shaking, 300 ml. of chlorosulfonic acid. The reaction mixture was heated on the steam bath for 2 hr., then poured onto 500 g. of ice. The yellow, powdery solid which was deposited was removed by filtration, washed with water, and dried over potassium hydroxide in a desiccator. The product amounted to 103 g., m.p. 142–146°. Recrystallization from benzene afforded the analytical sample, m.p. 147–149°; λ_{max} (anhydride C=O) 5.62, 5.77, (SO_2) 7.68, 8.58 μ.

Anal. Calcd. for $C_9H_6ClNO_5S$: C, 39.21; H, 2.19; Cl, 12.86; N, 5.08; S, 11.63. Found: C, 39.47; H, 2.28; Cl, 12.7; N, 5.42; S, 11.5.

5-Chloro-2-methylamino-N-(2-morpholinoethyl)benzamide (Ii). Method A.—To a solution of 6.5 g. of N-(β-aminoethyl)morpholine in 40 ml. of absolute ethanol was added 10.5 g. of 5-chloro-N-methylisatoic anhydride. After the evolution of carbon dioxide had abated, the reaction mixture was heated for 10 min. on the steam bath. The solvent was removed *in vacuo* on a rotary evaporator. The residual oil crystallized on cooling to afford 9.8 g. of product, m.p. 129–132°. Recrystallization from ethanol gave 8.7 g. of analytically pure material, m.p. 130–132°, λ_{max} (C=O) 6.15 μ.

Method B.—A solution of 2 g. of IIa in 5 ml. of morpholine was heated under reflux for 1 hr. The excess morpholine was then removed *in vacuo* on a rotary evaporator. The residual oil was washed with water. Upon the addition of a few drops of methanol to the residue, crystallization resulted. There was obtained 0.6 g. of Ii, m.p. 130–133.5°, whose identity was confirmed by a mixture melting point and infrared spectral comparison with an authentic sample.

2-Amino-5-chloro-N-ethylbenzamide was prepared from 5-chloroisatoic anhydride and 33% aqueous ethylamine. Recrystallization from aqueous ethanol afforded a sample with m.p. 118–120°; λ_{max} (C=O) 6.14, (amide II) 6.45 μ.

Anal. Calcd. for $C_9H_{11}ClN_2O$: C, 54.41; H, 5.58; Cl, 17.85; N, 14.10. Found: C, 54.55; H, 5.53; Cl, 17.9; N, 13.82.

N-Phenylisatoic Anhydride.—A solution of 5 g. of N-phenylanthranilic acid[7] in 20 ml. of ethyl chloroformate was heated under reflux for 10 hr. The excess ethyl chloroformate was removed *in vacuo* on a rotary evaporator. The residual solid amounted to 3.6 g., m.p. 172–179°. Recrystallization of the product from ethanol raised the melting point to 177–179°; λ_{max} (anhydride C=O) 5.64, 5.76 μ.

Anal. Calcd. for $C_{14}H_9NO_3$: C, 70.29; H, 3.79; N, 5.86. Found: C, 70.21; H, 3.83; N, 5.65.

2-Anilino-N-ethylbenzamide was prepared from N-phenylisatoic anhydride and 33% aqueous ethylamine. After recrystallization from cyclohexane, the analytical sample had m.p. 73–75°; λ_{max} (C=O) 6.14, (amide II) 6.48 μ.

Anal. Calcd. for $C_{15}H_{16}N_2O$: C, 74.97; H, 6.71; N, 11.66. Found: C, 74.86; H, 6.85; N, 11.74.

3,4,5,6-Tetrachloro-2-chloromethylamino-N-ethylbenzamide.—A solution of 4 g. of Ib in 30 ml. of sulfuryl chloride was heated under reflux for 1 hr. The excess sulfuryl chloride was removed *in vacuo* on a rotary evaporator. The residue was recrystallized from benzene–petroleum ether (b.p. 30–60°) affording 2.1 g. of product, m.p. 130–131.5°; λ_{max} (C=O doublet) 5.96, 6.06, (amide II) 6.58 μ.

The expected hydrogen ratio of 3:2:2 in the n.m.r. spectrum was confirmed by the following resonance signals (in δ-values): triplet centered at 1.15 ($-CH_3$), multiplet centered at 3.32 ($-CH_2$), and a singlet at 3.42 ($-CH_2Cl$).

