taken up in hot DMF, filtered, and water was added to precipitate the crude product which was collected, affording 0.33 g (91% yield) of a colorless solid, mp 389–391°. Repeated crystallization from DMF–water solvent pair gave an analytical sample of **18**, mp 390–392°.

Anal. Calcd for $C_{25}H_{18}N_2O$: C, 83.13; H, 5.01. Found: C, 82.91; H, 5.02.

An attempt to reduce **18** using lithium aluminum hydride in anhydrous diglyme yielded only unreduced **18** and none of the desired **2a**.

3,10-Diphenyl-6,7-dioxo-5,6,7,8-tetrahydrodibenzo[*e*,*g*] [1,4]-diazocine (19).—Two grams (6.0 mmol) of **13**, mp 225.0–227.0°, was dissolved in 250 ml of anhydrous toluene and to this refluxing solution 0.93 ml (7.5 mmol) of oxalyl chloride in 100 ml of anhydrous toluene was added dropwise with stirring. A colorless solid separated immediately. After refluxing for an additional 30 min, the reaction mixture was cooled, filtered, washed with toluene, and dried at 125° for 24 hr. The product proved to be insoluble in several solvents, and was finally triturated with hot DMF and filtered. This process was repeated twice, affording 1.9 g (82% yield) of **19** as a colorless powder, mp above 400°.

Anal. Calcd for $C_{26}H_{18}N_2O_2$: C, 79.99; H, 4.64. Found: C, 79.65; H, 4.26.

Lithium aluminum hydride reduction of **19** in anhydrous diglyme yielded only recovered **19** and none of the desired reduction product **2b**.

Registry No.—**1a**, 42447-99-4; **1b**, 42448-00-0; **1c**, 42448-01-1; **1d**, 42448-02-2; **3**, 42448-03-3; **5**, 18062-89-0; **6**, 42271-42-1; **7**, 42271-43-2; **7** acetyl derivative, 42271-44-3; **8**, 42271-45-4; **9**, 42271-46-5; **10**, 4085-18-1; **11**, 2499-68-5; **12**, 2499-69-6; **13**, 2499-76-5; **17**, 42448-04-4; **18**, 42448-05-5; **19**, 42448-06-6; diphenyl ether, 101-84-8; 4-nitrobiphenyl, 92-93-3; methylene iodide, 75-11-6; 1,2-dibromoethane, 106-93-4; 1,3-dibromopropane, 109-64-8; 1,4-dibromobutane, 110-52-1.

A New Ring Expansion Reaction. V. The Decomposition of the Magnesium Salts of Various 1-(1-Bromo-1-methylethyl)-1-cycloalkanols. Electrophilic Addition to Isopropylidenecycloalkanes

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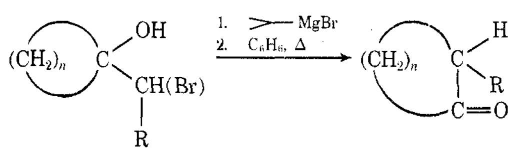
The synthesis of some 2,2-dimethylcycloalkanones is described. They were prepared from the decomposition of the magnesium salts of various halohydrins by a ring-enlargement procedure previously described. The necessary halohydrins were prepared from an electrophilic addition reaction with aqueous NBS and the isopropylidenecycloalkanes. The reasons for the observed selective orientation of the bromo and hydroxyl groups are discussed.

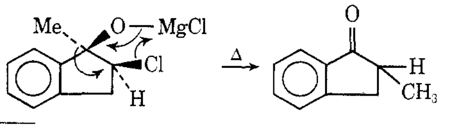
Preliminary papers[1] have reported a new ring-enlargement procedure[2] entailing the decomposition of the magnesium salts of appropriate halohydrins (eq 1).



(1)

R = CH_3 and C_6H_5; *n* = 4, 5, 6, and 7

Our results were in accord with those of Geissman and Akawie,[3] who extensively studied the reaction producing ketones *via* the decomposition of the magnesium salts of halohydrins. They observed that primary halides rearrange only when a good migrating group is involved but that secondary and tertiary halides rearrange regardless of the migrating group. From their stereochemical studies, they concluded that the halo and hydroxyl groups must be cis (or be able to attain the cis conformation in nonrigid systems) to effect the rearrangement. Trans isomers lead to extensive decomposition, making an epoxide intermediate for the reaction unlikely and leaving as most plausible a pinacol-type mechanism (eq 2).



