-CHOAc), 3.97 (q, bridgehead H's), 1.92 (s, -OCOCH₃); lit.[27] mp 56-57°.

Anal. Calcd for C₁₃H₁₂O₂: C, 77.98; H, 6.04. Found: C, 77.79; H, 6.18.

The *crude* solvolysis product (0.13 g) was also hydrogenated in absolute ethanol (2.5 hr, 5% Pd-C) to afford *only anti*-7-benzonorbornenol (11, 0.12 g), the spectra and glpc behavior of which matched that of authentic 11. No nmr resonance at δ 3.97 due to the saturated *syn* epimer[25] could be detected, even at high amplitude.

The small quantity of bromide 7 available necessitated a smaller scale product study. Bromide 7 (0.1 g) was allowed to stand in 70% dioxane (5 ml) containing lutidine (0.058 g, 1.2 equiv) at room temperature for 22 hr. Processing as before gave *syn*-7-benzonorbornadienol (14, 0.061 g, 85%): mp 94-94.8° after three recrystallizations from petroleum ether (bp 30-60°); ir λ^{KBr} 3.01, 3.34, 9.22, 9.41, 13.71, and 14.40; δ^{CDCl_3} 7.0-7.6 (m, ArH, A₂B₂), 6.7 (t, HC=CH), 4.1-4.4 (broad m, CHOH), 3.73 (q, bridgehead H's, J$_{bridgehead vinyl}$ = 2.5, J$_{bridgehead CHOH}$ = 1.5 cps), 2.1-2.6 (broad s, OH).

Anal. Calcd for C₁₁H₁₀O: C, 83.51; H, 6.37. Found: C, 83.43; H, 6.37.

The crude solvolysate showed no trace of the *anti* epimer 13, whose -CHOH resonance at δ 3.89 (m)[26] is readily discernible from that of 14 [δ 4.1-4.4 (m)]. Also, the two epimers have several differences in the ir that make contamination obvious, and the crude solvolysate showed only 14. Alcohol 14, like 13,

decomposed over Reoplex at 200°, apparently again yielding aldehydes of as yet unknown structure.

Some early attempts to study the rate of solvolysis of 7 in 80% ethanol containing 1.2 equiv of sodium acetate as described for the ether bromides afforded petroleum ether washes of the reaction material. Work-up of these as detailed for 1 led to an oily product that decomposed upon attempted glpc (see 14). Its spectra indicated it to be principally *syn*-7-ethoxybenzonorbornadiene [δ^{CCl_4} 6.8-7.4 (m, Ar, H, A₂B₂), 6.67 (t, HC=CH), 3.97 (t, -CHOEt), 3.77 (q, bridgehead H's, J$_{bridgehead vinyl}$ = 2, J$_{bridgehead CHOEt}$ = 1.5 cps), 3.39 (q, -OCH₂CH₃, J = 7 cps), 1.00 (t, -OCH₂CH₃)], although some acetate ester (λ^{neat} 5.79 μ) was also present. The triplet nature of the -CHOEt resonance indicated the *syn* stereochemistry of the ether.[28] Unfortunately, analytical material *via* glpc could not be obtained because of the lability of the compound.

Registry No.—1, 23526-72-9; 2, 23526-73-0; 3, 7605-11-0; 4, 23526-75-2; 5, 23537-58-8; 6, 7605-10-9; 7, 22436-26-6; *anti*-12, 23526-77-4; *syn*-12, 23552-88-7; 14, 23526-79-6; *anti*-7-benzonorbornadienyl acetate, 16031-3-9.

Acknowledgment.—We thank Dr. Henry F. Dabek, Jr., for the sample of bromide 5. We also appreciate the preprints of related work from Professor S. J. Cristol.

(27) Cristol and Nachtigall[12] in their preliminary report give this melting point. Our sample has not yet solidified, but the multiplet shown by the -CHOAc proton in the nmr spectrum and the other work described above support the structure.

(28) The stereochemistry of the proton at the bridge in 7-substituted benzonorbornenes and -dienes is better established by the nmr splittings than by chemical shifts. The matter has been discussed.[1a]

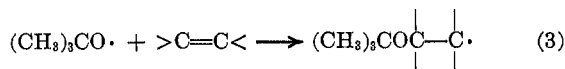# Reactions of Alkenes with Di-*t*-butyl Peroxide and *t*-Butyl Peroxypivalate

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A variety of alkenes structurally related to 4-vinylcyclohexene have been allowed to react with *t*-butoxy radicals from both di-*t*-butyl peroxide (DTBP) and *t*-butyl peroxypivalate (TBPP) to relate variations in reactivity and products to the structure of the alkenes. The major products were *t*-butyl alcohol and dehydro dimers when allylic hydrogen was present and vinyl unsaturation absent, as in the cycloalkenes (C₅-C₇). Addition dimers and polymer were also obtained when nonallylic radicals were formed in the presence of double bonds, as in cyclooctene and vinylcyclohexane. Minor amounts of acetone and *t*-butyl ethers were produced from β scisson and addition of *t*-butoxy radicals, respectively. More addition occurred with cyclooctene, alkenes with no allylic hydrogens, and conjugated alkenes. A decrease in relative reactivity toward hydrogen abstraction by *t*-butoxy radical was observed with increasing ring size from cyclopentene to cyclooctene. Other products from TBPP decomposition include carbon dioxide and products derived from *t*-butyl radical by addition, hydrogen transfer, and coupling reactions. Interactions of *t*-butyl and *t*-butoxy radicals, in or near the perester solvent cage, account for the formation of di-*t*-butyl ether and a portion of the *t*-butyl alcohol and isobutylene.

