Decomposition of Tertiary Alkyl Hypochlorites[1]

FREDERICK D. GREENE, MAXINE L. SAVITZ, FREDERICK D. OSTERHOLTZ, HANS H. LAU, WILLIAM N. SMITH, AND PAUL M. ZANET[2]

Department of Chemistry, Massachusetts Institute of Technology, Cambridge 39, Massachusetts

Received August 10, 1962

The scope of the decomposition of tertiary alkyl hypochlorites has been investigated (Table I). Decomposition proceeds by a free radical chain reaction of long chain length (Table II). Principal reactions of the intermediate alkoxy radicals are (1) fragmentation to ketone and alkyl radical and (2) intramolecular hydrogen abstraction. The relative ease of ejection of alkyl radical in the fragmentation of alkoxyl is isopropyl > ethyl > 1-norbornyl (1-bicyclo[2.2.1]heptyl) ~ methyl. Ring strain appears to be of importance in determining the direction of fragmentation—*e.g.*, in 1-isopropyl-1-cyclopentoxyl radical, rate of ring opening to the primary radical $(CH_3)_2CH—CO—(CH_2)_3—CH_2\cdot$ exceeds rate of ejection of isopropyl radical. Intramolecular hydrogen abstraction may predominate over fragmentation and occurs principally *via* "1,5" transfer of hydrogen, leading to α,δ-chlorohydrins. Subsequent cyclization renders this a convenient route to a number of substituted tetrahydrofurans. Intermolecular hydrogen abstraction from cyclohexene (solvent) competes poorly with "1,5" intramolecular hydrogen abstraction.

Alkyl hypochlorites, a class of compounds readily available from the corresponding alcohols, have been known for many years and have received attention principally as chlorinating agents[3] and oxidants.[4] Recently, attention has been directed to the thermal and photochemical decomposition of hypochlorites.[1a,5-7] The tertiary hypochlorites have been shown in a number of isolated examples to undergo decomposition to carbonyl compounds and alkyl chlorides. For a few

$$R_3C—O—Cl \longrightarrow R_2CO + RCl$$

of these cases, strong evidence exists for decomposition by a radical chain reaction.[8] This study reports the results of decomposition of a series of hypochlorites which serve to outline the scope and limitations of this degradation reaction of alcohols. Principal questions concern: (1) the generality of decomposition by a radical chain reaction, (2) the involvement of alkoxyl radicals and selectivity in fragmentation of these species, and (3) the reactions of alkoxyl radicals competitive with fragmentation, such as inter- and intramolecular hydrogen abstraction.

Results

The hypochlorites were prepared by the action of hypochlorous acid on the alcohols. The decompositions were effected thermally or photochemically in Freon 11 (trichlorofluoromethane), carbon tetrachloride, or cyclohexene. Products were isolated by gas phase chromatography. In most cases an accounting is made for 80–90% of the hypochlorite. (Decompositions in Freon 11 and in carbon tetrachloride occasionally have afforded high-boiling polyhalogenated material, believed to be products of olefin–solvent addition reactions.) The product compositions are fairly insensitive to initial concentrations of hypochlorite but optimum yields are obtained in the region 0.5–1.5 *M* under degassed and dry conditions. At high hypochlorite concentrations, an undesirable side reaction—intermolecular chlorination affording α-chloro ketones—may occur (**4**–**6**). The product data of this study are summarized in Table I.

Structural Assignments.—Identification of all of the products in Table I of known structure was made by direct comparison of infrared spectra and gas–liquid phase chromatography (g.l.p.c.) retention times with authentic samples. Of the new compounds of Table I, assignment of structure to alcohols of **3**, **11**, and **12** and to methyl 1-norbornyl ketone is based on mode of synthesis and infrared spectral data. Assignment of structure to the chlorohydrins from **8** and **9** is based on cyclization by the action of sodium hydride in ether to the corresponding tetrahydrofurans and comparison with samples made by independent routes. The structures of the olefins from **3** and **12** and the chloro olefins from **8** and **9** are based on identity with the products of dehydration of the corresponding tertiary alcohols. Assignment of the *exo*-methylene position to the double bond in the olefins from **3** and the chloro olefins from **8** and **9** is based on the strong terminal methylene absorption at 890 cm.$^{-1}$ in the infrared. The isopropylidene structure for the olefin from **12** is based on oxidation by osmium tetroxide and cleavage of the resulting diol by lead tetraacetate to give 2-norbornanone, established by direct comparison of the 2,4-dinitrophenylhydrazone derivative with an authentic sample. Assignment of structure to the chloro ketones from **5**, **6**, and **7** is based on infrared and n.m.r. data, outlined here in detail for the chloro ketone from **5**, 1-chloro-6-octanone. The analysis and infrared spectra indicate that the product is an acyclic saturated chloro ketone. The

N.m.r. of	CH_3—	—CH_2—	—$\overset{O}{\overset{\|}{C}}$—	—CH_2—	—$(CH_2)_3$—	—CH_2Cl
Description	Triplet	Quartet		Triplet	Multiplet	Triplet
tau	8.96	7.57		7.57	8.4	6.47
Approx. rel. area	3	2		2	6	2
J, c.p.s.	7.2	7.2		6.3		6.2

---

[1] (a) For a preliminary account of work in this area, see F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz, and W. N. Smith, *J. Am. Chem. Soc.*, **83**, 2196 (1961). (b) This work was supported by grants from the Sloan Foundation and the National Science Foundation.

[2] This paper is dedicated to the memory of Paul M. Zanet, who began the work of these laboratories on the hypochlorites.

[3] (a) For leading references, see C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, pp. 386–388; (b) C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108, 6113 (1960); (c) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

[4] *E.g.*, see G. S. Fonken, J. L. Thompson, and R. H. Levin, *ibid.*, **77**, 172 (1955); C. A. Grob and H. J. Schmid, *Helv. Chim. Acta*, **36**, 1763 (1953).

[5] C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **83**, 2207 (1961).

[6] J. S. Mills and V. Petrow, *Chem. Ind.* (London), 946 (1961); M. Akhtar and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 2213 (1961).

[7] J. W. Wilt and J. W. Hill, *J. Org. Chem.*, **26**, 3523 (1961); E. L. Jenner, *ibid.*, **27**, 1031 (1962); B. E. Englund, U.S. Patent 2,691,682 (Oct. 12, 1954).

[8] See F. D. Greene, *J. Am. Chem. Soc.*, **81**, 2688 (1959) and references cited therein; D. B. Denney and W. F. Beach, *J. Org. Chem.*, **24**, 108 (1959).

TABLE I

PRODUCTS OF DECOMPOSITION OF TERTIARY HYPOCHLORITES

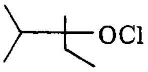
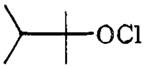
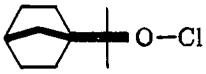
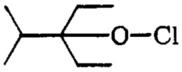
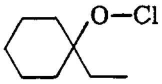
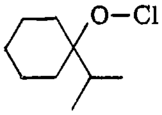
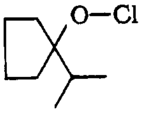
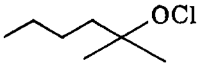
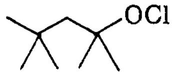
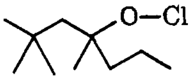
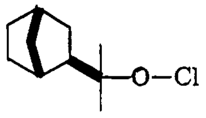
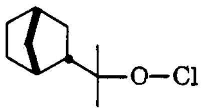
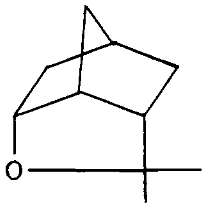
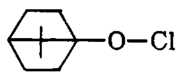
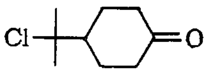
Hypochlorite	Solvent	Products	Yield, %
(1) 	CCl_4[a]	Isopropyl chloride, 2-butanone	95
		Ethyl chloride, 3-methyl-2-butanone	3
		Methyl chloride, 2-methyl-3-pentanone	$<$0.5[b]
(2) 	CCl_4[a]	Isopropyl chloride, acetone	96
		3-Methyl-2-butanone	$<$0.5[b]
	$CBrCl_3$[c]	Acetone	98
		Isopropyl chloride	38
		Isopropyl bromide, CCl_4	32
	Cyclohexene[c,d]	Isopropyl chloride, acetone	80
		3-Chlorocyclohexene	2
(3) 	$CFCl_3$[c]	1-Chloronorbornane, acetone	22
		Methyl 1-norbornyl ketone	5.2
		1-Isopropenylnorbornane	5
	Cyclohexene[c,d]	Dimethyl(1-norbornyl)carbinol	94
		1-Isopropenylnorbornane	3
		1-Chloronorbornane	(2)
		Norbornane	$<$0.5[b]
		3-Chlorocyclohexene	94
		4-Chlorocyclohexene	$<$3
		Cyclohexyl chloride	$<$0.5[b]
(4) 	CCl_4[a]	3-Pentanone	84
		2-Methyl-3-pentanone	3.7
		2-Chloro-3-pentanone[e]	(3)
	CCl_4[c]		[f]
(5) 	CCl_4[a]	Ethyl chloride, cyclohexanone	5
		1-Chloro-6-octanone	68
		1-Ethylcyclohexene	1
		2-Chlorocyclohexanone[e]	(1)
		1,X-Dichloro-6-octanones[e]	(5)
(6) 	CCl_4[a]	Isopropyl chloride, cyclohexanone	66
		$(CH_3)_2CHCO(CH_2)_4CH_2Cl$	13.5
		2-Chlorocyclohexanone	[g]
		1-Isopropylcyclohexene	$<$0.5[b]
		Isopropylidenecyclohexane	$<$0.5[b]
(7) 	$CFCl_3$[c]	$(CH_3)_2CHCO(CH_2)_3CH_2Cl$	94
		Isopropyl chloride, cyclopentanone	3.4
(8) 	$CFCl_3$[c]	$CH_3CHClCH_2CH_2C(CH_3)_2OH$	55
		n-Butyl chloride, acetone	15
		Methyl chloride, 2-hexanone	$<$0.5[b]
	Cyclohexene[c,d]	$CH_3CHClCH_2CH_2C(CH_3)_2OH$	75
		n-Butyl chloride, acetone	14
		$CH_3CHClCH_2CH_2C(CH_3){=}CH_2$	3
		2,2,5-Trimethyltetrahydrofuran	2
		3-Chlorocyclohexene	8
		4-Chlorocyclohexene	$<$0.5[b]
		Cyclohexyl chloride	$<$0.5[b]

