spinning-band column. A center fraction was collected for use, bp 60° (1 mm), $n^{25}\mathrm{D}$ 1.5211. *p*-Nitrophenylacetonitrile was recrystallized from a mixture of alcohol and water, mp 116–117°. *p*-Nitrocumene was prepared by the mixed acid nitration of freshly distilled cumene.[28] The compound was distilled through a 30-in. spinning-band column at a reflux ratio of 15:1. The fraction with bp 132° (13 mm), $n^{25}\mathrm{D}$ 1.5363, was collected and stored under nitrogen until used [lit.[29] bp 134° (13 mm), $n^{20}\mathrm{D}$ 1.5369]. 2,4-Dinitrocumene was prepared by the mixed acid nitration of pure cumene at 80° according to the method of Hansch and Helmkamp.[30] After a preliminary distillation the material was carefully fractionated under vacuum through a 30-in. spinning-band column at a reflux ratio of 15:1. Physical constants were bp 134–136° (0.5 mm), $n^{20}\mathrm{D}$ 1.5548 [lit.[31] bp 169–171° (11 mm), $n^{25}\mathrm{D}$ 1.5523]. 2,4-Dinitrotoluene (Eastman Kodak Co., pure grade) was used as received. *meso*-2,3-Diphenylbutane was prepared by the method of Conant and Blatt[32] by treatment of the Grignard reagent from α-phenethyl bromide with anhydrous cuprous chloride. The solid *meso* isomer obtained in 20% yield was recrystallized from ethanol, mp 126–127°. This compound was nitrated with nitric acid in acetic anhydride to yield *meso*-2,3-bis(*p*-nitrophenyl)butane,[33] mp 254–256° (recrystallized from acetic acid). *p*-Nitroethylbenzene was prepared by the mixed acid nitration of ethylbenzene.[28] After vacuum distillation through a spinning-band column the fraction of bp 125–125.4° (13 mm), $n^{20}\mathrm{D}$ 1.5458, was collected and stored under nitrogen until used [lit.[25] bp 126° (13 mm), $n^{20}\mathrm{D}$ 1.5459]. *p*-Nitrodiphenylmethane was prepared by the condensation of *p*-nitrobenzyl alcohol with benzene in the presence of sufuric acid.[34] The compound was recrystallized from ethanol, mp 31–32°. Bis(*p*-nitrophenyl)methane was prepared by the method of Parkes and Morley.[35] After several recrystallizations from acetic acid, pale orange needles were obtained, mp 186–187°. Bis(2,4-dinitrophenyl)methane was prepared by the nitration of diphenylmethane yielding yellow platelets from acetic acid, mp 173.5–175°, using potassium nitrate as the nitrating agent.[36] Mono-*p*-nitrotriphenylmethane was prepared as described by Curtin and Kauer,[37] mp 92–93° (recrystallized from hexane). Tris-*p*-nitrophenylmethane was prepared by the mixed-acid nitration of triphenylmethane at 0°.[38] The compound was recrystallized from a mixture of chloroform and ether, mp 212.5–214°. 2,4,6-Trinitrotoluene (Eastman Kodak Co., practical grade) was recrystallized five times from ethanol, mp 81–81.7°. *sym*-Trinitrobenzene (Eastman Kodak Co., pure grade) was recrystallized from acetic acid, mp 122–123°.

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[28] K. L. Nelson and H. C. Brown, *J. Am. Chem. Soc.*, **73**, 5605 (1951).

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Thermal Decomposition of *t*-Butylperoxy 6-Bromohexanoate. Lack of Evidence for Radical Displacement on Carbon and 1,5-Bridged Bromine Radicals[1a]

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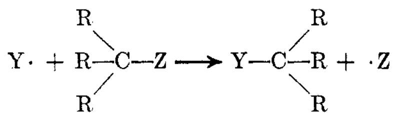
The products and rates of the thermal decomposition of *t*-butylperoxy 6-bromohexanoate (**2**) and *t*-butylperoxy hexanoate (**3**) in various solvents and the gas phase were studied. Cyclopentane was not produced under any conditions, which means that the 5-bromopentyl radical (**1**) does not undergo an intramolecular radical displacement reaction on carbon. Since the main products of the bromo per ester and the unsubstituted per ester are very similar, there is no evidence that the 5-bromopentyl radical forms a 1,5-bridged bromine radical (**4**). The similar rates of decomposition of the two per esters are also consistent with no 1,5-bromine participation.