(2)

This paper describes the synthesis of various 2,2-dimethylcycloalkanones by the new ring-enlargement procedure,[1] as starting materials for which we required halohydrins of the type depicted in **1**. In a preliminary communication,[4] we reported that isopropylidenecyclopentane, when treated with aqueous *N*-bromosuccinimide (NBS), yielded **1** (*n* = 4), the structural assignment for which was confirmed by the conversion of its magnesium salt to 2,2-dimethylcyclohexanone[5] in 54% overall yield. Additional confirmation has now been furnished by examination of the nmr spectrum, which reveals, from the location of the methyl signal (τ 8.2), that the bromine is indeed attached to the exocyclic carbon atom.[6] It was also reported[4] that isopropylidenecyclohexane, when treated with aqueous NBS, gave a halohydrin **2** *isomeric* with **1** (*n* = 5). The structure **2** was verified by decomposition of the magnesium salt, which yielded only 1-acetyl-1-methylcyclohexane in 66% overall yield. Further

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[1] A. J. Sisti, *J. Org. Chem.*, **33**, 453 (1968); **35**, 2670 (1970).

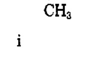
[2] For an excellent recent review, see C. D. Gutsche and D. Redmore, "Carbocyclic Ring Expansion Reactions," Academic Press, New York, N. Y., 1968.

[3] T. A. Geissman and R. I. Akawie, *J. Amer. Chem. Soc.* **73**, 1993 (1951).

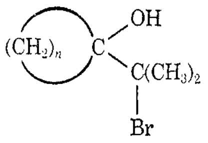
[4] A. J. Sisti, *Tetrahedron Lett.*, 3305 (1970).

[5] The vpc revealed the presence of a 5–10% contaminant, presumably methyl 1-methylcyclopentyl ketone based upon the same retention time as that of an authentic sample [A. J. Sisti and A. C. Vitale, *J. Org. Chem.*, **37** 4090 (1972)] and the nmr spectrum (τ 8.0 and 8.8, two small sharp singlets) It is presumed that the ketone arose from the rearrangement of small amounts of the corresponding epoxide and/or small amounts of the magnesium salt of the halohydrin isomeric with **1** (*n* = 4).

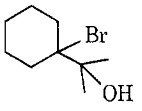
[6] R. M. Silverstein and G. C. Bassler, "Spectrometric Identification of Organic Compounds," Wiley, New York, N. Y., 1967, p 136. Model compounds i show the nmr methyl signal at τ 8.3 (doublet); see A. J. Sisti, *J. Org. Chem.*, **35**, 2670 (1970).



i

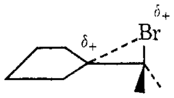


1 (n = 4, 5, and 6)

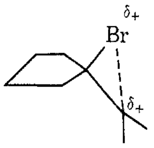


2

data now reported confirm that the hydroxyl group is bound to the exocyclic carbon atom[6] in **2** (CH_3 signal τ 8.6). The striking feature of the reactions of these two olefins is that the addition of the bromo and hydroxyl groups is regiospecifically *opposite* in the two cases. Since the reaction of aqueous NBS with an olefin proceeds *via* the bromonium ion,[7] these results were rationalized by invoking the concepts of *I* strain[8] and the unsymmetrical bromonium ion[9] as follows. Of the two possible unsymmetrical bromonium ions from isopropylidenecyclopentane (**3** and **3a**), the former



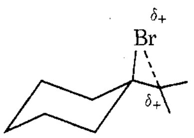
3



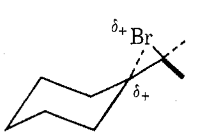
3a

should be the more stable since it would more nearly maintain sp^2 hybridization on the ring carbon in the transition state and thereby avoid or minimize four bond oppositions (two H–Br and two H–isopropyl oppositions) present in **3a**; **3** then reacts with water to yield **1** (n = 4).

In the case of isopropylidenecyclohexane, **4** should be more stable than **4a** since the transition state of the



4



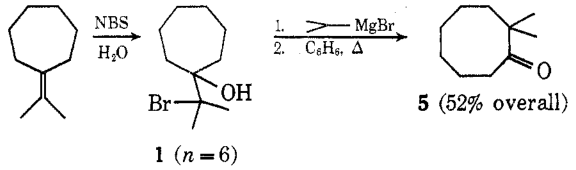
4a

former has essentially sp^3 hybridization on the ring carbon, and thus minimizes the two bond oppositions which are present in **4a** (two adjacent equatorial hydrogens opposed to the isopropyl group); **4** subsequently reacts with water to produce **2**.