TABLE I (*Continued*)

	Hypochlorite	Solvent	Products	Yield, %
(9)		$CFCl_3$[c]	Neopentyl chloride, acetone	55
			$(CH_3)_2C(CH_2Cl)CH_2C(CH_3)_2OH$	20
			2,2,4,4-Tetramethyltetrahydrofuran	5
			Methyl neopentyl ketone	<0.5[b]
			t-Amyl chloride	<0.5[b]
		Cyclohexene[c,d]	Neopentyl chloride, acetone	55
			$(CH_3)_2C(CH_2Cl)CH_2C(CH_3)_2OH$	25
			$(CH_3)_2C(CH_2Cl)CH_2C(CH_3){=}CH_2$	4
			2,2,4,4-Tetramethyltetrahydrofuran	2
			3-Chlorocyclohexene	8
			4-Chlorocyclohexene	<0.5[b]
			Cyclohexyl chloride	<0.5[b]
		Toluene	Neopentyl chloride, acetone	50
			$(CH_3)_2C(CH_2Cl)CH_2C(CH_3)_2OH$	20
			Benzyl chloride	6
(10)		$CFCl_3$[c]	Neopentyl chloride, 2-pentanone	25
			n-Propyl chloride, 4,4-dimethyl-2-pentanone	25
		Cyclohexene[h]	Neopentyl chloride, 2-pentanone	25
			n-Propyl chloride, 4,4-dimethyl-2-pentanone	25
			$(CH_3)_2C(CH_2Cl)CH_2C(CH_2CH_2CH_3){=}CH_2$[g]	(5)
			3-Chlorocyclohexene	7
(11)	 *exo*	CCl_4[c]	*exo*-Norbornyl chloride, acetone	80
			endo-Norbornyl chloride	<5
			Methyl 2-norbornyl ketone	<0.5[b]
(12)	 *endo*	CCl_4[c,i]		30
			2-Isopropylidenenorbornane	7
			exo-Norbornyl chloride	3.5
			Methyl 2-norbornyl ketone	<0.5[b]
(13)		CCl_4[a]		>95

[a] Thermal initiation at 80°. [b] Not present within the limits of detection of the analyses. [c] Weak ultraviolet initiation at 0°. [d] Initial concn. of ROCl, approx. 1.3 *M*. [e] By retention time only, tentative assignment. [f] Ratio of diethyl ketone to ethyl isopropyl ketone, 26:1. [g] By retention time and infrared spectrum, amount uncertain. [h] Violent self initiation. [i] In presence of pyridine.

appearance of only one methyl peak in the n.m.r. requires that the chlorine be attached at the remaining terminal position. The typical propionyl pattern in the n.m.r. requires the location of the chlorine at the opposite end of the chain, leading unambiguously to the structure shown. Assignment of structure to the chloro ketone from **13** is based on (a) conversion to derivatives of 4-isopropylcyclohexanone and (b) conversion to a dibenzal derivative identical in melting point with that of Wallach,[9] formed by the action of hydrochloric acid and benzaldehyde on nopinone (6,6-dimethylbicyclo[3.1.1]heptanone-2). Assignment of structure to the cyclic ether derived from **12** is based on strong absorption in the infrared at 1060 cm.$^{-1}$ and on identity with the product obtained by the action of lead tetraacetate on alcohol **12**.[10]

---

(9) O. Wallach, *Ann.*, **437**, 187 (1924).

(10) G. Cainelli, M. Lj. Mihailović, D. Arigoni, and O. Jeger, *Helv. Chim. Acta*, **42**, 1124 (1959); for some additional examples of this reaction, see O. Jeger, M. Lj. Mihailović, *et al.*, *ibid.*, **44**, 186, 502 (1961), and A. Bowers, E. Denot, L. Cuéllar Ibanez, Ma. E. Carbezas, and H. J. Ringold, *J. Org. Chem.*, **27**, 1862 (1962).

Effect of Reaction Conditions on Rate of Decomposition.—Solutions of the hypochlorites in carbon tetrachloride or in trichlorofluoromethane are stable in the dark for prolonged periods. Exposure to weak ultraviolet light, or heating of the solutions, or the addition of free radical sources effect rapid decomposition of the hypochlorites. Oxygen and *m*-dinitrobenzene markedly inhibit both the photochemical and the thermal decompositions. A lower limit of 1000 for chain length is estimated for 2,4,4-trimethyl-2-pentyl hypochlorite in toluene. Illustrative data on the effect of accelerators and inhibitors on the decomposition of this hypochlorite, **9**, are summarized in Table II. The effect of temperature on the product composition of this work has not been examined in detail other than to establish that the effect is small—*e.g.*, for case **4** the ratio of cleavage of isopropyl radical to cleavage of ethyl radical is 45 at 80°, 52 at 0°.

TABLE II

EFFECT OF REACTION CONDITIONS ON RATE OF DECOMPOSITION OF 2,4,4-TRIMETHYL-2-PENTYL HYPOCHLORITE (**9**)

Conditions	Solvent	Temp., °C.	Time, min.	Reaction, %
U,[a] dark	T[b]	80	800	99
U,[a] hν[c]	T[b]	0	7	99
D,[d] dark	T[b]	25	2540	<1
D,[d] AIBN[e]	T[b]	45	110	35[f]
D,[d] AIBN[g]	T[b]	45	150	25[h]
U,[a] hν[c]	F[i]	0	20	99
D,[d] hν[c]	F[i]	0	3	99
D,[d] hν, DNB[j]	F[i]	0	170	99

[a] Undegassed. [b] Toluene, ROCl concn., 1.15 *M*. [c] Weak irradiation with a Burton lamp. [d] Degassed. [e] Azobisisobutyronitrile, 0.0132 *M*. [f] Corresponds to a chain length of 1300 using k_1 of 0.004 hr.$^{-1}$ (ref. 3a, p. 513) for AIBN at 45° and a 20% correction for cage recombination [G. S. Hammond, C. S. Wu, O. D. Trapp, J. Warkentin, and R. T. Keyes, *J. Am. Chem. Soc.*, **82**, 5394 (1960)]. [g] AIBN, 0.0056 *M*. [h] Corresponds to chain length of 1800 (see *f*). [i] CFCl$_3$, ROCl concn., 0.80 *M*. [j] *m*-Dinitrobenzene, 0.6 *M*.

Discussion

Examination of Table I reveals that the decomposition of tertiary hypochlorites varies from a clean one-product reaction to complex multiproduct reactions affording ketones, chloro ketones, chlorohydrins, olefins, alkyl halides, and tetrahydrofurans. The principal features of these decompositions will be considered with reference to the three points outlined in the introduction: (1) generality of radical chain decomposition, (2) involvement of, and selectivity in cleavage of, alkoxyl radicals, and (3) reactions of alkoxyl radicals competitive with fragmentation.

Mechanism.—Previous studies have provided evidence that *t*-butyl hypochlorite[11] and 2-methyl-3-phenyl-2-butyl hypochlorite[8] decompose by chain reactions. Kinetic data (such as illustrated in Table II) and product data of this study provide strong support that this mode of decomposition is general for the tertiary hypochlorites. (For example, relevant product data supporting a chain mechanism are the formation of both isopropyl bromide and chloride from the decomposition of dimethylisopropylcarbinyl hypochlorite, **2**, in bromotrichloromethane and the predominance of the *exo* isomer in the 2-norbornyl chloride obtained from both **11** and **12**.) That all of the products of decomposition are derived from chain reactions is indicated by the independence of product composition on the type (heat or light) or quantity of initiator.[12]

Two principal chain mechanisms warrant consideration,[13] *A* and *B*. Both mechanisms involve an alkoxyl radical intermediate.

$$A.\quad R_3C{-}O{-}Cl + \cdot R \longrightarrow R_3C{-}O\cdot + Cl{-}R \qquad (1)$$

$$R_3C{-}O\cdot \longrightarrow R_2C{=}O + \cdot R \qquad (2)$$

$$B.\quad R_3C{-}O\cdot \longrightarrow R_2\dot{C}{-}O{-}R \qquad (1)$$

$$R_2{-}\dot{C}O{-}R + Cl{-}O{-}R' \longrightarrow R_2\overset{Cl}{\overset{|}{C}}{-}O{-}R + \cdot OR' \qquad (2)$$

$$R_2\overset{Cl}{\overset{|}{C}}{-}O{-}R \longrightarrow R_2C{=}O + RCl \qquad (3)$$

In *B* this intermediate undergoes rearrangement and subsequent conversion to an α-chloro ether. The α-chloro ether might then proceed to alkyl chloride and ketone by several possible mechanisms. Although our inability to prepare the appropriate α-chloro ethers has precluded the most direct approach to evaluation of this sequence, indirect evidence may be cited against the intermediacy of α-chloro ethers. (1) Decomposition of 2,4,4-trimethyl-2-pentyl hypochlorite in toluene saturated with water[14] still affords neopentyl chloride as the major product. (2) Rearrangement of α-chloro ethers,[15] equation *B*-3, appears to require higher temperatures than those employed in the decomposition of hypochlorites. (3) A number of α-chloro ethers has been prepared by the photochemical chlorination of ethers[15-17] under illumination conditions much more intense than those needed to effect decomposition of hypochlorites. (The formation of α-chlorotetrahydrofuran in good yield by photochlorination[17] seems of particular importance to the point under discussion.) Thus, although α-chloro ethers may be involved in some hypochlorite decomposition, there is no evidence to involve them in the examples of this study; and the preferred mechanism of decomposition is that shown in sequence *A*.[18] The principal paths of reaction then available to the alkoxyl radical are fragmentation and inter- and intramolecular hydrogen abstraction.