A type of radical reaction that has been observed in only a few special cases is radical displacement on carbon as illustrated by eq 1. Ogg and Polanyi[2] called



$$\mathrm{Y\cdot + R_3C{-}Z \longrightarrow Y{-}CR_3 + \cdot Z} \qquad (1)$$

this bimolecular homolytic substitution reaction an "SH2" reaction. The similarities between SH2 and SN2 reactions are obvious.

Early attempts to characterize the SH2 reaction by studying the racemization of optically active *sec*-butyl iodide in the presence of iodine were unsuccessful.[2,3] The study merely pointed out the enormous difficulties one encounters with free-radical reactions of this type.[3b]

Opening of cyclopropane rings by free-radical processes has been presented as an example of a homolytic displacement reaction.[4] However, because of the considerable "unsaturated" character of the cyclopropane ring,[5] the evidence obtained could be interpreted as the addition of a free radical into the cyclopropane ring followed by ring opening. Even if radical displacement on carbon is occurring, the carbon is part of a strained system and is consequently a special type of carbon.

Applequist has recently presented evidence for a radical substitution reaction on carbon by demonstrating the free-radical nature of the bromination of 9,10-dehydrodianthracene.[6] Again, the radical displacement is on a special type of carbon that is involved in a highly strained ring system. Friswell and Gowenlock have recently reported that the heptyl radical cyclizes to form cyclohexane by the displacement of a methyl radical.[7] However, the identity of cyclohexane was based on gas–liquid partition chromatography (glpc)

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[1] (a) Based on work by M. P. Doyle in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Iowa State University; (b) U. S. Public Health Service Fellow, 1966.

[2] R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 482 (1935).

[3] (a) R. A. Herrmann and R. M. Noyes, *J. Am. Chem. Soc.*, **78**, 5764 (1956); (b) R. M. Noyes, M. W. T. Pratt, and J. E. Bujake, Jr., *ibid.*, **83**, 1547 (1961); (c) S. W. Benson, *J. Chem. Phys.*, **38**, 1945 (1963).

[4] (a) R. A. Ogg, Jr., and W. J. Priest, *ibid.*, **7**, 736 (1939); (b) S. W. Benson, *ibid.*, **34**, 521 (1961); (c) M. S. Kharasch, M. Z. Fineman, and F. R. Mayo, *J. Am. Chem. Soc.*, **61**, 2139 (1939); (d) J. D. Roberts and P. H. Dirstine, *ibid.*, **83**, 1281 (1960); (e) D. E. Applequist, G. F. Fanta, and B. K. Henrikson, *ibid.*, **82**, 2368 (1960).

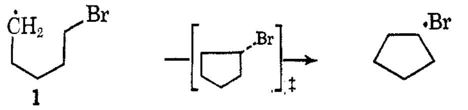
[5] C. Walling and P. S. Fredricks, *ibid.*, **84**, 3326 (1962).

[6] D. E. Applequist and R. Searle, *ibid.*, **86**, 1389 (1964).

[7] N. J. Friswell and B. G. Gowenlock, *Chem. Commun.* (London), 277 (1965).

retention times only and no yield was reported. Moreover, the heptyl radical was generated by treating heptyl bromide with sodium vapor at 300°; these severe reaction conditions could produce small amounts of cyclohexane by some other path.

In an attempt to observe a radical displacement reaction on an ordinary saturated carbon atom, we chose to study the reactions of the 5-bromopentyl radical (**1**) for several reasons. First, the radical could be conveniently generated by the thermal decomposition of *t*-butylperoxy 6-bromohexanoate (**2**).[8] Cyclization of the radical to form cyclopentane by an intramolecular radical displacement reaction (SHi) seemed quite likely since the energy required to break the carbon–bromine bond should be more than returned by the formation of the carbon–carbon bond.[9] Moreover, the five-membered ring in the transition state should not be unduely strained. Also, intramolecular 1,5-hydrogen migrations from alkyl chains to oxygen or nitrogen radicals are well known.[10] This suggests that the geometry of alkyl chains is such that radical displacement is most likely to occur on the five carbon. The removal of the hydrogen from the carbon that contains the bromine is unlikely since alicyclic alkyl radicals do not readily abstract intramolecular hydrogens. Of course, a bromine atom may affect the reactivity of hydrogen atoms that are attached to the same carbon.[11] Displacement on the five carbon is also favored since it is a primary carbon. Finally the product, cyclopentane, should be stable and easily detected by glpc. Thus, the products and rates of the thermal decomposition of *t*-butylperoxy 6-bromohexanoate and *t*-butylperoxy hexanoate in various solvents and the gas phase were studied.