The present work further examines this rationale and the synthetic utility of our ring-enlargement sequence by extending them to the cycloheptane, cyclooctane, and norbornane systems.

Results and Discussion

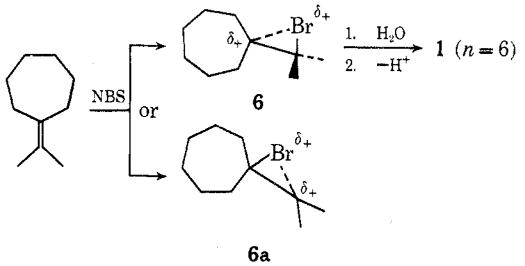
2,2-Dimethylcyclooctanone (5) from Isopropylidenecycloheptane.—The halohydrin[10] **1** (n = 6) was prepared from isopropylidenecycloheptane by treatment with aqueous NBS. The structure for **1** (n = 6) is based upon the nmr spectrum (the methyl signal at τ 8.2 indicates that the bromine is bound to the isopropyl carbon atom[6]), the ir spectrum, and the ring expansion to, almost exclusively, 2,2-dimethylcyclooctanone (**5**) (eq 3). The purity of **5** was established



(3)

by vpc and found to be about 90%.[11] The structure for **5** was confirmed by elemental analysis and the ir and nmr spectra.

The orientation observed from the electrophilic addition to isopropylidenecycloheptane was rationalized by the concepts of *I* strain[8] and the unsymmetrical bromonium ion[9] (eq 4). A change in hybridization



(4)

from sp^2 to sp^3 at the site of reaction in a seven-membered ring is beset with bond oppositions and is comparatively disfavored. Therefore, of the two possible unsymmetrical bromonium ions **6** and **6a**, **6** should be the more stable since it would maintain a trigonal or quasitrigonal geometry on the ring carbon in the transition state and thereby avoid or minimize four bond oppositions (two H–Br and two H–isopropyl) present in **6a**; **6** will then yield **1** (n = 6) after nucleophilic attack by water (eq 4).

3,3-Dimethyl[3.2.1]bicyclooctanone-2 (7) from 2-Isopropylidenenorbornane.—The necessary halohydrin[10] **8** was prepared from the olefin with aqueous NBS and was subsequently converted by ring enlargement to the bicyclic ketone **7** in 13% overall yield (eq 5). The poor yield is primarily attributed to the extensive decomposition of **8** during the ring enlargement reaction. The vpc analysis indicated that the product **7** was approximately 85% pure.[12] The structure of **8**

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(7) E. E. Van Tamelen and K. B. Sharpless, *Tetrahedron Lett.*, 2655 (1967).

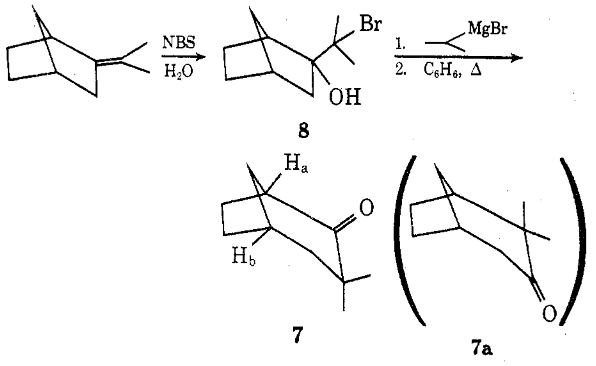
(8) H. C. Brown, R. S. Fletcher, and R. B. Johannesen, *J. Amer. Chem. Soc.*, **73**, 212 (1951).

(9) D. R. Dalton, V. P. Dutta, and D. C. Jones, *J. Amer. Chem. Soc.*, **90**, 5498 (1968).

(10) All halohydrins herein were handled under mild conditions during work-up and were used immediately without purification. Undoubtedly, their extreme lability is due to the presence of the tertiary bromo group and the relatively severe bond oppositions in **1**, **2**, and **8**.

(11) The impurity is probably 1-acetyl-1-methylcycloheptane (as suggested by the observation of two small sharp signals in the nmr spectrum at τ 8.0 and 8.9), probably arising from the rearrangement of the corresponding epoxide and/or small amounts of the magnesium salt of the halohydrin isomeric with **1** (n = 6).