Three modes of reaction are available to *t*-butoxy radicals generated in the presence of alkenes.

$$(CH_3)_3CO \cdot \longrightarrow CH_3COCH_3 + CH_3 \cdot \qquad (1)$$

$$(CH_3)_3CO \cdot + RH \longrightarrow (CH_3)_3COH + R \cdot \qquad (2)$$

$$(CH_3)_3CO \cdot + {>}C{=}C{<} \longrightarrow (CH_3)_3COC{-}C \cdot \qquad (3)$$

Acetone indicates those *t*-butoxy radicals that are wasted by β scission (eq 1), *t*-butyl alcohol measures hydrogen abstraction (eq 2), and *t*-butyl ethers provide a measure of the addition reaction (eq 3).

Previous studies have shown[2-4] that *t*-butoxy radicals preferentially abstract the secondary allylic hydrogens

of 4-vinylcyclohexene to form *t*-butyl alcohol and biallyls rather than add to either double bond. On the other hand, an investigation[5] of the liquid-phase oxidation of cyclic alkenes disclosed that some 70% of the cyclooctene reacted by addition of oxy and peroxy radicals, although other cycloolefins gave mostly products derived from allylic hydrogen abstraction. Moreover, the overall rate of oxidation decreased in progressing from cyclopentene to cyclooctene.

These results led us to examine the reaction of a variety of alkenes structurally related to 4-vinylcyclohexene with *t*-butoxy radicals obtained by photolysis of di-*t*-butyl peroxide (DTBP) and by thermal decomposition of *t*-butyl peroxypivalate (TBPP). The objective of this work was to relate the observed reaction products and the relative reactivities toward *t*-butoxy radical attack to the structure of the alkenes. Ques-

(1) Taken from the Ph.D. Thesis of C. W. Uzelmeier, Case Institute of Technology, 1967.

(2) J. R. Shelton and J. N. Henderson, *J. Org. Chem.*, 26, 2185 (1961); J. R. Shelton and A. E. Champ, *ibid.*, 28, 1393 (1963).

(3) W. J. Farrissey, *ibid.*, 29, 391 (1964).

(4) J. R. Shelton and J. F. Siuda, *ibid.*, 31, 2028 (1966).

(5) D. E. Van Sickle, F. R. Mayo, and R. M. Arluck, *J. Amer. Chem. Soc.*, 87, 4824 (1965).

TABLE I

PRODUCTS FROM PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE IN VARIOUS ALKENES

Alkene[a]	Acetone[b]	*t*-BuOH[b]	*t*-Butyl ether[b]	Dimer[c]	*t*-BuOH formed/ alkene consumed
Vinylcyclohexane	4.3	94	1.0	33	0.73
4-Vinylcyclohexene	2.3	92	2.0[d]	43	0.86
4-Ethylcyclohexene	2.0	94	2.2	63	0.90
1-Ethylcyclohexene	1.5	99	0.7	54	1.08
None	49	37	0	10[e,f]	...

[a] 2.24 *M* alkene and 0.37 *M* DTBP in benzene.   [b] Based on amount of DTBP decomposed after 24-hr photolysis at 86 ± 3°.   [b] Based on amount of *t*-BuOH formed.   [d] Contained a fourfold excess of adduct of internal double bond.   [e] Biphenyl.   [f] 15% toluene also formed.

TABLE II

PRODUCTS FROM PHOTOLYSIS OF DI-*t*-BUTYL PEROXIDE IN CYCLIC ALKENES AND RELATED COMPOUNDS

Hydrocarbon[a]	Acetone[b]	*t*-BuOH[b]	*t*-Butyl ether[b]	Dimer[c]	*t*-BuOH formed/ alkene consumed
Cyclopentene	1.6	98	4.4	61	0.90
Cyclohexene	d	98	3.4	54	1.03
Cycloheptene	3.2	97	3.1	54	0.88
Cyclooctene	4.0	82	3.4	55	0.68
1,5-Cyclooctadiene	1.6	89	3.7	48	0.98
Cyclododecene	2.2	95	d	d	1.24
Cyclohexane	5.1	88	...	4[e]	1.44[f]
Toluene	25	76	...	43	0.89[f]

[a] 2.28 *M* hydrocarbon and 0.38 *M* DTBP in benzene.   [b] Based on amount of DTBP decomposed after 24-hr photolysis at 86 ± 3°.   [c] Based on amount of *t*-BuOH formed.   [d] Not determined.   [e] 41% yield of solvent-derived product (cyclohexylbenzene).   [f] Relative to hydrocarbon consumed.

tions of particular interest were (1) the factors affecting the relative importance of the abstraction and addition reactions of the *t*-butoxy radical, (2) the effect of ring size in cycloalkenes on the reactivity of the double bond and associated allylic hydrogens, and (3) the relative reactivity of the tertiary allylic hydrogen of vinyl-substituted cycloalkenes and alkanes toward *t*-butoxy radical. In addition, it was desired to observe the reactions of alkenes with *t*-butyl radical from TBPP decomposition and to correlate variations in products and reactivities of this radical with alkene structure.

