water mixture and the greenish solid was filtered. The solid was washed with water and recrystallized from ethanol (Norit). Colorless rods, m.p. 172–174°, were obtained; 0.54 g. Concentration of the mother liquor gave an additional 0.09 g. A total of 0.63 g. (60%) was obtained.

An analytical sample was obtained by repeated recrystallization from ethanol; m.p. 177–178°.

Anal. Calcd. for $C_{15}H_9Cl_3O$: C, 57.82; H, 2.91. Found: C, 57.87; H, 3.34.

2-Chloro-9-keto-10-trichloromethyl-9,10-dihydroanthracene (IIIb). This compound was prepared using substantially the procedure given above for IIIa. The product, IIIb, (71%) melted at 144–145° (from ethanol).

Anal. Calcd. for $C_{15}H_8Cl_4O$: C, 52.06; H, 2.33. Found: C, 51.83; H, 2.21.

Preparation of 9-dichloromethylene-9,10-dihydroanthracene (IVa) *and oxidation to* Va. A mixture of 0.4 g. of the dihydro compound IIa and 20 ml. of anhydrous pyridine was protected from moisture and heated under reflux for 24 hr. The mixture was poured into an ice water mixture. The white precipitate was filtered and recrystallized from ethanol to give 0.18 g. of white needles, m.p. 84–86°. Concentration of the mother liquor gave an additional 0.13 g. for a total yield of 0.31 g. (89%).

A mixture of 0.12 g. of the above olefin, 0.6 g. of chromic anhydride, and 10 ml. of glacial acetic acid was heated under reflux for 4 hr. Worked up in the usual way this mixture gave 42% of the known anthraquinone Va; m.p. 282–284°.

2-Chloro-10-dichloromethylene-9,10-dihydroanthracene (IVb). This compound was prepared using substantially the procedure given above for IVa. The dihydro compound IIb on dehydrohalogenation with pyridine gave IVb (75%); m.p. 131–132°.

Anal. Calcd. for $C_{15}H_9Cl_3$: C, 60.94; H, 3.07. Found: C, 60.74; H, 3.12.

Oxidation of 2-chloro-10-dichloromethylene-9,10-dihydroanthracene (IVb). This oxidation was effected using chromic anhydride in substantially the way IVa was oxidized. The yield of the known 2-chloroanthraquinone (Vb), m.p. 212–213° was 54%.

Dehydrohalogenation of 2,7-dichloro-10-trichloromethyl-9,10-dihydroanthracene (IIc) *and subsequent oxidation to* Vc. The dihydrocompound IIc was dehydrohalogenated with pyridine as was IVa above. The tan solid was then oxidized with chromic anhydride in 53% yield to the known 2,7-dichloroanthraquinone, m.p. 231–232°.

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Addition of Halogens and Halogen Compounds to Allylic Chlorides. IV. Effect of Reactivity upon the Orientation of Electrophilic Olefinic Addition

J. REID SHELTON AND LIENG-HUANG LEE[1]

The orientation of electrophilic olefinic addition is governed by the various electronic effects (such as electromeric, hyperconjugative, and inductive) which are in turn influenced both by the presence of substituents in the olefinic compound and by the nature of the electrophilic reagent. Three generalizations summarize the experimentally observed behavior with a series of allylic chlorides and related compounds: (1) When both the reagent and the olefinic compound are of low reactivity, the orientation is controlled by electromeric or hyperconjugative electron displacements. If this type of displacement cannot be induced, the orientation is controlled by the inductive effect. (2) When either the reagent or the olefinic compound is of high reactivity, the orientation is controlled chiefly by the inductive effect, although hyperconjugative effects may also be involved. (3) When both the reagent and the olefinic compound are of high reactivity, the normal orientation is controlled by the inductive effect, plus a certain amount of random orientation. Increasing the number of chlorine atoms in the allylic position does not appear to reduce the electron density of the double bond sufficiently to alter the nature of the attack by electrophilic reagents.

