V.P.C. analysis. Mass spectral analysis was complicated by cracking at the lowest convenient voltage. Prof. Wiberg estimated a *minimum* of 88% dideuterio derivative was present, and stated that this figure was probably considerably low. The value of 97%, as obtained for IIIa, is probably more realistic, since both acetals were prepared from the same diol.

The infrared spectrum of IIIa shows strong C–D stretching at 4.5 and 4.8 μ. Additional bands not in the non-deuterated analog appear at 9.33m, 10.55s, 11.34s, 11.70m, 12.40m and 13.28mμ. The bands of the non-deuterated analog at 8.20, 10.78, 11.52 and 12.62 μ disappear completely, while those at 10.2 and 10.4 μ are attenuated to shoulders. The bands at 4.5, 4.8 and 12.4 μ are suitable for analysis. The spectrum of IIIb differs from that of its undeuterated analog in a similar way.

Pyrolysis of Deuterated Acetals.—The standard procedure used previously[1] was modified by using a 12 mm. o.d. tube with 12–20 mesh pumice. At 400°, conversion of IIIa to isobutoxypivalaldehyde was 70%, with 6% fragmentation. At 430°, only a trace of acetal remained but almost 30% was fragmented. The optimum temperature appeared to be about 425°, since for analysis of the mixture of IV and V it was desirable to have a minimum of unchanged acetal. The phenyl derivative IIIb was pyrolyzed at 355°.

The crude pyrolyzate of IIIa was collected in a receiver cooled in Dry Ice. It contained 57.2% of mixed IVa and Va, 2.5% of unchanged IIIa, 18.7% of isobutyraldehyde, 18.0% of other low-boiling fragments and 2.6% of high boiling products (V.P.C.). It was pumped at room temperature (1 mm.) to remove volatile products, and the residue was analyzed directly by n.m.r. The composition was 60% IV and 40% Va, calculated from the areas of the aldehyde C–H peak and the CH_2 and CHD peaks. Infrared analysis showed a composition of 57% IV and 43% V. In another run, 25% of the acetal IIIa survived. Because of the substantial correction required for this, the n.m.r. values of 54% IVa and 46% Va (corrected) are probably less reliable.

The crude pyrolyzate of IIIb contained 5.6% of isobutyraldehyde, 3.5% of benzaldehyde, 1.8% of other volatiles and 88.7% of product (V.P.C.; no column was found which would resolve a mixture of acetal and benzyloxypivalaldehyde). It was evacuated at 50–80° (30 mm.), and the residue then contained 1.6% of isobutyraldehyde, 3.6% of benzaldehyde, 0.87% of other volatiles and 94% product; n.m.r. showed 60% IVb, 35% Vb and 5% IIIb. Correcting for the unchanged acetal, the ratio of IVb to Vb was 61:39.

By-products in Acetal Pyrolysis.—Pyrolysis of a large sample of 2-isopropyl-5,5-dimethyl-*m*-dioxane (acetal 4) at 435° caused considerably more than normal fragmentation. V.P.C. analysis of the pyrolyzate showed 68.5% of isobutoxypivalaldehyde, 2.3% of acetal, 10.6% of isobutyraldehyde, 16.5% of other low-boiling materials and 2% of higher-boiling impurities. The volatile components were separated by distillation at bath temperature 60–80° (50 mm.) into a Dry Ice-cooled receiver. V.P.C.–T.O.F. analysis showed isobutylene (3%), acetone (trace), a pentadiene (1%), a pentene or dimethylcyclopropane (0.46%), pivalaldehyde (5%), methyl isopropyl ketone (6.9%) and two six-carbon hydrocarbons (traces), in addition to the 10.6% of isobutyraldehyde already determined. (The percentages are based on starting acetal.)

Examination of the by-products from other acetals was conducted similarly, but since the compositions were not determined quantitatively, the qualitative description given in the Discussion section will suffice.

Acknowledgment.—The research described in this series of papers was presented at the Gordon Conference on Organic Reactions and Processes on July 26, 1961. I am indebted to the members of the Conference who participated in stimulating discussions. I also appreciate the helpful and critical comments of Drs. J. E. Cole, Jr., and F. W. Swamer of this Laboratory.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, N. Y.]

Positive Halogen Compounds. IV. Radical Reactions of Chlorine and *t*-Butyl Hypochlorite with Some Small Ring Compounds[1]

BY CHEVES WALLING AND P. S. FREDRICKS

RECEIVED MARCH 28, 1962

The liquid phase photoreaction of cyclopropane with chlorine has been reinvestigated and found to give much 1,3-dichloropropane as well as cyclopropyl chloride. On this basis earlier results[2] on C–H bond reactivities in small rings have been re-evaluated. In contrast, little ring opening occurs with *t*-butyl hypochlorite and competitive reactions show decreasing C–H bond reactivities with decreasing ring size for C_6–C_3-cycloparaffins. *t*-Butyl hypochlorite chlorination of methyl- and 1,1-dimethylcyclopropanes occurs chiefly by attack on methyl to give chloromethylcyclopropanes and products arising from ring opening of the intermediate cyclopropylmethyl radicals. Competitive experiments show enhanced methyl reactivity compared with open chain compounds, interpreted as arising from homoallylic conjugation of cyclopropylmethyl radicals. *t*-Butyl hypochlorite reacts with ethylene and propylene oxides to give the corresponding chloroepoxides with little ring opening, and this reagent thus appears to be an excellent mild radical chlorinating agent for a variety of small ring compounds.