Anal. Calcd. for $C_{10}H_9Cl_5N_2O$: C, 34.27; H, 2.59; Cl, 50.59; N, 7.99. Found: C, 34.19; H, 3.16; Cl, 50.0; N, 7.96.

Acknowledgment.—The authors are indebted to Ronald D. Stewart for his technical assistance, to Dr. Gordon Ellis and staff for the spectral and microanalytical results, and to Mr. Bruce Hofmann for his helpful comments concerning the infrared spectra.

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[7] N-Phenylanthranilic acid is available from Aldrich Chemical Co., Inc., Milwaukee, Wis.

Reactions of Mixed Acetals with Di-*t*-butyl Peroxide[1]

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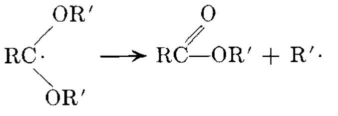
Received March 24, 1964

The mixed acetals of acetaldehyde undergo extensive fragmentation in reactions induced by di-*t*-butyl peroxide at 130°. The products of these reactions—namely, aldehydes, ketones, acetate esters, and hydrocarbons—can be explained in terms of β-elimination reactions of alkyl radicals from α-alkoxyalkyl free radicals. A comparison of the amounts of the acetate esters formed in these reactions gives the relative ease of β-elimination of alkyl radicals from the acetal-derived radicals $CH_3\dot{C}OR(OR')$. The relative β-elimination rates of various alkyl radicals from such acetal-derived radicals are discussed in terms of resonance and steric and polar factors.

Acetals have been shown to undergo rather extensive fragmentation in reactions induced by the thermal decomposition of di-*t*-butyl peroxide. In most cases, the major product of the reaction is an ester which results from the β-elimination of an alkyl radical from an α,α-dialkoxyalkyl radical as shown in eq. 1. For



$$RC\cdot(OR')_2 \longrightarrow RC(=O)\text{—}OR' + R'\cdot \qquad (1)$$

example, ethyl butyrate was obtained from the reaction of diethyl-*n*-butyral and di-*t*-butyl peroxide.[3] Similar reactions of cyclic acetals yield esters which are rearrangement products of the acetal as evidenced by the formation of methyl valerate from 2-methoxytetrahydropyran,[4] benzoate esters in the reactions of the cyclic acetals obtained from benzaldehyde and 1,2-glycols and 1,3-glycols,[5] and ethyl alkanoates in the photochemically induced reactions of the acetals obtained from ethylene glycol with various aldehydes.[6] The formation of aldehydes and ketones as products in these reactions results from similar fragmentation reactions of radicals formed by the abstraction of α-hydrogens from the alcohol moieties of the acetal.

The present study is concerned with the reactions of di-*t*-butyl peroxide with acetals of acetaldehyde having two different alkyl groups. Such mixed acetals are readily prepared by the acid-catalyzed reaction of a vinyl ether with an alcohol. Table I lists the mixed acetals used for our studies which were prepared in 40–

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[1] This work was supported by a grant from the National Science Foundation.

[2] Phillips Petroleum Research Fellow, 1963–1964. Taken from the thesis submitted by D. T. W. in partial fulfillment of the requirements for the Ph.D. degree from the University of Kansas, 1964.

[3] L. P. Kuhn and C. Wellman, *J. Org. Chem.*, **22**, 774 (1957).

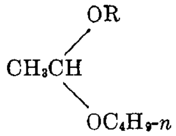
[4] E. S. Huyser, *ibid.*, **25**, 1820 (1960).

[5] E. S. Huyser and Z. Garcia, *ibid.*, **27**, 2716 (1962).

[6] D. Elad and R. D. Youssefyeh, *Tetrahedron Letters*, **No. 30**, 2189 (1963).

