	2	104		
	−19	100		
3*b* + 3*c*§	0	96 ± 2	2.20 ± 0.04	
		103 ± 3	2.17 ± 0.06	
3*d*§	0	102 ± 2		2.16 ± 0.06
		98 ± 1		2.04 ± 0.03

*Determined by n.m.r. spectroscopy with benzene as an internal standard. Errors are average errors from three integrations per run.

†Corrected to 100% isotopic purity of the trideuteriomethyl groups of 3*d* using the expression

$$\frac{7d}{7d(1-z)+7e(z)} = (7d/7e)$$

observed where z is the fraction of deuterium atoms in the trideuteriomethyl groups.

‡Concentrations: 0.13 *M* 3*a* and 0.81 *N* sodium hydroxide in methanol.

§Concentrations: 0.11 *M* substrate and 0.55 *N* sodium deuteroxide in methanol-d_4.

TABLE 2. Relative rates of disappearance of 3*b* and *c* in basic CD_3OD at 0°

Run	% Conversion*	3*b*/3*c*†	7*c*/7*b*‡
—	0	1.45	—
1	15	1.42	—
2	31	1.46	1.4
3	57	1.43	1.7

*Sufficient 0.55 *N* NaOD was added in each case to 0.11 *M* solutions of 3*b* + *c* to give the conversions shown.

†Measured by n.m.r. spectroscopy from relative peak heights of the signals at τ 8.19 of 3*c* and at τ 8.58 of 3*b*. The ratio of 3*b*/3*c* formed from 1*b* as determined by integration of these signals is 1.6.

‡Measured by n.m.r. spectroscopy from relative peak heights (normalized) of signals of 7*c* at τ 8.22 and of 7*b* at τ 8.70. On complete conversion this ratio is 2.2 as measured by integration of these signals (Table 1).

spectroscopy. The results in Table 2 show that the two bromohydroperoxides 3*b* and *c* both react at essentially the same rate. The ratio, 3*b*/3*c*, changes hardly at all up to 57% reaction. Isotope effects, k_H/k_D, of from 5–9 have been found in a variety of base-promoted elimination reactions of alkyl bromides (14). Thus, if the C—H or C—D and C—Br bonds were being broken simultaneously in the reaction of 3*b* and *c* then 3*c* should be consumed more rapidly than 3*b*, in contrast to what is observed.

The product ratio, 7*c*/7*b*, even at 31% conversion, shows that a migration of the hydroperoxy group has occurred. The ratios of 7*c*/7*b* given in Table 2 differ from those given in Table 1 because the former were determined from the relative peak heights of the signals due to the CH_3 groups of 7*c* and *b*. It was necessary to use the less accurate peak height method of analysis because the absorption of the allylic CH_3 group of 7*c* was too near that of the CH_3 groups at τ 8.20 of the starting material 3*c* for accurate integrations of the signals to be made.

The results suggest that 3*b* and *c* are converted by base to the same reactive bromine-free intermediate which can then lose either a proton or deuteron equally well, except for an isotope effect, to give the allylic hydroperoxides 7*b* and *c*.

The results obtained from the reaction between 3*d* and base are consistent with this. The major product of the reaction is 7*d*, formed by loss of hydrogen bromide, rather than 7*e*, formed by loss of deuterium bromide, and the product ratio, 7*d*/7*e*, is essentially the same as the ratio, 7*c*/7*b*, of products obtained from the mixture of 3*b* and *c*, Table 1.

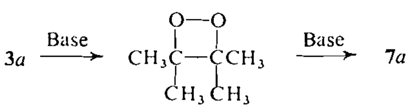
The results above were obtained before it was discovered that some 2,3-epoxy-2,3-dimethylbutane was formed under these conditions from samples of 3*a* which had been stored for some time. As a result of the method of analysis of the reaction mixtures the ratios, 7*c*/7*b* and 7*d*/7*e*, given in Table 1 are minimum and maximum values, respectively. For example, had 5% of epoxide actually been present in the reaction mixtures obtained from 3*b* + *c* and 3*d*, the corrected value for the ratio, 7*c*/7*b*, would be 2.6 and that for the ratio, 7*d*/7*e*, would be 1.8.

It is not known how much epoxide was formed during reaction of the deuterated bromohydroperoxides with base, but the amounts formed, if any, are probably quite small because fresh samples of the deuterated bromohydroperoxides were used so the ratios, 7*c*/7*b* and 7*d*/7*e*, are uncorrected. Barely detectable amounts, less than 1%, of epoxide were formed from fresh samples of 3*a*, while a maximum of about 12% was formed from some of the older samples of 3*a*, see below.

Spectroscopic Search for an Intermediate

At the time that these results were obtained it was thought that the intermediate formed during the conversion of the β-bromohydroperoxide, 3*a*, to the allylic hydroperoxide, 7*a*, might be tetramethyl-1,2-dioxetane (**8**), eq. 5*a*. The

[5*a*]



8

formation of **8** from 3*a* would be consistent with evidence which was accumulating (1, 4, 15) which suggested that 1,2-dioxetanes were formed in reactions between other suitably substituted hydroperoxides and base. Attempts were made to detect **8** by following the reaction between 3*a* and base in methanol between −17.5 and −37.5° by n.m.r. spectroscopy in the thermoregulated probe of a 100 MHz n.m.r. spectrometer. The reaction is rapid enough so that it can be monitored conveniently in this way at temperatures as low as −40°, Table 3. The rate of disappearance of 3*a* obeyed second order kinetics over the first 50–60% of reaction during which the reactions were followed.

Besides absorptions for starting material 3*a* and product 7*a*, a new absorption, a sharp singlet, appeared about 3 Hz downfield from the absorption of the *gem*-dimethyl group of the allylic hydroperoxide and increased in intensity as the reaction progressed until about 40% reaction, after which the intensity of this signal remained constant. It was determined that this signal was due to a compound having 12 equivalent protons by careful integration of the starting material and products before and during reaction using tetramethylsilane as internal standard. The signal was shown to be due to 2,3-epoxy-2,3-dimethylbutane by comparing the chemical shift of authentic material in methanol solution at the temperatures used and by peak enhancement on addition of small amounts of authentic material to reaction mixtures at low temperatures. About 12% of the epoxide was formed from the samples of bromohydroperoxide used for the rate studies. These samples had been stored for several weeks at 5°. When fresh samples of 3*a* were used in the reaction the signal due to the epoxide was barely detectable; less than 1% was formed. The epoxide presumably is formed from the corresponding bromohydrin which may be formed by the slow decomposition of the bromohydroperoxide, 3*a*.