In 1959, some results on the liquid-phase photochlorination of C_3–C_6-cycloparaffins were reported in a paper from this Laboratory.[2] The data indicated a continuous decrease in reactivity with decreasing ring size, without the unusual reactivity of cyclopentane predicted by Brown on the basis of "I-strain."[3] However, the results had two anomalous features. First, differences in reactivity were much less than those reported by Knox and Nelson[4] for gas-phase chlorination; second, relative reactivity differences decreased at lower temperatures. Tentatively, our results were ascribed to complex formation between small ring cycloparaffins (particularly cyclopropane) and chlorine atoms, analogous to that proposed by Russell[5] to account for the large solvent effects on selectivity observed in radical chlorinations employing molecular chlorine.[2,5]

We have now repeated the experiments with chlorine, and extended them to similar chlorinations using *t*-butyl hypochlorite. While we confirm the earlier results with C_4–C_6-cycloparaffins,

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(1) Support of this work by a Grant from the National Science Foundation is gratefully acknowledged.

(2) C. Walling and M. F. Mayahi, *J. Am. Chem. Soc.*, **81**, 1485 (1959).

(3) H. C. Brown, R. S. Fletcher and R. B. Johannesen, *ibid.*, **73**, 212 (1951).

(4) J. H. Knox and R. L. Nelson, *Trans. Faraday Soc.*, **55**, 937 (1959).

(5) G. A. Russell, *J. Am. Chem. Soc.*, **80**, 4997 (1958).

we find that the low-temperature liquid phase photochlorination of cyclopropane leads to considerable ring-opening as well as substitution. We have also investigated the competitive chlorination of methylcyclopropanes using both chlorine and *t*-butyl hypochlorite, and report some preliminary experiments on the *t*-butyl hypochlorite chlorination of epoxides.

Results and Discussion

Halogenation of Cyclopropane.—The gas-phase chlorination of cyclopropane, carried out photochemically below 100° or thermally up to 500°, has been shown by Roberts and Dirstine[6] to give cyclopropyl chloride in high yield. On further chlorination, the product is converted chiefly to 1,1-dichlorocyclopropane.[7] In our own photochemical experiments in the liquid phase, gas liquid chromatographic (G.L.C.) analysis showed cyclopropyl chloride as a product, together with higher-boiling materials originally assumed to be polychlorocyclopropanes. However, more careful investigation has now shown that these are in fact 1,3-dichloropropane, together with higher chlorination products derived from it. Table I gives typical product analyses.

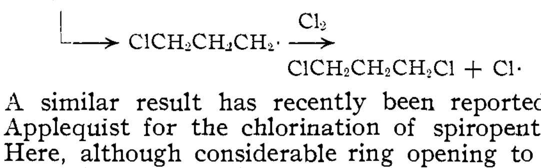
TABLE I

Cl_2 CHLORINATION OF CYCLOPROPANE

Temp., °C.	0	68	68
Solvent (*M*)	CCl_4 (5)	CCl_4 (5)	C_6H_6 (7.3)
Products, %[a]			
Cyclopropyl chloride	15.4	47.3	48.2
1,3-Dichloropropane	61.4	33.5	42.3
$C_3H_5Cl_3$ (2 isomers)	23.2	19.2	9.5

[a] Yields are determined from areas under peaks in G.L.C. analysis and refer to % of total chlorinated products detected.

Since mixtures of cyclopropane and chlorine are indefinitely stable in the dark, these products must also arise from the radical chain halogenation. Further, the fraction of product accounted for by ring opening increases markedly at lower temperatures, and we are forced to conclude that the radical chain process takes a rather different course under these conditions, sequence 2 being preferred to sequence 1.



(1)

(2)

A similar result has recently been reported by Applequist for the chlorination of spiropentane.[8] Here, although considerable ring opening to give 1,2-di-(chloromethyl)-cyclopropane also occurs in the gas phase, the amount increases at lower temperatures and is more marked in the liquid state. Actually, the analogous ring opening of cyclopropane by bromine atoms (bromine plus light or peroxides) in the liquid phase was reported by Kharasch[9] as long ago as 1939, and the gas phase ring opening by iodine atoms by Ogg and Priest in the same year.[10] In these cases the competing hydrogen abstraction is strongly endothermic, and Benson[11] has recently estimated the activation energy for the ring opening by iodine atoms as 17.5 kcal. If the formulation is correct, these reactions must all belong to the rather rare class of radical displacements on carbon, here facilitated both by the high strain energy of the cyclopropane ring, and its "unsaturated" character. This last should make the electronic structure of the transition state electronically similar to that involved in radical additions to olefins.