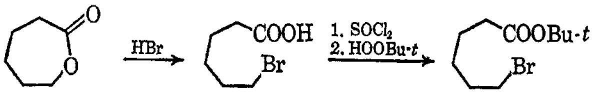


1

(2)

Results

6-Bromohexanoic acid was prepared by the reaction of ε-caprolactone with hydrobromic acid. The acid was converted to the *t*-butyl per ester by the method of Bartlett and Gortler.[12] The per ester was obtained in high yield and is stable at room temperature for days.



(3)

Thermal decomposition of 0.02–0.3 *M* solutions of **2** at 100° in heptane, benzene, chlorobenzene, and hexafluorobenzene yielded no detectable amount of cyclopentane. Decomposition of per ester **2** in the gas phase at 250° in a nitrogen atmosphere also produced no cyclopentane.

Yields of the products from the decomposition of per ester **2** in benzene are given in Table I.

TABLE I
PARTIAL PRODUCT ANALYSIS FROM DECOMPOSITION OF *t*-BUTYLPEROXY 6-BROMOHEXANOATE (2) AT 100° IN BENZENE

Product[a]	Yield,[b] % from 0.03 *M* solution of **2**	Yield, % from 0.326 *M* solution of **2**
5-Bromopentylbenzene	23	14
5-Bromopentyl *t*-butyl ether	15	12
1-Bromopentane	8	10
6-Bromohexanoic acid	6	25
Methyl 6-bromohexanoate	5	3
1,5-Dibromopentane	Trace	6
Pentane	?	Trace
1,10-Dibromodecane	?	Trace
Acetone and *t*-butyl alcohol	55	52
Isobutylene	?	8
Toluene	50	17

[a] Bromobenzene, 1-bromohexane, cyclopentane, hexane, 1-pentene, and pentyl *t*-butyl ether were shown to be absent. [b] Yields were determined by comparison of the area of the gas–liquid partition chromatography peak of the product with that of an added standard. Yields are accurate to within 10% of their reported value as shown by triplicate runs of *t*-butylperoxy hexanoate decompositions.

6-Bromohexanoic acid was separated and collected by glpc and identified by nuclear magnetic resonance (nmr). The 5-bromopentylbenzene and 5-bromopentyl *t*-butyl ether were identified in a similar fashion. Glpc retention times further confirm the production of 6-bromohexanoic acid. Additional identification of 5-bromopentylbenzene was obtained from its mass spectrum.

The *t*-butyl per ester of hexanoic acid, which was prepared by the method of Bartlett and Gortler,[12] was decomposed at 100° in benzene. Yields of the major products of this decomposition are presented in Table II.

TABLE II
PARTIAL PRODUCT ANALYSIS FROM DECOMPOSITION OF *t*-BUTYLPEROXY HEXANOATE (3) AT 100° IN BENZENE

Product[a]	Yield,[b] % from 0.050 *M* solution of 3	Yield, % from 0.140 *M* solution of 3
Pentylbenzene	11	16
Pentyl *t*-butyl ether	21	12
Pentane	8	15
Acetone	25	*c*
Toluene	23	9

[a] Decane, hexane, hexanoic acid, isobutylene, methyl hexanoate, 1-pentene, pentyl hexanoate, phenyl hexanoate, *t*-butyl alcohol, and *t*-butyl hexanoate were shown to be absent. [b] See footnote *b* of Table I. [c] Yield was not determined.

The first-order rate constants for the decompositions of undegassed solutions of per esters **2** and **3** in cyclohexane at 106° were 1.37×10^{-5} and 1.44×10^{-5} sec^{-1}, respectively. The kinetic runs gave excellent linear behavior over their full course.