TABLE 3. Rate of reaction between 3-bromo-2,3-dimethyl-2-butyl hydroperoxide (3*a*) and hydroxide ion in methanol*

Temperature (°C)	$[3a]_0$	$[\mathrm{NaOH}]_0$	k_2(graphical) × 10^4 ($M^{-1}\,s^{-1}$)
−37.5	0.22	0.83	1.0
−27.5	0.15	0.82	1.7
−17.5	0.23	0.58	3.5

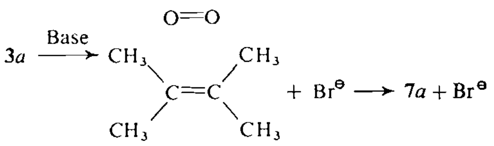
*At −17.5° $\Delta H^{\ddagger} = 6.9$ kcal/mol, $\Delta S^{\ddagger} = -47$ e.u. for disappearance of 3*a*.

No signals other than those due to 3*a*, 7*a*, and the epoxide could be detected above τ 8 in the n.m.r. spectrum of the reacting mixtures at low temperature. Careful integration indicated that there was no significant absorption other than those due to 3*a* and 7*a* at around τ 8.20.

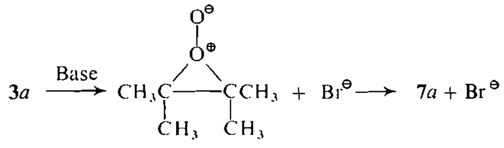
Authentic tetramethyl-1,2-dioxetane (**8**) was prepared some time after these experiments were carried out (5). It is not converted to 7*a* by base in methanol even in the presence of added bromide ion and in methanol solution it shows absorption at τ 8.53, so that it clearly is not the intermediate which is formed in the reaction between 3*a* and base.

There are two other routes involving symmetrical intermediates that appear to be plausible by which the allylic hydroperoxide may be formed from 3*a*. One route is fragmentation of the anion of 3*a* to give the alkene 1*a*, singlet oxygen, and bromide ion followed by reaction between 1*a* and singlet oxygen, eq. 5*b*. This

[5*b*]



route to the formation of 7*a* can be ruled out on two grounds. First, the reaction between singlet oxygen and 1*a* is not a diffusion controlled reaction (16) so that a significant amount of the singlet oxygen would be deactivated before it could react and the conversion of 3*a* to 7*a* by this route could not be quantitative. In fact, the yield is essentially quantitative. Second, if the reaction between 3*a* and base proceeded as in eq. 5*b* the singlet oxygen oxidation of the deuterated analogs of 1*a*, *b*, and *c* would give the same distributions of products as are obtained from the reactions of 3*b* + *c* and 3*d* with base. As is shown below, the actual product distributions are quite different from each other.

[6]


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The remaining plausible route, and one which we have not yet ruled out, for formation of 7*a* from 3*a* proceeds by way of the perepoxide **9**, eq. 6. Attempts to trap the intermediate **9** with added azide ion have been unsuccessful. A reaction between 3*a* and base in 40% water – 60% CD_3OD saturated with sodium azide (about 0.4 *N*) at 0° formed 7*a* exclusively as judged by the n.m.r. spectrum of the solution after reaction.

Intramolecular Isotope Effects in the Singlet Oxygen and Triphenyl Phosphite Ozonide Oxidation of 2,3-Dimethyl-2-butene

The partially deuterated alkenes 1*b* and *c* were oxidized in methanol to the corresponding mixtures of allylic hydroperoxides with singlet oxygen generated by dye photosensitization (3) and by the reaction between sodium hypochlorite and hydrogen peroxide (3*a*, 3*b*, 17). Mixtures of allylic hydroperoxides were produced whose compositions were analyzed directly by n.m.r. spectroscopy, as described above for the bromohydroperoxide reactions, after extraction into ether and subsequent complete removal of the ether under reduced pressure or after preparative isolation. In these oxidations the allylic hydroperoxides formed by loss of hydrogen rather than deuterium from carbon predominate only to a slight extent. The product ratios, expressed as isotope effects, k_H/k_D, in Table 4 show only a small variation with the source[6] of singlet oxygen and temperature. Indeed, all the values of k_H/k_D for the singlet oxygen oxidations are within 8% of 1.40.[7] The variations of k_H/k_D with temperature and solvent, which are undoubtedly present, are too small to be distinguishable in these experiments. However, the method of product analysis used is accurate enough to show clearly that the observed isotope effects in the singlet oxygen oxidations of the unsymmetrically deuterated alkene 1*b* and the symmetrically deuterated alkene 1*c* differ by no more than 8%. It is also clear that there is a significant difference between the ratios of allylic hydroperoxides formed in these oxidations of 1*b* and *c* and the ratio of allylic hydroperoxides formed by the reactions between base and the bromohydroperoxides of 1*b* and *c*, Table 1, even when the photooxygenation was carried out in the presence of base at −52° (run 8, Table 4). This shows that if any intermediates are formed in the singlet oxygen oxidation of the alkenes 1*b* and *c* they must be different from the intermediates formed in the reactions between base and the bromohydroperoxides of these alkenes.

Triphenyl phosphite ozonide (23) has been shown to oxidize 1*a* to the allylic hydroperoxide 7*a* at −30° and to decompose to triphenyl phosphate and singlet oxygen at −15° (27). It was suggested that 1*a* was oxidized by the singlet oxygen released. In an attempt to distinguish between this mode of oxidation and

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[6] A variety of sensitizers was used in order to test the then recent suggestion (18) that sensitizers with high triplet state energies produced more $^1\Sigma_g^+$ than $^1\Delta_g$ oxygen molecules and that these had different reactivities. The suggestion was made to explain the observed (19) sensitizer dependence of product distribution in oxidation of cholest-4-en-3β-ol. It has since been shown that this variation in product distribution is probably due to a direct reaction between sensitizer and substrate which competes with the singlet oxygen ($^1\Delta_g$) reaction and produces a different product (20), and that $^1\Sigma_g^+$ oxygen molecules are deactivated so rapidly by solvent that no reaction with substrate could take place (21).

[7] It has been reported briefly that isotope effects of 1.2 to 2.1 were obtained in the singlet oxygen oxidation of 1*b*, *c*, and 2,2,6,6,2′,2′,6′,6′-octadeuteriocyclohexylidenecyclohexane, unpublished work cited in ref. 22.

NOTE ADDED IN PROOF: These results have now been published (55) and those for 1*b* and *c* are in excellent agreement with the results presented here.

