

Reactions were carried out in sealed degassed tubes, placed in thermostats and irradiated by incandescent lamps essentially as in previous work.¹²

Analyses of reaction mixtures were carried out by G.L.C. techniques using either a Perkin-Elmer model 154 or, more frequently, an Aerograph A-350 instrument. Two columns were used with the Perkin-Elmer instrument, A (diisodecyl phthalate) and C (dimethyl siloxane polymer); and five with the Aerograph, Carbowax 20 M (polyethylene oxide), "DEGS" (diethylene glycol polysuccinate), "Craig" (butanediol polysuccinate), didecyl phthalate and silicone (GE SF 96) all on firebrick. Products from each hypochlorite were collected and identified (by infrared spectra, index of refraction and boiling point) as described below. In quantitative experiments to determine relative amounts of β -scission and attack on cyclohexane (Table I) peak areas for acetone (or alkyl chloride) were compared with peak areas for alcohol (or cyclohexyl chloride) and results converted to molar ratios by calibration of the instrument with known mixtures. Relative reactivities of hydrocarbons were determined by hydrocarbon disappearance (or appearance of chlorinated products) using internal standards as previously.¹² Experiments were run in triplicate and analyzed in duplicate. Reproducibility was 2-6%, and results are reported as the mean, with experimental error the deviation from the mean.

***t*-Butyl Hypochlorite.**—Products of decomposition in CCl_4 were analyzed on the A column at 55 and 115°. Acetone, *t*-butyl alcohol, chloroacetone and 1-chloro-2-methyl-2-propanol were collected and identified. Methylene chloride and isobutylene oxide, present in very small quantities, were identified only by retention time. Peaks identified as dichloroacetone and dichloroalcohol had the same retention times as products obtained by *t*-butyl hypochlorite chlorination of chloroacetone and 1-chloro-2-methyl-2-propanol, respectively.

***t*-Amyl Hypochlorite.**—Ethyl chloride, acetone, *t*-amyl alcohol and chloroacetone were collected (A column, 64°) and identified by comparison with authentic samples.

Chloromethylmethylcarbinyl Hypochlorite.—Methylene chloride, acetone, chloroacetone and 1-chloro-2-methyl-2-propanol were collected (C column, 115°) and identified.

Phenylmethylcarbinyl Hypochlorite.—Acetophenone was collected and identified. Acetone, chlorobenzene (traces) and phenylmethylcarbinol were identified by retention times (Craig and Carbowax columns).

Isopropylmethylcarbinyl Hypochlorite.—Isopropyl chloride, acetone and the carbinol were separated (dinonyl phthalate column, programmed 60-150°), collected and identified.

***t*-Butylmethylcarbinyl Hypochlorite.**—Acetone and *t*-butyl chloride were separated and identified (DEGS column, programmed 60-130°). No more than traces of carbinol were detected.

Benzylmethylcarbinyl Hypochlorite.—Acetone, benzyl chloride and the carbinol were collected and identified (dinonyl phthalate column programmed 60-160°). In the presence of cyclohexene, no carbinol was detected. In the hydrocarbon chlorinations (Tables IV-VI) chlorination products of cyclohexane, cyclopentane, toluene, ethylbenzene and 2,3-dimethylbutane were all collected and identified.

Methylethylisopropylcarbinyl Hypochlorite.—Ethyl chloride, isopropyl chloride, methyl isopropyl ketone and methyl ethyl ketone were all collected and identified (silicone column, programmed 60-180°).

Methylethylbenzylcarbinyl Hypochlorite.—Ethyl chloride, benzyl chloride, methyl ethyl ketone and methyl benzyl ketone were all collected and identified (Craig column, programmed 174-240°).

1-Methylcyclopentyl Hypochlorite.—Products were separated on a Carbowax column, programmed at 60-210°. The 6-chloro-2-hexanone was identified as its 2,4-dinitrophenylhydrazone, m.p. 81-82°.

1-Methylcyclohexyl Hypochlorite.—Products were separated as in the previous case. The 7-chloro-2-heptanone was identified as its 2,4-dinitrophenylhydrazone, m.p. 95-96°.

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Positive Halogen Compounds. VII. Intramolecular Chlorinations with Long Chain Hypochlorites¹

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The light induced radical chain decomposition of *t*-hypochlorites with side chains of three carbons or longer has been shown to occur largely *via* an intramolecular path (1,5-shift of hydrogen) to give δ -chloroalcohols in yields of 15-80% plus in some cases small quantities of ϵ -chloroalcohols. The competition with β -scission of the intermediate alkoxy radicals is concentration independent, and the intramolecular reaction is important even in reactive hydrocarbon solvents. Reactivity of δ -hydrogens lies in the order 1° < 2° < 3°, 1:9:47, paralleling intermolecular reactions of alkoxy radicals. With suitable precautions, δ -chloroalcohols can be obtained similarly from primary and secondary hypochlorites, and base catalyzed cyclization provides a convenient synthesis of a variety of tetrahydrofurans.

