ferentials of appropriate reaction parameters. It is suggested, therefore, that these two reactions under the present investigation will differ from each other rather drastically in nature, presumably in the mechanism in which electrons are supplied from the diene to the dienophile moiety in the transition state. Thus, the catalyzed reaction is assumed to start with electrophilic attack of β carbon of MA–$AlCl_3$ on the diene to give I, if the uncatalyzed reaction is to proceed through the four-center-type[10,12] pathways. There will be no reason to believe that the exchange interaction between 4 and 2′ positions begins *after* the initial bond (1–1′) is completed. The question of whether the two new bonds are formed simultaneously or sequentially is therefore a subtle problem of whether the potential-energy profile is one peaked or two peaked.

Although the heterolytic mechanism is probable as discussed here, the possibility of four-centered mechanism for the catalyzed reaction can not be definitely ruled out because the larger selectivity might possibly be explained by assuming a larger polarity of 1–1′ bond induced by the inductive effect of the complexed carboxylate group. It is possible that the reactivity–selectivity correlation may fail when the reactivities of reagents differ very extremely, even if the reactions belong to the same broad category of the reaction mechanisms.

Experimental Section

Butadiene, methyl acrylate, anhydrous aluminum chloride, and benzene used in this study are the same as those previously described.[2] Determination of the reaction product, methyl 3-cyclohexene-1-carboxylate, was carried out by gas–liquid partition chromatography (glpc) using tetraline as internal standard. The required calibration curve of glpc peak area ratio *vs.* molar ratio (the product *vs.* tetraline) was prepared by using an Ohkura Model 1200 instrument with Carbowax 6000 on Diasolid M (Nihon Chromato Industries Co., Ltd.).

Aluminum Chloride Catalyzed Reaction.—A 300-ml, three-necked round-bottomed flask, fitted with a mercury-sealed stirrer, an inlet for nitrogen, and another inlet guarded with a mantle for stream of dry nitrogen, was placed in a thermostat. A benzene solution (50 ml) of MA–$AlCl_3$ of a known concentration containing known amounts of tetraline and methyl acrylate was added to the above reaction flask which had been flushed with dry nitrogen. A dilute benzene solution (100 ml) of butadiene of a known concentration, which had been thermally equilibrated in the same bath, was rapidly added to the flask. After certain time intervals aliquats were taken out onto 25 ml of water to stop the reaction. The benzene layer was dried with anhydrous sodium sulfate and concentrated under reduced pressure. The concentrate was analyzed for the amount of the product formed by glpc.

Uncatalyzed Reaction.—A benzene solution containing methyl acrylate (6.407 moles/l.), butadiene (0.424 mole/l.), and tetraline (0.09513 mole/l.) was prepared by using a high vacuum line. Portions of this solution were transfered to small tubes (4 mm i.d. × 50 mm) in a closed system and were sealed off. After certain periods of reactions in a thermostat the tubes were opened and the contents were directly analyzed for the addend by glpc.

Registry No.—Butadiene, 106-99-0; acrylic acid methyl ester, 96-33-3.

[12] J. Hine, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1956, p 453.

9-Decalyl Free Radicals. Decomposition of *cis*- and *trans*-9-Decalylcarbinyl Hypochlorite[1a]

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9-Decalyl radicals have been examined by the free-radical chain decomposition of *cis*- and *trans*-9-decalylcarbinyl hypochlorite in fluorotrichloromethane. Chain lengths exceed 1000 for the decomposition of both hypochlorites. The major products are formaldehyde and *cis*- and *trans*-9-chlorodecalin. The product ratio, *trans*-RCl/*cis*-RCl, obtained from *trans*-hypochlorite is independent of initial hypochlorite concentration and favors the *trans*-chloride (30 to 1 at −40°, 15 to 1 at 0°). The product ratio from *cis*-hypochlorite is dependent on the initial concentration of hypochlorite and favors the *cis*-chloride at high concentration and low temperature (1.3 to 1 at 3 *M*, −80°); at low hypochlorite concentrations the product ratio is the same as that obtained at all concentrations from *trans*-hypochlorite. The results require two different 9-decalyl radicals: one from *cis*-hypochlorite that either isomerizes to the radical derived from *trans*-hypochlorite or abstracts chlorine from hypochlorite to give *cis*- (and possibly some *trans*-) 9-chlorodecalin; and one from *trans*-hypochlorite that reacts with hypochlorite to give both 9-chlorodecalins, mainly the *trans* isomer, but does not isomerize to the radical initially formed from the *cis*-hypochlorite. The relevance of these results to questions of conformation and radical geometry is discussed.

Stereochemistry of atom-transfer reactions to carbon radicals has been a subject of interest to us. A relevant question is the geometry of carbon radicals. Spectroscopic evidence indicates planarity for the methyl radical.[2] Much data from electron spin resonance spectroscopy have been interpreted in terms of planar carbon radicals.[3] A study of relative rates of chlorine abstraction from carbon tetrachloride *vs.* decarbonylation of acyl radicals has led to the conclusion that the bridgehead radicals, 1-[2.2.2]bicyclooctyl and 1-adamantyl, are more stable than *t*-butyl.[4] An esr study of fluorinated methyl radicals has provided a strong indication that these are nonplanar ($CF_3\cdot$ almost tetrahedral, with a gradual change toward planarity as fluorine is replaced by hydrogen).[5] Since a group such as methyl may be regarded as isoelectronic with fluorine atom, the study provides new impetus to the search

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[1] (a) Supported in part under Contract No. AT(30-1)-905 with the Atomic Energy Commission. Reproduction is permitted for any purpose of the U. S. Government; (b) National Institutes of Health Predoctoral Fellow, 1962–1965.

[2] G. Herzberg, *Proc. Roy. Soc.* (London), **A262**, 291 (1961).

[3] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963); J. R. Morton, *Chem. Rev.*, **64**, 453 (1964).

[4] D. E. Applequist and L. Kaplan, *J. Am. Chem. Soc.*, **87**, 2194 (1965).

[5] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **43**, 2704 (1965).

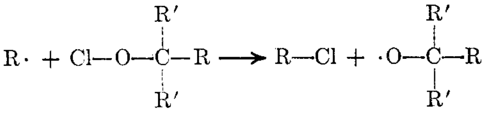
for a difference in structure in the series of primary, secondary, and tertiary alkyl radicals.

In the present investigation we have examined reactions of 9-decalyl radicals generated from diastereomerically related precursors of *cis* and *trans* ring fusion in order to see whether angular constraint might be adequate to lead to two, nonplanar 9-decalyl radicals. During the course of this work, a study of the decomposition of *cis*- and *trans*-*t*-butyl 9-decalinpercarboxylate in the presence of varying concentrations of oxygen was reported.[6] The general accord between the principal results of the two investigations is of special interest in view of the rather different substrates and conditions.