TABLE I

MIXED ACETALS PREPARED FOR REACTIONS WITH DI-*t*-BUTYL PEROXIDE

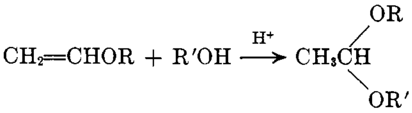


$CH_3CH(OR)(OC_4H_9\text{-}n)$

R	B.p., °C. (mm.)	$n^{21}D$	C, % Calcd.	C, % Found	H, % Calcd.	H, % Found
Isopropyl	37 (3)	1.4091[a]				
Allyl	41 (3)	1.4138[b]				
sec-Butyl	54 (4)	1.4090	68.97	68.94	12.64	12.56
t-Butyl	40 (3)	1.4067[c]				
Cyclopropylcarbinyl	50 (3)	1.4232	69.76	69.73	11.63	11.63
Cyclopentyl	45 (1)	1.4338	70.97	71.02	11.84	12.04
Cyclohexyl	75 (2)	1.4404[d]				
Cycloheptyl	91 (1)	1.4475	72.89	72.54	12.03	12.27
exo-Norbornyl	74 (1)	1.4521	73.58	73.10	11.32	11.40
endo-Norbornyl	82 (1)	1.4529	73.51	73.21	11.32	11.32
Benzyl	95 (1)	1.4779[e]	75.00	75.54	9.60	9.98
Cyclooctyl	105 (1)	1.5128	73.68	73.31	12.28	12.12

[a] M. F. Shostakowski and N. A. Gershtein [*J. Gen. Chem.* (USSR), **16**, 937 (1946)] reported $n^{20}D$ 1.3990. [b] Reported $n^{20}D$ 1.4140.[a] [c] Reported $n^{20}D$ 1.4068.[a] [d] Reported $n^{20}D$ 1.4415.[a] [e] B. I. Mikhantev, A. V. Tarasova, V. A. Sklyarov, and E. I. Fedorov [*Trudy Voronezh Gosudarst Univ.*, **57**, 177 (1959)] reported $n^{20}D$ 1.4820.

70% yields by the reaction of *n*-butyl vinyl ether with the appropriate alcohols.

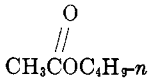
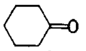
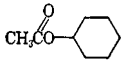


$$CH_2{=}CHOR + R'OH \xrightarrow{H^+} CH_3CH(OR)(OR') \qquad (2)$$

A complete analysis of the liquid products obtained from the reaction of di-*t*-butyl peroxide and *n*-butylcyclohexyl acetal at 130° was made. These products and their distribution, determined by gas chromatographic analysis of the reaction mixture, are shown in Table II.

TABLE II

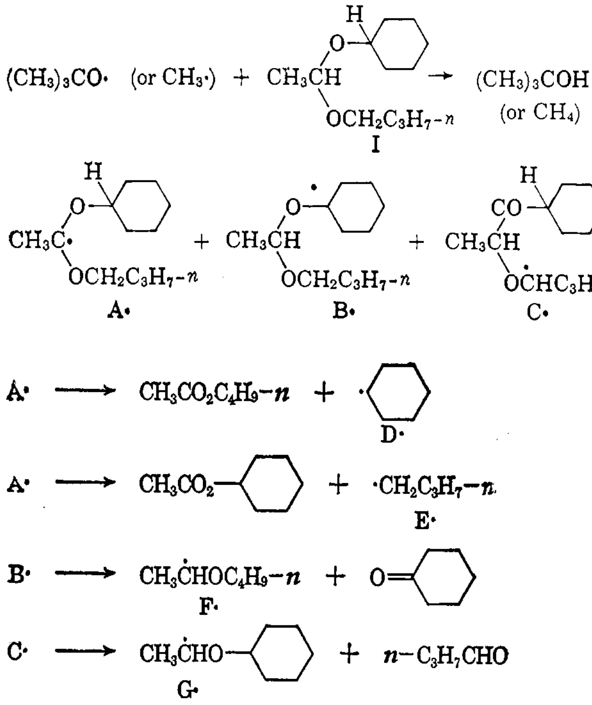
PRODUCTS OF THE REACTION OF *n*-BUTYLCYCLOHEXYL ACETAL (3.0 MMOLE) WITH DI-*t*-BUTYL PEROXIDE (0.26 MMOLE) AT 130° FOR 18 HR.