The literature of organic chemistry provides an abundance of information on the orientation and mechanism of additions of halogen and halogen compounds to unsaturated compounds containing various kinds and numbers of substituents. Some apparent contradictions and inconsistencies in the results reported prompted the present investigation of the addition of halogens and halogen compounds to a selected series of allylic chlorides and related compounds. Part I of this series of papers[2] was concerned with the addition of hydrogen chloride and hydrogen iodide, Part II dealt with the additions of hypochlorous acid, and Part III in-

volved a study of the relative rates of halogen addition. The object of this concluding paper of the series is to review the experimental results and point out the relationships and possible theoretical interpretations of the data. A comparison of olefinic addition and certain aspects of aromatic substitution will be made as an aid to the interpretation of the observed behavior.

DISCUSSION

Effect of allylic halogen. The principal products obtained by the addition of hydrogen chloride, hydrogen iodide, and hypochlorous acid to a series of allylic chlorides and related compounds are summarized in Table I. The addition of hydrogen chloride and hydrogen iodide to propene is according to Markownikoff's rule. Similar orientation of the additions of hydrogen chloride and hydrogen iodide is observed in the case of allyl chloride in

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(1) This is an abstract of a part of the doctoral thesis submitted by Lieng-huang Lee. Present address: The Dow Chemical Company, Midland, Mich.

(2) Part I, *J. Org. Chem.*, **23**, 1876 (1958); Part II, *J. Org. Chem.*, **24**, 1271 (1959); Part III, *J. Org. Chem.*, **25**, 428 (1960).

TABLE I

Addition Products of Allylic Chlorides and Related Compounds

Reagents	HCl	HI	HOCl (Cl⁺)	
			Primary Chloride	Secondary Chloride
Propene	CH_2—CH(Cl)—CH_3	CH_3—CH(I)—CH_3	$ClCH_2$—CH(OH)—CH_3 90%	CH_2(OH)—CH(Cl)—CH_3 10%
Allyl chloride	CH_3—CH(Cl)—CH_2Cl	CH_3—CH(I)—CH_2Cl	$ClCH_2$—CH(OH)—CH_2Cl 30%	CH_2(OH)—CH(Cl)—CH_2Cl 70%
3,3-Dichloropropene	$ClCH_2$=CH—CH_2Cl^a	CH_3—CH(I)—$CHCl_2$	$ClCH_2$—CH(OH)—$CHCl_2$ 2%	CH_2(OH)—CH(Cl)—$CHCl_2$ 98%
3,3,3-Trichloropropene	Cl_2C=CH—CH_2Cl^a	ICH_2—CH_2—CCl_3	...	CH_2(OH)—CH(Cl)—CCl_3 100%
1,3-Dichlorochloropropene	...	I(Cl)CH—CH_2—CH_2Cl	Cl_2CH—CH(OH)CH_2Cl	...
1,1,3-Trichloropropene	...	I(Cl_2)C—CH_2—CH_2Cl	Cl_3C—CH(OH)CH_2Cl	...

[a] Isomerized product.

spite of the electron-attracting effect of the *alpha* chlorine atom which might be expected to polarize the double bond in the opposite direction. This has been explained[3] on the basis that the hyperconjugative effect associated with the *alpha* hydrogen atoms is the controlling factor, and makes electrons available at the demand of the electrophilic reagent.

Under the experimental conditions employed, hydrogen chloride added only with difficulty to 3,3-dichloropropene, and no addition product was obtained with 3,3,3-trichloropropene. This inactivity may be attributed in part to the deactivating effect of the additional allylic halogen. The inertness of this compound to electrophilic addition has been confirmed by others.[4] The products isolated in each case were isomers of the starting material resulting from an allylic rearrangement:

$$CH_2{=}CH{-}CHCl_2 \rightleftarrows [CH_2{=}\overset{\frown}{CH}{-}CHCl] + Cl^-$$
$$\rightleftarrows ClCH_2{-}CH{=}CHCl$$
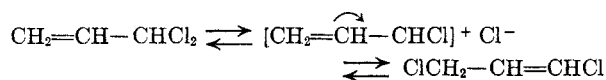
This isomerization (which may result from a nucleophilic attack by chloride ion) provides an additional explanation for the decreased reactivity toward addition of electrophilic reagents since a strongly deactivating vinyl halide is formed.

