attachment through all three carboxyl groups must prevent contact of the ortho hydrogens with active sites.

The exchange of side-chain hydrogen atoms observed by Tiers in toluene and by Bonner in phenylacetamide, and the lack of exchange in the aliphatic C–H groups of isopropyl benzoate, are the results to be expected in view of the demonstration by Fukushima and Gallagher[11] that the exchange at saturated carbon atoms of unsaturated steroids is confined to allylic positions.

[11] D. K. Fukushima and T. F. Gallagher, THIS JOURNAL, **77**, 139 (1955).

CHICAGO 37, ILL.

[CONTRIBUTION FROM STERLING CHEMISTRY LABORATORY, YALE UNIVERSITY]

The Electron-seeking Demands of Dichlorocarbene in its Addition to Olefins

BY W. VON E. DOERING AND WM. A. HENDERSON, JR.

RECEIVED MAY 16, 1958*

The relative reactivity of a number of aliphatic olefins in the addition of dichlorocarbene to form dichlorocyclopropane derivatives has been determined. Reactivity increases with increasing degree of substitution in accord with the hypothesis that dichlorocarbene is an electrophilic molecule. Dibromocarbene shows similar demands complicated perhaps by a steric factor.

The novel reaction of haloform, alkoxide ion and olefins,[1] recently discovered by Doering and Hoffmann, gives 1,1-dihalocyclopropane derivatives. The question may be asked whether the hypothetical intermediate, dihalocarbene, is an electrophilic reagent. A strong affirmative answer already has been given by Hine and Dowell[2] in competition experiments where the relative rates of reaction of dichlorocarbene with chloride, bromide, hydroxide and iodide ions compared to water parallel their nucleophilicities. Skell and Garner[3] have studied the matter by allowing a variety of olefins in pairs to compete for dibromocarbene in the addition reaction. These workers analyzed the products by distillation and were able to arrange a large number of olefins in an order of reactivity which paralleled that shown in bromination and epoxidation.

Independently we carried out a similar investigation allowing dichlorocarbene to choose between olefins offered in pairs. The range of olefins was limited to the lower molecular weights so that the products would be sufficiently volatile to permit convenient analysis by vapor phase chromatography (v.p.c.). The results confirm those of Skell and Garner.

Potassium *t*-butylate is dissolved in the olefin mixture and chloroform is added dropwise at -20 to $-10°$. The relative quantities of the two products in the reaction mixture is determined immediately by v.p.c. analysis, sensitivity having been determined by calibration with known mixtures of pure products. These sensitivities (perhaps better described as empirical correction factors) are incorporated in the body of the Experimental section and are used to correct the raw analyses. The ratio of the reaction rates is calculated from the expression $k_a/k_b = P_aO_b/P_bO_a$ where P is the mole per cent. of the product and O is the initial mole per cent. of the olefin. Since the starting olefin concentration is about 6–7 times that of the chloroform used, even in unfavorable cases the use of this simplified equation introduces less than a 10% error. As the olefin most frequently used in the

TABLE I

RELATIVE REACTIVITIES OF OLEFINS

	Reactants			
Olefin	:CCl$_2$^{a} log	:CBr$_2$^{a} log	Br^{+g} log	HO^{+i} log
2,3-Dimethylbutene-2	(1.73)^d	0.84, 0.97^e	(1.15)	
2-Methylbutene-2	1.37	.87, .94^e	(1.02)	0.98
Isobutylene	0.92 (0.89)^b	.57, .43^e	(0.74)	−0.15
2-Methylbutene-1	.74			
trans-Pentene-2	(.33)^c			−0.14
Ethyl vinyl ether	.27			
cis-Pentene-2	.21			
Cyclohexene	.00	.00		0.00
Hexene-1	− .73	(− .71)^{e,f}	(0.31)^h	−1.42
Pentene-1	− .86 (−0.78)^b	− .78		−1.48

^{a} Measured against cyclohexene as the reference standard unless otherwise indicated. ^{b} Measured in competition with hexene-1 as reference. ^{c} Measured in competition with *cis*-pentene-2. ^{d} Measured in competition with 2-methylbutene-2. ^{e} These data are taken from Skell and Garner[3] and have been adjusted to cyclohexene as standard and are tabulated as the logarithms. ^{f} Measured in competition with isobutylene. ^{g} These are the logarithms of the "reduced velocities of bromination at −78°" relative to ethylene taken from Anantakrishnan and Venkataraman.[4] ^{h} Propene. Calculated from the rates of epoxidation reported by Swern,[5] and referred to cyclohexene as standard.