TABLE 4. Intramolecular deuterium isotope effects in the oxidation of **1***b* to **7***b* + *c* and of **1***c* to **7***d* + *e**

Alkene	Run	Reagent (sensitizer)†	Solvent	Temperature (°C)	k_H/k_D‡
1*b*	1	$^1O_2$(MB)	CH_3OH	14	1.35 ± 0.01
	2			14	1.31 ± 0.01
	3			−52	1.35 ± 0.02
	4	$^1O_2$(RB)		14	1.38 ± 0.04
	5	$^1O_2$(Fl)		14	1.36 ± 0.03
	6	$^1O_2$(EY)		14	1.41 ± 0.01
	7			−52	1.44 ± 0.05
	8		CH_3OH–NaOH§	−52	1.30 ± 0.00
	9	H_2O_2–NaOCl	CH_3OH–H_2O	0	1.47 ± 0.01
	10	$(C_6H_5O)_3P\cdot O_3$	CH_2Cl_2	−28	1.45 ± 0.01
	11			−70	1.60 ± 0.04
	12			−70	1.65 ± 0.02
1*c*	13	$^1O_2$(MB)	CH_3OH	14	1.32 ± 0.03
	14			14	1.42 ± 0.05
	15			−52	1.53 ± 0.07
	16	$^1O_2$(RB)		14	1.37 ± 0.07
	17	$^1O_2$(Fl)		14	1.34 ± 0.06
	18	$^1O_2$(EY)		14	1.28 ± 0.06
	19			−52	1.46 ± 0.05
	20	$(C_6H_5O)_3P\cdot O_3$	CH_2Cl_2	−28	1.27 ± 0.00
	21			−70	1.31 ± 0.03
	22			−70	1.28 ± 0.05

*Alkene concentrations 0.045 *M* except in runs 1, 8–13, and 20–22. Runs 1, 8–10, 13, and 20 were preparative runs beginning with higher concentrations of alkene: 0.44 *M* in runs 1 and 13, 0.089 *M* in run 8, 0.2 *M* in run 9, and 0.1 *M* in runs 10 and 20. Runs 11, 12, 21, and 22 were made with 0.2 *M* olefin.

†MB = Methylene Blue, RB = Rose Bengal, Fl = Fluorescein, EY = Eosin-Y.

‡Determined by n.m.r. k_H/k_D = **7***c*/**7***b* in oxidation of **1***b* and **7***d*/**7***e* in oxidation of **1***c*. The latter ratio is corrected to 100% isotopic purity as indicated in Table 1. Errors are average errors obtained from at least three integrations per run.

§0.83 *N* NaOH.

a possible direct reaction between the alkene **1***a* and the ozonide, the alkenes **1***b* and *c* were allowed to react with the triphenyl phosphite ozonide at −28° in dichloromethane and the products isolated. The isotope effect in each case is not significantly different from those observed in the oxidations of these alkenes by singlet oxygen generated by unambiguous routes. The oxidations with triphenyl phosphite ozonide were repeated[8] at −70° after it was shown that there is a direct reaction between the ozonide and **1***a* at this temperature which produces **7***a* (24). The reactions were carried out in duplicate with each alkene at the same time. The difference in isotope effects between the two alkenes is somewhat larger in the reactions at −70° than it is at −28° and we feel that at −70° this difference is greater than the probable experimental error of about 8%.

Intermolecular Deuterium Isotope Effects in the Singlet Oxygen Oxidation of cis- and trans-1,2-Dimethylstilbene

The intramolecular isotope effects in the singlet oxygen oxidation of **1***b* and *c* are quite small. This is not unexpected in view of the high reactivity of **1***a* toward singlet oxygen (16, 25). The energy of activation for the reaction between singlet oxygen and **1***a* is reported to be 0.5 kcal/mol (25*c*). A brief study was made to determine whether the magnitude of the isotope effect would be greater in the oxidation of a less reactive alkene than it is in the oxidation of **1***b* and *c*. The dimethylstilbenes, *cis*- and *trans*-**2***a*, were chosen as substrates for this study as they are readily prepared and were expected to be less reactive toward singlet oxygen than is **1***a*. This expectation was substantiated qualitatively by finding that the methylene blue photosensitized oxidation of 0.014 mol of *cis*-**2**, the more reactive of the two isomers, required 2 h while the oxidation, under identical conditions, of

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[8] We thank Dr. J.-Y. Ding for performing these experiments.

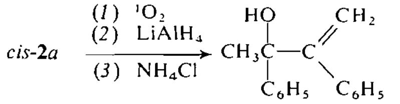
TABLE 5. Isotope effects in the singlet oxygen oxidation of *cis*- and *trans*-1,2-dimethylstilbene in methanol at 14°

Isomer	Sensitizer*	% Reaction†	Ratio 2*a*/2*b* Initial	Ratio 2*a*/2*b* Final	k_H/k_D‡
cis	MB	73	1.05	0.97	1.07
	EY	69	1.05	0.95	1.09
trans	MB	49	1.10	1.02	1.13

*MB = Methylene Blue, EY = Eosin-Y.
†Of undeuterated starting material.
‡Calculated by the method of ref. 27.

0.012 mol of **1***a*, required 45 min. After reduction of the intermediate hydroperoxide a 48% yield of 2,3-diphenyl-3-butene-2-ol (**10**) was isolated from the oxidation of *cis*-**2***a*, eq. 7.

[7]



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In a competitive oxidation (25*a*) it was found that *cis*-**2***a* was about 10 times as reactive as *trans*-**2***a* toward singlet oxygen, in agreement with a previous report that *cis*-**2***a* is more reactive than *trans*-**2***a* (26).

The intermolecular isotope effects in the singlet oxygen oxidations were determined by oxidizing mixtures of *cis*-**2***a* and *cis*-**2***b* and of *trans*-**2***a* and *trans*-**2***b* to partial completion in methanol. The unreacted alkenes were isolated by column chromatography. The composition of the initial and final mixtures of alkenes was determined by mass spectrometry using an ionizing voltage of 9.5 eV. The mass spectrometric analysis of weighed mixtures of *cis*-**2***a* and *b* and of *trans*-**2***a* and *b* reproduced the synthetic ratios to within 2% so it is felt that the isotope effects determined in this way should be accurate to within about 10% or less. The isotope effects, Table 5, are even smaller than those obtained in the singlet oxygen oxidations of **1***b* and *c*. Also, they are the same for both *cis*- and *trans*-**2***a* even though *trans*-**2***a* is less reactive than *cis*-**2***a* toward singlet oxygen.

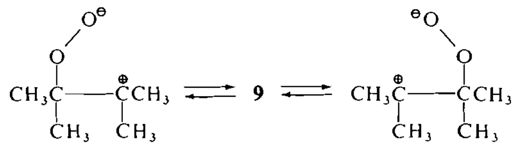
Discussion

Conversion of **3** *to* **7**

The product distribution observed in the conversion of the mixture of **3***b* + *c* to **7***b* + *c* indicates that migration of the hydroperoxy group occurs in the reaction. This migration cannot occur by fragmentation to singlet oxygen and alkene followed by recombination, eq. 5, or by way of tetramethyl-1,2-dioxetane (5). This appears to leave, as a result of this process of elimination, formation and subsequent reorganization of the perepoxide **9** as the pathway for migration of the hydroperoxy group. The perepoxide **9** must be a short-lived species, at least in the reaction medium used, as attempts to detect it by n.m.r. spectroscopy at temperatures as low as −37° gave no evidence for its existence. Attempts to trap **9** with azide ion also failed. Under the reaction conditions used **9** could be converted to **7** either by an intramolecular reorganization or by reaction with base.