---

(11) A. D. Yoffe, *Chem. Ind.* (London), 963 (1954).

(12) Exclusive of temperature dependence: The effect of temperature on the product compositions of Table I is small. Similar effects are reported in ref. 5 and 20.

(13) A third possible mechanism,

$$Cl\cdot + R_3C{-}O{-}Cl \longrightarrow Cl{-}R + R_2\dot{C}{-}O{-}Cl$$

$$R_2\dot{C}{-}O{-}Cl \longrightarrow R_2CO + Cl\cdot$$

may be rejected directly for *tertiary* hypochlorites on several grounds: It leads to the wrong prediction of structure for alkyl halide from cases such as 11 and that reported in reference 8; and it ascribes a selectivity and behavior to atomic chlorine that is not in accord with other information on this species—*e.g.*, see ref. 3a, chap. 8. This type of chain may be operative when the R undergoing attack by chlorine atom is hydrogen—*i.e.*, with primary or secondary hypochlorites (unpublished work of these laboratories).

(14) α-Halo ethers are rapidly hydrolyzed: see P. Ballinger, P. B. D. de la Mare, G. Kohnstam, and B. M. Prestt, *J. Chem. Soc.*, 3641 (1955) and references cited therein; F. Straus and H. J. Weber, *Ann.*, **498**, 105, 128 (1932).

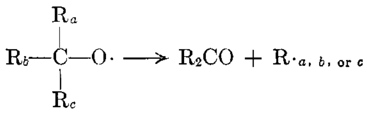
(15) (a) L. Summers, *Chem. Revs.*, **55**, 301 (1955); (b) R. K. Summerbell and D. R. Berger, *J. Am. Chem. Soc.*, **79**, 6504 (1957), **81**, 633 (1959); (c) For a study of the unimolecular decomposition of α-chloroethyl methyl ether to hydrogen chloride and methyl vinyl ether, see P. J. Thomas, *J. Chem. Soc.*, 136 (1961).

(16) H. Böhme and A. Dörries, *Ber.*, **89**, 723 (1956).

(17) H. Gross, *Angew. Chem.*, **72**, 268 (1960).

(18) Rearrangement of type *B*-1 *does* appear to occur in triarylmethoxyl radicals, ref. 3a, p. 473.

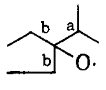
Selectivity in Fragmentation.—Examination of the cases **1**, **2**, **4**, **8**, **9**, **11**, and **13** indicates that the order of increasing ease of fragmentation of alkyl groups is


$$R_b\text{—}\overset{R_a}{\underset{R_c}{C}}\text{—O}\cdot \longrightarrow R_2CO + R\cdot_{a,\,b,\,\text{or }c}$$

methyl < primary alkyl < secondary, in confirmation of other data on alkoxyl radicals.[19,20] Rate of cleavage of a primary alkyl group exceeds rate of cleavage of methyl by factors as large as one hundred (**8**, **9**). Rate of cleavage of *sec*-alkyl (isopropyl) exceeds rate of cleavage of *n*-alkyl (ethyl) by factors of thirty (case **1**) and fifty (case **4**). This order of fragmentation is in the order of increasing radical stability, increasing carbonium ion stability, or simply increasing size. Case **3** is of special interest in this connection. The 1-norbornyl group represents a group of large size but of demonstrated instability as an ion,[21] and of lower radical stability than a secondary radical.[22] In case 3, the preference for ejection of the tertiary (but bridgehead) 1-norbornyl radical *vs.* ejection of methyl is only four to one. The smallness of this ratio must be attributed either to the reluctance of cleavage of this 1-norbornyl group or to a great decrease in selectivity of *all* fragmentation paths in compound **3**, a situation that might obtain in this alkoxyl radical due to strain produced by the presence of the bulky bridgehead group. Experiments described (under *Hydrogen Atom Abstraction*) provide compelling evidence that the alkoxyl radical of **3** is longer lived than that of **2**, thereby excluding this second possibility. One concludes that a principal factor in the order of fragmentation is the stability, rather than the size, of the departing group.[23]

In the recent report of Kochi,[20] the relative intramolecular cleavage rates of *n*-alkyl groups from *t*-alkoxyl radicals at 25° are methyl (~0.003), ethyl (1.0), *n*-propyl (0.65), *n*-butyl (0.43). It was noted that a linear correlation exists between the logarithms of the relative cleavage rates for ethyl, *n*-propyl, and *n*-butyl *vs.* the corresponding carbon-hydrogen bond dissociation energies.[24] This correlation is an interesting one, but appears to be of limited application. As pointed out by the author,[20] methyl is cleaved more slowly than predicted from the correlation; and from the present work, isopropyl is cleaved more rapidly than predicted. Competition between alternative fragmentation paths may be expected to be dependent on many factors: the stability of the ejected radical and the product ketone, the importance of strain in the reactant alkoxyl radical, the degree of brokenness of the carbon–carbon bond at the transition state, the importance of ionic character in the transition state. A detailed consideration of the relative importance of these factors must await the accumulation of more data.

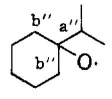
Examination of cases **4**, **5**, **6**, and **7** indicates the importance of ring strain in dictating the direction of cleavage. One notes a large preference for opening of a five-membered ring *vs.* ejection of ethyl (700-fold from the comparison of *b′ vs. b* in **7** and **4**, and making the assumption that $a \cong a'$). The preference for opening a six-membered ring *vs.* ejection of ethyl is much smaller (fourfold: *b″ vs. b* in **6** and **4**). The orders are in accord with the strain associated with these rings (five-membered ring, 6 kcal. per mole; six-membered ring, 1 kcal. per mole).[25] The 700-fold preference for opening the five-membered ring corresponds to a difference in free energy of 3.5 kcal. per mole at the temperature of the experiment and suggests that a major portion of the ring strain has been released at the transition state of the ring-opening step. (As indicated above, this is based on the *assumption* that $a \cong a'$.)



4

a/b

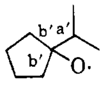
50:1



6

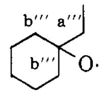
a/b

11:1



7

1:14

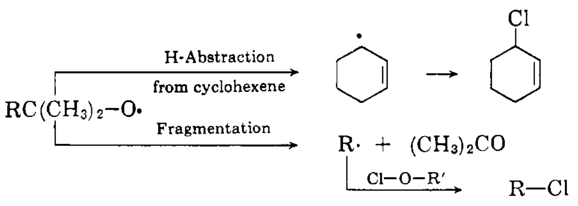


5

1:7

Examples **5** and **6** afford an intermolecular comparison of ease of fragmentation of isopropyl *vs.* ethyl. The value, 77 to 1, is moderately close to the *intra*molecular value from case **4** of 50 to 1 for these groups.

Hydrogen Atom Abstraction.—Competition between hydrogen abstraction by the *t*-butoxyl radical *vs.* fragmentation has been employed to determine the relative reactivities of a large number of kinds of carbon-hydrogen bonds.[3] In the decomposition of hypochlorites, competition between hydrogen abstraction from a single substrate, cyclohexene, by alkoxyl radicals *vs.* fragmentation may be employed to provide an index of the relative stabilities of the alkoxyl radicals. Such an index is based on the assumption that the hydrogen abstraction reaction is independent of the structure of the alkoxyl radical. (This method was originally used in the determination of the following order of stability of alkoxyl radicals [derived from dialkyl peroxides] at 195°: methoxyl > ethoxyl > *n*-butoxyl > isopropoxyl > isobutoxyl ≅ *t*-butoxyl.)[26] The principal feature of the data of Table III is the much greater difficulty of ejection of the 1-norbornyl radical than of the *n*-butyl, neopentyl, or isopropyl radicals—a strong indication (as pointed out above)



---

(19) See P. Gray and A. Williams, *Chem. Revs.*, **59**, 239 (1959); *Trans. Faraday Soc.*, **55**, 760 (1959).

(20) J. K. Kochi, *J. Am. Chem. Soc.*, **84**, 1193 (1962).

(21) See P. von R. Schleyer and R. D. Nicholas, *J. Am. Chem. Soc.*, **83**, 2700 (1961) and references cited therein.

(22) E. C. Kooyman and G. C. Vegter, *Tetrahedron*, **4**, 382 (1958).

(23) The question of the degree of ionic character to the transition state of the fragmentation reaction will be discussed in a later paper.

(24) For a thorough re-examination of bond dissociation data in simple hydrocarbons, see B. Steiner, C. F. Giese, and M. G. Inghram, *J. Chem. Phys.*, **34**, 189 (1961).

(25) V. Prelog, *Bull. soc. chim. France*, 1433 (1960).

(26) F. F. Rust, F. H. Seubold, Jr., and W. E. Vaughan, *J. Am. Chem. Soc.*, **72**, 338 (1950).

TABLE III

CHAIN DECOMPOSITION OF $RC(CH_3)_2$-O—Cl IN CYCLOHEXENE

	R	C_6H_9Cl,[a] %	RCl, %
	Methyl	>95	
8	Butyl	8[b]	14[c]
9	Neopentyl	8[b]	55[d]
2	Isopropyl	2[b]	80
3	1-Norbornyl	94	(2)

[a] 3-Chlorocyclohexene (>93%) and 4-chlorocyclohexene (<7%). [b] May not be formed exclusively from R′—O. [c] Plus 78% chlorohydrin and chloro olefin (see Table I). [d] Plus 29% chlorohydrin and chloro olefin (see Table I).

that the stability, not the size, of the ejected fragment is of overriding importance in the fragmentation reaction.