Product	Amount, mmoles
CH_3CHO	Trace
CH_3COCH_3	0.075
C_6H_{12}	0.13
$n\text{-}C_4H_9OC_2H_5$	0.13
$t\text{-}C_4H_9OH$	0.48
$n\text{-}C_3H_7CHO$	0.05
$C_6H_{11}OC_2H_5$	0.04
 $CH_3\overset{\overset{O}{\|}}{C}OC_4H_9\text{-}n$	0.20
	0.113
	0.074

These products are very likely produced in the sequence of reactions shown in eq. 3–14, a reaction scheme that might be predicted on the basis of earlier work. Although the sequence 6–14 is a self-propagating chain reaction, the amounts of the products suggest that the kinetic chain length is short. The chains very likely are terminated by various coupling reactions of the chain-carrying radicals. This could explain why various predictable quantitative relationships among the products produced in the sequence 6–14 are not found in the quantitative data in Table II.

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow 2(CH_3)_3CO\cdot \qquad (3)$$

$$(CH_3)_3CO\cdot \longrightarrow CH_3\cdot + CH_3COCH_3 \qquad (4)$$



(5)

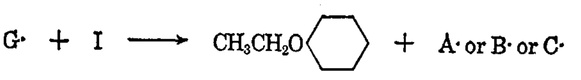
(6)

(7)

(8)

(9)

$$F\cdot + I \longrightarrow CH_3CH_2OC_4H_9\text{-}n + A\cdot \text{ or } B\cdot \text{ or } C\cdot \qquad (10)$$



(11)

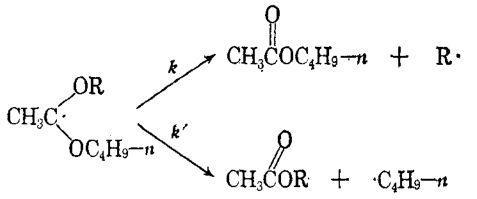
$$F\cdot \longrightarrow CH_3CHO + E\cdot \qquad (12)$$

$$G\cdot \longrightarrow CH_2CHO + D\cdot \qquad (13)$$

$$D\cdot \text{ (or } E\cdot) + I \longrightarrow C_6H_{12} \text{ (or } n\text{-}C_4H_{10}) + A\cdot \text{ or } B\cdot \text{ or } C\cdot \qquad (14)$$

One useful quantitative relationship that can be deduced from such product analysis and is not influenced by any termination process concerns the two fragmentation routes of radical A· shown in reactions 6 and 7.

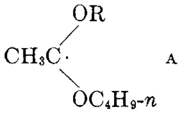
The relative amount of *n*-butyl acetate formed in the reaction with respect to cyclohexyl acetate is a quantitative measure of the relative ease of β-elimination of a cyclohexyl radical with respect to an *n*-butyl radical from A·. Similarly, the relative reactivities of β-elimination of other alkyl radicals from acetal derived radicals such as A· with respect to each other can be determined from the relative amounts of the two esters formed in the reactions of other mixed acetals with di-*t*-butyl peroxide. In our studies, each of the mixed acetals had the *n*-butyl group in common. Determination of the relative amount of the *n*-butyl acetate with respect to the other alkyl acetate produced in the reaction of the mixed acetal with the peroxide would be a measure of the relative rate of β-elimination from the acetal-derived radical of this alkyl group with respect to the *n*-butyl group. Table III lists the relative rates of elimination of a series of alkyl radicals with respect to the *n*-butyl radical determined by the quantitative gas chromatographic analysis of the acetate esters formed in the reactions of the corresponding mixed acetals.



(15)

TABLE III

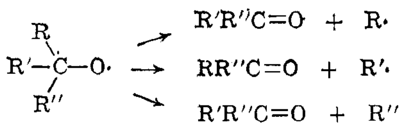
RELATIVE RATES OF β-ELIMINATION OF ALKYL RADICALS FROM



AT 130°

R	k/k'	No. of runs	Av. dev.
Isopropyl	5.66	3	0.24
Allyl	>25	3	
n-Butyl	1.00		
sec-Butyl	4.10	4	0.16
t-Butyl	18.7	4	0.6
Cyclopropylcarbinyl	3.89	3	0.11
Cyclopentyl	2.53	4	0.19
Cyclohexyl	2.36	4	0.21
Cycloheptyl	9.85	4	0.68
Cyclooctyl	17.2	4	2.4
exo-Norbornyl	2.20	5	0.17
endo-Norbornyl	0.87	4	0.04
Benzyl	22.4	4	1.2