Discussion

Several of the most important possible reactions of the 5-bromopentyl radical are depicted in Chart I. Lack of formation of cyclopentane and 1-pentene (yields 0.1%) indicate that these intramolecular reactions are less favorable than the intermolecular reactions. The yields of the products reported in Table I show that hydrogen abstraction either from the solvent or the

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[8] P. D. Bartlett and R. R. Hiatt, *J. Am. Chem. Soc.*, **80**, 1398 (1958), and references cited therein.

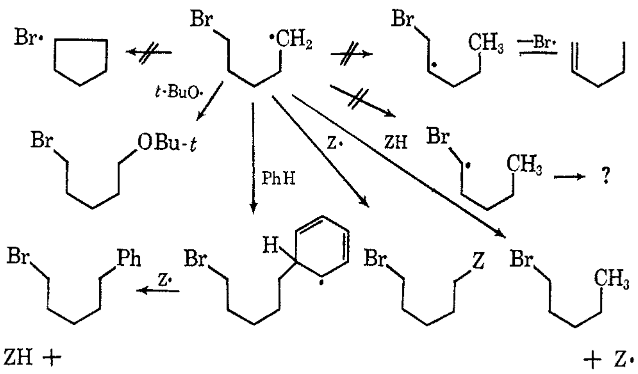
[9] C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, p 50.

[10] E.-A. I. Heiba and R. M. Dessau, *J. Am. Chem. Soc.*, **88**, 1590 (1966), and references cited therein.

[11] Personal communication from Professor G. A. Russell and K. M. Desmond.

[12] P. D. Bartlett and L. B. Gortler, *J. Am. Chem. Soc.*, **85**, 1864 (1963).

CHART I



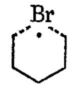
Z = any free radical

reactants and products, as well as addition into the solvent, is the main reaction of the 5-bromopentyl radical in benzene. The *t*-butyl ether probably arises from cage recombination of the 5-bromopentyl radical and the *t*-butylperoxy radical. Bartlett and Hiatt[8] have found that approximately 17% cage recombination occurs in chlorobenzene at 60° during the thermal decomposition of *t*-butylperoxy 2-phenyl-2-methylpropionate. The minor products, 1,5-dibromopentane and 1,10-dibromodecane, are explained by radical-coupling reactions. Pentane could result from the removal of a bromine atom to form a radical from either the undecomposed per ester or 1-bromopentane followed by hydrogen abstraction by that radical.

The formation of 6-bromohexanoic acid and its methyl ester is puzzling especially since the corresponding acid and ester are not formed during the decomposition of the unsubstituted per ester. In disagreement with our results, Trachtman and Miller[13] have found that 30% of the corresponding acid is produced during the decomposition of *t*-butylperoxy decanoate in chlorobenzene. Also, Starnes has found that 23% of 3,3,3-triphenylpropionic acid is formed during the decomposition of the *t*-butyl per ester of that acid in chlorobenzene.[14] None of these workers offered an explanation for the production of acids. The acids could result from hydrogen abstraction by the carboxy radicals, but this seems unlikely since decarboxylation of carboxy radicals is rapid.[15] Lorand has suggested that possibly the acids result from hydrolysis of the peresters by traces of water.[15] This latter suggestion seems likely since the yields of these acids are not constant.

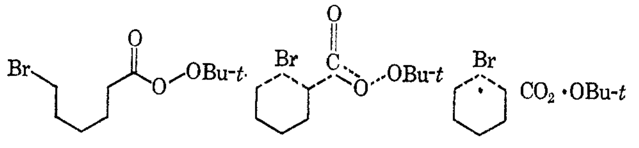
The radical displacement reaction on carbon shown in eq 2 must be very unfavorable since even reactions such as hydrogen abstraction and addition into benzene occur more readily. In most previously studied radical reactions, radical displacement on carbon did not occur because it was competing with other more favorable processes such as atom abstraction, addition, and coupling reactions. In the case of the 5-bromopentyl radical, the displacement reaction has an advantage over other types of reactions since it is intramolecular. Moreover, there are several other reasons that are mentioned in the introduction which suggest that the 5-bromopentyl radical is particularly likely to exhibit radical displacement on carbon. Nevertheless, the reaction failed to occur even when the radical was generated in relatively inert solvents such as benzene and hexafluorobenzene or in the gas phase in a nitrogen atmosphere. Thus, the energy requirements of this type of radical displacement reaction must be very high.