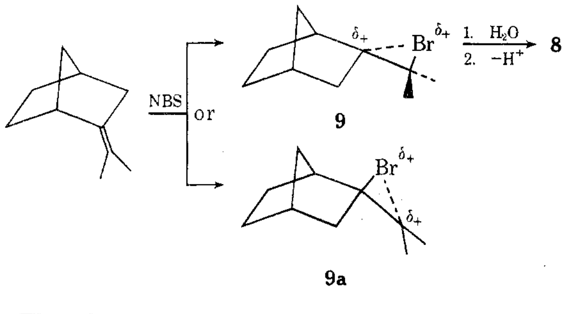
(12) Again the impurity is presumably 2-acetyl-2-methylnorbornane (on the basis of two small sharp signals in the nmr spectrum at τ 8.0 and 8.95) probably arising from rearrangement of small amounts of the corresponding epoxide and/or small amounts of the magnesium salt of the halohydrin isomeric with **8**.



(5)

was established from the ir spectrum, the nmr spectrum (signal position for the methyl group at τ 8.28), and conversion to the bicyclic ketone **7** (eq 5). The structure assigned to **7** is based upon the ir spectrum, elemental analysis (2,4-DNP), and the nmr spectrum, which confirmed structure **7** by the presence of signals at τ 7.3–7.4 (H_a multiplet), 7.6–7.7 (H_b multiplet), and 8.9 and 9.0 (the two methyl groups). Model compounds for these signal assignments have already been presented.[13] Additional support for the structural assignment was obtained from a deuterium exchange study. After the bicyclic ketone **7** was treated with trifluoroacetic acid-*d* (10% solution) for 24 hr at 80°, the nmr spectrum revealed that essentially no hydrogens were exchanged [the bicyclic ketone **7a**, the product, if the more substituted C-1–C-2 bond had migrated in **8** (eq 5), should have exchanged two hydrogens]. The reasons for the migratory preference of the less substituted C-2–C-3 bond in **8** have been discussed previously[13] and need not be repeated here.

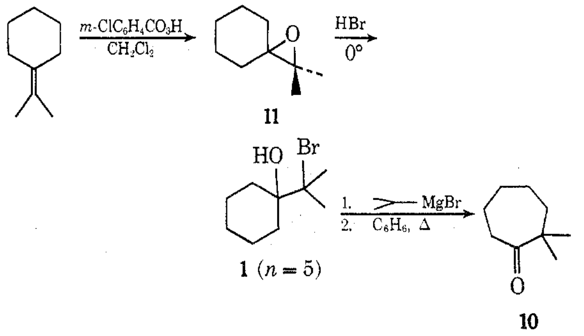
Since it is known that, in the norbornane system, bond oppositions are present between the groups on C-2 and C-3 and between the groups on C-5 and C-6, *I* strain[8] and the unsymmetrical bromonium ion[9] should adequately explain the production of **8**. Of the two possible unsymmetrical (exo) bromonium ions, **9** and **9a**, **9** is the more stable since it would more nearly maintain the quasitrigonal geometry at C-2 in the transition state and thus avoid or minimize two bond oppositions (H–Br and H–isopropyl) present in **9a**. Subsequent endo attack by water on **9** will yield **8**, the observed product (eq 6).



(6)

The above arguments presented to account for the orientation observed from all four olefins apply, provided that other effects are excluded or accounted for. Rationalizations based upon polar considerations do not seem fruitful, since both bromo carbonium ions from each olefin would be tertiary and should be of comparable stability. It also seems reasonable to suppose that the symmetrical bromonium ions and the corresponding unsymmetrical bromonium ions (**3**, **4**, **6**, and **9**) should be of comparable stabilities in terms of purely polar considerations. All these results therefore seem best explained by invoking the concepts of *I* strain[8] and the unsymmetrical bromonium ion,[9] as elaborated above.

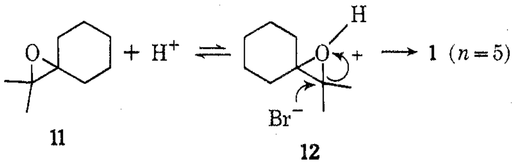
2,2-Dimethylcycloheptanone (10) from Isopropylidenecyclohexane.—It has already been demonstrated that the desired halohydrin **1** (*n* = 5) cannot be prepared directly from the olefin with aqueous NBS, since the isomeric halohydrin **2** is produced. Our alternate synthetic approach to the halohydrin **1** (*n* = 5) involved the hydrogen bromide cleavage of isopropylidenecyclohexane epoxide (**11**) (eq 7). The structure elucidation