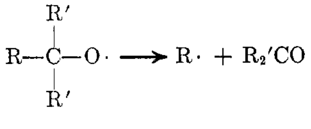
Results

Method.—Our approach has been to generate and consume the carbon radicals of interest *via* free-radical chain reactions; this technique permits the measurement of selectivities in atom-transfer reactions over a broad temperature range. Two reactions of this type have been examined: decomposition of alkyl hypochlorites[7] and reduction of alkyl halides by organotin hydrides.[8]

Previous studies have established the long-chain nature of the decomposition of tertiary alkyl hypochlorites.[7] The ease of ejection of a radical from an



$$R\cdot + Cl{-}O{-}\underset{R'}{\overset{R'}{C}}{-}R \longrightarrow R{-}Cl + \cdot O{-}\underset{R'}{\overset{R'}{C}}{-}R \qquad (1)$$



$$R{-}\underset{R'}{\overset{R'}{C}}{-}O\cdot \longrightarrow R\cdot + R_2'CO \qquad (2)$$

alkoxyl intermediate follows the order tertiary > secondary > primary > methyl. The examination of a particular radical may thus be made if the corresponding acid is accessible and if it can be converted to the tertiary alcohol, $RC(CH_3)_2OH$ (a conversion that proved difficult for R = 9-decalyl). The decomposition of primary and secondary hypochlorites is usually much more complex.[9] One type of structure, however, has provided clean results—decomposition of primary alkyl hypochlorites of "neopentyl-like" structure[9] (eq 1, R′ = H; R = tertiary alkyl). A system of this type, *cis*- and *trans*-9-decalylcarbinyl hypochlorite, RCH_2OCl, has been the object of this study.

Hypochlorites of *cis*- and *trans*-9-Decalylcarbinol.—Each hypochlorite was prepared by the action of hypochlorous acid (or better, chlorine monoxide) on the corresponding alcohol. Decomposition of *trans*-9-decalylcarbinyl hypochlorite in carbon tetrachloride afforded formaldehyde, a mixture of the two 9-decalyl chlorides, and a small amount of cyclic ether derived from intramolecular hydrogen abstraction in the alkoxyl radical.[10,11] Decomposition of the *cis*-hypochlorite afforded formaldehyde and the same two alkyl chlorides. The chlorides were separated by preparative-scale glpc employing a base-washed column.

***cis*- and *trans*-9-Decalyl Chloride.**—The skeletal structure of the alkyl chlorides is assigned on the basis of reduction by tributyltin hydride to mixtures of *cis*- and *trans*-decalin,[8] and elimination of hydrogen chloride by base to give mixtures of $\Delta^{1,9}$- and $\Delta^{9,10}$-octalin. The assignment of both products as tertiary chlorides is based on the nmr spectra, which show no peak below 2.3 ppm and hence indicate the absence of hydrogen α to chlorine. Assignment of stereochemistry is based on synthetic, elimination, and equilibration data summarized in Table I, and on mode of formation in the hypochlorite decompositions.

Addition of anhydrous hydrogen chloride at −78° to olefins in methylene chloride has been shown to favor *cis* addition, often with a considerably greater preference for *cis* than shown in Table I.[12]

Table I

cis- and *trans*-9-Decalyl Chloride

RCl	Equilibration, $ZnCl_2$, aq HCl, 46°	Addition of HCl to $\Delta^{9,10}$-octalin		Elimination, 3 *M* KOH EtOH → octalins $\Delta^{9,10}$ $\Delta^{1,9}$
		Anhydr HCl, CH_2Cl_2, −78°	Concd aq HCl, 25°	
trans	90	46	94	3.7 to 1
cis	10	54	6	1 to 9

Some thermodynamic data for 9-substituted decalins are summarized in Table II.

Table II

cis-9-R-Decalin ⇄ *trans*-9-R-Decalin

R	H	Cl	CH_3	COOH
$\Delta F°$ at 46°	-2.5^a	-1.3^b	-0.4^c	$(+)^d$

[a] N. Allinger and J. Coke, *J. Am. Chem. Soc.*, **81**, 4080 (1959), extrapolated value. [b] This work. [c] N. Allinger and J. Coke, *J. Org. Chem.*, **26**, 2096 (1961), extrapolated value. [d] Reference 26.

Product Ratios, *trans*-RCl/*cis*-RCl, from Decomposition of Hypochlorites.—The major aspect of this work has been the measurement of the ratio of 9-decalyl chlorides produced from the *trans*- and *cis*-hypochlorites under a variety of conditions. The chlorides were shown to be stable to the conditions of formation and analysis.[13] The results are summarized in Table III.

Chain Length.—In view of the differences in *trans*-RCl/*cis*-RCl produced from the *trans*- and *cis*-hypochlorites, it was necessary to ascertain what amount, if any, of the products was coming from nonchain (*e.g.*, SNi) paths Qualitative chain-length studies at 45° with initiation by azobisisobutyronitrile indicated that both *trans*- and *cis*-hypochlorite undergo free-radical chain decomposition of long chain length (>99.9% of the alkyl halides arise from chain paths). That the decompositions are of long chain length also at −80° is indicated by the marked inhibitory effect of oxygen and the rapid decomposition under degassed

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(6) P. D. Bartlett, R. E. Pincock, J. H. Rolston, W. G. Schindel, and L. A. Singer, *J. Am. Chem. Soc.*, **87**, 2590 (1965).

(7) F. D. Greene, C.-C. Chu, and J. S. Walia, *J. Org. Chem.*, **29**, 1285 (1964), and references cited therein.

(8) F. D. Greene and N. N. Lowry, *ibid.*, **32**, 882 (1967).

(9) F. D. Greene and J. S. Walia, in preparation.

(10) C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **85**, 1597 (1963).

(11) 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).

(12) M. J. S. Dewar and R. C. Fahey, *J. Am. Chem. Soc.*, **85**, 2245 (1963).

(13) One complication was the formation of small amounts of *cis*- and *trans*-RCl during the preparation of RCH_2OCl from RCH_2OH by HOCl. This was minimized by the use of Cl_2O in place of HOCl. The methods of analysis and illustration of the correction are given in the Experimental Section.

TABLE III

DECOMPOSITION OF 9-DECALYLCARBINYL HYPOCHLORITES IN FLUOROTRICHLOROMETHANE

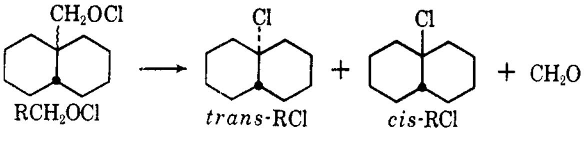
Temp, °C	Concn, mole/l.	(*trans*-RCl/*cis*-RCl)[a]	Yield of RCl, %
	cis-Hypochlorite		
0	3.0	2.2	52
	0.4	6.1	88
	0.08	17	50
−40	3.0	1.1	44
	2.0	1.4	25
	1.0[b]	1.7	35
	0.4	3.8	70
	0.1	10 ± 1	35
	0.008	29 ± 3	16
−78	3.0	0.75	25
	0.4	2.1	50
−120	2.5[c]	0.58	24
	1.5	0.55	28
	0.2[d]	1.4	28
	trans-Hypochlorite		
80	0.8	9	85[e]
	0.03	8	52
0	2.2	12	
	0.8	15	50
	0.08	13	
	0.005	15	
−40	3.3[b]	32 ± 2	35
	0.8	26	38
	0.009	27 ± 3	11
−78	0.22	49 ± 5	21[f]
−120	0.16[b,d]	>50	..[g]

[a] Estimated error, unless otherwise noted, ±5%; the data are the average of several runs. [b] One run only. [c] Medium is quite viscous. [d] Solvent is $CFCl_3$–isopentane. [e] 10% yield of cyclic ethers. [f] 40% yield of cyclic ethers. [g] Cyclic ethers/RCl = 5:1.

conditions, by the low intensity of light sufficient to initiate decomposition, and by the effect of concentration of *cis*-hypochlorite on the alkyl chloride ratios.