An intramolecular radical reaction involving hydrogen transfer was apparently first noted by Grob and Kammuler in 1937, who reported a 5% yield of 5,6-diphenyldecane from the decomposition of ϵ -phenylcaproyl peroxide.³ Hydrogen transfer was suggested as an explanation of free radical isomerization by Kossiakoff and Rice in 1943,⁴ and has subsequently been recognized as a factor in chain branching during ethylene polymerization,⁵ and as the source of certain products of autoxidation processes.^{6,7} Wawzonek⁸ and, in more detail, Corey⁹ have shown that such transfer is a key step in the Hofmann-Löffler-Freitag reaction (conversion of *N*-chloroamines to pyrrolidines), and numerous additional examples are recognized. In con-

trast to the behavior of carbonium ions, free radicals do not appear to undergo ready 1,2-migration of hydrogen.¹⁰ Rather, reaction occurs preferentially through quasi-6-membered transition states to give 1,5-hydrogen transfers. Barton has pointed out the synthetic possibilities of such 1,5-hydrogen transfers, and has used them most effectively in the steroid series by photolyzing appropriate nitrite esters.¹¹ Similar reactions of simple aliphatic nitrites to yield δ -hydroxynitroso compounds have recently been described by Kabasakalian and Townley.¹²

As Greene¹³ and we¹⁴ have shown, photolysis or thermal decomposition of *t*-hypochlorites provides a very convenient means of generating and studying the reactions of *t*-alkoxy radicals. When the alkoxy radical possesses a long enough side chain to permit a 1,5-

(1) Taken from the Ph.D. Thesis of Albert Padwa, Columbia University, 1962. Support of this work by the National Science Foundation is gratefully acknowledged.

(2) University Fellow, 1961-1962.

(3) C. A. Grob and H. Kammuler, *Helv. Chim. Acta*, **40**, 2139 (1937).

(4) A. Kossiakoff and F. O. Rice, *J. Am. Chem. Soc.*, **65**, 590 (1943).

(5) M. J. Roedel, *ibid.*, **75**, 6110 (1953); W. M. D. Bryant and R. C. Voter, *ibid.*, **75**, 6113 (1953); F. W. Billmeyer, Jr., *ibid.*, **75**, 6118 (1953).

(6) J. P. Wibaut and A. Strang, *Koninkl. Ned. Akad. Wetenschap Proc.*, **5B**, 102 (1951).

(7) F. F. Rust, *J. Am. Chem. Soc.*, **79**, 4000 (1957).

(8) S. Wawzonek and P. J. Thelen, *ibid.*, **72**, 2118 (1950).

(9) E. J. Corey and W. R. Hertler, *ibid.*, **82**, 1657 (1960).

(10) For a summary of evidence supporting this statement, cf. C. Walling, "Free Radical Rearrangements," in "Molecular Rearrangements," P. de Mayo, Ed., John Wiley & Sons, Inc., New York, N. Y., 1963.

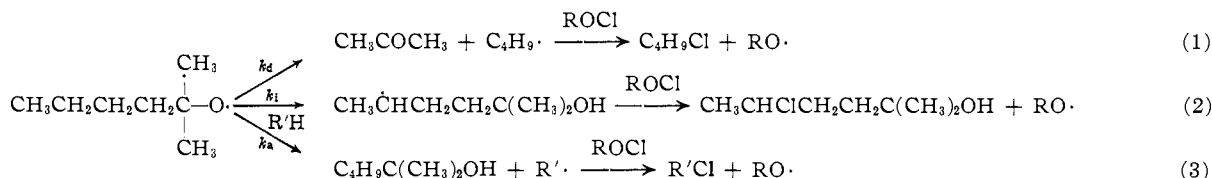
(11) D. H. R. Barton, J. M. Beaton, L. E. Geller and M. M. Pechet, *J. Am. Chem. Soc.*, **82**, 2640 (1960), and subsequent papers.

(12) P. Kabasakalian and E. R. Townley, *ibid.*, **84**, 2711 *et seq.* (1962).

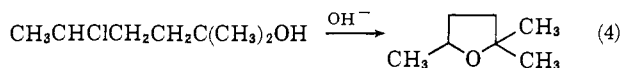
(13) F. D. Greene, *ibid.*, **81**, 2688 (1959).

(14) C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960), and subsequent papers.

hydrogen transfer, three competing chain reactions are possible, *e.g.*



This paper describes a study of these competitions and shows that in many cases sequence 2 gives δ -chloroalcohols in good yield. These in turn are readily cyclized with base to tetrahydrofurans, *e.g.*



Thus the over-all reaction provides a convenient synthetic route to such structures. Since this investigation was begun,¹⁵ somewhat parallel observations have been reported by Greene¹⁶ and by Barton.¹⁷

Results and Discussion

Reactions of Dimethylbutylcarbonyl Hypochlorite.—

This hypochlorite was chosen for initial studies to investigate the possibility of intramolecular chlorination and to investigate the effect of reaction conditions upon the process. It was prepared in solution in the desired solvent and decomposed photolytically without isolation, since it was found to undergo rapid induced decomposition at slightly above room temperature when solvent was removed. Results of a series of decompositions at 0° are shown in Table I. We see that