Allylic isomerization also was observed in the presence of hydrogen iodide, but by using a large excess of hydrogen iodide, addition to the allylic chlorides was effected in each case. However, the excess hydrogen iodide tended to reduce a portion of the product to the corresponding chloroalkane. The addition products of hydrogen iodide to propene, allyl chloride, and 3,3-dichloropropene

are all secondary iodides and again illustrate the controlling influence of the hyperconjugative effect. With 3,3,3-trichloropropene, a primary iodide was obtained as a result of the strong inductive electron-attracting effect of the —CX_3 group in the absence of *alpha* hydrogen. This finding is in accord with Henne and Kay's[5] observation on the addition of hydrogen chloride to 3,3,3-trifluoropropene.

The results obtained with hypochlorous acid as shown in Table I are quite different from those obtained with hydrogen chloride and hydrogen iodide. With propene, allyl chloride, and 3,3-dichloropropene, two products were obtained by attack of the positive halogen of hypochlorous acid on both primary and secondary carbon atoms. The relative amount of primary alcohol formed (as a result of initial attack of positive halogen on the secondary carbon) increases in a regular manner with the number of allylic chlorines present in the starting material. This increasing trend is analogous to the increase in the amount of *meta* substitution observed in aromatic substitution with the corresponding benzylic chlorides in the series from toluene to benzotrichloride.

The orientations in electrophilic aromatic substitution and in electrophilic addition to allylic halides (as well as to other olefinic compounds) are thus governed by the same electronic effects. The inductive effects and hyperconjugation appear to be the controlling factors. In propene and toluene the two effects supplement each other, but in the benzylic and allylic compounds the direction of the two effects are opposite (+T and —I):
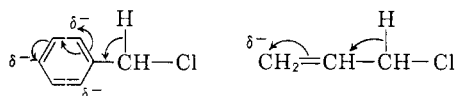
Inductive effect (—I)
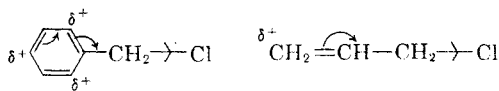
(3) E. E. Royals, *Advanced Organic Chemistry*, Prentice-Hall, Inc., New York, 1954. (a) p. 76; (b) p. 364.

(4) A. N. Nesmeyanov, R. Kh. Friedlina, L. I. Zakharkin, V. N. Kost, R. G. Petrova, A. B. Belyavsky, and A. B. Terentiev in *Vistas in Free-Radical Chemistry* by W. A. Waters, Pergamon, New York, 1959, pp. 235–41.

(5) A. L. Henne and S. Kay, *J. Am. Chem. Soc.*, **63**, 2558 (1941).

Hypercon-
jugative
effect $(+T)$

With an increase in the number of electron-at-
tracting substituents on the *alpha* carbon atom,
the inductive effect increases, while the oppor-
tunity for hyperconjugation decreases with the
diminishing number of *alpha* hydrogens. This
change is reflected in the increasing amount of
meta substitution in benzylic halides and in the
increasing amount of primary alcohol in the addi-
tion products of hypochlorous acid with allylic
halides. In 3,3,3-trichloropropene (and benzo-
trichloride) only the $-I$ effect remains. This is
confirmed by similar results reported for the addi-
tion of hypobromous acid to this compound.[4]

Effect of vinylic halogen. The effect of vinylic
halogen in combination with allylic halogen upon
the orientation and rate of addition was also in-
vestigated. The retarding effect upon rate is dis-
cussed in Part III,[2] and the effect upon orienta-
tion is included in Table I. With hydrogen iodide
addition, the entering halide went to the carbon
atom to which the vinyl halogen was attached
in each case, as is usually observed. Thus, while
hyperconjugation appeared to control the addition
of hydrogen iodide to allyl chloride, in the case of
1,3-dichloropropene and 1,1,3-trichloropropene, the
electromeric effect associated with the vinyl halo-
gen (and induced by the electrophilic reagent
at the moment of attack) appeared to be the pre-
dominant effect.
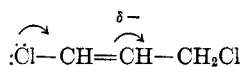
The addition of hypochlorous acid to these same
two compounds containing vinyl halogen along
with allylic halogen was more difficult and gave
opposite results in that attack by the electrophilic
reagent was on the carbon atom bearing the vinyl
halogen. This result can be explained on the basis
of the combined inductive effects of both the
vinylic and allylic halogen which lower the elec-
tron density around the central carbon and thus
serve to direct the electrophilic attack to the other
end of the double bond. The strong inductive