Discussion

Summary of Principal Findings in Decomposition of *trans*- and *cis*-9-Decalylcarbinyl Hypochlorite.—



(1) Decomposition of *trans*- and *cis*-hypochlorite proceeds by free-radical steps of long chain length. (2) The product ratio, *trans*-RCl/*cis*-RCl, obtained from *trans*-hypochlorite is *independent* of the initial concentration of hypochlorite, and favors the *trans*-chloride (30 to 1 at −40°). (3) The product ratio from *cis*-hypochlorite is *dependent* on the initial concentration of hypochlorite and favors the *cis*-chloride at high concentration and low temperature (1.3 to 1 at 3 *M*, −80°); at low hypochlorite concentration, the product ratio is the same as that obtained at all concentrations from *trans*-hypochlorite. (4) The product ratios, *trans*-RCl/*cis*-RCl, from either reactant show increasing retention of the stereochemistry of the reactant with decreasing temperature.

$$RCO_3C(CH_3)_3 \xrightarrow{50^\circ} R\cdot + CO_2 + \cdot OC(CH_3)_3$$

$$R\cdot + O_2 \longrightarrow ROO\cdot \xrightarrow{\text{solvent-H}} \underset{(\textit{trans}\text{ and }\textit{cis})}{ROOH}$$

$$ROOH \xrightarrow{LiAlH_4} ROH \quad \text{(method of analysis)}$$

Perester	O_2, atm	*trans*-ROH/*cis*-ROH
cis	1	7
	545	0.4
trans	1	7
	600	7

For the decomposition of *trans*- and *cis*-*t*-butyl 9-decalinpercarboxylate in the presence of oxygen,[6] the principal findings are the same: the product ratio, *trans*-ROH/*cis*-ROH, from *trans* perester is *independent* of oxygen pressure, and *trans*-ROH is the major product; the product ratio from *cis* perester is *dependent* on oxygen pressure, and at the highest pressures employed *cis*-ROH is the major product. A clear analysis and discussion of these findings has been presented,[6] much of which is directly applicable to the hypochlorite study of this paper and need not be repeated. Some further consideration will now be given to the relative rates of the various competing processes and the relation of this information to structural questions, for which purpose the numbering of rate constants in the perester study will be retained to facilitate comparison.

The hypochlorite results require two different product-determining radicals, one from the *cis* precursor ($R_c\cdot$) and one from the *trans* precursor ($R_t\cdot$). The product-determining step in the hypochlorite decompositions is chlorine transfer from RCH_2OCl to $R\cdot$.[14] Radical $R_t\cdot$ may react with RCH_2OCl to afford both *trans*- and *cis*-RCl, but does not isomerize to $R_c\cdot$. $R_c\cdot$ disappears by two processes of different kinetic order: second-order reaction with RCH_2OCl to afford RCl, and first-order isomerization to $R_t\cdot$. The results are summarized in Scheme I, p 878.

Rate Constant Ratios, k_1/k_2 and k_5/k_2.—From the over-all selectivities of formation of *trans*-RCl/*cis*-RCl from, for example, 2 *M* and 1 *M* initial hypochlorite concentration (Table III), one may calculate the selectivity ratio for that part of the reaction corresponding to the concentration range, 2 *M* to 1 *M* RCH_2OCl. Data for several ranges are summarized in Table IV.

TABLE IV

EFFECT OF CONCENTRATION ON THE RATIO OF *trans*/*cis*-9-DECALYL CHLORIDE OBTAINED FROM DECOMPOSITION OF *cis*-HYPOCHLORITE

Concn interval, *M*	% reacn	*trans*-RCl/*cis*-RCl
3–2	33	0.7
3–1	67	0.9
2–1	50	1.2
1–0.4	60	1.1
0.4–0.1	75	3
0.1–0.008	92	~9
0.008–0	100	30

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[14] The result (point 3, above) is only understandable if RCH_2OCl, and not solvent, is the halogen atom donor. Also, decomposition of *t*-butyl-$O^{36}Cl$ in CCl_4 affords $CH_3{}^{36}Cl$: A. A. Zavitsas, *J. Org. Chem.*, **29**, 3086 (1964).

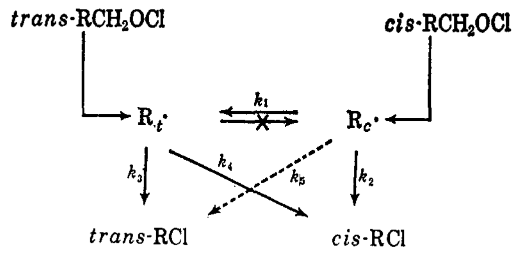
TABLE V

DEPENDENCE OF PRODUCT RATIO, *trans*-RCl/*cis*-RCl, ON RATE RATIOS k_1/k_2 AND k_5/k_2

		$(trans\text{-RCl}/cis\text{-RCl})_{\text{calcd}}$[a]			
[RCH$_2$OCl],[b] *M*	(*trans*-RCl/ *cis*-RCl)$_{\text{obsd}}$[c]	$k_1/k_2 = 0.85$ $k_5/k_2 = 0.45$ A	$k_1/k_2 = 0.85$ $k_5/k_2 = 0$ B	$k_1/k_2 = 1.75$ $k_5/k_2 = 0$ C	$k_1/k_2 = 0.3$ $k_5/k_2 = 0.6$ D
2.5	0.7	0.76 (0.75)[d]	0.34 (0.33)[d]	0.7	0.72
2.0	0.9	0.88	0.42	0.88	0.75
1.5	1.2	1.0	0.57	1.2	0.8
0.7	1.1	1.6 (1.5)[d]	1.2	2.5	1.0
0.25	3.0	3.7 (3.3)[d]	3.4 (3.0)[d]	7.0 (5.6)[d]	1.8 (1.7)[d]

[a] Equation 4. [b] Table IV, column 1. [c] Table IV, column 3. [d] Equation 3.

SCHEME I



By reference to Scheme I, with the usual steady-state assumptions, and the additional, reasonable assumption that the rate constant (*k*) for $R_t\cdot$ + ClO-CH$_2$R$_c$ is equal to *k* for $R_t\cdot$ + ClOCH$_2$R$_t$, one obtains eq 3.[15] At −40°, decomposition of *trans*-RCH$_2$OCl

$$\frac{d[trans\text{-RCl}]/dt}{d[cis\text{-RCl}]/dt} = \frac{\dfrac{k_1k_3}{k_3 + k_4}[R_c\cdot] + k_5[R_c\cdot][\text{RCH}_2\text{OCl}]}{\dfrac{k_1k_4}{k_3 + k_4}[R_c\cdot] + k_2[R_c\cdot][\text{RCH}_2\text{OCl}]} = \frac{k_3/(k_3 + k_4) + (k_5/k_1)[\text{RCH}_2\text{OCl}]}{k_4/(k_3 + k_4) + (k_2/k_1)[\text{RCH}_2\text{OCl}]} \quad (3)$$

affords *trans*-RCl/*cis*-RCl = 30/1 = k_3/k_4. By reference to the *trans*-RCl/*cis*-RCl ratios of Table IV, one sees that the first term of the denominator of eq 3 will be small compared with the second term, leading to the simplification (eq 4) for the selectivity, *trans*-RCl/

$$\frac{trans\text{-RCl}}{cis\text{-RCl}} \cong \frac{k_1}{k_2[\text{RCH}_2\text{OCl}]} + \frac{k_5}{k_2} \quad (4)$$

cis-RCl, at (relatively) constant hypochlorite concentration.

The best values for the two unknowns, derived from the first five entries of Table IV, are $k_1/k_2 = 0.85 \pm 0.40$ *M*,[16] and $k_5/k_2 = 0.45 \pm 0.35$. The degree of sensitivity of the product ratios, *trans*-RCl/*cis*-RCl, to the rate ratios, k_1/k_2 and k_5/k_2, is shown in Table V. Unparenthesized values have been calculated from eq 4; the values in parentheses have been calculated from the fuller equation (eq 3, also employing the "fixed" hypochlorite concentrations of the first five entries of Table IV).