TABLE I
PHOTODECOMPOSITION OF BUTYLDIMETHYLCARBONYL
HYPOCHLORITE (0°)

Solvent	Concn., <i>M</i>	—Products (% yield)—		
		Acetone, butyl chloride	2-Methyl- 5-chloro- 2-hexanol	2-Methyl- 2-hexanol
CCl ₄	1.7	13	80	3
C ₂ Cl ₄ F ₂	0.8	15	76	3
C ₂ Cl ₄ F ₂	3.2	13	77	5
C ₂ Cl ₄ F ₂	6.7	14	79	5
Cyclohexane	1.6	2	81	8
Toluene	1.4	3	78	4
Cyclohexene	1.7	Trace	75	18

the δ -chloro-alcohol is formed in high yield (75–80%) in all cases, and that in inert solvents (CCl₄ and C₂Cl₄F₂) the ratio of δ -chloroalcohol to cleavage products (acetone and *n*-butyl chloride) is essentially concentration independent. Since β -scission of alkoxy radicals (reaction 1) is a unimolecular process,¹⁸ this provides a convincing demonstration that the 1,5-hydrogen transfer is unimolecular and accordingly an intramolecular process as well. Even in 6.7 *M* hypochlorite solution very little 2-methyl-2-hexanol is formed by bimolecular reaction of the alkoxy radical with hypochlorite or its decomposition products, and this preference for intramolecular reaction is brought out even more strongly in the last three experiments where potential hydrogen

donors were used as solvents. Interestingly, here, while yields of 2-methyl-2-hexanol are increased, it is

almost entirely at the expense of cleavage products, not of δ -chloroalcohol. This result suggests that perhaps all the reactions of the alkoxy radical are fast compared to changes in conformational structures of the side chain, so that the yield of δ -chloroalcohol is largely fixed by that fraction of the molecules which have favorable conformations for intermolecular hydrogen abstraction, and only those alkoxy radicals with unfavorable conformations live long enough to undergo β -scission or attack on solvent. Also, in the single experiment performed we find no solvent effect of cyclohexene favoring β -scission such as we have reported previously in other systems.¹⁸

Other Tertiary Hypochlorites.—We have extended our studies to a number of other *t*-hypochlorites to determine the effect of structure on the competition between intramolecular chlorination and β -scission, and to see whether hydrogen transfers other than 1,5- can be induced to take place. Results are summarized in Table II. In general, yields of chloroalcohols were determined after cyclization with base to tetrahydrofurans (or tetrahydropyrans). From the table it is evident that in every system studied 1,5-hydrogen transfer is the preferred intramolecular reaction, and that the ease of hydrogen transfer lies in the order $t > s > p$. Thus attack on a primary H competes less well with β -scission than attack on secondary H (hypochlorites II and III *vs.* I). From examples VII and VIII relative reactivities per H at 40° are $p:s:t$; 1:9:47. This result agrees well with intermolecular chlorination data with *t*-butyl hypochlorite where the values are 1:12:44.¹⁹

In the two cyclic hypochlorites IX and X, intramolecular chlorination competes with β -scission involving ring opening. The lower yields with IX apparently reflect the more rapid opening of the five-membered ring which is also noted in competition with intermolecular reactions of 1-alkylcyclopentylloxy and cyclohexylloxy radicals.¹⁸

In no case have we been able to detect any products of 1,2-, 1,3-, 1,4- or 1,7-hydrogen shifts, but in compounds IV and V, where secondary hydrogens are available for 1,6-attack, reaction occurs about 1/15 as readily as the 1,5-process. In VI, where the 6-hydrogens are activated by neighboring phenyl, reactivity increases to approximately 1/9, again paralleling relative reactivities of *s*-aliphatic and *s*-benzyl hydrogens of 1:2.5 in intermolecular chlorination.^{14,19}

In their discussion of the Hofmann–Loeffler–Freitag reaction, Corey and Hertler⁹ have suggested that 1,5-hydrogen transfers are preferred since the quasi-six-membered transition state is the smallest in which C, H and N can approximate a linear conformation. The same explanation seems plausible here,²⁰ *i.e.*, a transi-

(19) C. Walling and W. Thaler, *ibid.*, **83**, 3877 (1961).

(15) For a preliminary report *cf.* C. Walling and A. Padwa, *J. Am. Chem. Soc.*, **83**, 2207 (1961).

(16) F. D. Greene, M. L. Savitz, H. H. Lau, F. D. Osterholtz and W. N. Smith, *ibid.*, **83**, 2196 (1961); 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).

(17) M. Akhtar and D. H. R. Barton, *J. Am. Chem. Soc.*, **83**, 2213 (1961).

(18) A general discussion of β -scission of alkoxy radicals appears in our preceding paper: C. Walling and A. Padwa, *ibid.*, **85**, 1593 (1963).