Although the intermediate under discussion has been formulated as a perepoxide the migration of the hydroperoxy group in the present system can also be formulated as proceeding by way of a pair of rapidly interconverting open chain zwitterions, eq. 8, in which case the

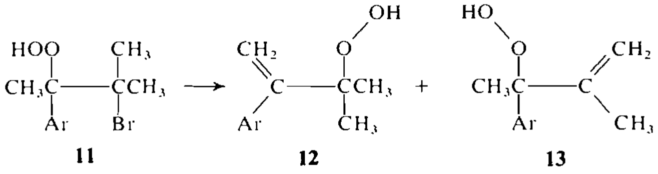
[8]



perepoxide would represent a transition state or an intermediate between the two zwitterions.

Evidence that such open chain zwitterions do not play a role in the conversion of bromohydroperoxides to allylic hydroperoxides comes from the reaction between base in methanol and 3-bromo-3-methyl-2-(4-methoxyphenyl)-2-butyl hydroperoxide (**11**), eq. 9, in which migration of the hydroperoxy group also clearly occurs. A mixture of the allylic hydroperoxides **12** and **13** is formed in a 6.3:1 ratio (2*b*). One would

[9]



Ar = 4-Methoxyphenyl

expect such a great difference in the stabilities of the two possible open chain zwitterions that might be derived from **11** that **12** should be the exclusive product. A perepoxide intermediate might be more likely to lead to the observed product distribution.

The perepoxides derived from **3** and **11** must form allylic hydroperoxides by a process with a very low activation energy and which may be concerted. This would account for the relatively small magnitude of the isotope effect observed in the conversion of **3** to **7** and the perhaps smaller than expected ratio of **12**:**13** formed from **11**. If the perepoxides rearranged in an intramolecular, concerted reaction the carbon, hydrogen, and oxygen atoms involved in the hydrogen transfer could not be colinear. This would also result in the formation of products with little discrimination as discussed below for the singlet oxygen reactions. In fact, if the perepoxide reaction is concerted the transition state geometry for this reaction must resemble quite closely that of the singlet oxygen reaction.

Until recently there appeared to be no authentic examples of compounds which had structures and which gave reactions analogous to those of **9**. Now, two classes of such "strained dipolar species" have been characterized definitively: the episulfoxides (28) and the aziridine *N*-oxides (29). When suitably substituted these materials rearrange thermally at relatively low temperatures to give allylic sulfenic acids and allylic hydroxylamines, respectively. Further, aziridine *N*-oxides do not rearrange to the four-membered ring compounds, 1,2-oxazetidines (29). In these respects the behavior of the proposed intermediate **9** parallels that of the above materials very closely.

It is possible to compare the neighboring group effect of the hydroperoxy anion with that of the oxide ion in the 2,3-dimethyl-3-bromo-2-butyl system. Because the bromohydroperoxide 3*a* is stable in neutral methanol for several days, at least, the perepoxide **9** must be formed from the conjugate base of 3*a*. Since no evidence was obtained for the formation of any of the dioxetane **8**, cyclization by the neighboring hydroperoxy anion with participation of the disubstituted oxygen to give **9** is at least 50 times faster than is cyclization with participation of the anionic oxygen to give **8**. This is the reverse of what occurs in the reactions between base and 3-bromo-2-methyl-2-butyl hydroperoxide (5) and 1-chloro-2-methyl-2-propyl hydroperoxide (30) in which only 1,2-dioxetanes are formed initially. Apparently, in a system such as 3*a* where a tertiary halide is to be displaced by the hydroperoxy anion, only a small amount of nucleophilic assistance is required so that the inherently more favorable cyclization to form a three-membered ring can compete effectively with the cyclization to form a four-membered ring. Even so, the disubstituted oxygen atom of the hydroperoxy anion is a much less effective neighboring group than is the oxide ion in the present system. From the observation, that in the reaction between base and samples of 3*a* which were contaminated with bromohydrin, epoxide formation was essentially complete by the time 50% of 3*a* had been consumed together with the estimate that the pK_a's of 3*a* ($pK_a \approx 13$ (31)) and the corresponding bromohydrin ($pK_a \approx 18$ (32)) differ by about five pK_a units, it can be reckoned that cyclization of oxide ion to epoxide is 10^4–10^6 times as fast as cyclization of hydroperoxy anion to **9**.

Mechanism of Singlet Oxygen Oxidation

Three mechanisms have been proposed for the oxygenation of alkenes to allylic hydroperoxides by singlet oxygen: (*1*) formation and subsequent reorganization of a perepoxide intermediate which was initially proposed to account for the large rate enhancement caused by increasing substitution of the double bond by alkyl groups (25*a*, 33); (*2*) formation and subsequent reorganization of a 1,2-dioxetane which was proposed when cleavage products were observed in photooxygenation of indene (34); (*3*) a concerted reaction in which the C—O and C—H bonds are formed simultaneously in a cyclic transition state. This latter mechanism was proposed to explain the geometric requirements of the photooxygenation reactions in steroids (35) and the lack of solvent and substituent effects on product distribution (3*a*, 3*b*, 36). Intervention of 1,2-dioxetanes as intermediates in the conversion of alkenes to allylic hydroperoxides by singlet oxygen can be disregarded as a general phenomenon as it has been shown that trimethyl- and tetramethyl-1,2-dioxetane are not converted to allylic hydroperoxides even when treated with base (5). The results of the present study certainly provide no evidence against a concerted mechanism and provide strong evidence that perepoxides are not formed in this reaction.

The perepoxide mechanism had appeared to receive experimental support when it was reported that photooxygenation of **1***a* and of 1,2-dimethylcyclohexene in the presence of azide ion resulted in the formation of high yields of hydroperoxy azides (37). It was suggested that azide ion trapped perepoxides formed by reaction of singlet oxygen with these alkenes. It has now been shown (38) that the formation of hydroperoxy azides is a radical reaction which has nothing to do with the allylic oxygenation reaction. Furthermore, the present work shows that the perepoxide derived from **7***a* cannot be trapped by azide ion anyway under reaction conditions similar to those which gave hydroperoxy azides from **1***a* (37).