(*) Manuscript originally received June 7, 1957.

[1] W. von E. Doering and A. K. Hoffmann, THIS JOURNAL, **76**, 6162 (1954).

[2] J. Hine and A. M. Dowell, Jr., *ibid.*, **76**, 2688 (1954).

[3] P. S. Skell and A. Y. Garner, *ibid.*, **78**, 5430 (1956).

[4] S. V. Anantakrishnan and R. Venkataraman, *Chem. Revs.*, **33**, 27 (1943).

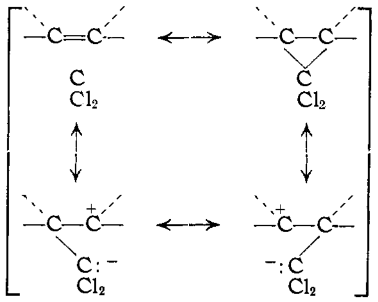
[5] D. Swern, *ibid.*, **45**, 1 (1949).

competition experiments, cyclohexene has become the natural (if nonetheless arbitrary) standard to which the other olefins are referred. In Table I, column 2, the logarithms of k_a(olefin)/k_0(cyclohexene) are shown. Where the ratio has not been measured directly, the reference standard is indicated and the data have been recalculated to cyclohexene as standard. Since all the reactions have been run at $-15 \pm 5°$, multiplication of the differences between any pairs of log k_a/k_0 by 1.18 translates into free energy of activation ($\Delta\Delta F^{\ddagger}$ in kcal.).

The validity of the competition method depends on the stability of the products. All the halocyclopropanes prepared here are stable to alkoxide ion under conditions far more drastic than those used in the reactions. The internal consistency of the method is demonstrated by completing a circle of competition runs. Two such examples, those involving isobutylene and pentene-1 with dichlorocarbene are to be found in Table I. The agreement within the two pairs of values is certainly satisfactory.

With the over-all differences being quite large—tetramethylethylene reacting 390 times faster than pentene-1—it is at once clear that the free energy of the activation in the addition of dichlorocarbene to an olefin is greater than zero and is sensitive to variation in structure. By contrast, methylene generated photochemically reacts indiscriminately with the carbon–hydrogen bond, the aromatic ring and the double bond.[6] Dihalocarbene (which fails to react with saturated hydrocarbons and benzene) is accordingly a much more stable, less reactive carbene than methylene.

The observed order of reactivity among the olefins toward dichlorocarbene increases with the degree of alkyl substitution: monosubstituted olefins < *sym*-di < *unsym*-di- < tri- < tetra-. This sequence is rationalized in terms of the hypothetical geometry of the transition state consistent with the completely *cis* nature of the addition of dibromocarbene to *cis*- and *trans*-butene.[7] Among the several resonance structures written to suggest the less localized character of the electrons, those with the carbon bearing the positive charge must be prominent. By analogy with the remarkable, stabilizing effect on negative charge, of the three chlorine atoms in the trichloromethide ion,[8] the singly non-bonded structures will be strongly polarized in the sense of olefin carbon atoms positive and the dihalocarbon negative.



It therefore follows that structural factors in an olefin which facilitate bearing positive charge will lower the energy of the transition state and increase the rate of reaction of that olefin (assuming no concomitant unfavorable change in the entropy of activation). It is well known that tert. carbonium ions are more stable than sec., which are in turn more stable than prim. Increasing the degree of substitution in the olefin is therefore expected to lead to contribution by increasingly lower energy structures in the transition state and therefore to more rapid reaction.

The fact that unsymmetrically disubstituted olefins react faster than symmetrically substituted can be interpreted to mean that contribution by one t. and one p. carbonium ion structure is more favorable than contribution by two s. structures. The enhanced rate of ethyl vinyl ether relative to 1-pentene (*ca.* 14 times) is easily rationalized by noting the contribution of a *third*, singly no-bonded structure in which oxygen bears the positive charge.