As indicated by examples **8**, **9**, **10**, and **12**[27] (Table I), decomposition of hypochlorites may result in the replacement in the alkyl portion of the hypochlorite of a carbon–hydrogen bond by a carbon–halogen bond. The selectivity in point of attack—four carbon atoms removed from the oxygen atom (1,5-hydrogen abstraction)[28]—is suggestive of intramolecular attack by the alkoxyl radical. Confirmation of the intramolecular nature is provided by the unimportance of attack on cyclohexene (as solvent) relative to attack on the alkyl portion of hypochlorite (Table III, **8** and **9**). Intramolecular hydrogen transfer reactions have been proposed in a number of reactions. Some of the principal cases have been summarized recently by Barton and Morgan.[29]

Preliminary results reported in an independent, and more detailed, examination of intramolecular chlorination with long chain hypochlorites[5] also indicate marked preference for 1,5-hydrogen abstraction by alkoxyl radical, and considerable discrimination in the abstraction reaction between primary, secondary, and tertiary hydrogens. Chlorohydrin formation from steroidal hypochlorites has also been reported recently.[6]

Competition between Fragmentation and Intramolecular Hydrogen Abstraction.—The rate of 1,5-abstraction of secondary C-H (per hydrogen) *vs.* fragmentation of *n*-alkyl (butyl) is 2.7 to 1 (**8**). The rate of fragmentation of ethyl *vs.* isopropyl is 1 to 50 (**4**). On a purely statistical basis these data would predict that ejection of a secondary radical would outweigh abstraction of a secondary hydrogen. Example **12** shows a tenfold preference (a minimum value) for abstraction of the single available hydrogen *vs.* fragmentation to the 2-norbornyl radical. Thus the steric situation of the δ-hydrogens with respect to the alkoxyl oxygen may be of overriding importance in the competition between intramolecular hydrogen abstraction and fragmentation.

Experimental

The order of description of experiments is: (1) preparation of reactants, standards, and products, (2) preparation and decomposition of the hypochlorites, and (3) control data. Preparations and decompositions are given in the order in which they are listed in Table I. Materials obtained commercially were purified when necessary to obtain material giving a single peak on g.l.p.c. columns and agreeing with reported physical constants. The constants for such compounds are not reproduced.

(1 and 2)

2,3-Dimethyl-3-pentanol, b.p. 137–137.5°, $n^{30}D$ 1.4241 (lit.,[30] b.p. 139–140°, $n^{25}D$ 1.4262) and **2,3-dimethyl-2-butanol**, b.p. 116.2–116.7°, $n^{30}D$ 1.4121 (lit.,[31] b.p. 117.91–117.95°, $n^{25}D$ 1.4151) were prepared by standard Grignard syntheses.

(3)

Norbornane-1-carboxylic acid was prepared from *endo*-norbornanecarboxylic acid by bromination and successive catalytic hydrogenolysis.[32] The acid had m.p. of 111–112° (lit., m.p. 112–113°).

Norbornane-1-carbonyl Chloride.—A 5.6-g. sample of norcamphane-1-carboxylic acid was treated with 8 g. of thionyl chloride under nitrogen and the temperature was maintained at 30–40° until the hydrogen chloride evolution had ceased. The excess of thionyl chloride was removed at aspirator pressure and the acid chloride was distilled at 47–47.5° at 2.1 mm., yield 85%. Treatment with concentrated ammonia converted the acid chloride to *norbornane-1-carboxamide*, m.p. 233–234° (recrystallized from chloroform).

Anal. Calcd. for $C_8H_{13}NO$: C, 69.02; H, 9.41; N, 10.06. Found: C, 68.72; H, 9.55; N, 9.92.

Anhydride of Norbornane-1-carboxylic Acid.—A solution of 1.58 g. of norcamphane-1-carbonyl chloride and 20 ml. of pyridine was allowed to stand at room temperature for 4 hr. at which time a copious precipitate was present. Moist either was added and the solution was washed successively with water, 6 *N* hydrochloric acid, 2 *N* sodium carbonate, and water. After drying over anhydrous magnesium sulfate, the ether was removed *in vacuo*. Crystallization from pentane at low temperatures gave the anhydride, m.p. 73.0–74.5°.

Anal. Calcd. $C_{16}H_{22}O_3$: C, 73.24; H, 8.45. Found: C, 73.19; H, 8.55.

Methyl 1-Norbornyl Ketone.—To an ethereal solution of methylmagnesium iodide, prepared from 3.55 g. of methyl iodide and 0.6 g. of magnesium, was added 2.56 g. of anhydrous cadmium chloride.[33] The ether was evaporated at 25° under nitrogen and replaced by 40 ml. of dry benzene. A 3.2-g. sample of norbornane-1-carbonyl chloride in 20 ml. of benzene was added dropwise at room temperature. The mixture was stirred for another 2 hr. and decomposed by addition of ice-cold 2 *N* hydrochloric acid. The water layer was extracted three times with ether. The combined ether–benzene layers were washed twice with 1 *N* sodium hydrogen sulfite, twice with 1 *N* sodium hydrogen carbonate, and dried over calcium chloride. After removal of the ether and the benzene, distillation of the residue at 73–74° (11 mm.) yielded 2.2 g. of ketone (80%). Some unchanged acid chloride was removed by passing a solution of the ketone in pentane through an aluminum oxide (base-washed) column. The ketone had b.p. 194–195°, $n^{27}D$ 1.4702.

Anal. Calcd. for $C_9H_{14}O$: C, 78.22; H, 10.21. Found: C, 78.77, 78.70; H, 10.63, 10.42.

A sample of the ketone was converted to the **2,4-dinitrophenylhydrazone**, m.p. 121–122°.

Anal. Calcd. for $C_{15}H_{18}O_4N_4$: C, 56.59; H, 5.71; N, 17.60. Found: C, 56.79; H, 5.69; N, 17.46.

Methyl Norbornane-1-carboxylate.—The above acid was converted by the action of an ethereal solution of diazomethane to

---

[27] Assuming that the precursor of the ether from **12** is the corresponding chlorohydrin.

[28] For example **8**, a specific search was made for the product of 1,6-hydrogen abstraction. Cyclization of the chlorohydrin fraction by base failed to reveal any 2,2-dimethyltetrahydropyran within the limits of the g.l.p.c. analysis (0.5%).

[29] D. H. R. Barton and L. R. Morgan, Jr., *J. Chem. Soc.*, 622 (1962). See also F. D. Greene, G. R. Van Norman, J. E. Cantrill, and R. D. Gilliom, *J. Org. Chem.*, **25**, 1790 (1960); E. J. Corey and W. R. Hertler, *J. Am. Chem. Soc.*, **82**, 1657 (1960); and T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **27**, 3067 (1962).

[30] P. M. Ginnings and M. Hauser, *J. Am. Chem. Soc.*, **60**, 2581 (1938); F. H. Norton and H. B. Haas, *ibid.*, **58**, 2147 (1936).

[31] G. B. Kistiakowsky, J. R. Ruhoff, H. A. Smith, and W. E. Vaughan, *ibid.*, **58**, 137 (1936); F. Hovoska, H. Lankelma, and J. Bishop, *ibid.*, **63**, 1097 (1941).

[32] H. Kwart and G. Null, *ibid.*, **80**, 248 (1958); W. R. Boehme, *ibid.*, **80**, 4740 (1958).

[33] D. A. Shirley, *Org. Reactions*, **VIII**, 45 (1954).

the methyl ester, b.p. 70–72° (11 mm.) [lit. 52–53° (1.8 mm.)[32]], n^{26}_{D} 1.4621 (lit.,[34] n^{26}_{D} 1.4633).

Dimethyl(1-norbornyl)carbinol.—To a cooled ethereal solution of methylmagnesium iodide, prepared from 20.8 g. of methyl iodide and 3.12 g. of magnesium in 40 ml. of ether under nitrogen atmosphere, was added a solution of 9.0 g. of the above ester in 10 ml. of ether over a period of 10 min. The mixture was stirred at room temperature for an additional 2 hr., and then decomposed by the addition of ice-cold saturated aqueous ammonium chloride solution. The water layer was extracted three times with ether. The combined ether layers were washed twice with 1 *N* sodium hydrogen sulfite solution, twice with 1 *N* sodium hydrogen carbonate solution, and dried over magnesium sulfate. Removal of the ether afforded a white solid, which was twice recrystallized from pentane at low temperatures, m.p. 67–68°, b.p. 57–59° at 1.6 mm., yield 89%. The alcohol is hygroscopic and should be kept in a desiccator over phosphorus pentoxide.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.87; H, 11.76. Found: C, 77.59; H, 11.73.

A sample of the above alcohol was treated with an equimolar amount of phenyl isocyanate for 3 days at room temperature,[35] and then for 1 hr. at 90°. The solid obtained was filtered, recrystallized from methanol, and extracted with cold hexane to free it from *sym*-diphenylurea. This extract was evaporated and the solid was recrystallized from methanol, yielding the **phenylurethane** of the above alcohol, m.p. 157–158°.

Anal. Calcd. for $C_{17}H_{23}NO_2$: C, 74.69; H, 8.48; N, 5.12. Found: C, 74.49; H, 8.32; N, 5.12.

1-Isopropenylnorbornane.—A 1.1-g. sample of the alcohol was distilled at atmospheric pressure in the presence of a trace of iodine. The distillate was dissolved in ether and the solution was washed twice with 1 *N* sodium bisulfite, with 1 *N* sodium hydrogen carbonate, and dried over calcium chloride. The ether was removed and the liquid was distilled at 11-mm. pressure yielding 82% of the olefin, b.p. 169–170°, n^{31}_{D} 1.4695. The gas chromatogram of the product exhibited only one peak; the infrared absorption spectrum exhibits bands at 3030, 1640, and 890 cm.$^{-1}$ (terminal methylene).

Anal. Calcd. for $C_{10}H_{16}$: C, 88.15; H, 11.84. Found: C, 88.12; H, 12.10.

Norbornane.—A solution of 0.170 g. of sublimed norbornylene in absolute methanol was added to a mixture of 0.034 g. of prereduced platinum oxide in absolute methanol. The theoretical amount of hydrogen was taken up in 15 min. The catalyst was removed by filtration and the mixture subjected to gas chromatography to determine retention time.