Even a cursory examination of the data in Table III shows that the relative ease with which most of these alkyl groups undergo β-elimination in this system is related to the resonance stabilization of the free alkyl radicals. For the saturated alkyl radicals, where stabilization of the radical presumably involves hyperconjugation, the order of reactivity is tertiary > secondary > primary. In the cases where allylic and benzylic resonance of the radical are involved, the radical is eliminated even more readily than a tertiary alkyl radical. Although it is not surprising that the stability of the eliminated radical should influence the activation energy requirement for the reaction, the degree to which this effect is operative in these reactions is considerably less than that reported for the β-elimination reactions of alkyl radicals from alkoxyl radicals as shown in reaction 16.[7-9] Both Greene and his co-workers[9a] and Walling and Padwa[9b] found secondary alkyl radicals undergo β-elimination from alkoxyl radicals from thirty to fifty times as readily as primary alkyl radicals. The *t*-butyl radical is eliminated over 300 times as readily as the ethyl group from alkoxyl radicals. Our work shows that the β-elimination of a secondary alkyl radical from the α,α-dialkoxyalkyl radicals derived from the mixed acetals is only about five times as facile as the elimination of a primary alkyl radical and the *t*-butyl radical is eliminated only about eighteen times as readily as the *n*-butyl radical. The rather marked difference in the relative ease of β-elimination of the simple alkyl radicals from these two systems could be due to one or more of the following reasons: (1) a carbon–carbon bond is broken in the alkoxyl-radical reactions and a carbon–oxygen bond is broken in the acetal-derived radical reactions; (2) relief of steric strain is greater in the reactions of the alkoxyl radicals, a factor which would aid the elimination of the more bulky secondary and tertiary radicals in the alkoxyl system; (3) a sizable polar contribution is possible in the reactions of the alkoxyl radicals but not in the reactions of the acetal-derived radicals; and (4) a temperature factor may be involved, our relative reactivities being measured at 130° and those in the alkoxyl-radical systems being determined at 80° or below.



(16)

The bond dissociation energies of both the carbon–carbon bond and the carbon–oxygen bond are about 80 kcal./mole[10] and in each case the elimination reaction is accompanied by the formation of a carbonyl function. Since the absolute enthalpy changes for the β-eliminations of primary and secondary alkyl radicals are about the same in both systems, it seems unlikely that this factor would be responsible for the observed differences in the rates of β-eliminaion.

Relief of back strain would be expected to be greater in the β-elimination of a secondary alkyl radical than of a primary alkyl radical from the alkoxyl radical.[9b] A similar relief of strain does not exist in the β-elimination reactions of alkyl groups from the acetal-derived radicals. This factor might account in part for the difference in the relative rates of elimination of primary and secondary radicals in these two systems.[11]

A polar contribution to the transition state of the reaction involving β-elimination of an alkyl group from

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[7] P. Gray and A. Williams, *Chem. Rev.*, **59**, 239 (1959); *Trans. Faraday Soc.*, **55**, 760 (1959).

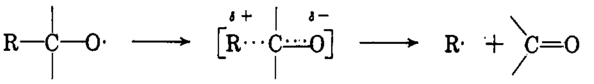
[8] J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

[9] (a) F. D. Greene, M. L. Savitz, F. D. Osterholtz, H. H. Lau, W. N. Smith, and P. M. Zanet, *J. Org. Chem.*, **28**, 55 (1963); (b) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1593 (1963).

[10] T. L. Cottrell, "The Strength of Chemical Bonds," Butterworths Scientific Publications, London, 1954.