In attempting to use this theoretical analysis to predict the relative rate of other olefins, it is helpful to know that ethylene itself apparently fails to react.[9] This failure must be due to the fact that *t*-butylate reacts with dichlorocarbene[10] faster than does ethylene. Accordingly, one would predict that ethyl crotonate or acrylonitrile and other negatively substituted olefins would fail to compete effectively. In such cases the unfavorable effect of raising the energy of one of the resonance structures contributing to the transition state would be aggravated by the resonance energy of conjugation in the starting state.

For the sake of clarity we include in Table I the relative reactivities in bromination and epoxidation so that the parallelism first pointed out by Skell and Garner[3] may be seen to apply to dichlorocarbene as well. It may be noted that bromination and epoxidation are believed to proceed through three-membered transition states in which the olefin carbon atoms bear a positive charge. The observation that these reactions respond to changes in olefin structure in roughly the same way as does dichlorocarbenation is in gratifying support of the theoretical analysis.

It also may be pointed out that no parallelism exists with the argentation constants (four pairs in common),[11] with the relative rates of hydration (one pair)[12] or with the heats of hydrogenation (seven pairs).[13]

The detailed geometrical and electronic structures of methylene and its substituted derivatives have not been established.[14] Although both the

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[6] W. von E. Doering, R. G. Buttery, R. G. Laughlin and N. Chaudhuri, THIS JOURNAL, **78**, 3224 (1956).

[7] W. von E. Doering and P. M. LaFlamme, *ibid.*, **78**, 5447 (1956).

[8] J. Horiuti and Y. Sakamoto, *Bull. Chem. Soc. Japan*, **11**, 627 (1936).

[9] W. von E. Doering and A. K. Hoffmann, unpublished observation.

[10] J. Hine, E. L. Pollitzer and H. Wagner, THIS JOURNAL, **75**, 5607 (1953).

[11] S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).

[12] H. J. Lucas and Y. P. Liu, *ibid.*, **56**, 2138 (1934).

[13] J. B. Conant and G. B. Kistiakowsky, *Chem. Revs.*, **20**, 181 (1937).

[14] In one recent paper, "The Structure of Carbene, CH_2," by P. S. Skell and R. C. Woodworth,[15] an sp^2 (presumably 120°),[2] singlet structure is proposed. In another, "The Structure of CH_2" by G. A. Gallup, *J. Chem. Phys.*, **26**, 716 (1957), MO calculations lead to the opposed conclusion that CH_2 is in a diradical (triplet) state with a

stereochemical evidence and the competition evidence of Skell and Garner[3] and this paper are consistently explained in terms of the simultaneous formation of both bonds of the ultimate cyclopropane ring and therefore in terms of a paired, singlet structure for dichloro- and dibromocarbene,[15] it is not clear either in theory or by analogy that a diradical structure would be less consistent.

In principle, the effect of replacing two chlorine atoms in dichlorocarbene by bromine atoms or iodine atoms can be evaluated by determining the relative response of the apposite carbenes to identical changes in olefin structure. The relative response or sensitivity is obtained easily by plotting the logarithms of the ratio of the rates of reaction (with pairs of olefins, all adjusted to a single arbitrary standard) of dichlorocarbene against those of dibromocarbene and determining the slope ($d[CCl_2]/d[CBr_2]$) of the line. A slope > 1 would signify a greater ability to discriminate, a higher sensitivity, a larger internal stabilization in dichlorocarbene.

In Table I, third column, the comparable data on the relative reactivity of dibromocarbene toward five olefins have been selected from Skell and Garner,[3] and, after readjustment to cyclohexene as standard, have been tabulated as the logarithms. Because simple distillation was the method of analysis used by them, competitions have been repeated using v.p.c. as the method of analysis. When plotted against the comparable dichlorocarbene reactivities the scatter about a hypothetical line is so large that no slope can be determined. One notices that relatively dibromocarbene reacts slower than dichlorocarbene, the greater the degree of substitution. This falling off may indicate the operation of a steric factor. We have undertaken further work with dichloro and dibromocarbene to establish this point more firmly. Susceptibility to steric factors would not in any event help one decide between linear and bent structures for the dihalocarbenes, even though it seems reasonable that a linear structure should be more sensitive than an angular one.

The authors thank Research Corporation, New York City, for the granting of a Summer Research Fellowship to Wm. A. Henderson, Jr.