Results and Discussion

Fate of the *t*-Butoxy Radical in the Presence of Alkenes.—Tables I and II show amounts of reactants consumed and products formed in the photolysis of DTBP in benzene solutions of alkenes. Results for cyclohexane and toluene are also included in Table II for comparison. The data show that in most cases the volatile products (alcohol, acetone, and ether) account for 95–100% of the *t*-butoxy radicals generated. An important exception is the case of cyclooctene, where *t*-butyl alcohol, acetone, and cyclooctyl *t*-butyl ether account for only 89.4% of the *t*-butoxy radicals, the remainder being present in the higher molecular weight residue formed by initiation as in eq 3 with one or more additions before termination by hydrogen abstraction. Nevertheless, with all substrates, hydrogen abstraction is the predominant reaction pathway of the *t*-butoxy radical when sufficiently reactive allylic hydrogens are present.

Table III shows the yields of products from the thermal decomposition of TBPP in benzene solutions of various alkenes and related compounds. The major *t*-butoxy radical product was again *t*-butyl alcohol, which is formed along with small but significant amounts of acetone and di-*t*-butyl ether. Their sums

quantitatively accounted for the *t*-butoxy radicals generated in all cases except cyclooctene (5.7% missing *t*-BuO·). Traces (<1%) of volatile *t*-butoxy radical addition products also were present. As expected, these products are formed in somewhat smaller amounts, since the perester only generates one oxy radical per mole and the same 6:1 molar ratio of substrate to radical source was used as in the DTBP reactions.

Considerable variation in the extent of *t*-butoxy radical addition to alkenes has been reported in the literature. Generally, addition to conjugated alkenes occurs readily.[6-8] In contrast, the addition of *t*-butoxy radicals to isolated double bonds occurs only to a minor extent in most cases. Walling and Thaler[8] observed 3–6% *t*-butoxy radical addition to a variety of butenes and methylbutenes. A notable fact of this work was the lack of high reactivity in terminal vinyl compounds (1-butene and *trans*-2-butene each gave ca. 3% adduct). Farmer and Moore[9] also noticed very little addition in studying the reactions of DTBP with cyclohexene and 1-heptene. Exceptions include intramolecular alkoxy radical addition in the photolysis of a steroidal nitrite[10] and the formation of 65% adduct when norbornene was allowed to react with *t*-butyl hypochlorite.[11]

The small amount of addition to most alkenes observed in our work (1–4%) closely parallels Walling and Thaler's data, even though their source of *t*-butoxy radicals was different (*t*-BuOCl). The *t*-butyl ethers obtained with 4-vinylcyclohexene and related systems

(6) M. S. Kharasch, F. S. Arimoto, and W. Nudenberg, *J. Org. Chem.,* **16,** 1556 (1951).

(7) J. K. Allen and R. G. Bevington, *Proc. Roy. Soc.,* **262,** 271 (1961).

(8) C. Walling and W. Thaler, *J. Amer. Chem. Soc.,* **83,** 3877 (1961).

(9) E. H. Farmer and C. G. Moore, *J. Chem. Soc.,* 131 (1951).

(10) A. L. Nussobaum, R. Wayne, E. Yuan, O. Z. Zarre, and E. P. Oliveto, *J. Amer. Chem. Soc.,* **87,** 2451 (1965).

(11) E. Tobler, D. E. Baltin, and D. F. Foster, *J. Org. Chem.,* **29,** 2834 (1964).

Table III
Thermal Decomposition of *t*-Butyl Peroxypivalate in Various Alkenes and Related Compounds

Product	Benzene	Toluene	4-VCH[b]	VCHA[c]	4-ECH[d]	1-ECH[e]	Cyclo-pentene	Cyclo-heptene	Cyclo-octene	1,5-COD[f]	Cyclo-hexane
t-Butyl alcohol	67	82	97	92	95	100	100	95	88	100	93
Acetone	30	16	1.4	3.5	1.8	0.8	1.3	1.7	2.7	1.3	7.3
Di-*t*-butyl ether	3.0	3.7	3.0	4.0	3.0	3.2	2.1	3.0	3.6	3.6	...[g]
Carbon dioxide	109	104	98	96	94	94	85	95	99	95	87
Isobutylene	18	7.0	19	11	13	10	13	9.7	11	9.0	11
Isobutane	14	10	11	3.6	15	15	15	8.3	6.0	14	8.8
Hexamethylethane	3.0	5.0	...	...	...	...	...	...	2.2	...	...
Dehydro dimer	2.0[h]	5.5	9	6.5[i]	19	19	14	14	12[i]	13	<1
t-Bu addition product	...[j]	...	21[k]	17	12}[l]	...	9.6	3.9}[l]	11	3.2	...[m]
t-Bu coupling product	...	11[n]	...	...	}	7.2	9.1	}	...	1.2	...
t-Butylated dimer	...	...	6.0	10	...	...	...	...	...	...	...