[11] Greene and co-workers[9a] concluded that relief of steric strain is not necessarily a principal factor in the relative ease of β-elimination of alkyl radicals from alkoxyl radicals on the grounds that the bulky 1-norbornyl radical is eliminated comparatively slowly from alkoxyl radicals. They have suggested that lack of resonance stabilization in the 1-norbornyl radical is largely responsible. Although this very likely may be the important factor when the elimination rates of secondary alkyl radicals are compared with that of the 1-norbornyl radical, Walling[9b] does suggest that the strain factor may be significant when comparisons of relative rates of β-elimination of primary, secondary, and tertiary alkyl radicals are made.

an alkoxyl radical may be important, whereas similar polar contributions may be of little significance in the reactions of the acetal-derived radicals. In the alkoxyl-radical reactions, the alkyl group can display electron-donor properties and the oxygen electron-acceptor properties in the transition state of the reaction.[9b] Since the ability of the secondary (and tertiary) alkyl radicals to act as donors in such reactions is greater than that of primary radicals, these polar contributions may significantly lower the activation energy requirements for elimination of secondary or tertiary alkyl radicals over that of the primary alkyl radicals. Generally, polar contributions to the transition state of a radical reaction are a significant factor in lowering the activation energy requirement if a reacting electron donor or acceptor radical produces an electron-acceptor or -donor radical, respectively. This requirement is met in the alkoxyl-radical fragmentation reaction shown in eq. 17, where the electron-donor alkyl radical is eliminated from the electron-acceptor alkoxyl radical. However, in the β-elimination of an electron-donor alkyl radical from an acetal-derived radical, the reacting radical, an α,α-dialkoxyalkyl radical, is also a good electron-donor radical. Consequently, it is questionable if the eliminated alkyl radical can display its donor properties in the acetal-derived radical fragmentation reactions to a degree similar to that encountered in the alkoxyl-radical fragmentation reactions.



$$R-\overset{|}{\underset{|}{C}}-O\cdot \longrightarrow \left[\overset{\delta+}{R}\cdots\overset{|}{\underset{|}{C}}\overset{\delta-}{\cdots O}\right] \longrightarrow R\cdot + {>}C{=}O \qquad (17)$$

It is unlikely that the temperature factor alone could account for the observed differences in these two systems. In our studies, the effect of temperature was not measured since we were limited to those temperatures at which di-*t*-butyl peroxide decomposed at a reasonable rate. Extrapolation of the data reported by both Greene[9a] and Walling[9b] to the temperatures used in our reactions shows that temperature does not affect the reactivity ratios for β-elimination of primary and secondary alkyl groups as markedly as observed in changing the system from alkoxyl to dialkoxyalkyl radicals.

A conclusion that might be reached from the foregoing discussion is that the relative rates of β-elimination of the simple alkyl radicals from acetal-derived radicals are determined for the most part by the resonance stabilization of the alkyl radical and are relatively free from polar and steric effects (however, see discussion of cyclic compounds). This conclusion is supported by the nearly additive effect of increasing the number of alkyl groups bonded to the carbon that will become the radical site in their ability to increase the ease of β-elimination of the radical. A secondary alkyl radical is eliminated about four times as readily as a primary alkyl radical, and a tertiary alkyl radical about four times as readily as a secondary alkyl radical. In hydrogen atom abstractions by electron-acceptor radicals, reactions in which polar contributions can become quite considerable, the effect of increasing the number of alkyl groups on the carbon from which the hydrogen is being abstracted is generally greater than that observed here and is by no means additive. Generally, tertiary alkyl radicals are formed by hydrogen abstraction more readily than secondary radicals which in turn are formed far more readily than primary radicals.[12]

The cyclopropylcarbinyl radical is apparently stabilized to some extent as evidenced by the fact that this primary alkyl radical is eliminated about four times as readily as the *n*-butyl radical. Rate enhancements have been observed in other reactions in which the cyclopropylcarbinyl radical is formed, namely, the decomposition of certain azonitriles[13] and peroxides[14] and in the free-radical addition of radicals to vinyl cyclopropane.[15] The nature of the stabilizing effect of the cyclopropyl group is certainly open for discussion. The polar contribution, a factor cited previously as possibly contributing to its formation in certain reactions,[15] is very likely not important in the β-elimination of the cyclopropylcarbinyl radical from the acetal-derived radical. This suggests that the cyclopropyl group may have a stabilizing effect on the radical itself.