Although the rate ratios of column A afford the best fit of the data over-all, the product ratio, *trans*-RCl/*cis*-RCl, is a rather insensitive function of what one assumes about k_5. The ratio, k_5/k_1, does appear to be less than 1; no value for k_1/k_2 will accommodate the observed ratios of *trans*-RCl/*cis*-RCl when used with a k_5/k_1 value greater than one (*e.g.*, Table V, column D).

The first conclusion of this analysis is that k_1 and k_2 are of comparable magnitude;[16] the free-energy of activation for the conversion of $R_c\cdot$ to $R_t\cdot$ is comparable to that for the abstraction of chlorine from RCH$_2$OCl by $R_c\cdot$. The value for the latter (and hence for the former) may be approximately 3–6 kcal/mole.[17] The second conclusion is that little can be said from these data concerning the interesting question of whether any *trans*-RCl is formed by direct reaction of $R_c\cdot$ with RCH$_2$OCl. At the lower limit, k_5/k_2 is close to 0; the best average value is about 0.5.

This situation also obtains with the decalyl perester-oxygen system.[6] The ingenious use of oxygen at high pressures is not without its hazards and experimental difficulties, and the amount of data is limited. There, also, k_1' and k_2' (for $R_c\cdot + O_2 \rightarrow ROO\cdot$)[18] appear to be of the same order of magnitude.[16] Even if some allowance is made for uncertainty in the oxygen concentration (ref 6, footnote 16), this fact would appear to favor the lower end of the 3–6-kcal range cited above. The data are uninformative on the question of the ratio of k_5'/k_2'.[18] In arriving at an estimate of k_1'/k_2', it was considered probable that $k_3' + k_4' = k_2' + k_5'$, and that $k_5' = 0$.[6] However, in illustration, values of $k_5'/k_2' = 0.45$ and $k_1'/k_2' = 0.7$ afford product ratios in accord with the observed ratios (calcd *cis*-ROH/*trans*-ROH for various oxygen concentrations: 0.1 at 0.001 *M*, 1 at 1 *M*, 1.4 at 2 *M*, 1.75 at 4 *M*, 2 at 8 *M*).

Structure of $R_c\cdot$ and $R_t\cdot$.—The evidence requires two different 9-decalyl radicals. Possibilities are the pyramidal radicals, py-$R_c\cdot$ and py-$R_t\cdot$ and, the planar radicals, pl-$R_c\cdot$ and pl-$R_t\cdot$. At first thought, it might be supposed that planarity at C-9 would remove all distinction between $R_c\cdot$ and $R_t\cdot$. However, these two species are derived from *cis*- and *trans*-decalyl precursors, and, even if $R_c\cdot$ and $R_t\cdot$ are planar at C-9, conformational differences may still exist elsewhere. The two species, pl-$R_c\cdot$ and pl-$R_t\cdot$, do not become equivalent until shmething close to a boat-to-boat transformation is effected in one of the rings.[19]

For py-$R_c\cdot$ → py-$R_t\cdot$ the activation barrier (3–6 kcal/mole)[17] might be ascribed to various possible elements of strain associated with flattening the bridgehead radical, C-9. However, a barrier of this small magnitude would not appear to be inconsistent with the energy needed to effect the conformational change

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[15] In ref 6, $k_0 = k_2 + k_5$, $a = k_2/(k_2 + k_5)$, $b = k_4/(k_3 + k_4)$.

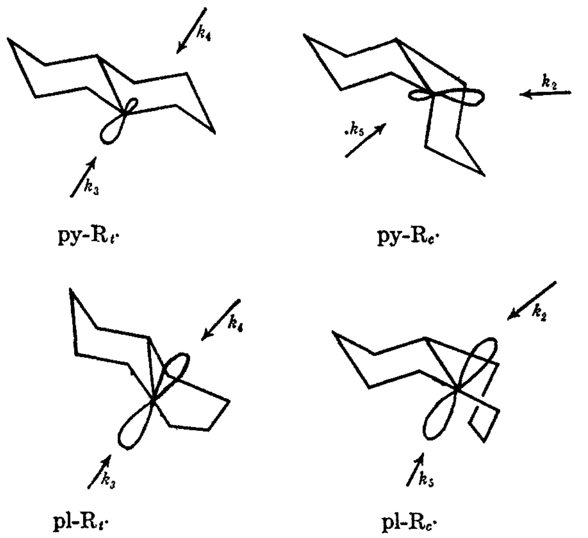
[16] Interpretation of rate constant ratios of *k* values differing in kinetic order poses some problems. The ratio will contain concentration units; for all second-order rate constants discussed here, the units are M^{-1} sec^{-1}.

[17] A. A. Zavitsas and S. Ehrenson, *J. Am. Chem. Soc.*, **87**, 2841 (1965), and by application of the Hirschfelder rules (A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley and Sons, Inc., New York, N. Y., 1963, p 106).

[18] Employing primed rate constants for the reactions related to Chart I but derived from the perester–oxygen system.[6]

[19] A different view of this has been expressed.[6] We feel that the smallness of the energy barrier in question warrants retention of consideration of both planar possibilities, pl-$R_t\cdot$ and pl-$R_c\cdot$.

CHART I



py-R$_t$· py-R$_c$·

pl-R$_t$· pl-R$_c$·

of pl-R$_c$· → pl-R$_t$·, particularly if this barrier is nearer to 3 than to 6 kcal/mole (see foregoing discussion, and also Chart I).

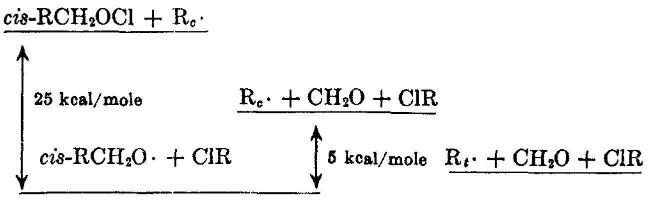
From the data on the ratio, *trans*-RCl/*cis*-RCl, obtained from *trans*-hypochlorite, the differences in the activation parameters for steps k_3 and k_4 have been calculated. The difference between the activation

$$k_3/k_4 \text{ at } -40° = 30/1$$
$$\Delta\Delta F^{\ddagger}_{4-3} = 1.5 \text{ kcal/mole}$$
$$\Delta\Delta H^{\ddagger}_{4-3} = 1.5 \pm 0.1 \text{ kcal/mole}$$
$$\Delta\Delta S^{\ddagger} = 0$$

energies for k_3 and k_4 is an appreciable fraction of the estimated total activation energy of 3–6 kcal/mole for k_3.[17]

Thermochemical Considerations.—The foregoing discussion has focused on the two-step sequence of eq 1 and 2. An additional factor that may have some bearing on the over-all selectivity ratio, *trans*-RCl/*cis*-RCl, is the possibility of one-step conversion (eq 5). Unimolecular examples of one-step (two-bond) decompositions have been observed, notably with peresters;[20,21] also decomposition of dimethyl-*t*-butylcarbinyl hypochlorite is believed to be a one-step process.[17]

$$\text{RCH}_2\text{OCl} + \text{R}_c\cdot \longrightarrow \text{R}\cdot + \text{CH}_2\text{O} + \text{ClR} \qquad (5)$$



Efforts to distinguish the two routes, eq 1 and 2 *vs.* eq 5, by trapping of the alkoxyl radical have been unsuccessful. Its transient existence in at least a portion of the reaction of *trans*-hypochlorite is indicated by the formation of the cyclic ethers. If the one-step conversion of eq 5 were operative, how much of the 25 kcal/mole[22] liberated by this change would be retained by the decalyl moiety? If the amount exceeded 3–6 kcal—the barrier separating thermoneutral R$_c$· from R$_t$·—then reaction *via* eq 5 would lead to R$_t$· directly, resulting in a common product composition from *cis*- and *trans*-hypochlorite.[23] Obviously this does not account for the major fraction of *cis*-hypochlorite decomposition; however, *some* of the *trans*-RCl formed from *cis*-RCH$_2$OCl may arise in this way. This would require a decrease in the k_5/k_2 ratio discussed above.