(4)

2-Methyl-3-ethyl-3-pentanol was prepared by the reaction of methyl isobutyrate and ethylmagnesium bromide, b.p. 62° at 18 mm., n^{25}_{D} 1.4353 (lit.,[36] b.p. 53° at 10 mm., n^{20}_{D} 1.4372).

(5)

1-Ethylcyclohexanol was prepared by the procedure of Mosher,[37] m.p. 31–35° (lit.,[38] m.p. 33°), n^{25}_{D} 1.4628 (lit.,[37] n^{20}_{D} 1.4642), m.p. of *p*-nitrobenzoate 73–74° (lit.,[39] 73–74°). Dehydration[37] afforded a mixture of 1-ethylcyclohexene and 1-ethylidenecyclohexane for use in determination of retention times on g.l.p.c.

2-Chlorocyclohexanone was prepared by a standard procedure.[40]

(6)

1-Isopropylcyclohexanol was prepared by the procedure of Mosher,[37] b.p. 60° at 1.2 mm. n^{25}_{D} 1.4659 (lit.,[37] b.p. 80° at 1.8 mm.). Dehydration[37] afforded a mixture of isopropylidenecyclohexane and 1-isopropylcyclohexene for use in determination of g.l.p.c. retention times.

(7)

1-Isopropylcyclopentanol was prepared by the Grignard reaction[41] of 1,4-dibromobutane and ethyl isobutyrate in 50% yield, b.p. 62–63° at 11 mm., n^{26}_{D} 1.4545 (lit.,[41] b.p. 53° at 6 mm., n^{25}_{D} 1.4551).

(8)

2-Methyl-2-hexanol, b.p. 141–142°, n^{27}_{D} 1.4166 (lit.,[42] b.p. 141–143°, n^{20}_{D} 1.4186) was prepared by a standard Grignard reaction.[42] Distillation of the alcohol in the presence of a trace of iodine afforded a mixture of **2-methyl-1-hexene** and **2-methyl-2-hexene**, b.p. 90–92° (lit.,[43] b.p. 94–96°). Gas chromatography indicated a predominance of the former compound, infrared band at 890 cm.$^{-1}$.

2-Methylhexane-2,5-diol.—To a cooled ethereal solution of methylmagnesium iodide, prepared from 70.5 g. (0.500 mole) of methyl iodide and 12.0 g. (0.500 g.-atom) of magnesium in 100 ml. of ether under nitrogen atmosphere was added an ethereal solution of 250 g. (0.247 mole) of γ-valerolactone over a period of 1 hr. The mixture was refluxed for an additional hour, and decomposed by the addition of an ice-cold saturated aqueous ammonium chloride solution. The aqueous layer was extracted three times with ether. The combined ether layers were washed with 10% sodium bisulfite solution, 10% sodium bicarbonate solution and water and dried over magnesium sulfate. Filtration, removal of the ether, and distillation afforded the diol as the major fraction, b.p. 106–110° at 8 mm., (lit.,[44] b.p. 121° at 14 mm.).

2,2,5-Trimethyltetrahydrofuran.—To 0.60 g. of the above diol at 90° was added an equal amount of 60% sulfuric acid. The reddish brown layer was stirred for 30 min., extracted with ether washed with sodium bicarbonate solution and water and dried over magnesium sulfate. Distillation gave 0.150 g. of 2,2,5-trimethyltetrahydrofuran, b.p. 99–102° (lit.,[44] b.p. 102–103°), infrared absorption band at 1080 cm.$^{-1}$.

2,2-Dimethyl-3,4-dihydropyran was prepared by the Diels–Alder addition of isobutylene and acrolein according to the procedure of Smith, Norton, and Ballard, b.p. 55° at 75 mm., n^{25}_{D} 1.4390 (lit.,[45] b.p. 52–58° at 100 mm., n^{20}_{D} 1.4371).

2,2-Dimethyltetrahydropyran.—A solution of the above 2,2-dimethyl-3,4-dihydropyran in petroleum ether was added to a mixture of pre-reduced platinum oxide. The theoretical amount of hydrogen was taken up in 20 min. The catalyst was removed by filtration and mixture was subjected to gas chromatography. The retention time differed from that of 2,2,5-trimethyltetrahydrofuran.[46]

(9)

2,4,4-Trimethyl-2-pentanol was prepared from the chloride by the method of Brown and Berneis[45] with the modification of a reaction time of 30 hr. at 50–55°; b.p. 57–58° at 25 mm. n^{25}_{D} 1.4860 (lit.,[47] b.p. 146–146.5°).

Neopentyl chloride was prepared from neopentyl alcohol by the procedure of Gerrard and Tolcher, n^{25}_{D} 1.4020 (lit.,[48] n^{20}_{D} 1.4048).

Methyl neopentyl ketone was prepared by potassium dichromate–sulfuric acid oxidation of diisobutylene according to the procedure of Mosher and Cox, b.p. 123–125°, n^{25}_{D} 1.4013 (lit.,[49] b.p. 124–125°, n^{25}_{D} 1.4018).

2,4,4-Trimethylpentene-1 and -2.—The acid dehydration of 2,4,4-trimethyl-2-pentanol according to the procedure of Whitmore[50] gave 2,4,4-trimethyl-1-pentene in 80% yield and 2,4,4-trimethyl-2-pentene in 20% yield, indicated by gas chromatography.

2,4,4-Trimethyl-3,5-pentanediol was prepared by heating 68 g. of freshly distilled isobutyraldehyde and 136 g. of 13.5% potassium hydroxide for 12 hr. at 50° according to the procedure of Fossek, b.p. 83–86° at 5 mm., (lit.,[51] b.p. 222–223°).

2,2,4,4-Tetramethyltetrahydrofuran.—To 20 g. of the above glycol was added an equal amount of concd. sulfuric acid. The reddish-brown layer was stirred for 30 min. at 0°, poured into twenty times the amount of ice–water, extracted with ether, and dried over magnesium sulfate. Ether was removed and distillation afforded 10.5 g. of the tetrahydrofuran, b.p. 120–122°

---

[34] W. P. Whelan, Jr., dissertation, Columbia University, 1952.

[35] W. H. Perkin, Jr., and K. Matsubara, *J. Chem. Soc.*, **87**, 668 (1905).

[36] R. C. Huston, *et al.*, *J. Am. Chem. Soc.*, **70**, 1092 (1948).

[37] W. A. Mosher, *ibid.*, **62**, 552 (1940).

[38] P. Sabatier and A. Mailhe, *Compt. rend.*, **138**, 1321 (1903).

[39] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

[40] M. S. Newman, M. D. Farbman, and H. Hipsher, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, New York, N. Y., 1955, p. 188.

[41] G. S. Skinner and F. P. Florentine, Jr., *J. Am. Chem. Soc.*, **76**, 3200 (1954).

[42] J. Church, F. Whitmore, and R. McGrew, *ibid.*, **56**, 180 (1934).

[43] G. Edgar, G. Calingaert, and R. Marker, *ibid.*, **51**, 1483 (1929).

[44] M. S. Losanitsch, *Compt. Rend.*, **153**, 392 (1911).

[45] C. W. Smith, D. G. Norton, and S. A. Ballard, *J. Am. Chem. Soc.*, **73**, 5273 (1951).

[46] The gas–liquid phase chromatography columns used in this work are described in the section entitled *Decomposition of Alkyl Hypochlorites.*

[47] H. C. Brown and H. L. Berneis, *J. Am. Chem. Soc.*, **75**, 10 (1953).

[48] W. Gerrard and P. Tolcher, *J. Chem. Soc.*, 3640 (1954).

[49] W. Mosher and J. Cox, *J. Am. Chem. Soc.*, **72**, 3701 (1950).

[50] F. C. Whitmore, C. S. Rowland, S. N. Wrenn, and G. W. Kilmer *ibid.*, **64**, 2970 (1942).

[51] W. Fossek, *Monatsh.*, **4**, 663 (1883).

(lit.,[52] b.p. 120°) and higher boiling material. The infrared spectrum agreed with a published one.[52] The structure of 2,2,4,4-tetramethyltetrahydrofuran, previously assigned on the basis of infrared evidence, is strongly supported by the n.m.r. spectrum (four singlets of relative area 3:3:1:1 at τ of 8.91, 8.77, 8.40, and 6.6 in carbon tetrachloride).

(10)

2,2,4-Trimethyl-4-heptanol was prepared from propylmagnesium bromide and methyl neopentyl ketone according to the procedure of Moersch and Whitmore, b.p. 70–73° at 9 mm., n^{25}_{D} 1.4350 (lit.,[53] b.p. 59.6° at 7 mm., n^{20}_{D} 1.4373).

(11)

***exo*-5-Norbornene-2-carboxylic Acid.**—The Diels–Alder addition of freshly distilled cyclopentadiene with methyl acrylate afforded a 71% yield of a mixture of 75% *endo*- and 25% *exo*-methyl 5-norbornene-2-carboxylate.[54,55] The mixture was isomerized by the action of sodium methoxide to a 54% *exo*–46% *endo* mixture. This mixture was hydrolyzed by aqueous sodium hydroxide and the resulting acid mixture was separated into iodo lactone, m.p. 58–59° (lit.,[56] m.p. 58–59°) and *exo* acid by the procedure of ver Nooy and Rondestvedt. Two recrystallizations from petroleum ether gave *exo* acid of m.p. 40.2–40.8° (lit.,[56] 44–45°).