Evidence has existed for some time that supports strongly a concerted mechanism for the singlet oxygen oxygenation of alkenes. It is difficult to explain the conformational requirements of the allylic hydrogen which is to be removed by singlet oxygen (35) and the complete lack of reactivity of norbornene, methylenecyclopentene, and methylenecyclohexane towards singlet oxygen (39) in terms of either a dioxetane or a perepoxide mechanism without invoking an extremely unlikely reversible formation of these species. Such arguments have been made already (22).[9]

The magnitudes of the deuterium isotope effect in the photooxygenation of **1***b* and *c* and of **2***a* and *b* might appear to be rather small for a reaction in which a C—H or a C—D bond is broken in the rate determining step. There can be several reasons for this small isotope effect. The reaction has a very small energy of activation so that a large isotope effect is not to be expected. In the transition state for the concerted reaction, it is unlikely that the oxygen, hydrogen, and carbon atoms involved in the hydrogen transfer are colinear. It has been pointed out that in such a situation the isotope effect should be smaller than for a process in which all these atoms can be colinear (41). Finally, it is theoretically possible to have small and even inverse isotope effects for reactions in which hydrogen is transferred from carbon to oxygen (42).

Oxygenation by Triphenyl Phosphite Ozonide

The isotope effects observed on oxygenation of **1***b* and *c* by triphenyl phosphite ozonide at −70° in methylene chloride are quite similar to those observed on oxygenation of **1***b* and *c* by singlet oxygen at −52° in methanol which indicates that a perepoxide intermediate cannot be involved. Also, it has been shown that singlet oxygen does not intervene in the triphenyl phosphite ozonide oxygenation at low temperatures (24) so that still another mechanism is required for oxygenation by this reagent. This reaction gives a higher proportion of the product of C—H bond breaking with **1***b* than with **1***c* which suggests the formation of a transition state or intermediate in which the oxygen is bonded more strongly to the carbon bearing the CD_3 groups of **1***b* than to the other carbon atom than is the case in the singlet oxygen reaction. The difference in isotope effects between **1***b* and *c* is quite small, however, and may not be outside experimental error although it is reproducible.

It is remarkable that there are so many different routes for the conversion of **1***a* to **7***a*.

Experimental

General

Boiling points and melting points are uncorrected. The latter were taken on a Gallenkamp melting point apparatus. I.r. spectra were taken on Perkin–Elmer Model 421 and 337 spectrophotometers and only characteristic absorption bands are cited. Refractive indices were measured on a Bausch and Lomb Abbe-34 refractometer. N.m.r. spectra were determined in carbon tetrachloride and with tetra-

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[9] The argument made against a perepoxide intermediate in terms of *syn* and *anti* isomers (22) probably is not valid. These would undoubtedly interconvert rapidly by inversion about the tricoordinated oxygen atom (40).

methylsilane as internal standard, unless otherwise noted, using Varian analytical spectrometers Models A-60 and HR-100. Abbreviations used in reporting the n.m.r. spectra are b, broad; s, singlet; d, doublet; m, multiplet. Gas chromatography was carried out on an Aerograph A-90-P3 gas chromatograph using a 5 ft × 1/4 in. stainless steel column packed with 20% SF-96 on 60/80 Chromosorb P. Mass spectra were obtained on an A.E.I. MS-2-H mass spectrometer. Organic extracts were dried with magnesium sulfate unless otherwise indicated. Elemental analyses were performed by Mrs. Darlene Mahlow of this Department.

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

Materials

Deuterium oxide (99.8 atom %D) and acetone-d_6 (99.5 atom %D) were obtained from Merck, Sharp & Dohme of Canada, Ltd.

Deuteriosulfuric acid was prepared by the addition of anhydrous sulfur trioxide to deuterium oxide.

Trideuterioiodomethane (96.5 atom %D) was prepared by pyrolysis of perdeuteriotrimethyloxosulfonium iodide obtained by isotopic exchange of the undeuterated salt with deuterium oxide (43).

Perdeuterioacetone Cyanohydrin (3,3,3-Trideuterio-2-trideuteriomethyl-2-hydroxypropanenitrile)

The synthesis was patterned after the procedure used for the preparation of acetone cyanohydrin (44). A solution of 28 ml deuteriosulfuric acid in 79 ml of deuterium oxide was added to a cooled (ice-bath) solution of 25 g (0.39 mol) of acetone-d_6 and 22 g (0.45 mol) sodium cyanide in 48 ml deuterium oxide at such a rate as to keep the temperature of the reaction mixture below 15°. The solution was stirred for 15 min after the addition was complete and then continuously extracted with ether for 36 h. The dried ether extract was freed of solvent and the residue distilled to give 32 g (93%) of product, b.p. 78–80° (17 mm), n_D^{25} 1.3966 (lit. (44) for acetone cyanohydrin, b.p. 78–82° (15 mm), n_D^{19} 1.4002); i.r. ($CHCl_3$): 2400 to 2700, 2250 cm^{-1}; n.m.r. (neat) no absorption from τ 0–10.

Methyl 3,3,3-Trideuterio-2-trideuteriomethyl-2-hydroxyproponoate

Perdeuterioacetone cyanohydrin was hydrolyzed using a modification of the procedure for the hydrolysis of a related cyanohydrin (45). A solution of 32.5 g (0.35 mol) of the cyanohydrin and 35 ml concentrated hydrochloric acid in 14 ml water was heated at 95° for 2 h. Sodium sulfate, 12 g, was then added and the mixture cooled to − 15°. The resulting mixture was filtered and both the precipitate and the filtrate were extracted continuously with ether for 2 days. The extracts were combined, dried, and a small sample of 3,3,3-trideuterio-2-trideuteriomethyl-2-hydroxypropanoic acid, m.p. 75–76° (lit. (46) for 2-methyl-2-hydroxypropanoic acid, m.p. 79°), was isolated from a portion of the extracts; i.r. ($CHCl_3$): 2500 to 3600, 2230, 1730 cm^{-1}; n.m.r. ($CDCl_3$): τ 3.24 (s).

The remainder of the extracts was treated with 0.4 mol diazomethane in ether at 0°. Excess diazomethane was destroyed by addition of acetic acid in small portions. Removal of solvent and distillation of the residual oil gave 33.0 g (74%) of product, b.p. 133–134° (710 mm), n_D^{25} 1.4069 (lit. (47) for methyl 2-methyl-2-hydroxypropanoate, b.p. 137–139° (760 mm), $n_D^{19.3}$ 1.4112); i.r. ($CHCl_3$): 3250 to 3600, 2230, 2210, 1745 cm^{-1}; n.m.r. τ 6.31 (s, 3.10H), 6.67 (s, 1.0H).