Conclusions

Attention is directed to the use of the hypochlorite route in the study of specific radicals. Secondly, although the results on the decalyl system (this study and those of ref 6) do not require pyramidal radicals, they raise this as a serious possibility; these results and those on the fluorinated methyl radicals[5] and on bridgehead radicals[4] point to the need for more information in this area. Thirdly, lest this problem fall into some of the semantic and energetic difficulties that have beset the "classical *vs.* nonclassical ion" problem, one should raise the question, "how planar is a planar radical?" The methyl radical, for which the evidence points to a planar ground state,[2] has been assigned a symmetrical out-of-plane bending vibration of 580 cm^{-1}. This corresponds to a deviation from planarity[24] of 15° at the maximum distortion for the 0 energy level of the out-of-plane bending vibration; *i.e.*, the "planar" methyl radical in the ground state is changing from a +15° deviation from planarity (an H–C–H angle of 113° 50′) to a −15° deviation, at more than 10^{13} times per second. For the planar species, boron trimethyl[25] the out-of-plane deformation vibration is 336 cm^{-1}, corresponding to a deviation from planarity of 6° 45′ at maximum distortion. For a radical such as *t*-butyl, even if it were planar in the ground state, one would expect the out-of-plane vibration to be considerably less than for borontrimethyl. (For example, a value of 200 cm^{-1} would correspond to a deviation from planarity at maximum distortion of 8° 40′.) Lastly, the possibly obvious point should also be mentioned that the energy required to excite these bending vibrations is small, *e.g.*, less than 1 kcal/mole to go from the 0 energy out-of-plane vibration of borontrimethyl with a deviation from planarity at maximum distortion of 6° 45′ to the first excited level with a corresponding deviation of 11° 35′.

Experimental Section

***cis*- and *trans*-9-decalincarboxylic acids** were prepared by published procedures;[26] *cis* acid had mp 121.5–122° (lit.[26] mp 121.8–123°); *trans* acid had mp 134–135° (lit.[26] mp 134.5–135.5°). An improvement in the method of purification of the *trans* acid was made by taking advantage of the difference in pK_a values (*trans* acid, 8.66; *cis* acid, 8.16 in Methyl Cellosolve–water);[27]

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

[21] P. D. Bartlett and D. M. Simons, *ibid.*, **82**, 1753 (1960).

[22] Calculated from data in P. Gray and A. Williams, [*Chem. Rev.*, **59**, 239 (1959)] and a bond energy of 48 kcal/mole for OCl. For a lower estimate of OCl (44), see C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960), ref 13.

[23] Some experiments to test this possibility by examining product ratios for different leaving groups [*e.g.*, RCOO·, ROCO·, RC(CH$_3$)HO·] failed to yield definitive results; see N. N. Lowry, Ph.D. Thesis, Massachusetts Institute of Technology, 1965.

[24] The force constant (k) in dynes/cm = $4\pi^2c^2\bar{\nu}^2\mu$ with c in cm/sec, $\bar{\nu}$ in cm^{-1}, and μ, the reduced mass, in g. Maximum displacement in cm, $x = (h^2/4\pi^2k\mu)^{1/4}$ with h in erg sec.

[25] W. J. Lehmann, C. O. Wilson, Jr., and I. Shapiro, *J. Chem. Phys.*, **31**, 1071 (1959); L. A. Woodward, J. R. Hall, R. N. Dixon, and N. Sheppard, *Spectrochim. Acta*, **15**, 249 (1959).

[26] R. E. Pincock, E. Grigat, and P. D. Bartlett, *J. Am. Chem. Soc.*, **81**, 6332 (1959).

[27] P. F. Sommer, C. Pascual, V. P. Arya, and W. Simon, *Helv. Chim. Acta*, **46**, 1734 (1963).

the crude solid obtained from carbonylation under the conditions of preparation of *trans* acid was dissolved in ether and extracted four times with 10% sodium carbonate solution. The extracts were not combined; acidification of the first extract yielded *cis* acid, mp 118–119°; acidification of the remaining extracts gave crude *trans* acid, purified by repeated recrystallizations from acetone. The β-decalol used in the preparations, a mixture of diastereomers, was prepared by catalytic hydrogenation.[28]

Methyl *cis*- and *trans*-9-decalincarboxylates were prepared with diazomethane; *cis* ester had bp 54–57° (0.12 mm) (*Anal.* Calcd for $C_{12}H_{20}O_2$: C, 73.55; H, 10.21. Found: C, 73.35; H, 10.18.); *trans* ester,[29] had bp 38° (0.08 mm), $n^{25}D$ 1.4787.

***cis*- and *trans*-9-Decalylcarbinol.**—*cis*- and *trans*-9-decalylcarboxylic acids were reduced with lithium aluminum hydride as described in the literature[29] to yield *cis*-carbinol, mp 59.5–60.5° (lit.[29] mp 59–60°), and *trans*-carbinol, mp 84–85° (lit.[29] mp 77–78°, 84.2–84.6°).

Methyl *cis*-9-decalyl ketone was prepared by the action of excess methyllithium on the *cis* ester in ether solution (yield 90%), bp 64–65° (0.15 mm) [lit.[30] bp 82–85° (0.8 mm)]. The mass spectrum shows a parent ion at *m/e* 180 and a large peak at 137 (loss of acetyl). A sample of the ketone was converted into the 2,4-dinitrophenylhydrazone, mp 140.7–141.3° after recrystallization from aqueous ethanol (lit.[30] mp 140–140.5°).

In addition to the ketone, an olefin was formed in low yield, believed to be 2-(*cis*-9-decalyl)propene [infrared at 1650 and 890 cm^{-1}; nmr at δ 3.19 (vinyl CH_2), 1.8 (methyl), 1.5 (decalyl protons, broad)]. Efforts to obtain the tertiary alcohol, dimethyl (*cis*-9-decalyl)carbinol, from this reaction or from a number of variations employing methyl Grignard reagent or *cis*-9-decalylcarbonyl chloride were unsuccessful.

Methyl(*cis*-9-decalyl)carbinol was prepared by reduction of the ketone in ether by lithium aluminum hydride, mp 36.5–37.5°.

Anal. Calcd for $C_{12}H_{22}O$: C, 79.05; H, 12.17. Found: C, 79.17; H, 12.08.