Recently, much interest has been displayed in the possibility of bridged bromine radicals.[16] The 5-bromopentyl radical could bridge to form a 1,5-bridged bromine radical, **4**. Indeed, evidence has been reported that distant halogens form bridges in heterolytic reactions.[17] However, both the product and rate studies of the decomposition of *t*-butylperoxy 6-bromohexanoate give no evidence for the existence of **4**. The decomposition of a dilute solution of the bromo per ester (2) in benzene gives 23% 5-bromopentylbenzene, 15% 5-bromopentyl *t*-butyl ether, and 8% 1-bromopentane. The yields of these products are very comparable with those of the corresponding products obtained from the decomposition of the unsubstituted per ester **3** under similar conditions. Per ester **3** gives 11% pentylbenzene, 21% pentyl *t*-butyl ether, and 8% pentane. If the 5-bromine atom bridged to form **4**, the reactivity of the radical should be lowered. Since there is no evidence that the 5-bromine affects the reactivity of the pentyl radical, the existence of **4** seems unlikely.



4

If the bridged radical **4** is much more stable than a primary radical, the 6-bromine atom of per ester **2** could assist its thermal decomposition as is shown below.



2 **4**

Assistance of this type should lead to a substantial rate enhancement. However, the rate of decomposition of the bromo per ester **2** in cyclohexane is equal to that of the unsubstituted per ester **3**. Thus these rate data also give no evidence for the formation of the bridged bromine radical **4**.

Experimental Section

Materials and Methods.—Nmr spectra were taken either with a Varian Model A-60 or Model HR-60 spectrometer. Infrared spectra were obtained with a Perkin-Elmer Model 21 recording spectrometer. Mass spectra were obtained with an Atlas MAT Model CH 4 spectrometer. Melting points and boiling points are uncorrected. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich.

Glpc measurements were carried out on an Aerograph Model 202 gas chromatograph (Wilkens Instrument and Research, Inc.) fitted with dual thermal conductivity detectors. Use was made of 5-ft columns of 20% silicone SF-96 on Chromosorb W, 6-ft columns of 20% Ucon 50 HB 2000, 20% fluorosilicone QF-1,

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[13] M. Trachtman and J. G. Miller, *J. Am. Chem. Soc.*, **84**, 4828 (1962).

[14] W. H. Starnes, Jr., *ibid.*, **85**, 3708 (1963).

[15] J. P. Lorand, Ph.D. Thesis, Harvard University, 1964.

[16] (a) M. P. Cava, M. Krieger, R. Pohlke, and D. Mangold, *J. Am. Chem. Soc.*, **88**, 2615 (1966); (b) P. S. Skell, D. L. Tuleen, and P. D. Readio, *ibid.*, **85**, 2849 (1963); (c) P. S. Skell and P. D. Readio, *ibid.*, **86**, 3334 (1964).

[17] (a) P. E. Peterson and E. V. P. Tao, *ibid.*, **86**, 4503 (1964); (b) P. E. Peterson and R. J. Bopp, 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966, Abstracts, p 3S; (c) R. E. Glick, Ph.D. Thesis, University of California at Los Angeles, 1954.

20% Carbowax 20 M, and 20% β,β′-oxydipropionitrile, all on Chromosorb P. Unless otherwise noted, product identification was carried out by comparison of glpc retention times and by peak enhancement of the product peaks by authentic samples on at least three different columns. As an example of the separation obtained, authentic samples of the products from the decomposition of *t*-butylperoxy 6-bromohexanoate were eluted from the silicone SF-96 columns in the following order:[18] isobutylene (1.2), pentane (1.7), *t*-butyl alcohol (2.0), 1-pentene (2.1) acetone (2.7), cyclopentane (3.8), benzene (10–14), 1-bromopentane (17.0), pentyl *t*-butyl ether (19.6), 1,5-dibromopentane (25.7), 5-bromopentyl *t*-butyl ether (26.5), methyl 6-bromohexanoate (27.1), 6-bromohexanoic acid (29.1), 5-bromopentyl benzene (30.80), and 1,10-dibromodecane (34.2). Products from the decomposition of *t*-butylperoxy hexanoate were eluted from the QF-1 columns in the order given:[18] isobutylene (0.7), 1-pentene (1.7), pentane (1.8), *t*-butyl alcohol (7.0), benzene (8–12), toluene (15.0), pentyl *t*-butyl ether (16.6), decane (18.0), methyl hexanoate (21.0), pentyl benzene (23.80), hexanoic acid (24), biphenyl (29.8), and phenyl hexanoate (32.4). Products were assumed to have a relative thermal conductivity of 1.0.