The increase in ring opening with lowering of temperature implies that, compared with displacement on hydrogen to give a cyclopropyl radical, the ring opening reaction has a lower activation energy, but a smaller probability.[12] In connection with our earlier experiments on cycloparaffin halogenation it was suggested that halogen atoms are able to form complexes with cyclopropane analogous to those with aromatic molecules which seem well established.[5,13] In support of this suggestion we reported[2] that the isomer distribution obtained on chlorination of 2,3-dimethylbutane was significantly altered when the reaction was carried out in cyclopropane as solvent. Unfortunately we have been unable to confirm this result, and find that the isomer distribution obtained on chlorination of either 2,3-dimethylbutane or butane are the same in the presence and absence of cyclopropane.[14] Even without this piece of evidence, however, the possibility that complexes play some role in the low temperature liquid phase reactions of chlorine atoms with cyclopropane cannot be ruled out,[15] and there is no doubt that the reaction is in some way unusual. We have made a careful investigation of the products of chlorination of cyclobutane, and find only cyclobutyl chloride and no 1,4-dichlorobutane. Here, although the ring strain is almost as large as in cyclopropane,[11] there is less indication of "unsaturated" character.

Photochlorination of cyclopropane with *t*-butyl hypochlorite at either 0 or 68° gives predominantly cyclopropyl chloride and only very small G.L.C. peaks which could be 1,3-dichloropropane. Here the *t*-butoxy radical serves as chain carrier and shows only a small solvent sensitivity in its re-

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[6] J. D. Roberts and P. H. Dirstine, *J. Am. Chem. Soc.*, **67**, 1281 (1945).

[7] P. G. Stevens, *ibid.*, **68**, 620 (1946).

[8] D. E. Applequist, G. F. Fanta and B. W. Henrikson, *ibid.*, **82**, 2368 (1960).

[9] M. S. Kharasch, M. Z. Fineman and F. R. Mayo, *ibid.*, **61**, 2139 (1939).

[10] R. A. Ogg, Jr., and W. J. Priest, *J. Chem. Phys.*, **7**, 736 (1939).

[11] S. W. Benson, *ibid.*, **34**, 521 (1961).

[12] Alternatively, one might suggest (by analogy to double-bond additions) that the opening is reversible. However, since C–C and C–Cl bonds have almost the same strength, the back reaction would be *endothermic* by the strain energy of cyclopropane, (∽29 kcal.)[11] and can be ruled out.

[13] S. J. Rand and R. L. Strong, *J. Am. Chem. Soc.*, **82**, 5 (1960).

[14] Our former conclusion was based upon G.L.C. analysis of products, and may have been based upon misidentification of some of the polychloropropane peaks observed.

[15] Since halogen molecules form complexes with olefins similar to those with aromatic solvents, similar complexing might be expected with halogen atoms. However, Russell[5] was unable to detect any solvent effects in chlorinations conducted in unsaturated solvents, concluding that, if such complexing occurs, it leads directly to halogen atom addition. The analogous situation may obtain here.

actions.[16] We may also note that the failure of the ring-opening reaction occurs in spite of the low reactivity of the C–H bond in cyclopropane toward the *t*-butoxy radical. At 68° the latter undergoes almost 50% decomposition to acetone and methyl radical (appearing as methyl chloride), and 20% even at 0°.

Competitive Chlorination of Cycloparaffins.—Relative reactivities of two species R_1H and R_2H in competitive radical chain halogenation depend upon the rates of the competing processes

$$X\cdot + R_1H \xrightarrow{k_1} HX + R_1\cdot \tag{3}$$

$$X\cdot + R_2H \xrightarrow{k_2} HX + R_2\cdot \tag{4}$$

where $X\cdot$ represents a halogen atom or other chain-carrying radical. The ratio k_1/k_2 is usually computed from the relation

$$\frac{\log\ [R_1H]_0/[R_1H]}{\log\ [R_2H]_0/[R_2H]} = \frac{k_1}{k_2} \tag{5}$$

the change in concentration of the two substrates either being measured directly, or calculated from the concentrations of chlorinated products formed. Direct measurement of change of substrate concentration has the advantage that it avoids complications arising from further reaction of initial products, and was used in our earlier paper.[2] However, since it assumes that 3 and 4 represent the sole path by which substrate is consumed, it evidently requires correction for reactions involving cyclopropane in which ring opening occurs. Table II shows the results obtained when our earlier measurements are so corrected (using product distributions from Table I). Also included are new measurements for the other cycloparaffins. While agreement with earlier values are reasonable, we consider the new values (based on careful measurement of areas under G.L.C. traces) are more reliable. Table III shows a similar set of relative reactivities for *t*-butyl hypochlorite chlorination.