Preparation of *cis*-9-Decalylcarbinyl Hypochlorite. A. Sodium Hypochlorite Method.[11]—*cis*-9-Decalylcarbinol (1.8 g, 0.011 mole) in 4 ml of carbon tetrachloride (or trichlorofluoromethane, Freon 11) was cooled to 0° and added to a cooled solution of sodium hypochlorite (40 ml, 2.3 *M*). The alcohol flask was rinsed with 1 ml of solvent and this solution was added to the reaction mixture. Two milliliters of glacial acetic acid was added, and the resulting, two-phase mixture was stirred in the dark at 0° for 1 hr, then poured into an amber separatory funnel. The two layers were separated, and the organic layer was washed twice with 5% aqueous sodium bicarbonate and once with water, dried ($MgSO_4$) in the refrigerator, and filtered into a 10-ml volumetric flask. The flask was rinsed with solvent and the hypochlorite solution was diluted to 10 ml. Iodometric titration indicated 40–70% conversion of alcohol to hypochlorite and vapor phase chromatographic analysis showed 10–50% yield of decalyl chloride. The alkyl hypochlorite solution was protected from light at all stages of its preparation and stored in the refrigerator or freezer until use. It was stable under these conditions for several weeks.

B. Chlorine Monoxide Method.—An excess of chlorine monoxide[31] solution in trichlorofluoromethane and a sample of *cis*-9-decalylcarbinol were allowed to stand over magnesium sulfate for 30 min. At the end of this time the solution was filtered into an amber separatory funnel, and the flask and filtrate were washed well with fresh solvent, and worked up as described for the preparation of alkyl hypochlorite with sodium hypochlorite. Iodometric titration indicated 70–80% conversion of alcohol to hypochlorite; analysis by vapor phase chromatography showed decalyl chloride to be present in 3 to 8% yield.

Analysis for Decalyl Chlorides in Hypochlorite Solutions Prior to Subjection to Decomposition Conditions.—An aliquot of hypochlorite solution was transferred in the dark to a foil-wrapped flask containing a measured amount of *o*-dichlorobenzene, and an excess of aqueous acidic potassium iodide was added. The two phase-mixture was stirred for 5 min and then excess sodium thiosulfate was added. The organic layer was separated, washed well with water, and analyzed by vapor phase chromatography. The *cis*- and *trans*-chlorides present were determined by comparing peak areas of the decalyl chlorides and the standard, *o*-dichlorobenzene. [Sample calculation: initial concentration of *cis*-hypochlorite, 0.008 *M* in trichlorofluoromethane at 0°. Peak area ratios: (a) prior to decomposition, standard (100), *trans*-chloride (15.0), *cis*-chloride (8.0); (b) after decomposition, standard (100), *trans*-chloride (320), *cis*-chloride (24.5). Apparent ratio of *trans*-chloride to *cis*-chloride = 320/24.5 = 13; corrected ratio = (320 − 15)/(24.5 − 8) = 18.]

Determination of the initial amounts of *cis*- and *trans*-chloride was made for each series of experiments, and the appropriate correction was applied to calculation of the *cis*-to-*trans*-chloride ratios associated with the various decomposition conditions. Correction was of consequence only for runs employing low initial concentrations in the *cis*-hypochlorite series.[32]

Vapor Phase Chromatography.—All vapor phase chromatography of chlorodecalins was done on a column of 20% Carbowax 20 M on Chromosorb W (80–100 mesh) which had been base washed and then water washed to pH 8. This was accomplished by soaking the untreated Chromosorb W for several minutes in a solution of 10% sodium hydroxide. The water layer was decanted and the remaining solid was washed with water until the washings were pH 8. The solid was then filtered, dried overnight in an oven, and coated with Carbowax 20 M. This type of column worked well with tertiary chlorides; no loss of hydrogen chloride on the column preheater was observed unless the column was old, had been misused, or the temperature was too high. Attempts to analyze 9-chlorodecalins on columns of SE-30 or silicone oil (710) failed; loss of hydrogen chloride was complete and the only peaks observed were broad owing to octalin formation. The polar coating XF-1150 worked moderately well for the 9-chlorodecalins.

Decomposition of *cis*-9-Decalylcarbinyl Hypochlorite.—Samples of hypochlorite were added to foil-wrapped tubes by means of a syringe, degassed three times at 0.005 mm, and sealed. The ampoules were stored in liquid nitrogen until ready for use.

For decomposition of concentrated solutions of hypochlorite an aliquot of the stock solution was placed in a foil-wrapped, graduated centrifuge tube and nitrogen was passed through the solution for 10–30 min, removing all of the solvent; the solution was cooled in an ice bath during this time. The tube was then placed in a bath at the desired temperature, the foil was removed, and the volume of the yellow liquid was noted and used to calculate the concentration of hypochlorite.

For photolytic decompositions the tubes were warmed to the reaction temperature, the foil was removed, and the tubes were irradiated with a weak ultraviolet source (Burton Manufacturing Co., Van Nuys, Calif., 2.2 w). In all cases the decomposition showed an induction period of about 30 sec followed by vigorous bubbling of the solution for about 30 sec (for reaction at 0°). Reaction at lower temperatures took somewhat longer and the decomposition was smoother; even at −120° decomposition was complete in 30 min. At the end of the reaction time the solution was colorless and a white deposit coated the walls of the tube. The tubes were opened, standard *o*-dichlorobenzene solution was added for yield determination, and the solution was analyzed by vapor phase chromatography.[11]

The vapor phase chromatogram of the reaction mixture showed two products only: a main peak owing to *trans*-9-chlorodecalin (retention time at 126° was 23.0 min) and a smaller peak (retention time at 126° was 29.8 min). The products were isolated by vapor phase chromatography and distilled in a molecular still. (The full infrared spectra are in the thesis of N. N. L.[1b] on p 118.)

Anal. Calcd for $C_{10}H_{17}Cl$: C, 69.54; H, 9.92; Cl, 20.53. Found (for *trans*-9-chlorodecalin): C, 69.86; H, 9.83; Cl, 20.43. Found (for *cis*-9-chlorodecalin): C, 69.40; H, 9.70; Cl, 20.29.

The white solid (polymeric formaldehyde) formed a 2,4-dinitrophenylhydrazone, mp 163–164°; authentic formaldehyde

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[28] A. C. Cope, R. Cotter, and R. Pike, *Org. Syn.*, in press.

[29] W. G. Dauben and J. B. Rogan, *J. Am. Chem. Soc.*, **79**, 5002 (1957).

[30] R. K. Hill, R. T. Conley, and O. T. Chortyk, *ibid.*, **87**, 5646 (1965).

[31] G. H. Cady, *Inorg. Syn.*, **5**, 158 (1957), procedure A.

[32] The reason for formation of the alkyl chloride during the preparation of *cis*-9-decalylcarbinyl hypochlorite is not known; all preparations were carried out in dark red vessels and all solutions were transferred in a darkened room. The hypochlorite solutions once prepared were stable in the freezer for several weeks; so the formation of the alkyl chloride resulted from the preparation procedure rather than the instability of the hypochlorite. Furthermore, the amount of *cis*-9-decalyl chloride relative to the *trans* isomer present in the impurity is considerably higher than is observed under photoinitiated decomposition at 0° indicating that the presence of the chlorides is not due to adventitious exposure of the solution to light during the preparation.

2,4-dinitrophenylhydrazone had mp 163–164°. The mixture melting point showed no depression.

Preparation and Decomposition of *trans*-9-Decalylcarbinyl Hypochlorite.—This hypochlorite was prepared as described for the *cis* isomer. The conversion to hypochlorite using the sodium hypochlorite method was 80–90%; yield of decalyl chloride was less than 1%. The yield of *trans*-9-decalylcarbinyl hypochlorite from the preparation involving chlorine monoxide was 100%.

Decomposition of *trans*-9-decalylcarbinyl hypochlorite was carried out as described for *cis*-9-decalylcarbinyl hypochlorite, affording *cis*- and *trans*-9-decalyl chloride, identified by vpc retention time and infrared spectra. Treatment of the decomposition solution with 2,4-dinitrophenylhydrazine solution yielded the 2,4-dinitrophenylhydrazone derivative formaldehyde, mp 163–164°, mmp 163–164°.