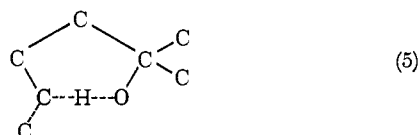
(20) In our previous work involving decomposition of *t*-hypochlorites with short side chains in which 1,5-hydrogen shifts are not possible, no intramolecular chlorination was detected.¹⁸ Even β -phenylethyl dimethyl carbonyl hypochlorite gives solely acetone and β -phenylethyl chloride. However, reactions involving smaller cyclic transition states have been reported in other radical systems; *cf.* H. E. De La Mare and F. F. Rust, *ibid.*, **81**, 2691 (1959); A. A. Reuter and T. N. Shatkina, *Tetrahedron*, **18**, 305 (1960).

TABLE II
PHOTODECOMPOSITION OF *t*-ALKYL HYPOCHLORITES
(0.5–1.8 *M* IN CCl₄)

<i>T.</i> , °C.	Intramolecular	Products, % ^a chlorination	β - Scission ^b
I			13
0	(80)		
II			59
0	(17)		63
40	(16)		68
80	(16)		
III			43
0	(29)		48
40	(27)		55
80	(26)		
IV			..
0	(5.5)(80.5)		..
70	(5.3)(74.3)		
V			..
0	(5.0)(82.3)		..
70	(4.9)(74.1)		
VI			..
0	(7.7)(73.3)		..
70	(7.6)(66.4)		
VII			..
0	(73)	(12)	..
VIII			..
	(52)	(20)	
IX			81°
0	(10)		86°
80	(6)		
X			18 ^d
0	(63)		26 ^d
80	(45)		

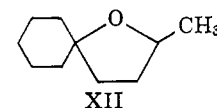
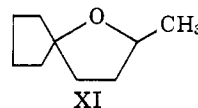
^a Numbers indicate yield of chlorine substitution at indicated carbon. ^b To give acetone and alkyl chloride unless indicated. ^c To 1-chloro-5-nonanone. ^d To 1-chloro-6-decanone.

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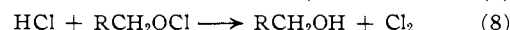
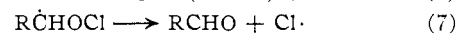
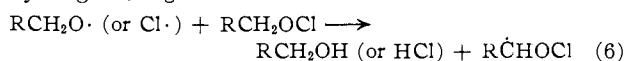
Larger ring transition states should be of similar energy but lower probability, and it is evident that activation energies for 1,5- and 1,6-transfers must be almost identical, since the ratios of yields in Table II are essentially temperature independent.

Base treatment of the chloroalcohols obtained from the hypochlorites of Table II in general gave the corresponding tetrahydrofurans (or tetrahydropyrans) in excellent yield, including the interesting oxaspirane structures XI and XII from IX and X, respectively.



Cyclization not unexpectedly failed for the tertiary chloride 2-chloro-2,5-dimethyl-5-nonanol from VIII which gave only a mixture of 2,5-dimethyl-1-nonene and 2,5-dimethyl-2-nonene. Similar results have been reported for the cyclization of δ -chloroamines containing tertiary chlorine.⁹

Primary and Secondary Hypochlorites.—Primary and secondary hypochlorites are relatively unstable; Chattaway and Backeberg²¹ stated that they decompose explosively when exposed to bright light. Subsequently Fort and Denivelle²² have reported that the products of decomposition are chiefly the corresponding aldehyde (or ketone) and HCl, plus alcohol and Cl₂, and it has been suggested²³ that these products arise from additional chain steps involving attack on α -hydrogens, *e.g.*



In our preliminary report¹⁵ we stated that we had been unable to observe intramolecular chlorination with primary or secondary hypochlorites, but subsequently Jenner has reported successful reaction,²⁴ and we have found that, with proper attention to experiment conditions, δ -chloroalcohols can be produced in yields approaching those obtained with tertiary hypochlorites. Results with *n*-butyl, *n*-pentyl and 2-hexyl hypochlorites are listed in Table III which shows that the competing attack on α -hydrogen can be suppressed by dilution with an inert solvent and (more important) by removing HCl either by adding NaHCO₃ (pyridine is ineffective) or best by refluxing the system under reduced pressure.

In addition to yielding alcohol and aldehyde as by-products we find (as has Jenner) that the primary hypochlorites give some ester. Although we have not investigated its formation, it may be most simply accounted for as arising from chlorination of aldehyde to chloride (a known reaction between *t*-butyl hypochlorite and aromatic aldehydes²⁵) followed by reaction with alcohol.