TABLE II

RELATIVE REACTIVITIES OF CYCLOPARAFFINS TOWARD HYDROGEN ABSTRACTION BY CHLORINE ATOMS[a]

Cycloparaffin	Conditions		Relative reactivities This paper	Relative reactivities Ref. 2
Cyclopentane	5 *M* CCl_4	68°	0.85	0.90
		0°	.95	.94
Cyclobutane	5 *M* CCl_4	68°	.67	.85
		0°	.84	1.03
	7.3 *M* C_6H_6	68°	.76	0.85
Cyclopropane	5 *M* CCl_4	68°	.100[b]	.210
		0°	.048[b]	.315
	7.3 *M* C_6H_6	68°	.136[b]	.283

[a] Per hydrogen, cyclohexane hydrogen taken as density. [b] Data of ref. 2 corrected for cyclopropyl chloride actually found in product.

In both chlorinations we now find a slight drop in reactivity from C_6 to C_4, and a large decrease for cyclopropane. For all the *t*-butyl hypochlorite reactions, selectivity increases as the temperature is lowered, the expected result if the slower reaction has the higher activation energy. In the chlorine series, cyclopropane now appears normal, but the small decrease in selectivity in reactions of cyclopentane and cyclobutane at lower temperatures still remains, indicating anomalously small entropies of activation for chlorine atom attack on these molecules.

TABLE III

RELATIVE REACTIVITIES OF CYCLOPARAFFINS TOWARD *t*-BUTOXY RADICALS[a]

Cycloparaffin	Conditions	Relative reactivities
Cyclopentane	68° CCl_4	1.04 ± 0.04
	0° CCl_4	0.89 ± .04
Cyclobutane	40° $CFCl_3$	.71 ± .05
	0° $CFCl_3$	.51 ± .04
Cyclopropane	68° $CFCl_3$	.027 ± .003
	0° $CFCl_3$	.010 ± .002
Neopentane	68° $CFCl_3$	.13 ± .01
	0° $CFCl_3$	.054 ± .003

[a] See note *a*, Table II.

Two factors may contribute to the low reactivity of cyclopropane toward hydrogen abstraction: first, the high bond dissociation energy of the C_3H_5–H bond,[17] and second the expectation that any sp^2 character of the carbon in cyclopropane[18] will increase its electronegativity, and decrease the ease of attack by the strongly electron-attracting chlorine atom or *t*-butoxy radical. Table IV summarizes available data[19] on cyclopropane reactivities toward various radicals *vs.* neopentane as standard. Although conditions are far from strictly comparable, it is probably significant that, among the reactions of $Cl\cdot$ (gas phase) $MeO\cdot$, $t\text{-}BuO\cdot$ and $CH_3\cdot$ (which have almost the same energetics), the methyl radical (the only radical in the series lacking strong electron-accepting properties) shows the least preference for neopentane. This at least suggests that the reactivity of cyclopropane toward oxygen and halogen radicals is somewhat decreased by C–H bond polarization.

TABLE IV

RELATIVE REACTIVITIES OF C–H BONDS, CYCLOPROPANE: NEOPENTANE

Radical	*T*, °C.	Rel. reactivities
$F\cdot$	25	1.0[19]
$Cl\cdot$ (gas)	250	0.028[19]
$Cl\cdot$ (liq.)	68	.13
$CH_3\cdot$	182	.65[19]
$CH_3O\cdot$	250	.4[19]
$t\text{-}C_4H_9O\cdot$	68	.21
Oxidn. ($HO_2\cdot$)	350	.45[19]

Finally we may note that, even after correction for the ring opening reaction, the relative reactivity of cyclopropane toward hydrogen abstraction at low temperatures in the liquid phase which we observe is many times reported for the gas-phase reaction at 250°. While this may still be accounted for by chlorine atom complexing in

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[16] C. Walling and B. B. Jacknow, *J. Am. Chem. Soc.*, **82**, 6108 (1960).

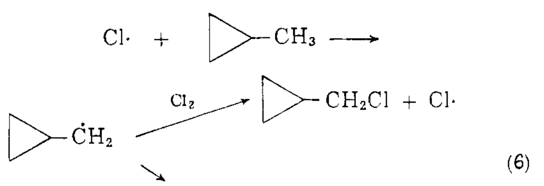
[17] No direct measurement of *D* (cyclo-C_3H_5H) is available. However, since rates and activation energies for hydrogen abstraction by a variety of radicals is close to that for methane, it must be close to 102 kcal./mole.

[18] C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, **40**, 1 (1949).

[19] W. E. Falconer, J. H. Knox and A. F. Trotman-Dickenson, *J. Chem. Soc.*, 782 (1961).

the liquid phase, a careful kinetic study of both systems would seem to be in order to illuminate the difference.