The pyrolysis apparatus consisted of a vertical Pyrex tube packed with Pyrex helices. The materials were dropped on the top of the column of helices, carried through the hot tube by a flow of dry prepurified nitrogen, and collected in a trap using ice water as a coolant.

Heptane from Eastman and reagent grade benzene from Mallinckrodt were distilled before use. Chlorobenzene from Matheson Coleman and Bell was distilled from potassium hydroxide and dried by passing through phosphorus pentoxide as recommended by Martin.[19] Eastman Red Label cyclohexane was washed with concentrated sulfuric acid to remove any alkenes, washed with water three times, dried by filtering through anhydrous sodium sulfate, and distilled before use. Hexafluorobenzene from Imperial Smelting, Ltd., was purified by distillation and glpc.

Hexyl bromide was prepared from the corresponding alcohol by treatment with hydrobromic acid.[20] Methyl 6-bromohexanoate, methyl hexanoate, and phenyl hexanoate were prepared by reaction of the respective acid chlorides with an excess of alcohol and an equivalent amount of either pyridine or N,N-dimethylaniline.[21]

The *t*-butyl hydroperoxide obtained from K and K Laboratories was separated from the 30% water by dissolving in petroleum ether[15] (bp 30–60°) and extracting three times with a saturated sodium chloride solution. The organic layer was passed through anhydrous magnesium sulfate and the petroleum ether was removed at 0° under reduced pressure. The remaining liquid was distilled; the fraction boiling at 34–35° (20 mm) was collected [lit.[22] bp 33–34° (17 mm)].

Cyclopentane, 1,5-dibromopentane, and pentane were obtained from Matheson Coleman and Bell; decane, 1,10-dibromodecane, and 1-pentene were obtained from Eastman; pentylbenzene was obtained from City Chemical Corp. These materials were used without further purification.

ε-Caprolactone was prepared by the method of Starcher and Phillips[23] with the use of *m*-chloroperbenzoic acid instead of peracetic acid.

6-Bromohexanoic acid was prepared by the method of Fox, *et al.*,[24] bp 147° (4 mm) [lit.[25] bp 164–170° (20 mm)]. Recrystallization from petroleum ether yielded white crystals, mp 33.2–33.5° (lit.[25] mp 35°).

***t*-Butylperoxy 6-bromohexanoate** (**2**) was prepared by the method of Bartlett and Gortler[12] in 70% yield. The infrared spectrum of the colorless liquid showed a peak at 1786 cm^{-1}. The nmr spectrum showed peaks at δ 1.30 (singlet, 9 H), 1.30–2.05 (complex, 6 H), 2.15–2.4 (split unsymmetrical triplet, 2 H), and 3.25–3.5 (triplet, 2 H).

Anal. Calcd for $C_{10}H_{19}BrO_3$: C, 44.96; H, 7.17; Br. 29.91. Found: C, 45.07; H, 7.21; Br, 29.94.

***t*-Butylperoxy hexanoate** (**3**) was prepared by the same method used to prepare per ester **2**. The infrared spectrum of **3** showed a carbonyl absorption at 1783 cm^{-1}. The nmr spectrum showed peaks at δ 0.80–1.1 (unsymmetrical split triplet, 3 H), 1.30 (singlet, 9 H), 1.30–2.05 (complex, 6 H), and 2.15–2.40 (unsymmetrical split triplet, 2 H).

Anal. Calcd for $C_{10}H_{20}O_3$: C, 63.80; H, 10.71. Found: C, 63.43; H, 10.66.