The relative ease with which the cycloalkyl radicals undergo β-elimination from acetal-derived radicals is consistent with observations made on the relative ease of formation of the cycloalkyl radicals in other reactions. In free-radical halogenations with bromotrichloromethane[16] and with chlorine in carbon disulfide,[17] the order of reactivity of the C_5 to C_8 cycloalkanes toward hydrogen abstraction is $C_8 > C_7 > C_5 > C_6$. Similarly, the rates of decomposition of the appropriate azonitriles yielding the α-cyanocycloalkyl radicals are in the order $C_8 > C_7 > C_5 > C_6$.[18] There is no apparent reason why the resonance stability of the cycloalkyl radicals should vary so markedly. On the other hand, conformational strain might be expected to be less in the cycloalkyl radical than in the acetal-derived radical from which it is eliminated.[19] Since the relief of conformation strain would be greatest in the cyclooctyl case and somewhat less in the cycloheptyl case, it is not surprising that the cyclooctyl and cycloheptyl radicals undergo β-elimination readily and in the observed order of reactivity. The lower reactivity of the cyclopentyl and cyclohexyl radicals compared with other secondary alkyl radicals may be caused in part to an increase in internal angular strain in these cycloalkyl groups resulting from the introduction of an sp^2-hybridized carbon in the ring.

The data found for the relative rates of β-elimination of the 2-norbornyl radical from the *exo*- and *endo*-2-norbornyl-*n*-butyl acetal-derived radicals presents a somewhat puzzling anomaly in that β-elimination of the 2-norbornyl radical from the *endo* isomer is only 40% as fast as from the *exo* isomer. The similarity in the relative rates of β-elimination of the 2-norbornyl radical from the *exo* isomer to that of the cyclohexyl radical is not unexpected. Although anchimeric assistance of the 6-carbon appears to be an important factor in deter-

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[12] *Cf.* C. Walling, "Free Radicals in Solution," John Wiley and Sons, Inc., New York, N. Y., 1957, pp. 357, 358; also, E. S. Huyser, *J. Org. Chem.*, **26**, 3261 (1961).

[13] G. C. Overberger and A. Lebovits, *J. Am. Chem. Soc.*, **76**, 2722 (1954).

[14] H. Hart and D. P. Wyman, *ibid.*, **81**, 4891 (1959); H. Hart and R. A. Caprini, *ibid.*, **84**, 3697 (1962).

[15] E. S. Huyser and J. D. Taliaferro, *J. Org. Chem.*, **28**, 3442 (1963).

[16] E. S. Huyser, H. Schimke, and R. L. Burham, *ibid.*, **28**, 2141 (1963).

[17] G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958).

[18] C. G. Overberger, H. Biletch, A. B. Finestone, J. Lilker, and J. Herbert, *ibid.*, **75**, 2078 (1953).

[19] For a discussion of these conformational effects in cyclic compounds, see E. L. Eliel, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, pp. 121, 122.

mining the relative rates of formation of the 2-norbornyl cation from various *exo*-2-norbornyl derivatives, such anchimeric effects are not found in the decompositions of peresters leading to the 2-norbornyl radicals.[20] It seems reasonable to assume that the difference in the ease of elimination of the 2-norbornyl radical from the two different acetal-derived radicals is not due to an increase in rate of β-elimination from the *exo* isomer acetal radical but rather to a decrease in the rate of the elimination from the *endo* isomer. The reason for the decrease in the rate of elimination of the 2-norbornyl radical from the *endo* isomer may involve a steric interference of some sort from the 5- and 6-hydrogens of the bicyclic system, an effect not operative in the case of the *exo* isomer. It is interesting to note that Bartlett and Pincock[20a] found that *endo*-2-carbo-*t*-butylperoxynorbornane decomposed at a rate about one-fourth that of the *exo*-2-carbo-*t*-butylperoxynorbornane.[20a]

Experimental[21]

Materials.—The following alcohols were commercial materials (Matheson Coleman and Bell) used without further purification: isopropyl alcohol, allyl alcohol, *sec*-butyl alcohol, *t*-butyl alcohol, cyclopentyl alcohol, cyclohexyl alcohol, and benzyl alcohol. Cycloheptyl alcohol (b.p. 96° at 26 mm.) was prepared in 90% yield by the sodium borohydride reduction of cycloheptanone (Aldrich). Cyclooctyl alcohol (b.p. 60-62° at 2 mm.) was prepared in 78% yield by the hydroboration of cyclooctene (Aldrich). Cyclopropyl carbinyl alcohol (b.p. 121–122°) was prepared in 44% yield by lithium aluminum hydride reduction of cyclopropane carboxylic acid (Aldrich). *exo*-Norborneol was obtained commercially (Aldrich) and used without further purification (m.p. 127–129°). *endo*-Norborneol (m.p. 147–148°) was prepared by the sodium borohydride reduction of norcamphor (Aldrich). *n*-Butyl vinyl ether (Matheson Coleman and Bell) was redistilled before using. The di-*t*-butyl peroxide was obtained from the Lucidol Corporation and used without further purification.