(7)

for the product **1** (*n* = 5) was based upon the ir spectrum, the nmr spectrum,[6] and conversion to 2,2-dimethylcycloheptanone (**10**) in 57% overall yield (eq 7). The structure for **10** was assigned from the ir and nmr spectra and conversion to a known derivative. The vpc of **10** established the purity as 85%.[14]

The two most plausible mechanisms for the production of a halohydrin from the epoxide **11** both reasonably lead to **1** (*n* = 5). If the symmetrical oxonium ion **12** were involved, bromide ion should preferentially attack the exocyclic carbon atom (eq 8), since it is



(8)

known that SN2 reactions upon the cyclohexyl system are sluggish[15] compared with those upon its acyclic counterpart; alternatively, of the two unsymmetrical oxonium ions, **13** and **13a**, the former should be the more stable since it more nearly maintains the sp^3 hybridization on the ring carbon in the transition state and bond oppositions present in **13a** are thereby avoided or minimized (eq 9); attack by bromide ion on **13** will then yield **1** (*n* = 5). Attempts to account for the product due to a difference in stability between **13** and **13a** based on polar considerations are unconvincing, since they should be of comparable stability. The

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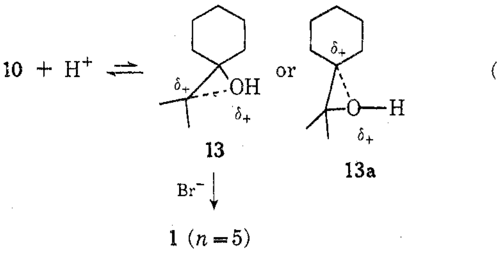
(13) A. J. Sisti, G. M. Rusch, and H. Sukhon, *J. Org. Chem.*, **36**, 2030 (1971); A. J. Sisti, *ibid.*, **35**, 2670 (1970).

(14) The major contaminant is believed to be 1-acetyl-1-methylcyclohexane, confirmation being obtained from the nmr spectrum, which revealed two small sharp signals at τ 8.0 and 8.9; an authentic sample (ref 4) had the same retention time as the impurity. The source of the ketone is probably the rearrangement of small amounts of the corresponding epoxide and/or small amounts of the magnesium salt of the isomeric halohydrin **2**.

(15) E. L. Eliel in "Steric Effects of Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, pp 123–125; P. J. Fierens, *Bull. Soc. Chim. Belg.*, **61**, 427, 609 (1952).



(9)

mechanism involving the unsymmetrical oxonium ion **13** is preferred, because it is known that under acidic conditions highly substituted epoxides undergo cleavage by the SN1 mechanism.[16]

The epoxides from isopropylidenecyclopentane and isopropylidencycloheptane were prepared and subjected to cleavage with 48% hydrogen bromide in an attempt to synthesize the halohydrins isomeric with **1** (n = 4 and 6). However, in each case, extensive decomposition ensued—polymerization (cyclopentane system) and dehydrohalogenation[17] and dehydration (cycloheptyl system)—as evidenced by the ir and nmr spectra.

Presently, other electrophilic and free-radical additions to the isopropylidenecycloalkanes herein mentioned are being undertaken.

Experimental Section[18]

1-(1-Bromo-1-methylethyl)-1-cycloalkanols were prepared from the appropriate isopropylidenecycloalkanes (Columbia Organic Chemicals Co.) (100–150 mmol), an equivalent amount of N-bromosuccinimide (NBS), and 100–150 ml of water according to a previously described procedure,[19] except that the reaction temperature was maintained between 10 and 20°, and, after all the NBS had reacted, the mixture was stirred for 5 min. All halohydrins were used immediately without purification.[10]

Halohydrin 1 (n = 4) was a colorless oil: ir 3480 cm^{-1}; nmr τ 8.2 [sharp s, $-C(Br)(CH_3)_2$]; **1** (n = 4) gave an instantaneous precipitate of AgBr when treated with alcoholic $AgNO_3$.

Halohydrin 1 (n = 6) was a light yellow oil: ir 3560 and 3480 cm^{-1}; nmr τ 8.2 [sharp s, $-C(Br)(CH_3)_2$]; **1** (n = 6) gave an instantaneous precipitate of AgBr with alcoholic $AgNO_3$.

Halohydrin 2 was a colorless oil: ir 3540 and 3460 cm^{-1}; nmr ($CDCl_3$) τ 8.6 [sharp s, $-C(OH)(CH_3)_2$]; **2** gave an instantaneous precipitate of AgBr when treated with alcoholic $AgNO_3$.