[a] From 0.06 mol of hydrocarbon and 0.01 mol of TBPP in 42 ml of benzene after 7 hr at 70°. [b] 4-Vinylcyclohexene. [c] Vinylcyclohexane. [d] 4-Ethylcyclohexene. [e] 1-Ethylcyclohexene. [f] 1,5-Cyclooctadiene. [g] Not determined. [h] Biphenyl. [i] Also includes addition dimer. [j] 12% toluene. [k] At terminal vinyl bond. [l] Inseparable by glpc. [m] 11% cyclohexylbenzene also formed. [n] Neopentylbenzene.

Table IV
Characterization of Dimeric Products

Dimer of	Bromine no. Obsd	Bromine no. Calcd[a]	Mol wt Obsd	Mol wt Calcd[b]	Nmr paraffinic/olefinic proton ratio Obsd	Nmr paraffinic/olefinic proton ratio Calcd[b]
4-Vinylcyclohexene	269	299	216	214	1.6	1.2
Vinylcyclohexane	99	145	227	218	11.0	3.7[c]
4-Ethylcyclohexene	139	145	220	218	6.6	5.5
1-Ethylcyclohexene	144	145	218	218	13.3	12.0
Cyclopentene	240	238	169	134	2.5	2.5
Cyclohexene	191	198	177	162	3.9	3.5
Cycloheptene	168	163	205	190	4.5	4.5
Cyclooctene	110	147	220	218	9.6	5.5
1,5-Cyclooctadiene	188	299	218	214	2.1	1.75

[a] Grams of bromine per 100 g of dehydro dimer structure. [b] For dehydro dimer structure. [c] If coupled through tertiary position, 12.0 if coupled through primary position.

indicate that the terminal vinyl bond is less susceptible to addition of *t*-butoxy radicals than *cis* internal unsaturation. Similar results were obtained for the addition of acetoxy to alkenes.[12]

Cyclooctene was the exception in that 14% addition occurred in the DTBP reaction compared with 82% hydrogen abstraction; yet even in this case abstraction was the predominant reaction. This is in contrast to the observation[5] that in autoxidation, cyclooctene reacted 70% by addition with only 30% abstraction by alkoxy radicals. Possibly the difference lies in the nature of the alkoxy radical, which in autoxidation is the 3-cyclooctenyloxy type.

Fate of the Substrate Radical.—Substrate radicals formed by hydrogen abstraction may either couple to form dehydro dimers, or add to a double bond to give a dimer radical which may propagate by addition to monomer, or terminate either by coupling or hydrogen abstraction. Equation 2 predicts that the ratio of alcohol formed to alkene consumed should be unity, but every addition of a radical to a double bond increases by one the number of alkene molecules consumed and reduces correspondingly the unsaturation of the total product. On the other hand, biallyls resulting from preferential coupling of radicals formed by abstraction of allylic hydrogen can compete effectively with the monomer as hydrogen donors in the later stages of the reaction and thus increase the formation of alco-

hol. Coupling of monomeric and dimeric radicals leads to the formation of dehydro trimers and tetramers which retain the unsaturation level characteristic of the monomer.

Data showing consumption of alkene relative to appearance of *t*-butyl alcohol in the DTBP reactions are included in Tables I and II. The cyclic alkenes (cyclopentene, cyclohexene, cycloheptene, and 1- and 4-ethylcyclohexene) most closely conform to eq 2 owing to the high reactivity of their allylic hydrogens toward *t*-butoxy radicals. The resulting radicals are resonance stabilized and relatively unreactive toward addition to a cyclic double bond. Opposing effects of small amounts of *t*-butoxy radical addition to the monomer and hydrogen abstraction from the dimer maintain the ratio of alcohol formed to alkene consumed near unity. Ratios greater than unity reported for cyclododecene and cyclohexane indicate that hydrogen is abstracted from species other than starting material. Since it is known[13] that secondary alkyl radicals of the cyclohexyl type add to aromatic solvents in preference to dimerization, it would be expected that the cyclohexadienyl radical intermediates formed in this process would act as hydrogen donors.

Distillation of the reaction mixtures at reduced pressure afforded a dimer fraction and a residue composed of trimer and higher molecular weight products. These were characterized as shown in Tables IV and V by infrared, nmr, and glpc analysis, and by determination

(12) J. C. Martin, J. W. Taylor, and E. H. Drew, *J. Amer. Chem. Soc.*, **89**, 129 (1967).

(13) J. R. Shelton and C. W. Uzelmeier, *ibid.*, **88**, 5222 (1966).