In addition, two unresolved peaks were observed by vapor phase chromatography (retention times at 130° were 38 and 47 min) which are attributed to the cyclic ethers, 11-oxatricyclo[5.3.2.0^{2,7}]dodecane and 11-oxatricyclo[7.2.1.0^{4,9}]dodecane. Analyses and spectra were run on the mixture.

Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.37; H, 11.13.

The infrared spectrum of the mixture showed a strong band at 1025 cm^{-1} (COC); the mass spectrum showed a parent peak at *m/e* 166 ($C_{11}H_{18}O$).

Approximate Chain Lengths of the Decomposition of *cis*- and *trans*-9-Decalylcarbinyl Hypochlorites.—Standard hypochlorite solution was pipetted into three, foil-wrapped test tubes; to one of these a known amount of standard azobisisobutyronitrile (AIBN) solution was added. The tubes were degassed and sealed. The sample containing AIBN and one noninitiated sample were heated in an oil bath for a period of time, removed, cooled in an ice bath, and opened. The hypochlorite concentrations were determined by iodometric titration. Sample calculation for *cis*-9-decalylcarbinyl hypochlorite in carbon tetrachloride at 45°: time, 40 min; $k_{AIBN} = 8.1 \times 10^{-7}$;[33] cage recombination, 57%;[34] initial AIBN concentration, 5.26×10^{-3} *M*; *free* radicals from AIBN in the 40-min period, 8.6×10^{-6} *M*; decomposition of hypochlorite owing to AIBN, 0.042 *M* (*i.e.*, the difference between hypochlorite concentrations in the initiated and noninitiated tubes after 40 min at 45° in the dark); chain length, 4800. Other values of chain lengths obtained in this way were *cis*-hypochlorite, 4000 and 10,000; *trans*-hypochlorite, 2000 ± 800 (four determinations).

Octalins.—A mixture rich in the Δ^{9-10} and the Δ^{1-9} isomers was prepared[35] and analyzed[36] by available procedures. Pure Δ^{9-10}-octalin is most conveniently prepared by a recent modification.[37]

9-Chlorodecalins. A. Addition of Hydrogen Chloride to $\Delta^{9,10}$-Octalin under Nonpolar Conditions.[12]—$\Delta^{9,10}$-Octalin (0.090 g, 0.066 mmole) was dissolved in 3 ml of methylene chloride and cooled to −78°, and dry hydrogen chloride was bubbled through the solution for 30 min. At the end of this time the solvent and hydrogen chloride were removed on a rotary evaporator, ether was added, and the solution was dried ($MgSO_4$), filtered, and analyzed directly by vapor phase chromatography (Table I). The products were isolated by vapor phase chromatography and the infrared spectra were identical with those of *cis*- and *trans*-9-chlorodecalins obtained from the hypochlorite decompositions.

B. Addition of Saturated Aqueous Hydrogen Chloride to Octalin.[38]—A sample of octalins (3.2 g, 0.0235 mole) containing approximately 58% $\Delta^{9,10}$-octalin and 33% $\Delta^{1,9}$-octalin was added to 25 ml of concentrated hydrochloric acid that had been saturated with hydrogen chloride gas. The mixture was allowed to stand at room temperature for 3 days. The brownish red layers were separated and the reaction flask was rinsed with ether and water. The ether layer was washed with water until the washings were neutral to litmus and dried (Na_2SO_4), and the ether was removed at reduced pressure. Distillation yielded 2.9 g (0.0168 mole, 71.5%) of crude 9-chlorodecalin, bp 39–41° (0.2 mm) [lit.[38] bp 89–95° (14 mm), 98–102° (15 mm)]. The infrared spectrum of the chlorodecalin was identical with that of *trans*-9-chlorodecalin. The vapor phase chromatogram of the oil showed that two chlorodecalins were present in ratios of approximately 17 to 1. The larger peak was identified as *trans*-9-chlorodecalin; the smaller peak was *cis*-9-chlorodecalin (as determined by infrared spectroscopy).

C. Reaction of Decalin, *t*-Butyl Chloride, and Aluminum Chloride.[39]—Commercial decalin (52.0 g, 0.377 mole) and *t*-butyl chloride (20.0 g, 0.216 mole) were mixed at room temperature with a magnetic stirrer. Aluminum chloride (2.5 g) was added and the mixture was stirred for 30 sec. Water was added to hydrolyze the aluminum chloride. The two layers were separated and the flask was rinsed with ether. The combined organic layers were extracted one time with 10% sodium carbonate solution and dried ($MgSO_4$). The solution was filtered and the ether was removed under reduced pressure. The residual brown oil was distilled at 0.1 mm. Three fractions were collected: 35.3 g (bp 26–28°, shown by vapor phase chromatography to be principally decalin with a trace of chlorodecalin), 3.96 g (bp 29–40, containing decalin and three chlorodecalin isomers), and 3.21 g (bp 40–44°, containing products in approximately equal amounts). The three products were collected by vapor phase chromatography. The compound with shortest retention time proved to be *trans*-9-chlorodecalin (infrared spectra superimposable); the second two compounds had infrared spectra different from both of the 9-chlorodecalins, and are presumed to be secondary chlorodecalins.

D. Photochemical chlorination of decalin was attempted by the method of Russell[40] in carbon bisulfide. Analysis by vpc showed the presence of many products in spite of low conversion (4%): *trans*-9-chlorodecalin, 1.7%; *cis*-9-chlorodecalin was obscured in the vpc by the presence of a compound presumed to be a secondary chloride (together the peaks amounted to 0.4%).

9-Bromodecalin.—A solution of $\Delta^{9,10}$-octalin (0.50 g, 0.0037 mole) in 9 ml of methylene chloride was cooled in a Dry Ice–acetone bath and hydrogen bromide was bubbled through the solution for 10 min. The flask was wrapped in aluminum foil during this time to prevent light-catalyzed addition. The solution was allowed to stand in the dark for 20 min and then moved to a rotary evaporator and concentrated to remove hydrogen bromide. The solution was then diluted with ether, dried ($MgSO_4$), filtered, and concentrated. The residual oil was distilled in a molecular still at a bath temperature of 40–60° at 0.5 mm. The oil thus obtained solidified in the freezer, mp 18–20°. The material was unstable to analysis by vapor phase chromatography and decomposed completely to octalin at preheater and column temperatures of 115°. On the basis of the similarity of the infrared spectra of the decalyl bromide and *trans*-9-decalyl chloride, the bromide is assumed to be predominantly *trans*.

Anal. Calcd for $C_{10}H_{17}Br$: C, 55.30; H, 7.83; Br, 36.87. Found: C, 55.33; H, 7.83; Br, 36.78.

Equilibration of *cis*- and *trans*-9-Chlorodecalin.—Chlorodecalin (10.0 mg), zinc chloride (98 mg), and concentrated hydrochloric acid (to make 0.5 ml of solution) were mixed in a test tube fitted with a ground-glass stopper and heated in an oil bath 46° for 6 days. At the end of this time the test tube was opened and the contents were poured into water in a separatory funnel. The test tube was washed with several portions of water and also pentane and the washings were added to the separatory funnel. The pentane layer was separated and the water layer was washed three times with pentane; the pentane extracts were combined, dried ($MgSO_4$), concentrated at reduced pressure, and analyzed by vapor phase chromatography (see Table VI above).