$$Cl \longrightarrow CH=CH\overset{\delta+}{\longleftarrow}CH_2 \longrightarrow Cl$$
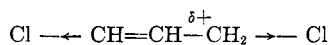
effect of the vinylic halogen has been shown in
Part III[2] and by others[6a] to be 1000 times more ef-
fective than allylic halogen in deactivating the
double bond. The fact that a change in the nature

of the reagent can change the relative importance of
the electronic effects which govern the mode of
addition to a given olefin requires further explana-
tion.

Effect of nature and reactivity of reagent. A com-
parison of the results in Table I with hydrogen
iodide and hypochlorous acid shows other instances
in which a change in the nature of the reagent
changes the point of electrophilic attack. For
example with hypochlorous acid two products
were obtained with propene, allyl chloride, and
3,3-dichloropropene where hydrogen iodide gave
predominantly single products. With both allyl
chloride and 3,3-dichloropropene hydrogen iodide
gave evidence of initial electrophilic attack on the
primary carbon while hypochlorous acid attacked
predominantly on the secondary carbon. De la
Mare and Pritchard[7] demonstrated that a small
portion of the chlorohydrin with the primary
alcohol group formed by addition of hypochlorous
acid to allyl chloride comes from exchange of the
substituent and entering groups, and suggested
that the rest of the product could be explained
by a migration of the entering group from the
point of initial attack to the neighboring carbon.
An alternative explanation is available in terms of
the effect of the nature and reactivity of the rea-
gent upon the relative contribution of the various
electronic effects involved.

Brown and his co-workers[8,9] have found that the
nature and reactivity of the reagent is an important
factor in determining the isomer distribution in
electrophilic aromatic substitution. In a similar
way, a highly reactive reagent like the Cl^+ ion
from hypochlorous acid might be expected to show
less selectivity in electrophilic addition to reactive
olefinic compounds, such as propene, due to an
increased random attack to form both possible
isomers. This is in accord with the results in Table
I for hypochlorous acid addition as compared with
the addition of the less reactive halide molecules.

Higher reactivity may also reduce the necessity
of a stage of rigorous polarization of the π-elec-
trons of the double bond prior to reaction. This
would explain why the mode of addition of hypo-
chlorous acid to allylic chlorides appears to be
mainly controlled by the permanent inductive ef-
fect rather than by conjugative effects induced at
the time of reaction.

Electrophilic mechanism. The interpretation of
the experimental results obtained in this series of
studies is based on the assumption that the attack
is electrophilic in each case. As the number of
allylic halogens is increased, the electron density
of the double bond is reduced so that the possibility

(6) C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N. Y., 1953. (a) p. 667; (b) p. 666; (c) p. 650, Hughes and Peeling, un-published work. (d) p. 258, Cohn, Hughes, and Jones, un-published work.

(7) P. B. D. De la Mare and J. G. Pritchard, *J. Chem. Soc.*, 3910, 3990 (1954).

(8) H. C. Brown and K. L. Nelson, *J. Am. Chem. Soc.*, 75, 6292 (1953).

(9) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, 77, 2300, 2306, 2310 (1955).

of a change in the nature of the reaction from electrophilic to nucleophilic attack by the reagent must be considered. Two evidences suggest that the nature of the attack remained unchanged. First, the addition of bromine[10] to the di- and trichloropropenes was found to be slower than that of chlorine (Part III).[2] Second, no evidence of addition of nucleophilic reagents, such as sodium bisulfite and ammonia to 3,3-dichloropropene and 3,3,3-trichloropropene was found in this study.

Some instances of nucleophilic attack on allylic halides have been reported. For example, 3,3,3-trifluoropropene does react with ethanol in a base-catalyzed reaction to give some addition by nucleophilic attack[11] along with solvolysis of allylic fluoride. Similarly, 3,3,3-trichloropropene is subject to nucleophilic attack in basic media[12] to give isomerized substitution products by an S_N2' mechanism. In the present study, some 3,3-dichloro-2-propen-1-ol was obtained by an analogous substitution in the attempted reaction with aqueous sodium bisulfite.