Experimental

Materials.—Except as noted below, solvents, hydrocarbons and alcohols were commercial materials, distilled and purity checked by G.L.C. before use. Alcohols which were not available were prepared by Grignard reactions as follows: 1-butylcyclopentanol from cyclopentanone and butyl bromide; yield 64%, b.p. 192–192.5°, *n*_D²⁵ 1.4517; 1-butylcyclohexanol from cyclohexanone and butyl bromide; yield 65%, b.p. 97–98° (9 mm.), *n*_D²⁵ 1.4633; propyldimethylcarbinol from 2-pentanone and methyl iodide; yield 74%, b.p. 120–121°, *n*_D²⁵ 1.4094; butyldimethylcarbinol from acetone and butyl bromide; yield 76%, b.p. 59–59.5° (21 mm.), *n*_D²⁵ 1.4155; isobutyldimethylcarbinol from acetone and isobutyl bromide; yield 62%, b.p. 133–133.5°, *n*_D²⁵ 1.4158; pentyldimethylcarbinol from 2-heptanone and methyl iodide; yield 68%, b.p. 161–161.5°, *n*_D²⁵ 1.4222; hexyldimethylcarbinol from 2-octanone and methyl iodide; yield 57%, b.p. 172–173°, *n*_D²⁵ 1.4263; methylpropylbutylcarbinol from 2-pentanone and butyl bromide; yield 68%, b.p. 78.5–79° (15 mm.), *n*_D²⁵ 1.4306; methylbutylisopentylcarbinol from 2-hexanone and isopentyl bromide; yield 54%, b.p. 89–90° (25 mm.) *n*_D²⁵ 1.4349; 2-methyl-4-phenyl-2-butanol from ethyl β -phenylpropionate (prepared by esterification of the acid) and methyl

(21) F. D. Chattaway and O. G. Backeberg, *J. Chem. Soc.*, 2999 (1923).

(22) R. Fort and L. Denivelle, *Bull. Soc. chim. France*, 1109 (1954).

(23) C. Walling, "Free Radicals in Solution," John Wiley & Sons, Inc., New York, N. Y., 1957, p. 388.

(24) E. L. Jenner, *J. Org. Chem.*, **27**, 1031 (1962).

(25) D. Ginsberg, *J. Am. Chem. Soc.*, **73**, 702 (1951).

TABLE III
 INTRAMOLECULAR CHLORINATION OF PRIMARY AND SECONDARY HYPOCHLORITES

Hypochlorite, <i>M</i>	<i>T</i> , °C.	Base	Products, %				
			δ-Chloroalcohol ^a	Alcohol	Aldehyde (or ketone)	Ester ^b	
<i>n</i> -C ₄ H ₉ OCl, 1.7	0	NaHCO ₃	18.1	32	8	19.2	
	70 ^c	NaHCO ₃	23.6	30.8	5	14	
	40	C ₄ H ₄ N	...	10	85	...	
<i>n</i> -C ₆ H ₁₁ OCl, 0.30	0	...	35.6	27	7	4	
	1.64	...	36.6	27	7	4	
	0.30	...	38	26	7	3	
	1.64	...	41.2	24.3	8	4	
	0.30	...	42	22	8	3	
	1.41	70 ^c	NaHCO ₃	54	16.2	6	2
	1.41	40	C ₄ H ₄ N	...	8	90	...
<i>n</i> -C ₄ H ₉ CH(OCl)CH ₃ ,	1.28	0	...	49.8	23.2	17.3	...
	0.62	0	...	56.3	21.3	15	...
	1.28	40	...	54.7	17.9	15.2	...
	0.62	40 ^c	...	65	16.6	14.6	...
	1.28	70	...	50.4	19.9	14.2	...
	0.62	70	...	60	18.4	15.2	...

^a 4-Chloro-1-butanol, 4-chloro-1-pentanol and 5-chloro-2-hexanol, respectively. ^b *n*-Butyl butyrate and *n*-pentyl valerate, respectively. ^c Solution refluxed under reduced pressure to remove HCl.

iodide; yield 69%, b.p. 87–87.5° (0.5 mm.), *n*_D²⁵ 1.5099; 2-methyl-6-phenyl-2-hexanol: 4-phenyl-1-butanol was prepared from ethylene oxide and β-phenylethyl bromide (yield 40%, b.p. 107° (2.5 mm.), *n*_D²⁵ 1.5212) and converted to 4-phenyl-1-bromobutane by refluxing with 48% HBr and H₂SO₄; yield 70%, b.p. 97° (1 mm.), *n*_D²⁵ 1.5386. Conversion to the Grignard reagent and reaction with acetone gave the desired alcohol; yield 60%, b.p. 104–105° (0.8 mm.), *n*_D²⁵ 1.5034. Alkyl hypochlorites were prepared in solvent from the alcohol and hypochlorous acid as described previously¹⁸ and used without isolation. Hypochlorite decompositions were for the most part carried out in sealed degassed tubes as reported previously.^{14,19} Experiments with primary and secondary hypochlorites were carried out under N₂ in a small thermostated flask equipped with a Dry Ice condenser when reflux was employed.

Analysis of Products.—Products were separated and collected by G.L.C. using an Aerograph A-350 instrument and diethylene glycol polysuccinate (DEGS), butanediol polysuccinate (Craig) and Carbowax columns. Since some of the δ-chloroalcohols decomposed on the G.L.C. columns, they were usually first converted to tetrahydrofurans by base treatment. For quantitative analysis internal standards were added before the base treatment. Product identifications for each hypochlorite are given below.