Pentyl *t*-butyl ether was prepared from pentyl alcohol and *t*-butyl alcohol on a small scale using the procedure of Norris and Rigby.[26] The water layer was separated from the azeotropic mixture and washed twice with ethyl ether. The combined organic layers were passed through anhydrous magnesium sulfate and the ether was removed by distillation under reduced pressure. The resultant solution was distilled; the fraction boiling at 132–133° was shown by glpc analysis to be a 60–40 mixture of pentyl alcohol and pentyl *t*-butyl ether. This mixture was chromatographed on a silica gel column with heptane, benzene, and chloroform as eluents. A colorless liquid was obtained after the solvents were removed by distillation under vacuum.

The infrared spectrum of the product showed a carbon–oxygen single bond stretch at 1031 and a *t*-butyl absorption at 1196 cm^{-1}. The nmr spectrum showed peaks at δ 0.65–1.05 (unsymmetrical split triplet, 3 H), 1.05–1.6 (complex multiplet, 6 H), 1.12 (singlet, 9 H), and 3.1–3.4 (unsymmetrical split triplet, 2 H).

Anal. Calcd for $C_9H_{20}O$: C, 74.93; H, 13.97. Found: C, 74.68; H, 13.84.

Per ester decompositions were carried out in sealed Pyrex tubes. The per ester was added to a clean, dry, constricted test tube followed by introduction of the solvent. The solution was degassed three times before the tube was sealed under vacuum. After decomposition of the per ester the tubes were cooled to −78° and opened. The reaction mixture was transferred to a vial and the internal standard was added. The solution was analyzed by glpc. The composition of solutions and reaction times are shown in Table III.

Product Studies.—All major products were identified by comparison of retention times and by peak enhancement with authentic samples on at least three different columns[27] (description of columns given above) except 5-bromopentyl *t*-butyl ether and 5-bromopentylbenzene. These two products, along with 6-bromoheptanoic acid, were identified by nmr after their collection by glpc on the silicon SF-96 columns. The nmr spectrum of the 5-bromopentylbenzene showed peaks at δ 1.25–2.0 (complex multiplet, 6 H), 2.4–2.8 (split unsymmetrical triplet, 2 H), 3.2–3.5 (triplet, 2 H), and 7.2 (singlet, 5 H). The mass spectrum showed molecular ion peaks at *m/e* 226 and 228 and an intense peak at *m/e* 91.

TABLE III

COMPOSITION OF SOLUTIONS AND REACTION TIMES USED IN THE DECOMPOSITION OF PER ESTERS 2 AND 3 AT 100°

Per ester	Solvent	Amt of per ester, g (mmole)	Amt of solvent, g	Concn, *M*	Decompn time, hr
2	Heptane	0.024 (0.0898)	2.65	0.0232	65
2	Chlorobenzene	0.0303 (0.113)	3.75	0.0206	90
2	Hexafluorobenzene	0.0133 (0.0498)	2.46	0.0172	69
2	Benzene	0.0535 (0.200)	5.68	0.0319	76
2	Benzene	0.668 (2.50)	6.73	0.326	76
3	Benzene	0.0465 (0.247)	4.39	0.0494	93
3	Benzene	0.0442 (0.234)	4.39	0.0468	93
3	Benzene	0.0445 (0.236)	4.39	0.0472	93

The nmr of 5-bromopentyl *t*-butyl ether gave peaks at δ 1.1 (singlet, 5 H), 1.2–1.8 (complex, 6 H), and 3.2–3.5 (roughly

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[18] The retention times given in parentheses are expressed in minutes.

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[27] Methyl 6-bromohexanoate was identified on only two columns.

overlapping triplets, 4 H). The integration of the *t*-butyl group is low and is probably a result of the partial decomposition of the product. The presence of the sharp singlet does indicate a *t*-butyl group and the rest of the spectrum is similar to that of 5-bromopentanol.

Gas Phase Pyrolysis of *t*-Butylperoxy 6-Bromohexanoate (2).—Quantities of 0.4 g of per ester were decomposed in the gas phase at 300 and 250°. The flow rate of nitrogen through the column was 100 ml/min which led to a residence time of 10 sec at the high temperature. Nmr spectra of the products showed the major components to be 1-bromopentane and acetone. A significant amount of tars was formed. Analysis of the products by glpc showed no cyclopentane. To ensure that the column temperature was not high enough to remove a bromine from **2**, 1-bromopentane was subjected to the same pyrolysis conditions. Greater than 95% of the 1-bromopentane was recovered.