TABLE V
CHARACTERIZATION OF DISTILLATION RESIDUES

Residue from	Wt formed[a]	Mol wt[b]	Bromine no.[c]	Residual unsaturation,[d] %
Norbornene	56	437 (4.6)	27	16
Vinylcyclohexane	25	517 (4.7)	45	31
Cyclooctene	14	458 (4.2)	42	29
4-Vinylcyclohexene	12	529 (4.9)	146	50
1,5-Cyclooctadiene	8.8	407 (3.8)	144	45
Cycloheptene	8.8	314 (3.3)	146	89
1-Ethylcyclohexene	8.2	366 (3.3)	177	110
Cyclohexene	7.4	315 (3.8)	170	89
4-Ethylcyclohexene	6.8	382 (3.5)	122	82
Cyclopentene	6.7	235 (3.5)	189	80

[a] Grams of residue normalized to 100% DTBP decomposition (0.10 mol). [b] *Via* vapor pressure osmometry; average number of monomer units shown in parentheses. [c] Grams of bromine per 100 g of sample. [d] Calculated from the observed bromine number of the residue and the theoretical value of the dehydro dimer.

of yields, molecular weight, and residual unsaturation. True dehydro dimers of the cyclic alkenes are formed in relatively high yield. Small amounts of residue are also formed, which are characterized by 80% retention of unsaturation and appear to be mixtures of dehydro trimers and tetramers. Toluene reacts similarly with *t*-butoxy radicals to give *t*-butyl alcohol and bibenzyl, although more β scission (eq 1) occurs in this case.

Cyclooctene and the alkenes containing terminal vinyl unsaturation showed greater tendencies to add carbon radicals. Olefin consumption was somewhat greater than alcohol production for 4-vinylcyclohexene, and was considerably greater for cyclooctene and vinylcyclohexane. Dimers possessed less unsaturation, and consisted of mixtures of addition and dehydro dimers. Moreover, larger amounts of residue were obtained (especially with vinylcyclohexane and cyclooctene), which were typified by very low unsaturation and higher molecular weight. This is consistent with the previously demonstrated reactivity of alkyl radicals toward addition to the terminal vinyl bond.[14-17]

Consideration of the vinylcyclohexane dimer fraction is helpful in understanding both the addition and coupling reactions. Analysis by glpc, ir, and nmr is consistent with a mixture of 0% 1, 33% 2, 60% 3, and 7% 4.
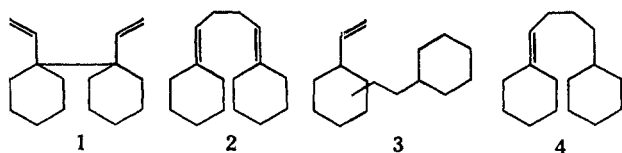
Abstraction of the tertiary allylic hydrogen produces a radical which adds in part to produce 4, but which mainly couples through the primary allylic position to give 2 (rather than the more highly hindered dehydro dimer 1). The essential feature of the vinylcyclohexane (and cyclooctene) system is the ability of *t*-butoxy radicals to abstract nonallylic hydrogens, thereby generating a higher energy radical which preferentially adds to olefinic unsaturation to give 3. Cadogan and co-

(14) J. R. Shelton and H. G. Gilde, *J. Org. Chem.*, **29**, 482 (1964).
(15) J. R. Shelton and A. E. Champ, *ibid.*, **30**, 4183 (1965).
(16) J. R. Shelton and E. E. Borchert, *Can. J. Chem.*, **46**, 3833 (1968).
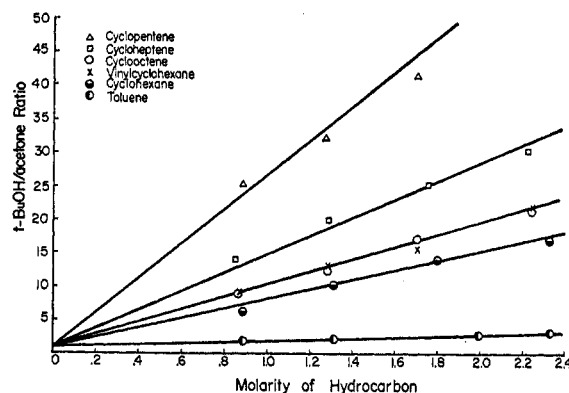(17) M. S. Karasch and M. Sage, *J. Org. Chem.*, **14**, 537 (1949).

Figure 1.—Plot of *t*-BuOH to acetone ratios *vs.* [RH] in benzene (from DTBP photolysis).

workers[18] similarly generated cyclohexyl radicals from the reaction of benzoyl peroxide with a large excess of cyclohexane in the presence of 1-octene and obtained 1-cyclohexyloctane in 42% yield.