The gas chromatographic analyses were performed on an Aerograph A-90P and recorded on a Sargent recorder (Model SR) fitted with a Disc Integrator. Columns (10 to 15 ft. by 0.25 inch) packed with the following substrates on Chromosorb P were used for the analyses: (a) 15% E-600 (Dow Chemical Company); (b) 15% Theed (Fisher Chemical Company); and (c) a mixture of 7% L-699 (Nalco Chemical Company) and 7% Ucon-nonpolar (Wilkins Instrument and Research, Inc.). In many instances, the esters produced in the reaction were identified by comparison of their retention times with those of authentic samples on more than one of the above-mentioned columns as well as other columns in seeking a column and conditions suitable for the quantitative analysis of the reaction mixture.

Preparation of Mixed Acetals.—Equimolar amounts of *n*-butyl vinyl ether and the alcohol were mixed along with a trace of *p*-toluenesulfonic acid. Almost immediate reaction ensued as evidenced by the evolution of heat. The reaction temperature was kept below 60° by swirling the reaction flask in an ice bath. In most cases, the reaction was essentially over in about 30 min. A few pellets of sodium hydroxide were added to the mixture and the mixed acetal was distilled from the reaction mixture under reduced pressure. A center cut (usually about 40–70% of the theoretical amount) was collected and used for analysis and for reaction with di-*t*-butyl peroxide. The acetals prepared in this manner, along with their boiling points and refractive indices, are listed in Table I.

Reaction of *n*-Butylcyclohexyl Acetal with Di-*t*-butyl Peroxide.—A reaction mixture consisting of *n*-butylcyclohexyl acetal (0.60 g., 3.0 mmoles) and di-*t*-butyl peroxide (0.0379 g., 0.26 mmoles) was sealed in a Pyrex tube and heated for 18 hr. at 130° in a refluxing chlorobenzene bath. The contents of the tube were analyzed by gas chromatographic analysis on the combination L-699 and Ucon-nonpolar column. The lower boiling components (acetaldehyde, acetone, cyclohexane, butyraldehyde, and *t*-butyl alcohol) were identified by comparison of their retention times with those of authentic samples at a temperature of 50°. A higher column temperature (120°) was employed for the higher boiling components. The quantitative estimations of the components were made by comparison of their peak areas with that of cyclopentyl acetate which was added in a known amount to a weighed portion of the reaction mixture. The necessary correction factors relating the peak area ratios to the mole ratios were made from the chromatograms of known mixtures of cyclopentyl acetate with each component. The data collected in this experiment are shown in Table II.

Determination of Relative Rates of Alkyl-Radical Elimination from Mixed Acetal Radicals.—The following general procedure was used for the determination of the relative rates of elimination of alkyl radicals from acetal radicals. A mixture consisting of the acetal and di-*t*-butyl peroxide in an approximate ratio of 10:1 was sealed in a Pyrex tube and heated for 18 hr. at 130° in a refluxing chlorobenzene bath. The resulting reaction mixture was subjected to gas chromatographic analysis on various columns at various column temperatures and helium flow rates until chromatographic conditions were found that would separate the two esters formed in the reaction from other products of the reaction. The ratio of the two esters formed was determined from their peak areas. The necessary correction factor required to equate the peak area ratio to the mole ratio was obtained from chromatograms of known mixtures of authentic samples of the two esters. From three to five different runs were made for each acetal. The data are reported in Table III.

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(20) (a) P. D. Bartlett and E. Pincock, *J. Am. Chem. Soc.*, **84**, 2445 (1962); (b) M. M. Martin and D. C. De Yongh, *ibid.*, **84**, 3526 (1962).

(21) Boiling points and melting points are uncorrected. Analyses were performed by Weiler and Strauss, Oxford, England.