3-Methyl-1,1,1-trideuterio-2-trideuteriomethyl-2,3-butanediol

A solution of 33 g (0.27 mol) of the above ester in 150 ml ether was added to a solution of methylmagnesium iodide prepared from 26.4 g (1.1 mol) magnesium and 200 g (1.45 mol) iodomethane in 1 l ether. The reaction mixture was stirred 4 h after the addition was complete and then poured into a mixture of ice and 1.1 mol hydrochloric acid. The ether layer was separated and the aqueous layer continuously extracted with ether for 2 days. The combined ether extracts were dried thoroughly, first with magnesium sulfate, then with molecular sieves (4 A) and finally poured through a column (4 × 20 cm) of molecular sieves. The solution was concentrated and the residue distilled to give 20 g (88%) of colorless oil, b.p. 164–167° (710 mm) (lit. (48) for pinacol, b.p. 172°); n.m.r.: τ 7.23 (s, 2.0H), 8.82 (s, 6.10H).

1,1,1-Trideuterio-2-trideuteriomethyl-3-methyl-2-butene (1b)

The procedure (10) for the preparation of 2,3-dimethyl-2-butene was adapted. This reaction gave a poor yield of product if the pinacol was not dried thoroughly as described. The above deuterated pinacol, 27.0 g (0.218 mol) was heated with 32.2 g (0.218 mol) of freshly distilled ethyl orthoformate under a 10 cm Vigreux column for 10 h after which the slow distillation of ethanol ceased. Two drops of acetic acid were added and the mixture was heated at 175° until no more product distilled (8 h) into the ice-cooled receiver. The product was redistilled to give 10.9 g (54%) of an oil, b.p. 69.5–70.5° (710 mm) (lit. (49) for 2,3-dimethyl-2-butene, b.p. 73°); i.r. (CCl_4): 2250, 2180, 2060 cm^{-1}; n.m.r.: τ 8.40 (s). Mass spectral analysis (12) at 12 eV, mol % d_n: 0.51 d_3, 0.10 d_4, 2.5 d_5, 96.88 d_6. The mass spectrum taken at 70 eV had the following peaks in the $M^{\oplus} - CX_3$ (X = D or H) region, *m/e* (% relative intensity): 69 (2), 70 (5), 71 (6), 72 (100), 73 (11), 74 (6), 75 (93), 76 (5).

2,3-Bis(trideuteriomethyl)-2,3-butanediol

A solution of 28 g (0.33 mol) dry, freshly distilled 2,3-butanedione in 200 ml ether was added at a rate to maintain mild reflux to a solution of trideuteriomethyl magnesium iodide prepared from 120 g (0.83 mol) trideuterioiodomethane and 18 g (0.75 mol) magnesium in 1500 ml ether contained in a Morton flask. High speed stirring was used during the addition and for 8 h afterwards. Work-up and drying of the product was carried out as described above for the preparation of the other deuterated pinacol to give 34 g (79%) of product, b.p. 163–168° (710 mm); n.m.r.: τ 6.49 (s, 2.0H), τ 8.78 (s, 6.1H).

In exploratory runs using undeuterated materials the yield of pinacol was found to be 30% or less when ordinary stirring was used in the Grignard reaction.

2,3-Bis(trideuteriomethyl)-2,3-dimethyl-2-butene (1c)

This reaction was carried out as described for the preparation of **1***b*. From 34 g (0.28 mol) of the above pinacol and 41 g (0.28 mol) ethyl orthoformate 14 g (56%) of product was obtained, b.p. 69–70.5° (710 mm); i.r. (CCl_4): 2235, 2180, 2130, 2060 cm^{-1}; n.m.r.: τ 8.41 (s). Mass spectral analysis (12) at 9.5 eV, mol % d_n: 0.31 d_2, 0.77 d_3, 3.09 d_4, 18.4 d_5, 77.43 d_6. The mass spectrum taken at 70 eV had the following peaks in the $M^+ - CX_3$ (X = D or H) region, m/e (% relative intensity): 67 (2), 68 (2), 69 (4), 70 (9), 71 (16), 72 (100), 73 (11), 74 (22), 75 (79), 76 (3).

*cis- and trans-1,2-Bis(trideuteriomethyl)-stilbene (cis- and trans-**2b**)*

The adsorbed water on 300 g basic alumina was replaced by deuterium oxide with a series of exchanges (50) which involved heating the alumina to 200° under 1 mm pressure followed by cooling and shaking the alumina with 18 g deuterium oxide. This process was repeated until the moisture collected on heating the alumina contained 0.4% protium (four exchanges). The resulting alumina was placed into two long (5 ft × 17 mm) chromatography columns and a solution of 30 g acetophenone in pentane was passed through the columns. The methyl group of the recovered acetophenone was 93% deuterated as determined by n.m.r. spectroscopy. Treatment of this material with lithium aluminum hydride in ether and hydrolysis of the reaction mixture gave 2,2,2-trideuterio-1-phenylethanol in 91% yield, b.p. 97–98° (18 mm), n_D^{25} 1.5245 (lit. (51) for 1-phenylethanol, b.p. 103–104° (20 mm), n_D^{25} 1.5251). This product was treated with a 5% excess of thionyl chloride in benzene to give 2,2,2-trideuterio-1-chloro-1-phenylethane in 90% yield, b.p. 76–77° (13 mm), n_D^{25} 1.5235 (lit. (52) for 1-chloro-1-phenylethane, b.p. 75° (14 mm), n_D^{19} 1.5275), and then converted to the deuterated 1,2-dimethylstilbenes, *cis*- and *trans*-**2b**, with sodium amide using the procedure described (53) for the preparation of the undeuterated analogs. The products were fractionally crystallized from methanol. Samples of both isomers were obtained in pure form as determined by g.c. and n.m.r. spectroscopy, *cis*-**2b**, m.p. 63–64°, *trans*-**2b**, m.p. 103–104° (lit. (53) for *cis*-**2a**, m.p. 65–66°, *trans*-**2a**, m.p. 105–106°); i.r. (CCl_4): *cis*-**2b**, 2230, 2210, 2115, 2060 cm^{-1}, *trans*-**2b**, 2230, 2210, 2110, 2060 cm^{-1}; n.m.r.: *cis*-**2b**, τ 3.09 (s), *trans*-**2b**, τ 2.50 (s); mass spectral analysis (12) at 9.5 eV, mol % d_n: *cis*-**2b**, 0.17 d_0, 0.14 d_1, 0.09 d_2, 0.90 d_3, 6.45 d_4, 30.68 d_5, 61.60 d_6; *trans*-**2b**, 0.07 d_0, 0.03 d_1, 0.09 d_2, 0.90 d_3, 6.65 d_4, 30.80 d_5, 61.47 d_6.