Butyldimethylcarbinyl Hypochlorite.—Analysis was on a DEGS column programmed at 60–210°. Butyl chloride and acetone were collected and compared with authentic materials. The predominant product, 2-methyl-5-chloro-2-hexanol, was collected, gave an immediate precipitate with AgNO₃, and showed a strong hydroxyl band at 2.9 μ in the infrared.

Anal. Calcd. for C₇H₁₆ClO: C, 55.81; H, 10.04; Cl, 23.53. Found: C, 55.54; H, 9.99; Cl, 23.90.

When a reaction mixture was refluxed for 10–12 hr. with 5% KOH in methanol the clear solution became cloudy and KCl precipitated. The mixture was poured into water, extracted continuously with ether overnight, and the ether removed under a short column. Analysis by G.L.C. showed complete disappearance of the chloroalcohol peak, and appearance of another of shorter retention time. This was isolated and identified as 2,2,5-trimethyltetrahydrofuran (b.p. 102–103°, *n*_D²⁵ 1.4019) by analysis (*Anal.* Calcd. for C₇H₁₆O: C, 73.63; H, 12.36. Found: C, 73.31; H, 12.46.) and by comparison with an authentic sample, prepared by treating δ-valerolactone with methylmagnesium iodide and dehydrating the resulting glycol by distilling with aqueous acid. Conversion of δ-chloroalcohol to tetrahydrofuran was essentially quantitative, since only trace quantities of unsaturated alcohol were detected. The cyclization was carried out in the same manner on other δ-chloroalcohols with equal success except as noted below.

Propyldimethylcarbinyl Hypochlorite.—Reaction products were separated on a DEGS column programmed at 60–180°. Acetone and *n*-propyl chloride were isolated and identified as above. The 2-methyl-5-chloro-2-pentanol was cyclized to 2,2-dimethyltetrahydrofuran, b.p. 93–94°, *n*_D²⁵ 1.4044, identified by comparison with authentic material and analysis.

Anal. Calcd. for C₆H₁₂O: C, 71.95; H, 12.07. Found: C, 71.72; H, 12.04.

Isobutyldimethylcarbinyl Hypochlorite.—Products were separated as above; isobutyl chloride and acetone were collected and identified. The 2,4-dimethyl-5-chloro-2-pentanol was cyclized to 2,2,4-trimethyltetrahydrofuran and identified by spectra and analysis; infrared: strong ether band at 9.2 μ; n.m.r.: multiplet at 8.59 τ vs. tetramethylsilane (methyl and methylene) and doublet at 6.46 (C–H α to oxygen), ratio of areas 6:1.

Anal. Calcd. for C₇H₁₄O: C, 73.63; H, 12.36. Found: C, 73.81; H, 12.42.

Pentyldimethylcarbinyl Hypochlorite.—Products were separated on a DEGS column at 60–210°. Acetone and *n*-pentyl chloride were separated and identified. The chloroalcohols were cyclized to a mixture of 2,2-dimethyl-5-ethyltetrahydrofuran and 2,2,6-trimethyltetrahydropyran. These could not be entirely resolved by G.L.C. on any of several columns, the pyran appearing as a shoulder of longer retention time on the major peak. The first half of the peak was collected and identified as the furan by comparison of its infrared spectrum with an authentic sample and by analysis.

Anal. Calcd. for C₈H₁₆O: C, 74.94; H, 12.58. Found: C, 74.60; H, 12.63.

The second half of the peak was collected and analyzed, showing it to be a mixture of C₈H₁₆O isomers (Found: C, 74.75; H, 12.52). It had an infrared spectrum and index of refraction identical with a 4:1 mixture of authentic furan and pyran, and the authentic pyran showed the same retention time on G.L.C. analysis as the shoulder observed on analysis of the cyclized reaction mixture.

Hexyldimethylcarbinyl Hypochlorite.—Products were separated as above; *n*-hexyl chloride and acetone were collected and identified. The chloro alcohols were cyclized and again obtained as a major peak with a poorly resolved shoulder of longer retention time. The major peak was collected (b.p. 148–149°, *n*_D²⁵ 1.4171) and identified as 2,2-dimethyl-5-propyltetrahydrofuran on the basis of spectra and analysis; infrared: strong ether band at 9.5 μ; n.m.r.: multiplet at 8.58 τ, multiplet at 6.16 τ, ratio of areas 17:1.

Anal. Calcd. for C₉H₁₈O: C, 76.00; H, 12.65. Found: C, 76.38; H, 12.58.

The shoulder was collected and identified as 2,2-dimethyl-6-ethylpyran (admixed with the furan) on the basis of analysis (C, 75.62; H, 12.56) and infrared spectrum (strong ether band at 9.5 μ, no –OH or carbonyl).

2-Methyl-6-phenyl-2-hexyl Hypochlorite.—Reaction products were separated on a Craig column at 60–250°. Acetone and 1-chloro-4-phenylbutane were collected and identified. The chloroalcohols were cyclized, again giving a major peak followed by a shoulder. The peak was collected (b.p. about 250°, *n*_D²⁵ 1.5005) and identified as 2,2-dimethyl-5-benzyltetrahydrofuran on the basis of spectra and analysis; infrared strong ether band at 9.4 μ; n.m.r.: singlet at 8.84 τ (methyl-H), multiplet at 8.37 τ (methylene-H), doublet at 7.30 τ (benzyl-H), multiplet at 6.01 τ (–H α to O) and singlet at 2.96 τ (phenyl-H), ratio of areas approximately 6:4:2:1:5.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.05; H, 9.54. Found: C, 82.27; H, 9.50.