Substitution also occurred in the attempted reaction of the di- and trichloropropenes with anhydrous ammonia. However, the failure to observe nucleophilic addition reactions with 3,3,3-trichloropropene is convincing evidence that, with the reagents and conditions used in this study, the addition products obtained resulted from electrophilic attack in each case.

Combined effect of reactivities of both reactants. Kinetic studies[6b] show that the order of reactivity for halogen addition is: $X^+ > X$-$Y > X_2 > HX$. When reagents of different reactivities are combined with olefins of different reactivities, three situations are encountered as demonstrated in part III of this series:

1. When both the reagent and the olefin are relatively unreactive, as in the case of hydrogen halides with the di- and trichloropropenes (both vinyl and allylic types), an electromeric or hyperconjugative electron displacement must be induced in order to polarize the π-electrons of the double bond and produce reaction. Thus, these dynamic effects control the orientation of addition except for the case of 3,3,3-trichloroprene where no electromeric shift or hydrogen-hyperconjugation is possible, and consequently, the inductive effect controls the mode of addition.

2. When either the reagent or the olefin is of high reactivity, as in the case of hypochlorous acid with the di- and trichloropropenes, or hydrogen halides

with propene, the permanent polarization of the molecule due to the inductive effect is sufficient to permit reaction and to determine the orientation of addition. Hyperconjugation may also be involved to some extent but it is apparently not a controlling factor for such a combination of reactivities. This is in accord with the results reported[6c] for the combination of hydrogen iodide with reactive olefins, and for the mononitration of alkylbenzenes.[6d]

3. When both the reagent and the olefinic compound are of high reactivity, as in the case of hypochlorous acid and propene, the reaction is very rapid and the permanent polarization of the molecule due to the inductive effect is sufficient to give reaction and to determine the predominant orientation of the addition. The greater rate of reaction results in lower selectivity as reflected in the increased random attack to give both possible isomers.

Thus, the orientation of electrophilic addition is governed by combinations of the various electronic effects possible. The relative contribution of the individual effects is dependent upon the nature and reactivity of both the olefinic compound and the electrophilic reagent.

EXPERIMENTAL

A. *Additions to allylic chlorides and related compounds.* The methods of preparation of the chloropropenes used for this study are described in Part I of this series of papers.[2] The procedures and the experimental results discussed in this paper are presented in Parts I–III.

B. *Attempted reactions with nucleophilic reagents.* 1. *Sodium bisulfite and 3,3,3-trichloropropene.* 3,3,3-Trichloropropene (3 g., 0.021 mole) containing hydroquinone (0.006 g.) was refluxed with 10 ml. of a saturated (30%) solution of sodium bisulfite (0.028 mole) for 20 hr. (Hydroquinone was used to inhibit free-radical addition.) After the reaction was completed, the organic layer was separated and washed with water and dried over sodium sulfate. The aqueous portion was evaporated to dryness and extracted with ethyl alcohol. The extract was treated with barium chloride. The organic portion was found to be 3,3-dichloro-2-propen-1-ol, a hydrolyzed product of 1,1,3-trichloropropene. No addition product was found in the aqueous portion.

2. *Anhydrous ammonia with di- and trichloropropene.* Anhydrous ammonia (4 ml., 0.19 mole) was condensed into two Carius tubes. Tube 1 contained 3,3-dichloropropene (3 g., 0.029 mole); tube 2 contained 3,3,3-trichloropropene (5 g., 0.034 mole). Both tubes were sealed and left standing at room temperature for 114 hr. At the end of the reaction, crystalline ammonium chloride was found in both tubes. The contents were washed with water and dried over anhydrous sodium sulfate. In both tubes, only the substituted chlorides were found, and no addition products were detected.

(10) P. B. D. De la Mare and P. W. Robertson, *J. Chem. Soc.*, 2838 (1950).

(11) A. L. Henne, M. A. Smook, and R. L. Pelley, *J. Am. Chem. Soc.*, **72**, 4756 (1950).

(12) A. N. Nesmeyanov, R. Kh. Friedlina, and L. I. Zakharkin, *Quart. Rev. (London)*, **10**, 330 (1956).