Halogenation of Methylcyclopropanes.—The photochlorination of methylcyclopropane by chlorine has been studied in some detail by Roberts and co-workers[20,21] who find that, in the vapor phase, attack occurs chiefly on the methyl group to yield cyclopropylcarbinyl and allylcarbinyl chlorides in roughly equal quantities, together with some ring-chlorinated material. Using methyl-^{13}C-cyclopropane, they showed that the allylcarbinyl chloride had the composition $^{13}CH_2{=}CHCH_2CH_2Cl$, consistent with the reaction scheme



(6)

rather than the participation of a "non-classical" radical which could produce carbon scrambling analogous to the behavior of the cyclopropylcarbinyl carbonium ion.[22]

Even without intervention of a highly delocalized intermediate radical, it is possible that homoallylic conjugation could give some stability to the cyclopropylmethyl radical and thus produce an enhanced reactivity of the methyl groups of methylcyclopropanes toward radical attack.

The products formed in the liquid-phase photochlorination of methylcyclopropane by chlorine and *t*-butyl hypochlorite are listed in Tables V and VI. These experiments were carried out using a large excess of hydrocarbon (6:1 volume ratio). Larger amounts of chlorinating agent changed the product composition considerably, in particular increasing the amount of polychlorinated material.

TABLE V

REACTION OF METHYLCYCLOPROPANE WITH CHLORINE

	68°	0°
Cyclopropylcarbinyl chloride	55.6 ± 0.5%	56.3
2-Chlorobutane	9.8 ± .2	6.1
1,3-Dichlorobutane	8.0 ± .1	7.3
1,3-Dichloro-2-methylpropane	3.5 ± .1	5.5
1,2,4-Trichlorobutane	Trace	Trace
Unidentified (C_4H_7Cl)	6.2 ± 0.1	2.4
Unidentified (higher-boiling)	16.9 ± 0.7	22.4

TABLE VI

REACTION OF METHYLCYCLOPROPANE WITH *t*-BUTYL HYPOCHLORITE

	68°	0°
Cyclopropylcarbinyl chloride	27.9 ± 0.9%	42.0 ± 0.3
Allylcarbinyl chloride	19.6 ± .7	4.2 ± .2
Cyclobutyl chloride (?)	10.2 ± .2	8.9 ± .2
Unidentified C_4H_7Cl[a]	15.4 ± 1.6	10.2 ± .2
Unidentified, high boiling[b]	26.9 ± 0.9	34.7 ± .3

[a] Two peaks, probably ring chlorinated material. [b] Approximately eight products.

In the chlorine reaction we find less ring opening of the intermediate cyclopropylmethyl radical than reported by Roberts. In fact, no allylcarbinyl chloride was isolated, and only traces of 1,2,4-trichlorobutane (its expected addition product with chlorine). However, other reaction-products derived from allylcarbinyl chloride may be included in the unidentified polychlorides obtained. Since our experiments involve lower temperatures and higher chlorine concentrations than the gas-phase reactions, this result is consistent with scheme 6 if the ring opening of the cyclopropylmethyl radical is indeed a process of appreciable activation energy, occurring subsequent to the hydrogen abstraction from methylcyclopropane. Of the other products observed, 1,3-dichlorobutane and 1,3-dichloro-2-methylpropane presumably come from radical displacement on carbon with opening of the cyclopropane ring. The 2-chlorobutane appears to be the consequence of electrophilic ring-opening by HCl, since it also forms slowly when methylcyclopropane is saturated with dry HCl.

In the *t*-butyl hypochlorite experiments, ring opening of the cyclopropylmethyl radical is more evident and clearly temperature dependent, again consistent with a scheme analogous to sequence 6 if attack of the cyclopropylmethyl radical on *t*-butyl hypochlorite is somewhat slower than on Cl_2. In this system a small amount of product tentatively identified as cyclobutyl chloride was also detected. Although it showed the same retention time as authentic material on both dinonyl phthalate and silicone G.L.C. columns it unfortunately could not be resolved from other materials in sufficient quantity for more unequivocal identification. If really present, it indicates the occurrence (and irreversibility) of the reaction

(7)

since no allylcarbinyl chloride was detected in our chlorinations of cyclobutane.

1,1-Dimethylcyclopropane was also smoothly chlorinated by *t*-butyl hypochlorite to give predominantly the chloromethyl derivative, 67.1 ± 0.8% at 68° and 52.4 ± 1.5% at 0°, identified by n.m.r. and infrared spectra, together with a variety of other products. With chlorine a 67.3% yield was also observed at 0° if samples were analyzed immediately after reaction. Here, however, electrophilic ring opening by HCl is rapid, and as high as 45% 2-methyl-2-chlorobutane was found in samples which had been allowed to stand.