The shoulder was collected and identified as 2,2-dimethyl-6-phenylpyran (mixed with the furan) on the basis of analysis (C, 82.31; H, 9.58) and infrared spectrum.

β -Phenylethylmethylcarbonyl Hypochlorite.—Products of a decomposition in CCl_4 were separated as above. Acetone and β -phenylethyl chloride were collected and identified. The only other product was a small amount of the parent carbinol.

Methylpropylbutylcarbonyl Hypochlorite.—Products were separated on a DEGS column at 60–230°. Propyl chloride, butyl chloride, 2-pentanone and 2-hexanone were collected and identified by comparison with authentic samples. The chloroalcohols were cyclized and the furans collected separately. The 2,5-dimethyl-2-propyltetrahydrofuran, b.p. 146–147°, n_D^{25} 1.4197, was identified by spectra and analysis; infrared: strong ether band at 9.4 μ ; n.m.r.: multiplet at 8.58 τ and at 6.11 τ , ratio of areas 17:1.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.65. Found: C, 76.12; H, 12.61.

The 2-methyl-2-butyltetrahydrofuran, b.p. 148–149°, was identified similarly, the n.m.r. results providing the basis for distinguishing between the two; infrared: strong ether band at 9.3 μ ; n.m.r.: multiplet at 8.57 τ , triplet at 6.46 τ , ratio of areas 8:1.

Anal. Found: C, 75.65; H, 12.56.

Methylbutylisopentylcarbonyl Hypochlorite.—Products were separated as above. Butyl chloride, isopentyl chloride, 2-hexanone and 5-methyl-2-hexanone were collected and identified. Base treatment of the reaction mixture gave three new products which were separated and collected: 2,5-dimethyl-2-isopentyltetrahydrofuran from the 2,5-dimethyl-8-chloro-5-nonanol present, and two olefins, 2,5-dimethyl-2-nonene-5-ol and 2,5-dimethyl-1-nonene-5-ol (in a ratio of 4.5:1), from the 2,5-dimethyl-2-chloro-5-nonanol present. All were identified by spectra and analysis.

2,5-Dimethyl-2-isopentyltetrahydrofuran: infrared strong ether band at 9.2 μ ; n.m.r.: multiplets at 8.88, 8.15 and a multiplet at 5.98 τ ratio of areas 12:9:1. *Anal.* Calcd. for $C_{11}H_{22}O$: C, 77.58; H, 13.02. Found: C, 77.23; H, 12.97.

2,5-Dimethyl-2-nonene-5-ol: decolorized Br_2 in CCl_4 instantly; infrared: hydroxyl at 2.9 μ , olefin at 10.4 μ ; n.m.r.: singlet at

6.97 τ , triplet at 4.87 τ , ratio of areas ca. 1:1. *Anal.* Calcd. for $C_{11}H_{20}O$: C, 77.58; H, 13.02. Found: C, 77.14; H, 12.93.

2,5-Dimethyl-1-nonene-5-ol: decolorized Br_2 in CCl_4 instantly; infrared: hydroxyl at 2.9 μ , 1-olefin at 10.1 and 10.75 μ ; n.m.r.: singlets at 6.94 and 5.42 τ , ratio 1:2.

1-Butylcyclopentyl Hypochlorite.—Products were separated on a Carbowax column at 60–210°. The 1-chloro-5-nonanone was collected and identified by infrared spectrum (carbonyl at 5.85 μ) and analysis.

Anal. Calcd. for $C_9H_{17}ClO$: C, 61.18; H, 9.70; Cl, 20.07. Found: C, 61.54; H, 9.63; Cl, 19.98.

The 1-(3-chlorobutyl)-cyclopentanol was cyclized to 2-methyl-1-oxaspiro-[4.4]-nonane, b.p. 179–180°, n_D^{25} 1.4524; infrared: strong ether band at 9.2 μ ; n.m.r.: doublet and multiplet at 8.87 and 8.42 τ , multiplet at 6.13 τ , ratio ca. 15:1.

Anal. Calcd. for $C_9H_{16}O$: C, 77.16; H, 11.42. Found: C, 77.23; H, 11.36.

1-Butylcyclohexyl Hypochlorite.—Products were separated as above. 10-Chloro-5-dacanone was collected and identified by infrared spectrum (carbonyl at 5.87 μ) and analysis.

Anal. Calcd. for $C_{10}H_{19}ClO$: C, 62.98; H, 10.0; Cl, 18.59. Found: C, 62.42; H, 9.97; Cl, 18.06.