Dimethyl(*exo*-norbornyl)carbinol.—A sample of the above acid was converted by diazomethane to the methyl ester, b.p. 82–83° at 15 mm. (lit.,[55] b.p. 86.5° at 17 mm.). The ester was hydrogenated in methanol at 2 atm. with platinum oxide, giving methyl *exo*-norbornanecarboxylate, b.p. 88–89° at 18 mm., n^{25}_{D} 1.4653 (lit.,[55] b.p. 84° at 15 mm., n^{20}_{D} 1.4643). To an ether solution of methylmagnesium iodide, prepared from 26 g. (0.18 mole) of methyl iodide and 4.3 g. (0.18 g.-atom) of magnesium was added an ether solution of 13.0 g. (0.094 mole) of the above ester over a period of 1 hr. The reaction mixture was heated at reflux for an additional hour, cooled, and excess Grignard reagent was decomposed by the addition of a saturated aqueous ammonium chloride solution. The ether layer was washed with 10% sodium bisulfite solution, 10% sodium bicarbonate solution, and dried over magnesium sulfate. Filtration, removal of the ether, and distillation of the residual yellow oil from potassium carbonate afforded 11.0 g. of pure dimethyl(*exo*-norbornyl)carbinol, b.p. 99–100° at 22 mm., n^{25}_{D} 1.4668.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.92; H, 11.68. Found: C, 77.86; H, 11.96.

***exo*- and *endo*-Norbornyl chloride** were prepared by published procedures: *exo* chloride, b.p. 59° at 20 mm., n^{25}_{D} 1.4905 (lit.,[57a] b.p. 88–89° at 74 mm.); *endo* chloride, b.p. 60–61° at 22 mm., n^{25}_{D} 1.4845 (lit.,[57b] b.p. 51–53° at 17 mm., n^{25}_{D} 1.4835).

(12)

***endo*-5-Norbornene-2-carboxylic Acid..**—The Diels–Alder addition of freshly distilled cyclopentadiene to acrylic acid afforded a 60% yield of adduct, b.p. 103–106° at 2 mm., (lit.,[58] b.p. 129–130° at 13 mm.) which solidified in the receiver. Successive recrystallizations from petroleum ether afforded the pure *endo* acid, m.p. 43–44° (lit.,[56] m.p. 44–45°), mixed m.p. with *exo* acid, 32–34°.

Dimethyl(*endo*-norbornyl)carbinol.—A sample of the above acid was converted by the action of an ethereal solution of diazomethane to the methyl ester, b.p. 63–64° at 8 mm., (lit.,[55] b.p. 88–89° at 18 mm.). The ester, 16.5 g., was hydrogenated with 500 mg. of platinum oxide in 125 ml. of absolute methanol to give 15.9 g. of methyl *endo*-norbornanecarboxylate, b.p. 67–68° at 8 mm. (lit.,[55] b.p. 70° at 10 mm.). The Grignard reaction was performed as described for the *exo* carbinol giving 8.3 g. of pure dimethyl(*endo*-norbornyl)carbinol b.p. 78° at 8 mm.

Anal. Calcd. for $C_{10}H_{18}O$: C, 77.92; H, 11.68. Found: C, 77.93, H, 11.45.

2-Isopropylidenenorbornane.—To a 3.8-g. sample of the *endo*-carbinol was added an equal amount of 15% sulfuric acid. The mixture was refluxed for 1 hr., extracted with ether, and dried with magnesium sulfate. Removal of ether and distillation through a small Claisen head gave 2.2 g. of colorless 2-isopropylidenenorbornane, b.p. 67° at 21 mm., infrared absorption bands at 3080 cm.$^{-1}$, 1640 cm.$^{-1}$, no band at 890 cm.$^{-1}$.

Anal. Calcd. for $C_{10}H_{16}$: C, 88.24; H, 11.76. Found: C, 88.16; H, 11.84.

Conversion of 2-Isopropylidenenorbornane to 2-Norbornanone.—To a solution of 500 mg. (3.7 mmoles) of 2-isopropylidenenorbornane and 15 ml. of pyridine was added 1.0 g. (3.94 mmoles) of osmium tetroxide. The deep red solution was stirred magnetically for 80 min. and the pyridine was removed *via* a water aspirator. To the brown residue was added 17 ml. of 95% ethanol, 17 ml. of dried benzene, 7.0 g. of mannitol, and a solution of 7.0 g. of potassium hydroxide in 17 ml. of water and 35 ml. of ethanol.[59] After refluxing for 16 hr. the bulk of the solvent was removed with the water aspirator. The remaining mixture was extracted with ether, washed with water, and dried over magnesium sulfate. The diol was not isolated, but used immediately for oxidation with lead tetraacetate. To the above benzene solution of diol was added 1.8 g. of lead tetraacetate. The solution was stirred for 90 min. at 30°. The reaction mixture was washed with 10% potassium iodide solution and extracted with ether. The ether solution was decolorized with 10% sodium thiosulfate, washed with 10% sodium bicarbonate, water, and dried over magnesium sulfate. Some of the ether was removed on a steam bath. The rest of the solution was shaken with a solution of 1.0 g. of 2,4-dinitrophenylhydrazine in 20 ml. of 75% ethanol containing 4 ml. of concd. sulfuric acid. Removal of the solvent yielded a 2,4-dinitrophenylhydrazone which after two recrystallizations from ethanol melted at 128–129°, mixed melting point with an authentic sample, 129–130°.

Methyl 2-Norbornyl Ketone.—An *endo*–*exo* mixture was prepared by the procedure of Berson and Suzuki, b.p. 125–127° at 22 mm. (lit.,[60] b.p. 87° at 19 mm.).

3-Chlorocyclohexene.—**A.** The reaction of 12.0 g. of *t*-butyl hypochlorite, 50 ml. of cyclohexene, and 0.200 g. of benzoyl peroxide according to the procedure of Grob, Kny, and Gagneux afforded 4.3 g. of 3-chlorocyclohexene, b.p. 63–64° at 40 mm., n^{25}_{D} 1.4838, (lit.,[61] b.p. 76–78° at 80 mm., n^{20}_{D} 1.4860). Gas chromatographic analysis indicated 94% of desired product and 6% of 4-chlorocyclohexene. After two distillations, gas chromatography indicated 77.6% of the desired product and 22.4% of 4-chlorocyclohexene. Pure 3-chlorocyclohexene was obtained by gas chromatography collection. Repassage of the collected peak showed only the same peak.

B. A solution of 25 ml. (0.25 mole) of purified cyclohexene, 20.0 g. (0.15 mole) of recrystallized N-chlorosuccinimide, 38 ml. of reagent carbon tetrachloride, and 0.500 g. of benzoyl peroxide was refluxed under nitrogen and irradiated with a Westinghouse sun lamp for 14 hr. Filtration of the solution and distillation gave 2.0 g. of chlorocyclohexene mixture, b.p. 64–66° at 40 mm. which was shown to be 73% 3-chlorocyclohexene and 27% 4-chlorocyclohexene by gas chromatography.

4-Chlorocyclohexanol was prepared by the reaction of 1,4-cyclohexanediol and hydrochloric acid according to the procedure of Owens and Robins, b.p. 74–77° at 13 mm., n^{25}_{D} 1.4985 (lit.,[62] b.p. 80–85° at 5 mm., n^{16}_{D} 1.4964).

4-Chlorocyclohexene.—To a solution of 7.2 g. of 4-chlorocyclohexanol, 5.5 g. of freshly distilled pyridine, and 20 ml. of reagent chloroform was added 8.3 g. of thionyl chloride dropwise. The mixture was allowed to reflux for 1 hr. and was washed three times with water. The water was washed with ether which was combined with the chloroform and was dried over magnesium sulfate. Distillation afforded 0.32 g. of forerun, 2.2 g. of 4-chlorocyclohexene, b.p. 38–45° at 13 mm., and 0.88 g. of material, b.p. 65–68° at 13 mm. The infrared spectrum of the 4-chlorocyclohexene was identical with the spectrum of the component of shorter retention time from the reaction of *t*-butyl hypochlorite and cyclohexene.

---

(52) F. Rust and D. Collamer, *J. Am. Chem. Soc.*, **76**, 1055 (1954).

(53) G. Moersch and F. C. Whitmore, *ibid.*, **71**, 819 (1949).

(54) J. D. Roberts, E. R. Trumbell, Jr., W. Bennett, and R. Armstrong, *ibid.*, **72**, 3116 (1950).

(55) A. C. Cope, E. Ciganek, and N. A. LeBel, *ibid.*, **81**, 2799 (1959).

(56) C. D. ver Nooy and C. S. Rondestvedt, Jr., *ibid.*, **77**, 3583 (1955).

(57) (a) J. D. Roberts, L. Urbanek, and R. Armstrong, *ibid.*, **71**, 3049 (1949); (b) J. D. Roberts, W. Bennett, and R. Armstrong, *ibid.*, **72**, 3329 (1950).

(58) K. Alder, G. Stein, E. Rolland, and G. Schulze, *Ann.*, **514**, 211 (1934).

(59) G. Buchi, M. Wittenau, and D. White, *J. Am. Chem. Soc.*, **81**, 1968 (1959).

(60) J. Berson and S. Suzuki, *ibid.*, **81**, 4088 (1959).

(61) C. A. Grob, H. Kny, and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).

(62) P. Owens and R. Robins, *J. Chem. Soc.*, 325 (1949).

(13)

7,7-Dimethyl-1-norbornanol (1-apocamphanol) was prepared by the method of Hawthorne, Emmons, and McCallum,[63] m.p. 160–161° (lit.,[63] m.p. 160°).

Conversion of Alcohols to Tetrahydrofurans by the Action of Lead Tetraacetate.[10] **2,2,4,4-Tetramethyltetrahydrofuran.**—A solution of 0.500 g. of 2,4,4-trimethyl-2-pentanol and 1.0 g. of lead tetraacetate (dried at reduced pressure in a desiccator) in 25 ml. of dry benzene was refluxed for 4 days. The reaction mixture was washed with 10% potassium iodide solution (a precipitate of lead iodide formed) and the colloidal mixture was extracted with ether. The organic layers were combined, decolorized with 10% sodium thiosulfate solution, washed successively with 10% sodium bicarbonate solution and water, and dried over magnesium sulfate. The bulk of the solvent was removed through a Vigreux column; 2,2,4,4-tetramethyltetrahydrofuran was collected by gas chromatography of the residue (yield, 15%; when the reaction was stopped after 37 hr., this yield was 7.5%). The gas chromatography retention time and infrared spectrum of the ether agreed with those of an authentic sample.