*2,3-Diphenyl-1-butene-3-ol, (**10**)*

A solution of 3 g (0.013 mol) of *cis*-**2a** (53) in 30 ml methanol was photooxidized at 14° using methylene blue as sensitizer in the apparatus previously described (1). Oxygen uptake became very slow after 2 h when 350 ml (112%) had been consumed. The solution was poured into 100 ml ice-water and the resulting mixture extracted twice with 50 ml ether. The combined extracts were washed with water and with saturated aqueous sodium chloride solution. After drying, the ether solution was added to a stirred slurry of 0.5 g lithium aluminum hydride in 25 ml ether. The mixture was heated under reflux for 30 min and then hydrolyzed with 15% potassium hydroxide. The precipitate was stirred several times with ether and the combined ether solutions dried and concentrated. The residue was distilled to give 1.5 g (48%) of a colorless oil, b.p. 101–104° (0.1 mm), n_D^{25} 1.5809; i.r. ($CHCl_3$): 3560, 3300–3500, 3060, 1640, 905 cm^{-1}; n.m.r.: τ 2.5–3.2 (m, 10.4H), 4.55 (d, J = 1.5 Hz, 0.94H), 4.82 (d, J = 1.5 Hz, 1.01H), 8.05 (s, 0.90H), 8.40 (s, 2.80H).

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.67; H, 7.19. Found: C, 85.63; H, 7.00.

*3-Bromo-2,3-bis(trideuteriomethyl)-2-butyl Hydroperoxide (**3d**)*

This material was prepared from the corresponding deuterated alkene **1c**, 98% hydrogen peroxide, and 1,3-dibromo-5,5-dimethylhydantoin according to the procedure described for the preparation of 3-bromo-2,3-dimethyl-2-butyl hydroperoxide (**3a**) (1), m.p. 90–92° (lit. (1) for **3a**, m.p. 93–94°); i.r. (CCl_4): 3550, 3200–3500, 2250 and 2160 cm^{-1}; n.m.r.: τ 2.4 (bs, 0.90H), 8.20 (s, 3.0H), 8.57 (s, 3.0H). Iodometric titration indicated that **3d** contained 97.0% of the theoretical amount of active oxygen.

*3-Bromo-4,4,4-trideuterio-3-trideuteriomethyl-2-methyl-2-butyl Hydroperoxide (**3b**) and 3-Bromo-1,1,1-trideuterio-2-trideuteriomethyl-3-methyl-2-butyl Hydroperoxide (**3c**)*

A mixture of **3b** and **c** was prepared from the corresponding alkene **1b** by the procedure described for the preparation of **1a** (1), m.p. 91–93°; i.r. (CCl_4): 3550, 3200–3500, 2240, 2130 cm^{-1}; n.m.r.: τ 2.1 (bs), 8.20 (s), 8.53 (s). The ratio of the areas of the latter signals was 1:1.60 as determined by careful integration. From four integrations the average ratio of the areas of the corresponding signals in the spectrum of the undeuterated compound **1a** was 1.00 ± 0.02. Iodometric titration indicated that the mixture of **3b** and **c** contained 97.4% of the theoretical amount of active oxygen.

*2-Bromo-2,3-dimethyl-3-methoxybutane (**6**)*

To a stirred solution of 5 g (0.06 mol) **1a** and 9.6 g (0.3 mol) of methanol in 50 ml ether at −40° was added 8.1 g (0.03 mol) of 1,3-dibromo-5,5-dimethylhydantoin in small portions over 10 min. The resulting mixture was allowed to warm to 23° and then was shaken four times with 50 ml water. The organic layer was dried and concentrated and the residue distilled to give 9.2 g (79%) of colorless oil, b.p. 75–77° (15 mm), which crystallized on standing. The solid was recrystallized from methanol to give 7.3 g white needles, m.p. 71–73°; n.m.r.: τ 6.70 (s, 3.0H), 8.26 (s, 6.0H), and 8.67 (s, 6.1H).

*Material Balance and Rate of Reaction Between Base and **1a***

Material Balance

A methanol solution 0.39 M in **1a** and 0.25 M in benzene was made up and the areas of the n.m.r. signals due to benzene and to the methyl groups of **1a** were carefully measured. Three n.m.r. tubes were prepared at −70° with one part of this solution and two parts of a 1.22 M solution of sodium hydroxide in methanol. The tubes were sealed and individual tubes were warmed to −19, 2, and 25°. After standing for 28 h, long enough for complete reaction to occur at −19°, the areas of the n.m.r. signals due to benzene and to the methyl groups of the product allylic hydroperoxide **7a** were carefully measured. The results are given in Table 1.

Reaction Rates

Volumetric solutions of **1a** and tetramethylsilane and of sodium hydroxide in methanol were prepared. Aliquots of these solutions were transferred to n.m.r. tubes at −78° and mixed. The tubes were placed in the temperature controlled probe of the 100 MHz n.m.r. spectrometer. The areas of the signals due to the *gem*-dimethyl group on the carbon bearing the hydroperoxy group of the starting material **1***a*, the *gem*-dimethyl group of product **7***a*, and tetramethylsilane were determined periodically. The apparent second order rate constants for the disappearance of **1***a* were determined from the slopes of plots of $1/(a-b)\ \ln b(a-x)/a(b-x)$ *vs.* time (54) where a and b represent the initial concentrations of hydroxide ion and **1***a*, respectively, and x is the instantaneous concentration of **1***a*. Reactions were followed to *ca.* 60% completion and the plots gave good straight lines. The results are given in Table 3.

Reaction between Deuterated Bromohydroperoxides 3b + c and 3d and Base

To n.m.r. sample tubes at −70° were added 0.15 ml of a solution made from 0.07 g deuterated bromohydroperoxide, 0.018 g benzene, 1.0 ml methanol-d_4, and 0.30 ml of a solution made from 0.038 g sodium, 0.046 g deuterium oxide, and 2.0 ml methanol-d_4. The contents of the tubes were mixed at −70° and then the tubes were placed in an ice bath for 6 h. The relative amounts of the deuterated allylic hydroperoxides were determined by integration of the n.m.r. signals at τ 8.2 (allylic CH_3) and 8.7 (*gem*-CH_3's). The ratio, **7***c*/**7***b*, was obtained by dividing twice the area of the signal at τ 8.2 by the area of the signal at τ 8.7. To account for the fact that the trideuteriomethyl groups of **1***c* were only 95.3% deuterated the ratio, **7***d*/**7***e*, was obtained using the expression

$$\frac{\text{area at } \tau\, 8.7}{\text{area at } \tau\, 8.2} = \frac{3a(100-y) + 0.14a(100-y) + 3ay + 0.14ay}{3a(100-y) + 0.141ay}$$

$$= \frac{314}{2.86y}$$

where a is the area due to one proton and y is the % **3***d* in the product mixture. The results are given in Table 1.