The 1-(3-chlorobutyl)-cyclohexanol was cyclized to 2-methyl-1-oxaspiro-4.5-decane, b.p. 186–187°, n_D^{25} 1.4555; infrared: strong ether band at 9.2 μ ; n.m.r.: doublet and multiplet at 8.88 and 8.44 τ , multiplet at 6.07 τ , ratio of areas 17:1.

***n*-Butyl Hypochlorite.**—Products were separated on a DEGS column at 62–210°. Butyraldehyde, 1-butanol, butyl butyrate, butyl chloride and 4-chloro-1-butanol were collected and compared with authentic materials.

***n*-Pentyl Hypochlorite.**—Products were separated as above. Valeraldehyde, *n*-pentyl valerate and 1-pentanol were collected and compared with authentic samples. 4-Chloro-1-pentanol was cyclized to 2-methyltetrahydrofuran, collected (b.p. 80–81°, n_D^{25} 1.4044) and compared with authentic material.

2-Hexyl Hypochlorite.—Products were separated as above. The 2-hexanol and 2-hexanone were collected and identified. The 5-chloro-2-hexanol was cyclized to 2,5-dimethyltetrahydrofuran (b.p. 92–93°, n_D^{25} 1.4019) and compared with a known sample.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE OHIO STATE UNIVERSITY, COLUMBUS, O., AND THE CENTRAL RESEARCH DEPARTMENT, MINNESOTA MINING AND MANUFACTURING CO., ST. PAUL, MINN.]

Halogenation, Dehydrohalogenation and Dehalogenation of Stilbene Photo-dimers (1,2,3,4-Tetraphenylcyclobutanes)

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Photo-dimerization of *trans*-stilbene in benzene yields 1,2,3,4-tetraphenylcyclobutane (I) and 1,2,3,4-*cis*-3,4-tetraphenylcyclobutane (II). Reactions of I with *N*-bromosuccinimide and II with sulfuryl chloride give 1,2,3,4-tetraphenyl-1,3-butadiene (IX). Photo-dimer II is resistant to *N*-bromosuccinimide. Chlorination of I with sulfuryl chloride produces 1-chloro-1,2,3,4-tetraphenylcyclobutane (VII); reactions of VII with alumina or potassium *t*-butoxide give IX. Photochemical chlorination (2 equiv.) of I results in 1,2-dichloro-1,2,3,4-tetraphenylcyclobutane (X). Reactions of X with zinc, phenyllithium, phenylsodium and lithium *N,N*-diethylamide, respectively, give IX. Chlorination of I, II and IX and subsequent chromatography of the product on alumina yield 3,6-diphenyl-1,2,4,5-dibenzopentalene (XVIII). The stereochemistries of I, II, VII and X were investigated by n.m.r. methods.

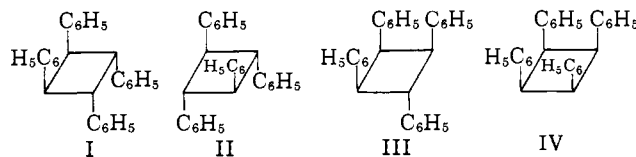
In order to obtain information which may contribute to the synthesis of a stabilized cyclobutadiene³ and/or its possible pseudoaromatic ionic derivatives, the halogenation, dehydrohalogenation and dehalogenation of two photo-dimers of stilbene (isomeric 1,2,3,4-tetraphenylcyclobutanes) have been investigated.

(1) (a) Abstracted in part from the Ph.D. dissertation of W. J. Link, The Ohio State University, Columbus, O., March, 1960. (b) This research was supported as indicated: Allied Chemical Corporation Fellow, 1957–1958; General Electric Company Fellow, 1958–1959; National Science Foundation Summer Teaching Fellow, E. I. du Pont Research Fellow, Petroleum Research Fund Fellow 454-A (American Chemical Society) and National Science Foundation Postdoctoral Fellow, 1959–1960.

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(3) Tetraphenylcyclobutadiene derivatives have been reported by (a) W. Hubel, *et al.*, *J. Inorg. Nucl. Chem.*, **9**, 204 (1959); (b) H. H. Freedman, *J. Am. Chem. Soc.*, **83**, 2194, 2195 (1961); (c) H. H. Freedman, *J. Org. Chem.*, **27**, 2298 (1962); and (d) H. H. Freedman and A. M. Frantz, Jr., *Abstr. of 141st Natl. Meeting of the American Chemical Society*, 1962, p. 26-O.

There are four possible isomeric 1,2,3,4-tetraphenylcyclobutanes (I–IV); what are believed to be two of the isomers have been reported previously. Isomer I, 1,2,3,4-*trans*-2,3,4-tetraphenylcyclobutane, has been obtained by solar (2 years^{4a}; 3 days^{4b}; no yields were



reported) or ultraviolet^{4c} (8 days, 7% yield) irradiation of *trans*-stilbene in benzene. The gross structure of the photo-dimer was based on its chemical properties;

(4) (a) G. Ciamician and P. Silber, *Ber.*, **35**, 4128 (1902); (b) H. Stobbe, *ibid.*, **47**, 2701 (1914); (c) M. Pailer and J. Muller, *Monatsh.*, **79**, 615 (1948).