Kinetic Studies.—The rates of decomposition of per esters **2** and **3** were followed by the infrared method of Bartlett and Hiatt.[8] Aliquots of stock solutions of per ester in cyclohexane were placed in constricted test tubes, sealed without degassing, heated for measured intervals, quenched by cooling, and stored at 0° until measurement. The rate was followed by observing the decrease in transmittance of the carbonyl band. Constants were calculated as described by Bartlett and Hiatt.[8]

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Nucleophilic Reactivity of the Carbon–Carbon Double Bond. VI. The Use of Urea as a Base in Acetolysis Reactions

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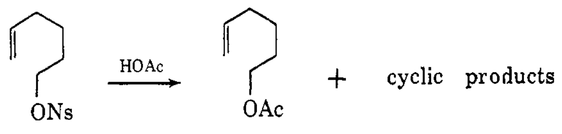
In the study of acetolysis reactions where it is necessary to neutralize the strong acid liberated, urea possesses certain advantages over sodium acetate as a base to be added to the solution. It is (a) too weakly nucleophilic to superpose a displacement reaction on the solvolysis, (b) not basic enough to give rise to acetate ions, yet (c) basic enough to neutralize sulfonic acids. Being an uncharged base urea produces no initial salt effect upon solvolytic reactions. On the other hand, the product solution containing the conjugate acid of urea is somewhat more acidic than pure acetic acid, and there is a class of sensitive substrates which it does not adequately protect against acid-catalyzed reactions.

When an alkyl arenesulfonate is solvolyzed in a nonbasic solvent, a strong arenesulfonic acid is produced. In many cases, the products and reactants are not stable to such a strong acid and are rearranged or transformed to tars by cationic polymerization. By addition of a sufficiently strong base to the reaction solution, the sulfonic acid produced is converted to an inert sulfonate salt, and thus the products and reactants are protected from the strong acid. The most commonly used base in acetolysis has been sodium or potassium acetate.[2] However, these acetates, good nucleophiles, can affect the product composition through direct displacement and can affect the rate both by this mechanism and by a kinetic salt effect. Because product studies are often run at relatively high solute concentrations, the correlation of product information with rate information is impaired.

An example is found in the study of double-bond participation in the acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate[3] (**1**). The acetolysis of 5-hexenyl *p*-nitrobenzenesulfonate is 1.6 times as fast as that of *n*-hexyl *p*-nitrobenzenesulfonate. This means that, if the relative rate constant for the unassisted solvolysis is 1.0, then that for the assisted reaction is 0.6. Thus, if the cyclohexyl cation is obtained from the assisted reaction, then one should obtain (0.6) (100)/(1.6) = 37% cyclic products, since the solvolysis of cyclohexyl arenesulfonates gives no acyclic products. Correction for the inductive effect of the double bond raises this estimate.[3,4] However, with sodium acetate as the base, only 18% cyclic products are obtained. This could mean that the *k* for the unassisted reaction is not equal to that of the saturated analog, that there are different salt effects on the unassisted and assisted reaction, that the assisted reaction does not lead to a true cyclohexyl cation and therefore does not give cyclic products exclusively, or that a considerable amount of direct displacement by the acetate ion gives more open acetate. Calculations based upon this last interpretation[3] have afforded reasonable agreement between the expectations based upon rates and the product compositions observed. As a further check on this interpretation and in search of improved practice for future solvolysis studies, it appeared desirable to use a nonnucleophilic base so that no S_N2 reaction between the substrate and base would occur. We have sought a poorly nucleophilic base which would be weak enough not to be protonated by acetic acid, but strong enough to be protonated by the sulfonic acid. This type of base would not displace the arenesulfonate itself, it would not give rise to an equivalent of acetate ions, yet it would preserve the products from attack by the sulfonic acid. Urea appeared as a promising candidate.



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[2] See, as an early example, S. Winstein and D. Trifan, *J. Am. Chem. Soc.*, **74**, 1153 (1952), and many other cases included in Bartlett, "Nonclassical Ions," W. A. Benjamin, Inc., New York, N. Y., 1965.

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