Photosensitized Oxidation of the Deuterated Alkenes 1b and c

The photosensitized oxidation of the alkenes **1***b* and *c* was carried out using the apparatus previously described (1). In preparative reactions, a solution of 1 g (0.01 mol) of the alkene and 15 mg methylene blue in 25 ml methanol was irradiated at 14° until oxygen uptake became very slow (*ca.* 45 min, *ca.* 120% oxygen uptake). The solution was then poured into 100 ml ice-water and the resulting mixture extracted with ether, 3 × 50 ml. The combined ether extracts were dried and concentrated and the residual oil distilled. From **1***b* there was obtained 0.65 g (48%) of a mixture of the deuterated allylic hydroperoxides **7***b* and *c*, b.p. 57–59° (17 mm); n_D^{29} 1.4375 (lit. (1) for **1***a*, b.p. 55° (12 mm); n_D^{20} 1.4428). From the oxidation of **1***c* there was obtained 0.70 g (56%) of a mixture of the deuterated allylic hydroperoxides **7***d* and *e*, b.p. 58–60° (17 mm), n_D^{29} 1.4379.

A series of oxidations with various sensitizers was carried out in the same apparatus using solutions 0.044 *M* in alkene **1***b* or *c*. The solutions were irradiated for 15 min, long enough for complete reaction to occur. For the runs at −52° the solutions were cooled by blowing cold nitrogen gas through the jacket of the apparatus. The temperature of the solution was checked just before and just after irradiation. One oxidation of **1***b* was carried out at −52° in the presence of 0.83 *M* sodium hydroxide. This reaction mixture was kept at −65° for 1.5 h after irradiation and then warmed to 0° over a 2 h period before work-up. After irradiation the reaction mixtures were worked-up as described above, except that the ether extracts were concentrated to a film under reduced pressure. Carbon tetrachloride (2 ml) was then added and the resulting solution was again concentrated to a film under reduced pressure. The residue was taken up in 0.5 ml carbon tetrachloride and the relative amounts of the deuterated allylic hydroperoxides were determined as described for the reaction between the deuterated bromohydroperoxides and base. In the analysis of the product of oxidation of the undeuterated alkene **1***a* carried out in this way, it was found that the ratio of twice the area of the signal at τ 8.2 divided by the area of the signal at τ 8.7 was 1.01 ± 0.03 so no correction was applied to the results obtained from deuterated materials which are given in Table 4.

Oxidation of the Deuterated Alkenes 1b and c with Triphenyl Phosphite Ozonide

A stream of ozone was introduced into a solution of 2.2 g (0.007 mol) of redistilled triphenyl phosphite in 40 ml methylene chloride at −75° until a blue color persisted in the solution. Excess ozone was flushed out with a stream of nitrogen and a solution of 0.6 g (0.006 mol) of deuterated alkene **1***b* or *c* in 5 ml methylene chloride was added. The resulting solution was mixed and then allowed to stand at −28° for 2.5 h. The methylene chloride was removed through a short fractionating column and the residue was distilled to give the corresponding allylic hydroperoxides. From **1***b* there was obtained 0.36 g (49%) of product, b.p. 50–56° (12 mm), n_D^{25} 1.4398, and from **1***c* 0.28 g (40%) of product, b.p. 49–53° (15 mm), n_D^{25} 1.4395. The composition of each mixture was determined as in the photooxidation reactions.

These reactions were repeated later at lower temperatures. One-milliliter solutions 0.4 *M* in triphenyl phosphite ozonide and 0.2 *M* in deuterated alkene, made up as described above, were allowed to stand at −70° for 4 h (24) and then analyzed directly by n.m.r. spectroscopy at 100 MHz. A run with undeuterated alkene **1***a* was made under these conditions and it was found on n.m.r. analysis that twice the area of the signal at τ 8.2 divided by the area of the signal at τ 8.7 was 1.05 ± 0.03. The results shown in Table 4, runs 11, 12, 21, and 22, are corrected for this.

Deuterium Isotope Effects in Photosensitized Oxidation of cis- and trans-1,2-Dimethylstilbene (cis- and trans-2a)

A solution of 0.520 g (2.5 mmol) of *trans*-1,2-dimethylstilbene (*trans*-**2***a*) (53) and 0.534 g (2.5 mmol) of *trans*-1,2-bis-(trideuteriomethyl)-stilbene (*trans*-**2***b*) in 40 ml methanol was prepared. Solvent was removed from an aliquot of this solution and the residue analyzed by mass spectrometry at 9.5 eV. The remainder of the solution, after addition of 15 mg methylene blue, was irradiated at 14° in the apparatus described (1) until 49% of *trans*-**2***a* had been consumed as determined by n.m.r. spectroscopy. The reaction mixture was then worked-up as described for the preparation of 2,3-diphenyl-1-butene-3-ol above. The concentrated residue obtained from the lithium aluminum hydride reduction was absorbed on a 1 cm × 15 cm column of basic alumina. Elution of the column with 50 ml pentane and removal of the pentane from the element left the mixture of unreacted alkenes of which the relative amounts of deuterated and undeuterated materials were determined by analysis (12) of the parent region of the mass spectrum taken at 9.5 eV. There were only traces of ions formed with m/e ratios below those of the parent ions at this voltage. The isotope effect, k_H/k_D, was calculated from the relative amounts of the alkenes remaining (25*b*, 27). The same procedure was used in the oxidation of mixtures of *cis*-**2***a* and *cis*-**2***b*. The results are presented in Table 5.

Relative Rates of Photosensitized Oxidation of cis- and trans-1,2-Dimethylstilbene (cis- and trans-2a)

A solution of 0.253 g *cis*-**2***a*, 0.251 g *trans*-**2***a*, 0.204 g bibenzyl, and 15 mg methylene blue was made up in 40 ml methanol and analyzed by g.c. (165°). Solvent was removed from an aliquot and the residue analyzed by n.m.r. spectroscopy. The methanol solution was irradiated in the apparatus described (1). Aliquots were removed after 25, 30, and 35 min and analyzed by g.c. The hydrocarbons remaining in each aliquot were isolated using the procedure described in the intermolecular isotope effect experiments, above, and their relative amounts also determined by n.m.r. spectroscopy. The relative rates of oxidations, k_{cis}/k_{trans}, were calculated from the relative amounts of materials remaining (25*b*, 27), and were determined at 25, 30, and 35 min to be 9, 11, and 13 by g.c. analysis and 6, 7, and 8 by n.m.r. spectroscopic analysis.

Reaction between 2,3-Dimethyl-3-bromo-2-butyl Hydroperoxide (3a) and Base in the Presence of Azide Ion

To a heterogeneous mixture of 9.5 mg (0.24 mequiv) of sodium hydroxide and 35.7 mg (0.55 mequiv) of sodium azide in 1.0 ml of 40:60 water–methanol-d_3 solution at 0° was added 25 mg (0.13 mmol) of **3***a*. The resulting mixture was allowed to stand at 0° for 6 h with occasional shaking and then filtered. The n.m.r. spectrum of the filtrate was identical to that from a reaction carried out under identical conditions in the absence of sodium azide. There was no evidence for the formation from **3***a* of any material in addition to the allylic hydroperoxide **7***a*.

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