Table VI

Initial	Final, *trans*-RCl/ *cis*-RCl
cis-RCl	89/11
	89/11
trans-RCl	90/10
	89/11

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[33] J. P. van Hook and A. V. Tobolsky, *J. Am. Chem. Soc.*, **80**, 779 (1958).

[34] G. S. Hammond, C. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keys, *ibid.*, **82**, 5394 (1960).

[35] W. G. Dauben, E. C. Martin, and G. J. Fonken, *J. Org. Chem.*, **23**, 1205 (1958).

[36] J. W. Powell and M. C. Whiting, *Tetrahedron*, **12**, 163 (1961).

[37] R. A. Benkeser and E. M. Kaiser, *J. Org. Chem.*, **29**, 955 (1964).

[38] W. P. Long, Ph.D. Thesis in Chemistry, Harvard University, 1955.

[39] P. D. Bartlett, F. E. Condon, and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

[40] G. A. Russell, *ibid.*, **80**, 4987 (1958).

Basic Elimination of Hydrogen Chloride from 9-Halodecalins.—A 4.4-mg sample (0.0256 mmole) of *cis*- (or *trans*-) 9-chlorodecalin was weighed into a small tube fitted with a cold-finger condenser and 50 μl. of 5.1 *M* (0.255 mmole) potassium hydroxide in ethanol was added. The solution was heated at 55–60° for 24 hr. Water was added and the resulting, cloudy water layer was washed twice with pentane (or hexane or ethyl ether), the organic layer was dried ($MgSO_4$), and the bulk of the solvent was removed on a steam bath using a Vigreux column. The solution was further concentrated under a stream of nitrogen and the products were analyzed[36] by vapor phase chromatography without further work-up. In determination of yields a standard, *o*-dichlorobenzene, was added to the reaction before the addition of water. *cis*-9-Chlorodecalin gave a ratio of $\Delta^{9,10}$-octalin to $\Delta^{1,9}$-octalin of 1 to 9; *trans*-9-chlorodecalin gave the same octalins in the ratio 3.7 to 1; 9-bromodecalin (18 hr at 40° in 3.5 *M* ethanolic KOH) gave these octalins in the ratio 3 to 1.

Registry No.—*cis*-9-Decalylcarbinyl hypochlorite, 7731-61-5; *trans*-9-decalylcarbinyl hypochlorite, 7731-62-6; methyl *cis*-9-decalincarboxylate, 4630-78-8; methyl *cis*-9-decalyl ketone, 5682-42-8; 2-(*cis*-9-decalyl)propene, 7731-65-9; methyl(*cis*-9-decalyl)carbinol, 7775-55-5; *cis*-9-chlorodecalin, 5597-83-1; *trans*-9-chlorodecalin, 5597-82-0; 11-oxatricyclo$[5.3.2.0^{2,7}]$dodecane, 7771-18-8; 11-oxatricyclo$[7.2.1.0^{4,9}]$dodecane, 7731-68-2; 9-bromodecalin, 7731-69-3.

Stereoselectivity in Hydrogen Atom Transfer. Reduction of *cis*- and *trans*-9-Chlorodecalins with Organotin Hydrides[1a]

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The free-radical chain reaction of *trans*- and *cis*-9-chlorodecalin with tri-*n*-butyltin hydride affords in high yield the same mixture from each chloride of *trans*- and *cis*-decalin in which *trans* predominates (3.5/1 at 130°, 6/1 at 60°, 11/1 at 0°). The same product ratio is obtained by use of triphenyltin hydride or dibutyltin dihydride. The reductions may be effected at 0° with initiation by azobisisobutyronitrile and weak ultraviolet irradiation. Reaction of 9-chlorodecalin with tri-*n*-butyltin deuteride in toluene affords 9-deuteriodecalin; this process constitutes a specific method for the introduction of deuterium, and indicates a high hydrogen atom transfer activity for tri-*n*-butyltin hydride.

Organotin hydrides effect the reduction of a variety of organic functional groups,[2] probably by a range of mechanisms. For the reduction of alkyl halides to alkanes, the evidence points to a free-radical chain reaction, for which the chain-propagating steps of eq 1 and 2 have been suggested.[2] This reaction has been

$$RX + R'_3SnH \longrightarrow RH + R'_3SnX$$

$$R\cdot + HSnR'_3 \longrightarrow RH + \cdot SnR'_3 \qquad (1)$$

$$RX + \cdot SnR'_3 \longrightarrow R\cdot + XSnR'_3 \qquad (2)$$

of interest to us in that it provides an opportunity for studying the stereochemistry of hydrogen atom transfer to specific radicals (R·). The present study describes the application of this reaction to 9-decalyl radicals.

Results

trans- and *cis*-9-chlorodecalin[3] were prepared by the addition of anhydrous hydrogen chloride to $\Delta^{9,10}$-octalin or by the decomposition of *cis*-9-decalylcarbinyl hypochlorite and separated by preparative-scale glpc. Reaction of either of the 9-chlorodecalins with tri-*n*-butyltin hydride afforded in high yield a mixture of *trans*- and *cis*-decalin in which the former predominated. The same product ratio, *trans*-RH/*cis*-RH, was obtained from each chloride. As with previous cases, the reductions appear to proceed by free-radical chain reaction.[2,4] At 80° a source of radical initiators is needed. Azobisisobutyronitrile was employed at 0.5 to 1 mole % of the hydride. Reduction was complete in 0.5 hr at 80° under these conditions; thus the chain length is long. At 130°, the AIBN may be omitted; probably the reaction is self-initiated. Reduction may also be effected at 0° with chain initiation by means of photochemical decomposition of azo compound. Irradiation of 9-chlorodecalin and tri-*n*-butyltin hydride in the absence of added azo compound was not effective.

Reductions of *trans*- and *cis*-9-chlorodecalin with di-*n*-butyltin dihydride and triphenyltin hydride were examined to see if the use of these hydrides, more reactive[2,4a] than tri-*n*-butyltin hydride, would result in any dependence of the product ratio, *trans*-RH/*cis*-RH, on the stereochemistry of the initial chloride. *cis*- and *trans*-9-chlorodecalin still afforded a common product composition, and the ratio of *trans*-decalin to *cis*-decalin was essentially the same as that obtained from the tri-*n*-butyltin hydride in spite of the rather different steric situations in the three hydrides. The use of di-*n*-butyltin dihydride as solvent also did not alter the product ratio. The results are summarized in Table I.

Although one of the products of the reaction (R_3SnCl) is a weak Lewis acid, no isomerization of the tertiary chlorides occurs prior to their reduction. Both chlorides were shown to be stable to the reaction conditions by analysis for alkyl chloride after partial reaction. The products were also shown to be stable to the reaction conditions. (Free-radical isomerization of *cis*- to *trans*-decalin has been observed but requires more severe conditions than those employed here.)[5]

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[1] (a) Supported in part by the Atomic Energy Commission under Contract No. AT(30-1)-905. Reproduction is permitted for any purpose of the U. S. Government; (b) National Institutes of Health Predoctoral Fellow, 1962–1965.

[2] H. G. Kuivila. "Advances in Organometallic Chemistry," Vol. 1, Academic Press Inc., New York, 1964, pp 47–87; see also C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, **31**, 3381 (1966).

[3] F. D. Greene and N. N. Lowry, *ibid.*, **32**, 875 (1967).

[4] (a) H. G. Kuivila and L. W. Menapace, *ibid.*, **28**, 2165 (1963); (b) L. W. Menapace and H. G. Kuivila, *J. Am. Chem. Soc.*, **86**, 3047 (1964).

[5] R. M. Roberts and J. J. Madison, *ibid.*, **81**, 5839 (1959).