With a knowledge of product compositions, competitive reactions can be used to determine methyl group reactivities of the methylcyclopropanes. Data for *t*-butyl hypochlorite are summarized in Table VII. Since the proportion of unidentified products which arise from methyl group attack is unknown, the actual values for relative reactivities must be between those given. Nevertheless, the methyl hydrogens of the cyclopropanes are

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[20] J. D. Roberts and R. H. Mazur, *J. Am. Chem. Soc.*, **73**, 2509 (1951).

[21] E. Renk, P. R. Shafer, W. H. Graham, R. H. Mazur and J. D. Roberts, *ibid.*, **83**, 1987 (1961).

[22] *Cf.* R. H. Mazur, W. N. White, D. A. Semenow, C. C. Lee, M. S. Silver and J. D. Roberts, *ibid.*, **81**, 4390 (1959), and subsequent papers.

definitely more easily attacked than those of neopentane (a hydrocarbon with typical normal primary C–H bonds.) While our results thus indicate significant stabilization of cyclopropylmethyl radicals by homoallylic conjugation, the effect is much smaller than the stabilization observed in allylic radicals. On the same scale, the reactivities of primary allylic C–H bonds are in the range of 12–20.[23]

The instability of methylcyclopropanes toward HCl makes any relative reactivity results toward Cl_2 still more uncertain. Competitive reaction with cyclopentane at 0° gives a relative reactivity of 0.56 ± 0.08. Assuming (from Table V) that 56% of the product arises from methyl C–H attack, this corresponds to a relative reactivity per C–H of 1.05, or, compared with a primary C–H, approximately 12. Again this high reactivity seems beyond experimental error.

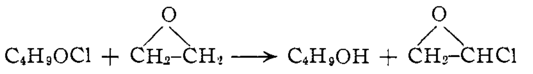
TABLE VII

RELATIVE REACTIVITIES OF METHYL C–H's (*vs.* NEOPENTANE) TOWARD *t*-BUTYL HYPOCHLORITE

Cyclopropane	T, °C.	Rel. reactivites a	Rel. reactivites b
Methyl-	68	3.7	2.1
	0	6.8	3.8
1,1-Dimethyl-	68	4.1	2.8
	0	6.3	3.3

[a] Assuming all products arise from methyl C–H attack. [b] Unidentified products assumed not to arise from methyl C–H attack.

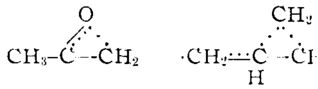
Reaction of *t*-Butyl Hypochlorite with Epoxides.—The smooth reaction of *t*-butyl hypochlorite with small carbocyclic rings encouraged us to carry out preliminary experiments on the analogous chlorination of epoxides. Irradiation of the hypochlorite in excess ethylene oxide at either 0° or 70° yielded a single major chlorination product (90–95%) together with two minor unidentified higher-boiling substances. The major component, collected by G.L.C., was identified by infrared and n.m.r. spectra as the monochlorinated epoxide, providing a very simple route to this material.



$$C_4H_9OCl + CH_2{-}CH_2\,(O) \longrightarrow C_4H_9OH + CH_2{-}CHCl\,(O) \quad (8)$$

Similar chlorination of propylene oxide gave somewhat more complex results. Again, a major product (41.2% at 70°, 48.1% at 0°) was resolved by G.L.C., together with five unidentified higher-boiling materials. The major product again had an infrared spectrum consistent with a chlorinated epoxide, and its n.m.r. spectrum unequivocally identified it as 2-chloropropylene oxide.

Aside from its possible synthetic utility, this result is interesting for two reasons. First, in contrast to the reaction of methylcyclopropane, attack occurs here primarily on the 3-membered ring, presumably because of the high electron availability adjacent to the ether oxygen. In addition the resulting radical may derive stabilization from structures such as I, and evidently these are more effective than those of type II which promote reaction on the methyl group in methylcyclopropane. Second, even if structures such as I stabilize the resulting radical, little ring opening occurs since only traces of chloroacetone were detected among the higher boiling products, *i.e.*, reaction 10 is unimportant



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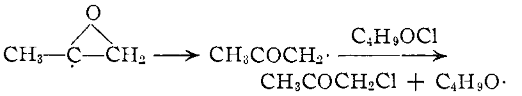

$$CH_3{-}C{-}CH_2\,(O) \longrightarrow CH_3COCH_2\cdot \xrightarrow{C_4H_9OCl} CH_3COCH_2Cl + C_4H_9O\cdot \quad (10)$$

This is in contrast to the findings of Gritter and Wallace[24] who have investigated the reaction of propylene oxide with *t*-butoxy radicals from *t*-butyl peroxide at 150°. At this higher temperature ring opening of the intermediate radical is extensive, and they also report products arising from ring opening by direct displacement on carbon. Similar materials may also be present among our unidentified higher boiling minor products.