When the reaction was carried out in heptane as solvent with a 4-day reflux period and work-up as described above, the products were 2,2,4,4-tetramethyltetrahydrofuran (3%), unchanged alcohol (65%), 2,4,4-trimethyl-2-pentyl acetate (5%, see below) and a mixture of heptanones (10%, assigned on the basis of the 1710-cm.$^{-1}$ band and a prominent mass spectral peak at m/e 114).

2,2,5-Trimethyltetrahydrofuran was obtained from 2-methyl-2-hexanol and lead tetraacetate in benzene in 3% yield after a 19-hr. reflux period. It was isolated by g.l.p.c. and had identical infrared spectrum and g.l.p.c. retention time with that of authentic material.

3,3-Dimethyl-2-oxatricyclo[4.2.1.0^{4,8}]nonane.—The lead tetraacetate procedure with dimethyl(*endo*-norbornyl)carbinol in benzene at reflux for 16 hr. gave a 45% conversion of alcohol to the ether. The infrared spectrum was identical to that of the product from the decomposition of the corresponding hypochlorite (**12**). (Combustion analysis, performed on several samples collected from gas chromatography, failed to give satisfactory data.)

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 78.36; H, 10.47.

2,4,4-Trimethyl-2-pentyl Acetate.—To a solution of 5.0 g. (0.038 mole) of freshly distilled 2,4,4-trimethyl-2-pentanol and 4.6 g. (0.038 mole) of freshly distilled N,N-dimethylaniline in 20 ml. of dry ether was added dropwise 3.2 g. (0.038 mole) of freshly distilled acetyl chloride.[64] The mixture was heated with a water bath for 2 hr. and a white precipitate of N,N-dimethylaniline hydrochloride formed. Water (20 ml.) was added. The mixture was extracted with ether. The ether layer was washed with 10% sulfuric acid and dried over magnesium sulfate. Filtration, removal of ether, and distillation afforded 0.65 g. of forerun, 2.50 g. of acetate, b.p. 59–61° at 13 mm., $n^{25}D$ 1.4351.

Anal. Calcd. for $C_{10}H_{20}O_2$: C, 69.77; H, 11.63. Found: C, 69.77; H, 11.67.

Preparation of Alkyl Hypochlorites.—The hypochlorites were prepared by the action of aqueous hypochlorous acid on the alcohol, neat or dissolved in carbon tetrachloride or Freon 11 (trichlorofluoromethane).

Because of the sensitivity of the hypochlorites to light the preparations and purifications were carried out in amber glass vessels or vessels otherwise protected from light. The general procedure is described in detail for example 5.

A. **Aqueous Sodium Hypochlorite.**—A mixture of 160 g. (1.5 moles) of sodium carbonate, 306 g. of 70% calcium hypochlorite (1.5 moles) (Olin-Matheson H.T.H.), and 1 l. of water was stirred for 1 hr., filtered, and the filter cake was washed with 50–100 ml. of water. The yellow filtrate, approximately 2.8 *M*, was stored in the dark at 5° and was stable for many weeks.

B. **1-Ethylcyclohexyl Hypochlorite** (**5**).—To 50 ml. of the aqueous hypochlorite solution, cooled to 0°, was added with stirring a solution of 6.42 g. (0.0506 mole) of 1-ethylcyclohexanol in 10 ml. of carbon tetrachloride (reagent grade) containing 5.7 ml. (0.1 mole) of glacial acetic acid. The mixture was stirred in the dark at 0° for 45 min. The layers were separated and the water layer was washed three times with 10-ml. portions of carbon tetrachloride. The combined carbon tetrachloride fractions were washed with three 10-ml. portions of 3% aqueous sodium bicarbonate, once with 10 ml. of water, and dried over magnesium sulfate at 5°; yield of hypochlorite: 85% by iodometric analysis.

Decomposition of Alkyl Hypochlorites.—The decompositions were effected under a variety of conditions (Tables I, II, and III). Light initiation (by means of a weak ultraviolet source—a Burton Ultraviolet Black Lamp, Model 1910, Burton Manufacturing Co., Santa Monica, California) was faster and usually afforded less secondary products than thermal decomposition. The procedure is described in detail for example **5**, and briefly for those cases in which decomposition of a hypochlorite represents the only mode of synthesis for new compounds obtained in this work.

A. **Decomposition of 1-Ethylcyclohexyl Hypochlorite** (**5**).—A 1.8 *M* solution of the hypochlorite in carbon tetrachloride prepared by the method described above was heated at reflux under nitrogen until a negative starch iodine test was obtained (8 hr.). Analysis of the solution by vapor phase chromatography [Dow-Corning Hi-Vac grease (30%) on Chromosorb P[65] (60/80 mesh)] at 135° indicated peaks (relative to carbon tetrachloride, 1.0) at 0.49, 1.0, 2.07, 2.32, 3.86, 4.75, 11.2, and a triplet from 19.3–21.8. The minor peaks at 0.49, 2.07, and 4.75 were shown by retention time to be ethyl chloride, 1-ethylcyclohexene, and 2-chlorocyclohexanone. The major peaks at 1.0, 2.32, and 3.86 were collected from a preparative-scale g.l.p.c. column and shown by comparison of infrared spectra with those of authentic samples to be pure carbon tetrachloride, cyclohexanone, and 1-ethylcyclohexanol. The 11.2 peak and the 19.3–21.8 triplet were collected; both showed strong carbonyl absorption.

A sample of the major component (the 11.2 peak) was obtained by distillation of the reaction mixture through a 30-cm. Holtzman column. The fraction of b.p. 52–53° at 0.2 mm. was shown by g.l.p.c. analysis to be the 11.2-component (over 95%). The fraction was chromatographed on Woelm activity III alumina in petroleum ether. Short path distillation of the main fraction afforded the pure chloro ketone, 1-chloro-6-octanone (infrared, 1715 cm.$^{-1}$, 790 cm.$^{-1}$; the n.m.r. spectrum is described under *Results*).

Anal. Calcd. for $C_8H_{15}ClO$: C, 59.07; H, 9.30; Cl, 21.80. Found: C, 59.00; H, 9.16; Cl, 21.93.

The 2,4-dinitrophenylhydrazone had m.p. of 100–104° (yellow form; upon cooling of the melt it is converted to orange form, m.p. 69–70°; this material is reconverted upon recrystallization from ethanol to the material of m.p. 100–104°), λ_{max} in chloroform 364 mμ (log ϵ 4.37).

Anal. Calcd. for $C_{14}H_{19}N_4O_4Cl$: C, 49.05; H, 5.59; Cl, 10.34. Found: C, 48.80; H, 5.48; Cl, 10.41).

B. **Analysis of Product Compositions.**—The yield data of Table I were obtained by gas–liquid phase chromatography analysis of solutions from decompositions obtained under degassed conditions. The columns employed for the examples of Table I were: 30% w./w. Dow–Corning Hi-Vac grease on Chromosorb P[65], 60/80 mesh (**4**, **5**, **6**); 30% w./w. Dow Corning silicone oil 550 on Chromosorb P, 80/100 mesh (before coating, the Chromosorb was soaked in 1% aqueous sodium hydroxide, then washed with water to pH 7-8, and dried) (**1**, **2**, **3**, **7**, **8**, **9**, **10**, **11**,[66] **12**); 30% w./w. γ-methyl-γ-nitropimelonitrile on Chromosorb P, 80/100 mesh, washed with aqueous sodium hydroxide before coating (**1**, **2**). The general procedure will be described in detail for case **5**.

C. **Quantitative Analysis of the Products of Decomposition of 1-Ethylcyclohexyl Hypochlorite** (**5**).—A 4.00-ml. sample of a 1.17 *M* solution of the hypochlorite in carbon tetrachloride was transferred to a tube with a constricted neck. The tube was degassed by three cycles of freezing, evacuating, and thawing (closed off from the vacuum source) and was then sealed *in vacuo*. The tube was heated for 10 hr. at 80°. After decomposition was complete, the tube was opened and a known amount of tetralin (retention time 8.3 relative to carbon tetrachloride 1.0 on Hi-Vac grease column) was added for use as an internal standard. In addition, a calibration mixture was prepared containing exactly known amounts of tetralin and of the major products of the decomposition in approximately the same proportions as the un-

---

(63) M. F. Hawthorne, W. D. Emmons, and K. S. McCallum, *J. Am. Chem. Soc.*, **80**, 6393 (1958).

(64) B. Abramovitch, J. Shrives, B. Hudson, and C. Hauser, *ibid.*, **65**, 986 (1943).

(65) Johns–Manville Corporation.

(66) None of these g.l.p.c. columns resolved *exo*- and *endo*-norbornyl chloride; the analysis for the *exo–endo* ratio was made by use of differences in the infrared.

known. This calibration mixture was analyzed by g.l.p.c. at the same time and under the same conditions as the unknown.

A simple proportionality was set up:

$$\frac{\text{Moles tetralin}}{\text{Peak area tetralin}} = k_x \frac{\text{moles } x}{\text{area } x} = k_y \frac{\text{moles } y}{\text{area } y} = \ldots \quad (1)$$

The areas of the peaks on the chromatogram for each component of both the calibration and the unknown mixtures were determined with a planimeter. The areas from the calibration mixture and the amount of each component of the calibration mixture were substituted into equation 1 and k was thereby determined for cyclohexanone, 1-ethylcyclohexanol, and 1-chloro-6-octanone. The areas obtained from the unknown mixture, the k's, and the amount of tetralin added to the unknown were then used to calculate the amount of each component present. A k of 1.0 was used for components not in the standard mixture.

1-Chloro-7-methyl-6-octanone was obtained from the thermal decomposition of a solution of the hypochlorite (6) in carbon tetrachloride and collection of the chloro ketone by use of a preparative-scale g.l.p.c. column.