Halohydrin 8 (prepared from 2-isopropylidenenorbornane[20] by the above procedure) was a dark yellow oil: ir 3550 and 3480 cm^{-1}; nmr τ 8.28 [sharp s, $-C(Br)(CH_3)_2$]; an instantaneous precipitate resulted when **8** was treated with alcoholic $AgNO_3$.

Isopropylidenecyclohexane epoxide 11 was prepared by the dropwise addition of a solution of 20.3 g (100 mmol) of m-chloroperbenzoic acid (Aldrich Chemical Co.) dissolved in 200 ml of CH_2Cl_2 to a vigorously stirred solution of 12.4 g (100 mmol) of isopropylidenecyclohexane[21] in 50 ml of CH_2Cl_2 (at room temperature). The reaction mixture was stirred at room temperature overnight. It was then filtered and the filtrate was washed twice with 25 ml of 20% $NaHSO_3$, twice with 50 ml of 10% $NaHCO_3$, and once with 100 ml of saturated aquaous NaCl. The organic solution was dried ($MgSO_4$), filtered, concentrated, and distilled through a 20-cm micro-Vigreux column and there was obtained 12.1 g (87%) of **11** as a colorless liquid: bp 61–62° (12 mm); nmr τ 8.7 (sharp s, 6 H) and 8.2–8.4 (m, 10 H).

Anal. Calcd for $C_9H_{16}O$: C, 77.09; H, 11.50. Found: C, 77.17; H, 11.51.

Ten grams (72 mmol) of the epoxide **11** was cleaved with 48% HBr at 0°[10] according to the procedure of Traynham.[22] The resulting dense oil **1** (n = 5) gave the following data: ir 3450 cm^{-1}; nmr τ 8.15 [sharp s, $-C(Br)(CH_3)_2$].

Isopropylidenecyclopentane epoxide was prepared from 11.0 g (100 mmol) of isopropylidenecyclopentane[21] and 20.3 g (100 mmol) of m-chloroperbenzoic acid as above. Distillation through a 20-cm micro-Vigreux column yielded 7.6 g (60%) of a colorless liquid: bp 56–57° (22 mm); nmr τ 8.7 (sharp s, 6 H) and 8.1–8.2 (m, 8 H).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.28; H, 11.16.

Upon treatment of isopropylidenecyclopentane epoxide with 48% hydrogen bromide according to the procedure of Traynham,[22] extensive decomposition and polymerization occurred immediately[17] along with extreme discoloration. No product characteristic of a halohydrin could be isolated.

Isopropylidenecycloheptane epoxide was prepared with 13.8 g (100 mmol) of isopropylidenecycloheptane (Columbia Organic Chemical Co.) and 20.3 g (100 mmol) of m-chloroperbenzoic acid as above. Distillation through a 20-cm micro-Vigreux column afforded 12.3 g (80%) of a colorless liquid: bp 74–75° (9 mm); nmr τ 8.6 (sharp s, 6 H) and 8.1–8.2 (m, 12 H).

Anal. Calcd for $C_{10}H_{18}O$: C, 77.86; H, 11.76. Found: C, 77.67; H, 11.70.

Treatment of isopropylidenecycloheptane epoxide with 48% HBr at 0° according to the procedure of Traynham[22] afforded an unstable oil which spontaneously fumed (HBr):[17] ir 1600 (vinyl hydrogen), 3500 cm^{-1} (w, OH); nmr ($CDCl_3$) τ 3.7–3.9 (m, vinyl hydrogen) and 5.0–5.1 (d, vinyl hydrogen).

2,2-Dimethylcycloalkanones were prepared by the dropwise addition of an equivalent amount of isopropylmagnesium bromide in ether (since the halohydrins were not purified,[10] the quantity of isopropyl bromide used in the formation of the Grignard reagent was equal to the number of moles of olefin employed for the preparation of the halohydrins) to 300 ml of a cooled anhydrous benzene solution of the halohydrin. After the addition, the solution was refluxed for 1 hr and subsequently decomposed with aqueous NH_4Cl. The separated organic portion was washed successively with water, 10% $NaHCO_3$ solution, and water, and then dried ($MgSO_4$), concentrated, and distilled.

2,2-Dimethylcyclohexanone: bp 55–57° (9 mm) (lit.[23] bp 169–170°); 10.2 g (79 mmol, 54% based upon 150 mmol of isopropylidenecyclopentane) isolated; ir 1710 cm^{-1}; nmr τ 8.98 [sharp s, $-COC(CH_3)_2$]; vpc (150°)[18] showed 90–95% purity;[5] 2,4-DNP mp 139–140° (lit.[23] mp 140–142°); mixture melting point produced no depression.