Experimental

Materials.—Cyclobutane,[25] methylcyclopropane[26] and 1,1-dimethylcyclopropane[27] were prepared by literature methods, and the first two purified by preparative scale G.L.C. The various reference materials not commercially available were also prepared by standard methods, and the purity of all materials checked by G.L.C. analysis.

Chlorination and Analysis.—All reactions were carried out in small sealed glass tubes and reaction initiated photochemically essentially as previously described.[2,16,23] Analysis was primarily by G.L.C. using either silicone or dinonyl phthalate columns, with collection of individual peaks and identification by infrared or n.m.r. spectra when required; n.m.r. spectra were measured on a Varian A-60 instrument at 60 megacycles. Relative yields were determined by G.L.C. peak areas, measured either with a planimeter or an electronic integrator. Details are given below for individual experiments.

Chlorination of Cyclopropane.—Reaction of 1.1 ml. of cyclopropane, 0.15 ml. of chlorine in 1–1.9 ml. of solvent gave the product compositions listed in Table I. Cyclopropyl chloride and 1,3-dichloropropane were identified by isolation and infrared spectra. No dichlorocyclopropanes were detected. Two peaks of longer retention time showed the same retention time and relative areas as those obtained on photochlorination of 1,3-dichloropropane, so they are presumably 1,1,3- and 1,2,3-trichloropropane.

Reactions of cyclopropane (2.0 ml.) and *t*-butyl hypochlorite (0.8 ml.) were run without solvent at 0° and 68°. The major peak on G.L.C. analysis, accounting for approximately 85% of the chlorinated product, was cyclopropyl chloride, plus less than 5% 1,3-dichloropropane, and two other small peaks appearing before 1,3-dichloropropane and absent in the chlorine experiments, which we believe to be dichlorocyclopropanes. At 0° the products from the hypochlorite were some 80% *t*-butyl alcohol plus roughly equal quantities of acetone, methyl chloride and 1-chloro-2-methyl-2-propanol. At 68°, yields of *t*-butyl alcohol and acetone were approximately equal, so it is evident that the efficiency of the chlorination is better at the lower temperature.

Chlorinations in Cyclopropane Solvent.—Photochlorinations of 2,3-dimethylbutane (0.5 ml.) in cyclopropane (2–3 ml.) were carried out with molecular chlorine at 0°. Determination of the isomer distribution gave *t/p* ratios (relative reactivities of tertiary to primary hydrogen) of 5.18 and 5.05, compared with our previous value[2] in no solvent of 4.96. Similar experiments with *n*-butane gave *s/p* ratios of 2.97 and 3.24 compared with a value in no solvent[2] of 3.09.

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[23] C. Walling and W. Thaler, *J. Am. Chem. Soc.*, **83**, 3877 (1961).

[24] R. J. Gritter and T. J. Wallace, *J. Org. Chem.*, **26**, 282 (1961).

[25] J. Cason and R. L. Way, *ibid.*, **14**, 31 (1949).

[26] H. C. Brown and M. Borkowski, *J. Am. Chem. Soc.*, **74**, 1894 (1952).

[27] R. L. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).

We consider these results within experimental error of each other, and conclude that our previous report of a solvent effect was in error.

Chlorination of Cyclobutane.—Reaction of cyclobutane (8 vol. plus an equal vol. of $CFCl_3$) with chlorine at 0° gave a single major product with an infrared spectrum identical with cyclobutyl chloride. Traces of polychlorinated material were formed, but no product with a retention time the same as authentic 1,4-dichlorobutane was detected. A similar chlorination using *t*-butyl hypochlorite also gave almost entirely cyclobutyl chloride and *t*-butyl alcohol.

Chlorination of Methylcyclopropane.—Reaction of 0.6 ml. of methylcyclopropane and 0.1 ml. of Cl_2 in 0.6 ml. of $CFCl_3$ gave the products shown in Table V. Cyclopropylcarbinyl chloride, the major product, was separated and identified by its infrared spectrum.[20] The other products were identified only by comparison of their retention times with known materials. 2-Chlorobutane was also detected as a reaction product when methylcyclopropane was saturated with dry HCl.

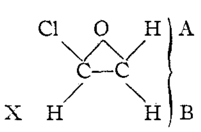
Chlorination with *t*-butyl hypochlorite gave the products listed in Table VI. Again cyclopropylcarbinyl chloride was separated and identified by its infrared spectrum. The other products were present in such small quantities that they could only be identified by retention time.

Chlorination of 1,1-Dimethylcyclopropane.—Reaction of 0.6 ml. of 1,1-dimethylcyclopropane with 0.1 ml. of Cl_2 at 0° in 0.6 ml. of $CFCl_3$ gave a product resolved into three G.L.C. peaks in the expected range for monochlorides. That with the shortest retention time increased markedly when samples were allowed to stand before analysis, and was also formed when 1,1-dimethylcyclopropane was saturated with dry HCl. It was identified as 2-chloro-2-methylbutane by retention time and infrared spectrum. The major product (67.3% of total monochlorides on a fresh sample) had infrared and n.m.r. spectra indicating 1-methyl-1-chloromethylcyclopropane. The third product (3–4%) was assumed to be a ring-chlorinated dimethylcyclopropane.