Relative Reactivities of Alkenes toward the *t*-Butoxy Radical.—Relative reactivities of the cyclic alkenes, vinylcyclohexane, cyclohexane, and toluene toward *t*-butoxy radicals were measured by two methods. The first involved measurement of *t*-butyl alcohol to acetone ratios at varying hydrocarbon concentrations using DTBP and TBPP as radical sources.[8] The relative magnitudes of slopes obtained from graphical treatment of the data (Figure 1) were a measure of the relative rates of hydrogen abstraction. The second method utilized competition between two substrates in reaction with *t*-butyl hypochlorite.[19] The results of these experiments are shown in Table VI and compared with existing literature data.

TABLE VI
RELATIVE REACTIVITIES (*k*) OF HYDROCARBONS TOWARD
THE *t*-BUTOXY RADICAL

Hydrocarbon	*k*(*t*-BuOH/acetone) DTBP (84 ± 4°)	TBPP (70°)	*k*(*t*-BuOCl) 65–70°	40° (lit. values)[a]
Toluene	1.0	1.0	1.0	1.0
Cyclohexane	8.2	2.7	4.1	6.0
Cyclooctene	11	7.5	6.2	...
Vinylcyclohexane	11	5.6	7.4[b]	11 (calcd)
Cycloheptene	14	13	16	...
Cyclohexene	...	...	27	51
Cyclopentene	27[c]	21	34	53

[a] Data of Walling and Thaler (see ref 8). [b] Chloride products: 55% β-chloroethylidenecyclohexane, 45% nonallylic vinylcyclohexyl chlorides. [c] 70–75°.

The relative reactivities of the cycloolefins in Table VI decrease as ring size increases from five to eight carbons, as also observed by Van Sickle, Mayo, and Arluck[5] in autoxidation. They pointed out that cyclopentene, being the most nearly planar of the ring systems, has a lower activation energy for abstraction because the developing allkyl radical is best able to achieve maximum overlap, while cyclooctene suffers from steric repulsions and two of the four allylic hydrogens are severely hindered from attack. As a result, attack at

(18) J. I. G. Cadogan, D. H. Hey, and S. H. Ong, *J. Chem. Soc.*, 1939 (1965).
(19) C. Walling and B. B. Jacknow, *J. Amer. Chem. Soc.*, **82**, 6108 (1960).

nonallylic positions becomes important, manifesting itself in the observed cyclooctene addition dimer.

Walling and Thaler's values[8] for the relative reactivities of various C–H bonds predict a reactivity for vinylcyclohexane of 1.8 relative to cyclohexane at 40° and 54% attack at the tertiary allylic hydrogen. Our results thus indicate that the tertiary allylic hydrogen of vinylcyclohexane is comparable in reactivity with an acyclic hydrogen of the same type.

Fate of the *t*-Butyl Radical from TBPP.—Various products were observed which reflected the alternatives open to the *t*-butyl radical—addition, gain or loss of hydrogen, dimerization, and mixed coupling.

In the presence of terminal vinyl unsaturation, preferential addition of *t*-butyl radicals occurred. When reactive allylic hydrogens were also present, as in 4-vinylcyclohexene, the adduct radical terminated by hydrogen abstraction or coupling with other allylic radicals. On the other hand, the *t*-butyl radical adduct of vinylcyclohexane tended to undergo further propagation.

The *t*-butyl radical showed a much lower inclination for addition when confronted with only *cis* internal unsaturation, as in the cycloalkenes, which gave a combination of addition and allylic coupling products. The more highly hindered trisubstituted double bond of 1-ethylcyclohexene did not add *t*-butyl radicals.

A bicyclo[3.3.0]octane derivative was formed in low yield by addition of *t*-butyl radicals to 1,5-cyclooctadiene. A similar *t*-butoxy radical addition product was observed in the reaction with DTBP. Other transannular radical additions to this diene have been observed.[20,21]

The relative amounts of isobutylene and isobutane varied with the substrate. In those cases where *t*-butyl radical addition predominated, the amount of isobutane formed was diminished. In contrast, those alkenes containing accessible allylic hydrogens but no terminal vinyl unsaturation gave more isobutane than isobutylene, indicative of allylic hydrogen abstraction by *t*-butyl radicals.

Small amounts of hexamethylethane (2–5%) produced by coupling of *t*-butyl radicals were observed in a few systems containing hydrogens of low reactivity. Disproportionation must have also occurred in these cases, but much of the isobutane and isobutylene formed in the more reactive systems must result from other hydrogen-transfer reactions.[16]
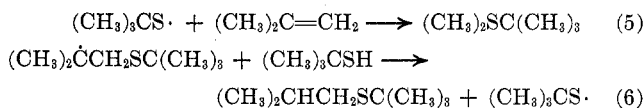
In no instance did the total of observed products account for all of the *t*-butyl radicals produced. This is in contrast to the quantitative recovery of carbon dioxide and *t*-butoxy radical products. Alkyl radical addition processes and polymerization reactions involving isobutylene evidently divert *t*-butyl reaction products to the residue.[22]