2,2-Dimethylcyclooctanone (**5**): bp 68–70° (2.5 mm); 8.0 g (52 mmol) isolated (52% based upon 100 mmol of isopropylidenecycloheptane); ir 1700 cm^{-1}; nmr τ 8.98 [sharp s, $-COC(CH_3)_2$]; vpc (200°)[18] demonstrated that **5** was 90% pure.[11]

Anal. Calcd for $C_{10}H_{18}O$: C, 77.92; H, 11.68. Found: C, 77.72; H, 11.50.

The 2,4-DNP was prepared as usual, mp 129–130° (EtOH).

Anal. Calcd for $C_{16}H_{22}N_4O_4$: C, 57.48; H, 6.58, N, 16.76. Found: C, 57.45; H, 6.50; N, 16.66.

2,2-Dimethylcycloheptanone (**10**): bp 81° (18 mm) [lit.[24] bp 82° (18 mm)]; 6.7 g (47 mmol) (67% based upon 72 mmol of the epoxide **11** or 57% based upon 83 mmol of isopropylidenecyclohexane) isolated; the amount of isopropyl bromide employed in the formation of the Grignard was equal to the number of moles of epoxide **11** used for the formation of the halohydrin **1** (n = 5); ir 1700 cm^{-1}; nmr τ 9.0 [sharp s, $-COC(CH_3)_2$]; vpc (200°)[18] demonstrated that **10** was 85% pure;[14] the semicarbazone had a melting point of 175–176° (lit.[24] mp 175°).

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[16] C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p 344; see also ref 15, p 112.

[17] It should be noted that the tertiary bromine on the ring carbon atom as opposed to the exocyclic tertiary bromine **1** (n = 4 and 6) would be more labile, since the magnitude of the bond oppositions (five- and seven-membered rings) would be increased and thus provide added impetus for the loss of bromide ion.

[18] All melting points are uncorrected. Infrared spectra, all of pure liquid films, were determined with a Perkin-Elmer Spectracord spectrophotometer. The nmr spectra of CCl_4 solutions, unless otherwise specified, were determined with a Varian A-60 instrument. The vpc analyses were performed with an F & M Scientific Model 720 duel column programmed temperature instrument; a 4-ft column packed with 20% Carbowax 4000 on Chromosorb W was employed at a pressure of 40 psi.

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1-Acetyl-1-methylcyclohexane: bp 68–70° (7 mm) [lit.[25] bp 80–85° (16 mm)]; 13.8 g (66% based upon 150 mmol of olefin) isolated; ir 1700 cm^{-1}; nmr τ 8.0 and 9.0 [sharp s, $H_3CCOCCH_3$]; vpc (130° and 150°)[18] showed a single compound. The 2,4-DNP had a melting point of 131–132° (lit.[26] mp 132°) and the semicarbazone melted at 183–185° (lit.[26] mp 186–187°).

3,3-Dimethyl[3.2.1]bicyclooctanone-2 (7): bp 30–40° (0.3 mm); ir 1710, 3050, and 1610 cm^{-1} (the latter indicated olefinic contamination); vpc (200°)[18] indicated three compounds present. The distillate, dissolved in petroleum ether (bp 30–60°), was placed upon a column containing 30 g of neutral alumina. Elution with petroleum ether yielded an unidentified olefin, ir 3050 and 1610 cm^{-1}, no carbonyl or hydroxyl absorptions present. Elution with 50% (v/v) benzene–petroleum ether yielded 2 g of **7** (13% based upon 100 mmol of 2-isopropylidenenorbornane used): ir 1705 cm^{-1}; vpc (200°)[18] indicated 85% purity;[12] nmr τ 8.9 and 9.0 [d, sharp $-COC(CH_3)_2$]; the 2,4-DNP had a melting point of 103–105° (EtOH).

Anal. Calcd for $C_{16}H_{20}N_4O_4$: C, 57.83; H, 6.02; N, 16.86. Found: C, 57.91; H, 6.16; N, 17.01.

A small amount of **7** was treated with trifluoroacetic acid-*d* (10% solution) at 80° for 24 hr; the nmr of the product showed no deuterium exchange.