When similar experiments were carried out using *t*-butyl hypochlorite, 1-methyl-1-chloromethylcyclopropane was again the major product (67% of total peak area at 68°, 52.5% at 0°) and was identified as above. At least three minor peaks with shorter retention times (17.6% total at 68°, 32.4% total at 0°) were also observed plus 15% of a higher-boiling product. By analogy to the reaction of methylcyclopropane, the low boiling products probably include products from the ring opening of the intermediate (1-methylpropyl) methyl radical.

Chlorination of Epoxides.—Photochlorination of 2.5 ml. of ethylene oxide with 0.25–0.5 ml. of *t*-butyl hypochlorite at 0° or 70° gave a single monochlorination product, *t*-butyl alcohol, and, at 70°, some acetone. The product was collected and identified as chloroepoxyethane by infrared and n.m.r. spectra. The infrared spectrum showed a strong peak at 11 μ (epoxide) and an otherwise plausible structure.

The n.m.r. spectrum was typical for an ABX system[27]



Chemical shift, $(CH_3)_4Si$ std., cycles		Coupling constants, cycles	
ν_X	297.2 ± 2	J_{AX}	2.68
ν_A	172.8 ± 2	J_{BX}	1.42
ν_B	168.4 ± 2	J_{AB}	4.7

Similar chlorination of propylene oxide gave a major product 41% of total peak area at 70°, 48% of 0°, five unidentified peaks of longer retention time, and not more than a trace of material with the retention time of chloroacetone.

TABLE VIII

COMPETITIVE CHLORINATIONS WITH Cl_2

R_1H	R_2H	Solvent and temp., °C.	k_1/k_2
Cyclobutane	Cyclohexane	CCl_4, 68	0.708
		CCl_4, 0	.795
Cyclobutane	Cyclopentane	CCl_4, 68	.63
		CCl_4, 0	.71
		C_6H_6, 68	.76
Methylcyclopropane	Cyclopentane	$CFCl_3$, 0	.48, 0.65

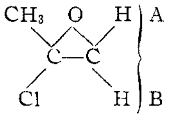
TABLE IX

COMPETITIVE CHLORINATIONS WITH *t*-BUTYL HYPOCHLORITE ($CFCl_3$ SOLVENT)

R_1H	R_2H	Temp., °C.	k_1/k_2[a]
Cyclopentane	Cyclohexane	68	0.87 ± 0.03[c]
		40	$.95 \pm .06$[c]
		0	$.74 \pm .04$[c]
Cyclobutane	Cyclopentane	40	$.50 \pm .02$
		0	$.46 \pm .03$
Cyclopropane	Neopentane	68	$.103 \pm .003$
		0	$.09 \pm .01$
Neopentane	Cyclopentane	68	.153[b]
		0	$.076 \pm .003$
Methylcyclopropane	Cyclopentane	68	.142[b]
		0	$.13 \pm .01$
Cyclopropane	Methylcyclopropane	0	.525[b]
n-Butane	Cyclopentane	0	$.305 \pm .002$
1,1-Dimethylcyclopropane	Cyclopentane	68	$.313 \pm .015$
		0	$.239 \pm .006$

[a] Experimental error represents spread of duplicate experiments. [b] Single experiment. [c] In CCl_4 solvent.

The major peak was collected, and showed an n.m.r. spectrum consistent with 2-chloropropylene oxide



Chemical shifts, cycles		Coupling constant cycles
ν_A	$= 177.5 \pm 2$	$J = 5.25 \pm 0.2$
ν_B	$= 162.9 \pm 2$	
ν_{CH_3}	$= 110.8 \pm 2$	

The ratio of areas (A + B):CH_3 was 65:97, and the methyl peak was unsplit.

Competitive experiments were carried out as described in our previous papers[2,15,23] and analyzed by disappearance of substrate hydrocarbons. The pairs employed and results are listed in Tables VIII and IX, using the symbols of eq. 3–5. Relative reactivities per C–H as listed in Tables II, III and VII were calculated in a step-wise manner when necessary (thus cyclopropane:cyclohexane *via* cyclopropane:neopentane:cyclopentane:cyclohexane) with the usual treatment of cumulative errors. For the methyl group reactivities of methylcyclopropanes it was assumed that only the cyclopropylcarbinyl chloride, allylcarbinyl chloride and cyclobutyl chloride (or 1-methyl-1-chloromethylcyclopropane) arose from attack on $-CH_3$, and the results corrected accordingly. Since some of the unidentified products may also have arisen from attack on $-CH_3$, relative reactivities in Table VII are, if anything, too low.

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[27] We wish to acknowledge the help of Dr. W. Neikam in obtaining and interpreting the n.m.r. spectra reported.