Cage Reactions with TBPP.—The constancy in yield of di-*t*-butyl ether (3–4%) over a wide range of substrates and reactant concentrations is suggestive of a cage combination of *t*-butyl and *t*-butoxy radicals following loss of carbon dioxide by the perester. Since yields of products of cage combinations depend on solvent viscosity,[23,24] TBPP was decomposed in mineral

oil at 70° for 24 hr. An 8.4% yield of di-*t*-butyl ether was observed, which represented approximately a 2.5-fold increase consistent with a cage effect. The higher ratio of isobutylene (13%) to isobutane (2.7%) formed in the more viscous solvent indicates that hydrogen transfer between *t*-butyl and *t*-butoxy radicals also occurs.

$$(CH_3)_3CO \cdot + (CH_3)_3C \cdot \longrightarrow$$
$$(CH_3)_3COH + (CH_3)_2C=CH_2 \quad (4)$$
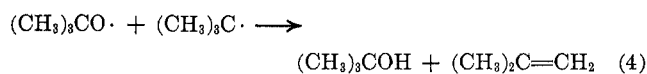
When 0.01 mol of TBPP was heated for 7 hr in benzene solution at 70° with 0.06 mol of 2-methyl-2-propanethiol, no di-*t*-butyl ether was obtained. However, this result cannot be attributed to scavenging of free radicals, since an induced decomposition of the peroxide through prior association with thiol could account for this observation. An 82% yield of di-*t*-butyl disulfide and 17% of *t*-butyl isobutyl sulfide (based on perester) was obtained. If the sulfide is formed by eq 5 and 6, 17% isobutylene must have been consumed. Formation of this much product resulting from loss of hydrogen by *t*-butyl radical in a system primed for proton donation by the thiol would have been unusual were it not for the occurrence of the reaction of eq 4 near or within the solvent cage.

$$(CH_3)_3CS \cdot + (CH_3)_2C=CH_2 \longrightarrow (CH_3)_2SC(CH_3)_3 \quad (5)$$
$$(CH_3)_2\dot{C}CH_2SC(CH_3)_3 + (CH_3)_3CSH \longrightarrow$$
$$(CH_3)_2CHCH_2SC(CH_3)_3 + (CH_3)_3CS \cdot \quad (6)$$

Experimental Section

Reagents.—4-Vinylcyclohexene, cyclooctene, and 1,5-cyclooctadiene were obtained from the Columbian Carbon Division of Cities Service Co. Cyclohexane and cyclohexene were products of Matheson Coleman and Bell. 3,3-Dimethyl-1-butene was obtained from Sinclair Petrochemicals. All hydrocarbons were distilled prior to use.

DTBP and TBPP (Lupersol 11) were obtained from the Lucidol Division, Wallace and Tiernan Inc. *t*-Butyl hypochlorite was prepared by the procedure of Gilliom and Ward.[25]

4-Ethylcyclohexene.—4-Vinylcyclohexene was allowed to react with 1 mol of hydrogen over Raney nickel in a Parr hydrogenator.[26] The crude product was brominated in CCl₄, and 4-ethylcyclohexene dibromide as removed by distillation, bp 140° (30 mm). Subsequent debromination with zinc–ethanol afforded 4-ethylcyclohexene, bp 130–131°, in 60% overall yield.

1-Ethylcyclohexene.—Reaction of ethereal ethylmagnesium bromide with cyclohexanone and dehydration of the resulting 1-ethylcyclohexanol with boiling 15% aqueous oxalic acid gave a 50% yield of 1-ethylcyclohexene, bp 133–134°.

Cyclopentene.—Dehydration of cyclopentanol with concentrated H₂SO₄ gave a 64% yield of cyclopentene, bp 44°.

Photolysis of DTBP.—The photolysis apparatus consisted of a Pyrex reaction vessel equipped with thermometer, condenser, nitrogen inlet, and Pyrex insert containing a GE H100-A4/T mercury lamp. The outer glass jacket of the lamp was removed to allow its insertion into the apparatus. Since DTBP shows a broad, regularly increasing absorption from 2200 to 3400 Å,[27] the wavelengths emitted by the lamp which were effective for DTBP decomposition were 3022, 3131, and 3341 Å.

The photolysis apparatus was charged with 0.60 mol of alkene, 0.10 mol of DTBP, and 190 ml of benzene, and flushed with nitrogen for 1 hr. The contents were then photolyzed for 24 hr at the reflux temperature, utilizing heat from the lamp regulated by a cooling stream of air. Under these conditions, 70–80% of the peroxide decomposed in most cases.