Anal. Calcd. for $C_{19}H_{17}ClO$: C, 61.17; H, 9.70; Cl, 20.07. Found: C, 61.11; H, 9.61; Cl, 20.19.

The n.m.r. spectrum in carbon tetrachloride at 60 Mc. showed a doublet at 9.05 τ (area, 6 protons; J, 6.5 c.p.s.), a multiplet at 8.5 τ (area, 6), a triplet superimposed on a multiplet at 7.6 τ (area, 3; J for the triplet, 7 c.p.s.), and a 1,2,1-triplet at 6.52 τ (area, 2; J, 6.5 c.p.s.).

1-Chloro-6-methyl-5-heptanone.—A 2.6-g. sample of 1-isopropylcyclopentanol in 20 ml. of carbon tetrachloride was converted to the hypochlorite (**7**) and decomposed by the slow distillation of the solvent under reduced pressure. The residual oil, 2.88 g. (principally the chloro ketone by g.l.p.c. analysis) was distilled, b.p. 101–102° at 12 mm., $n^{28}\text{D}$ 1.4419. The n.m.r. spectrum was markedly similar to that of 1-chloro-7-methyl-6-octanone, described above.

Anal. Calcd. for $C_8H_{15}ClO$: C, 59.07; H, 9.30; Cl, 21.80. Found: C, 59.06; H, 9.32; Cl, 22.35.

The **2,4-dinitrophenylhydrazone** had m.p. 83–84°.

Anal. Calcd. for $C_{14}H_{19}ClN_4O_4$: C, 49.05; H,, 5.59; Cl, 10.35; N, 16.35. Found: C, 48.74; H, 5.46; Cl, 10.35; N, 16.63.

5-Chloro-2-methyl-2-hexanol.—A 10-g. sample of 2-methyl-2-hexanol was converted to the hypochlorite (**8**) in Freon 11. The solvent was removed under reduced pressure and the pure hypochlorite was slowly added to a refluxing solution of 50 ml. of freshly distilled cyclohexene containing 0.2 g. of benzoyl peroxide. After the initial vigorous reaction, heating was continued for 30 min., solvent was removed under reduced pressure and the residue was distilled. The fraction of b.p. 78–79° at 10 mm., 4.5 g., was largely the chlorohydrin (90% by g.l.p.c. analysis). A sample was collected from a preparative-scale g.l.p.c. column.

Anal. Calcd. for $C_7H_{15}ClO$: C, 55.81; H, 9.97; Cl, 23.59. Found: C, 55.83; H, 10.13; Cl, 23.26.

5-Chloro-2-methyl-1-hexene.—Distillation of a mixture of the above chlorohydrin and potassium hydrogen sulfate afforded the olefin b.p. 42–44° at 10 mm., infrared absorption bands at 3080 cm.$^{-1}$, 1642 cm.$^{-1}$, 890 cm.$^{-1}$.

Anal. Calcd. for $C_7H_{13}Cl$: C, 63.40, H, 9.81, Cl, 26.79. Found: C, 63.81, H, 9.65, Cl, 26.71.

Conversion of 5-Chloro-2-methyl-2-hexanol to 2,2,5-Trimethyltetrahydrofuran.—A solution of 3.4 g. of the above chlorohydrin and 1.3 g. of 54% sodium hydride–mineral oil dispersion (Metal Hydrides, Inc.) in 5 ml. of ether was stirred for 2.5 hr.[67] The excess reagent was decomposed with water, the mixture was extracted with ether and distilled through a modified Claisen head to give a compound whose gas chromatography retention time and infrared spectrum were identical with authentic 2,2,5-trimethyltetrahydrofuran.

5-Chloro-2,4,4-trimethyl-2-pentanol was prepared from the corresponding hypochlorite (**9**) by the procedure described for the chlorohydrin from **8**. The chlorohydrin was principally in the fraction of b.p. 80–82° at 12 mm. A pure sample was collected from a preparative-scale g.l.p.c. column.

Anal. Calcd. for $C_8H_{17}ClO$: C, 58.36; H, 10.33; Cl, 21.58. Found: C, 58.56; H, 10.39; Cl, 21.71.

A sample of the chlorohydrin was converted to **2,2,4,4-tetramethyltetrahydrofuran** by the procedure described above for the 2,2,5-derivative.

5-Chloro-2,4,4-trimethyl-1-pentene.—Distillation of a mixture of the above chlorohydrin and potassium hydrogen sulfate afforded the olefin, b.p. 38–40° at 11 mm., infrared absorption bands at 3080, 1640, 890 cm.$^{-1}$.

Anal. Calcd. for $C_8H_{15}Cl$: C, 65.51; H, 10.24; Cl, 24.23. Found: C, 65.48; H, 9.99; Cl, 23.67.

5-Chloro-4,4-dimethyl-2-propyl-1-pentene was prepared by the photochemical decomposition of hypochlorite (**10**) in Freon 11 at 0° and collection of the products by g.l.p.c. The chloro olefin structural assignment is based on infrared (3080, 1640, 890 cm.$^{-1}$) and combustion data.

Anal. Calcd. for $C_{10}H_{19}ClO$: C, 68.77; H, 10.89; Cl, 20.34. Found: C, 68.69; H, 10.95; Cl, 20.16.

4-(α-Chloroisopropyl)cyclohexanone.—A 1.5-g. sample of 7,7-dimethyl-1-norbornanol in 45 ml. of carbon tetrachloride was converted to the hypochlorite (**13**). The dried solution was diluted to 100 ml. and the bulk of the solvent was removed by distillation. Removal of the residual solvent under reduced pressure afforded 1.8 g. of the chloro ketone, m.p. 61–62°. Recrystallization from benzene–hexane gave material of m.p. 61–62°.

Anal. Calcd. for $C_9H_{15}ClO$: C, 61.88; H, 8.65; Cl, 20.29. Found: C, 61.74; H, 8.77; Cl, 20.23.

A sample of the chloro ketone was dehydrochlorinated by refluxing in quinoline. The elimination product was hydrogenated in ethanol with palladium-on-carbon catalyst, stopping after the uptake of 1 mole. The product was converted in 55% over-all yield to the 2,4-dinitrophenylhydrazone, m.p. 118–119° (reported m.p. for DNP of 4-isopropylcyclohexanone,[68] 118–119°) and to the semicarbazone, m.p. 186–187° (lit.,[68] m.p. 186–187°).

2,6-Dibenzal-4-(α-chloroisopropyl)cyclohexanone.—To a suspension of 0.45 g. (0.0026 mole) of 4-(α-chloroisopropyl)cyclohexanone in 2 ml. of concd. hydrochloric acid and 2 ml. of absolute ethanol was added 0.54 g. (0.0051 mole) of benzaldehyde. The bright yellow precipitate which formed rapidly was filtered and washed with a small amount of dilute ethanol, giving 0.88 g. (98%), m.p. 144–148°. Two recrystallizations from carbon tetrachloride raised the melting point to 148–149° (reported[9] m.p. for a chlorodibenzal derivative from nopinone, 148–149°) λ_{max} 329 mμ (log ϵ 4.52) in ethanol [reported[69] for 3-methyl-2,6-dibenzalcyclohexanone: λ_{max} 328 mμ (log ϵ 4.54) in ethanol].

Anal. Calcd. for $C_{23}H_{23}ClO$: C, 78.70; H, 6.61; Cl, 10.10. Found: C, 78.92; H, 6.73; Cl, 10.06.

A Convenient Synthesis of Neopentyl Chloride.—A mixture of 10 g. of 2,4,4-trimethyl-2-pentanol in 60 ml. of Freon 11, 180 ml. of 1.68 M sodium hypochlorite solution, and 30 ml. of acetic acid was stirred for 20 min. at 0°. The Freon layer was separated, dried over magnesium sulfate, and decomposed by weak ultraviolet light. The solution was washed with two 25-ml. portions of concd. sulfuric acid, with 25 ml. of 5% aqueous sodium bicarbonate, and dried over magnesium sulfate. Removal of the solvent afforded pure neopentyl chloride, $n^{25}\text{D}$ 1.4021 (lit.,[48] $n^{20}\text{D}$ 1.4042) in 45% yield.

Decomposition of Hypochlorites in Cyclohexene and Toluene.—The alcohols were converted to the hypochlorites either without use of solvent or in Freon 11 followed by removal of the solvent under reduced pressure and then added to the desired solvent. Product analyses were made by the methods described above.

Hazards.—The principal hazards are associated with the sensitivity of the hypochlorites to light and peroxides. Attempts to distil some of the hypochlorites have led to vigorous decomposition, but many of the hypochlorites of this work have been kept in an undiluted state in the dark at 5° for days. A second source of hazard is the unexpected reactivity of certain combinations. For example, hypochlorites **2**, **3**, **8**, and **9** may be dissolved in cyclohexene without visible reaction; addition of hypochlorite **10** to cyclohexene produces violent decomposition. Addition of this hypochlorite, cooled to −15° (the hypochlorite freezes at −70°), to cyclohexene, cooled to −70°, still results in rapid decomposition, affording the products of chain decomposition of the hypochlorite (see Table I).[70]

Effect of inhibitors and accelerators was determined by sealed tube experiments. Conditions are given in Table II. Rate of disappearance of hypochlorite was followed by iodometric analysis.

---

[67] A. Rosowsky and D. S. Tarbell, *J. Org. Chem.*, **26**, 2255 (1961).

[68] M. D. Soffer and M. A. Jeunik, *J. Am. Chem. Soc.*, **77**, 1003 (1955).

[69] H. S. French and M. E. T. Holden, *ibid.*, **67**, 1239 (1945).

[70] This reactivity may be due to the formation of chain-initiating free radicals by a direct reaction between the hypochlorite and cyclohexene. For an example of this kind of reaction, see F. D. Greene, W. Adam, and J. E. Cantrill, *J. Am. Chem. Soc.*, **83**, 3461 (1961).