Registry No.—**1** (*n* = 4), 42393-47-5; **1** (*n* = 5), 42393-48-6; **1** (*n* = 6), 42393-49-7; **2**, 42393-50-0; **5**, 42393-51-1; **5** 2,4-DNP, 42393-52-2; **7**, 42393-53-3; **7** 2,4-DNP, 42393-54-4; **8**, 42393-55-5; **11**, 15446-32-9; *m*-chloroperbenzoic acid, 937-14-4; isopropylidenecyclohexane, 5749-72-4; isopropylidenecyclopentane epoxide, 42393-57-7; isopropylidenecyclopentane, 765-83-3; isopropylidenecycloheptane epoxide, 42393-59-9; isopropylidenecycloheptane, 7087-36-7.

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Intramolecular Propagation in the Oxidation of *n*-Alkanes. Autoxidation of *n*-Pentane and n-Octane

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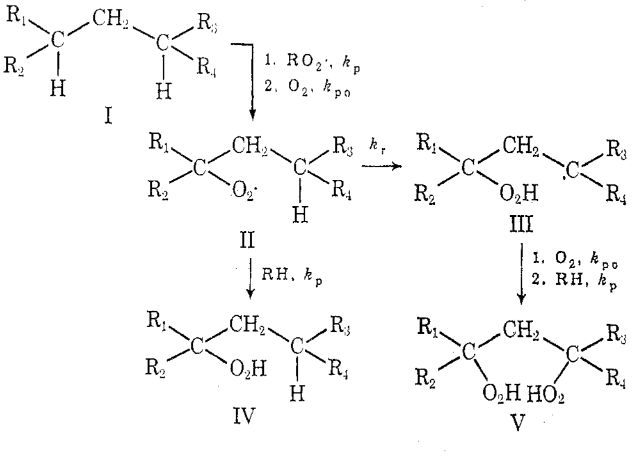
Initiated oxidations of liquid *n*-pentane and *n*-octane at 100 and 125°, respectively, give complex mixtures of products, including 34–76% pentyl hydroperoxides (mostly secondary monohydroperoxides) at <1% conversion and 19–54% octyl hydroperoxides at higher conversions. More cleavage products are found for octane than for pentane at all conversions. Bifunctional products from pentane include dihydroperoxide or diol and ketohydroperoxide with maximum yields of 10% on consumed oxygen. Added *tert*-BuO_2H markedly reduced this yield. Small amounts of octanediols were found following reduction but no reliable estimates of yields were possible. The absolute rate of intramolecular abstraction by *sec*-pentyl peroxy radicals is $^1/_{80}$ of that of 2,4-dimethyl-2-pentylperoxy radical and the ratio of attack by peroxy radicals at secondary and primary CH bonds is 38.5:1.

It was originally demonstrated by Rust[2] that, in the low-temperature liquid-phase oxidation[3] of certain branched alkanes, intramolecular transfer of a hydrogen atom to form bifunctional products is a major reaction path. Thus, good yields of 2,4-dihydroperoxy-2,4-dimethylpentane (Chart I) (R_1–R_4 = CH_3) could be obtained from the oxidation of 2,4-dimethylpentane (2,4-DMP); oxidation of 2,5-dimethylhexane gave a lower yield of the difunctional product. Recent work by Mill and Montorsi[4] showed that, at 100°, over 90% of the oxygen consumed by 2,4-DMP could be accounted for by hydroperoxide and that the ratio of mono- to difunctional hydroperoxide products was 1:7. The apparent generality of intramolecular propagation in the oxidation of alkanes with alternating *tertiary* hydrogens was confirmed by Van Sickle in the oxidation of 2,4,6-trimethylheptane[5] (2,4,6-TMH) [Chart I, R_1–R_3 = CH_3; R_4 = $CH_2CH(CH_3)_2$] where the major oxidation product is 2,4,6-trihydroperoxy-2,4,6-trimethylheptane and the calculated value for the ratio of rate constants of inter- to intramolecular propagation, k_p/k_r, is practically identical with that of 2,4-DMP[4] (0.015 M^{-1} *vs.* 0.013 M^{-1}).

CHART I



The question now arises as to what proportions of bifunctional reaction products are formed in low-temperature (100–125°) liquid-phase oxidations of *n*-alkanes. *A priori*, one might expect the reaction scheme in Chart I to be valid for the general case where R_1, R_3 = H and R_2, R_4 = any alkyl group. In gas-phase oxidations[6] above 200°, cyclic ethers, expected to arise from III of Chart I, are major products.

Although the liquid-phase oxidation of *n*-alkanes has been reported for various homologs, the results have not been analyzed from the standpoint of intra–intermolecular propagation. We now report the results of an investigation of the oxidation of *n*-pentane at 100° and *n*-octane at 125° where we have searched specifically for bifunctional products expected to be derived from intermediate III of Chart I.

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