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TABLE VII
QUANTITATIVE GLPC ANALYSIS OF REACTION MIXTURES

Column[a]	Temp, °C	Internal standard	Reactants and products separated
A	100	2-Butanone	Acetone, *t*-butyl alcohol, cyclohexene, cyclooctene, 1,5-COD, cyclopentene, di-*t*-butyl ether, DTBP, 4-ethylcyclohexene, hexamethylethane, toluene, 4-vinylcyclohexene
B	110	Ethylbenzene	Cycloheptene, vinylcyclohexane,
	180	Bicyclohexyl Cyclohexylbenzene	*t*-butyl ethers of 4-vinylcyclohexene, *t*-butyl radical addition products
C	125	Bicyclohexyl	*t*-Butyl radical coupling products,
	130	*o*-Dichlorobenzene (ODCB)	*t*-butyl ethers of 1,5-COD, cycloheptene, cyclooctene, 1-ethylcyclohexene, 4-ethylcyclohexene, vinylcyclohexane
	180	ODCB or bicyclohexyl	Dimers
D	25	Isopentane	Isobutane, isobutylene

[a] Column A: 12 ft × 0.25 in. 20% Carbowax 6000 on 60/80 mesh Chromosorb W.   Column B: 12 ft × 0.25 20% Hi-vac silicone grease on 40/60 mesh Chromosorb P.   Column C: 6 ft × 0.25 30% Carbowax 6000 on 60/80 mesh Chromosorb W.   Column D: 16 ft × 0.25 in. 30% Dowtherm A on 60/80 mesh Chromosorb W.

Thermal Decomposition of TBPP.—A 100-ml, two-necked flask was equipped with a condenser and rubber septum for admitting nitrogen. The top of the condenser was connected in series with two Miller absorption tubes containing drying agent and ascarite, respectively, and also with a trap kept at Dry Ice temperature. The stirred reaction mixture of 0.06 mol of alkene, 0.01 mol of TBPP, and 42 ml of benzene was flushed with nitrogen for 15 min, then allowed to react at 70° for 7 hr, after which nitrogen was again bubbled through the solution to remove dissolved volatile products to the absorption tubes and Dry Ice trap.

Characterization of Products.—*t*-Butyl alcohol and acetone were identified by their retention times on a 12 ft × 0.25 in. 20% Carbowax 6000 glpc column at 100°. Di-*t*-butyl ether was identified by comparison of glpc retention time and ir spectrum with those of an authentic sample.[28]

Carbon dioxide, isobutylene, and isobutane were identified by comparison of their retention times with those of authentic samples on both a 30 ft × 0.25 in. benzyl cyanide–AgNO₃ column and a 16 ft × 0.25 in. Dowtherm A column at room temperature.

Following their distillation from the reaction mixture, the dimers were characterized by their ir and nmr spectra, molecular weight, bromine number,[29] and where possible, by comparison with authentic material. Individual components of the dimers were collected upon emergence from the gas chromatograph and identified by ir and nmr spectra. The nonvolatile residues were characterized according to molecular weight and residual unsaturation.

Coupling products of alkenes were independently synthesized by allylic bromination with N-bromosuccinimide, followed by either self-coupling with magnesium to give dehydro dimers or cross-coupling with *t*-butyl Grignard reagent to give *t*-butyl-substituted alkenes.

t-Butyl radical addition products were identified by their ir spectra. Except for the addition product of 4-vinylcyclohexene, where bands owing to *cis* internal unsaturation were present (3030 and 660 cm⁻¹), the addition products of vinylcyclohexane, the cycloolefins, and 1,5-cyclooctadiene had no absorptions owing to residual unsaturation but did show the characteristic absorption of the *t*-butyl group (2960, 1390, and 1360 cm⁻¹).[30]

t-Butoxy radical addition products were readily identified by strong ir absorptions owing to the *t*-butyl group, the ether linkage, and any residual unsaturation. In the cyclohexene reaction, cyclohexyl *t*-butyl ether was independently synthesized by the method of Lawesson and Yang.[31] Elemental analyses were obtained for the *t*-butyl ethers of 4-vinylcyclohexene and 4-ethylcyclohexene.

Anal. Calcd for C₁₂H₂₂O: C, 79.12; H, 12.09; O, 8.79. Found: C, 79.21; H, 11.94; O, 8.85 (by difference). Calcd for C₁₂H₂₄O: C, 79.26; H, 13.04; O, 8.70. Found: C, 78.86; H, 13.12; O, 8.02 (by difference).

Photochemical Decompositions of *t*-Butyl Hypochlorite.—For competitive studies, 0.05 mol of each hydrocarbon, 0.01 mol of *t*-butyl hypochlorite, and 0.05 mol of chlorobenzene (added as an internal standard) were dissolved in 20 ml of benzene in a 50-ml, three-necked flask equipped with a thermometer, a rubber septum for admitting nitrogen, and a condenser connected to a bubbler. The system was flushed with nitrogen for 30 min and then irradiated with a 275-W Kenmore sun lamp situated to provide a reaction temperature of 65–70°. It was usually necessary to pass the alkenes through an alumina column immediately before use to remove hydroperoxides, which inhibited the chain chlorination. Under these conditions the yellow color of the hypochlorite was completely discharged in 30–60 min.

Quantitative Analysis of Volatile Products.—Carbon dioxide from the TBPP reactions was determined gravimetrically in a Miller absorption tube filled with ascarite and anhydrous CaSO₄.

The volatile products were analyzed quantitatively by glpc. An internal standard, which had previously been calibrated with the products for detector response, was added to the reaction mixture at its completion. Table VII lists the type of column, its temperature, and the internal standard used for separation and determination of reactants and products.

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