Experimental[16]

Reaction of Olefins, Chloroform and Potassium *t*-Butylate. (a) Pure Olefins.—The reaction of each olefin was carried out in an erlenmeyer flask equipped with a Dry Ice condenser and dropping funnel and immersed in a Dry Ice methanol-bath. Stirring was maintained with a magnetic stirrer.

To the flask containing 2 g. (0.027 mole) of potassium *t*-butylate prepared by the method of Doering and Hoffman,[1] 20 g. of olefin was added. The temperature of the bath then was adjusted and maintained between −20 and −10°, while 3 g. (0.025 mole) of purified chloroform was added dropwise to the stirred solution over the course of 20 min. After standing an additional 30 min., the solution was washed twice with an equal volume of water; the water extracts were then washed with 10 ml. of pentane and the combined organic layers were dried over sodium sulfate. The product was distilled at an appropriately reduced pressure.

The sensitivity of the Perkin–Elmer model 154 vapor fractometer, type "A" column to each cyclopropane derivative was compared relative to 1,1-dichloronorcarane. Four to six samples each (0.03 to 0.05 ml.) of known mixtures of the derivatives in question with 1,1-dichloronorcarane were passed through the column at appropriate temperatures (50 to 145°) at helium pressures of 5 to 20 lb. Temperature and pressure were maintained constant throughout all analyses of a given pair of products. Using the height times the half-height width of each product peak on the fractometer chart as a measure of the amount of each component present, the sensitivity for each product was determined.

Cyclohexene (Eastman Kodak Co. white label; 1 kg.) was purified by washing twice with 125-ml. portions of 15% sodium hydroxide and twice with 125-ml. portions of water. After being dried overnight over sodium sulfate, the cyclohexene was distilled through a 2-foot column packed with glass helices. The fraction boiling from 81.9–82.4° was collected. Reaction with chloroform and base afforded **1,1-dichloronorcarane**, b.p. 77–78° (13 mm.), $n^{25}D$ 1.5006 (reported[1] b.p. 78–79° (15 mm.), $n^{23}D$ 1.5014).

1-Hexene (Phillips reagent grade > 99%) afforded **1,1-dichloro-2-*n*-butylcyclopropane**, b.p. 71.6–72° (20 mm.), $n^{25}D$ 1.4479; sensitivity, 1.14. *Anal.* Calcd. for $C_7H_{12}Cl_2$: C, 50.3; H, 7.2; Cl, 42.4. Found: C, 50.1; H, 7.0; Cl, 42.4.

2,3-Dimethyl-2-butene, a sample of unknown origin kindly furnished by the Humble Oil and Refining Co., Inc., and identified by infrared spectrum and determined by v.p.c. to be of 94% purity, afforded **1,1-dichloro-2,2,3,3-tetramethylcyclopropane**, m.p. 49.8–50.5°; sensitivity, 0.91. *Anal.* Calcd. for $C_7H_{12}Cl_2$: C, 50.3; H, 7.2; Cl, 42.4. Found: C, 50.4; H, 7.2; Cl, 42.5.

cis-Pentene (Phillips technical grade: >95%) afforded ***cis*-1,1-dichloro-2-methyl-3-ethylcyclopropane**, b.p. 64.4–68.0° (49 mm.), $n^{20}D$ 1.4549; sensitivity, 0.94. *Anal.* Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 47.2; H, 6.5; Cl, 46.2.

2-Methyl-2-butene (Phillips technical grade: >95%) afforded **1,1-dichloro-2,2,3-trimethylcyclopropane**, b.p. 64.3–64.7° (47 mm.), $n^{20}D$ 1.4577; sensitivity, 0.82. *Anal.* Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 47.2; H, 6.7; Cl, 46.2.

2-Methyl-1-butene (Phillips technical grade: >95%) afforded **1,1-dichloro-2-methyl-2-ethylcyclopropane**, b.p. 59.0–59.5° (41 mm.), $n^{20}D$ 1.4555. *Anal.* Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 46.8; H, 6.4; Cl, 46.4.

1-Pentene (Phillips technical grade: >95%) afforded **1,1-dichloro-2-*n*-propylcyclopropane**, b.p. 68.2–68.5° (46 mm.), $n^{20}D$ 1.4488; sensitivity, 1.00. *Anal.* Calcd. for $C_6H_{10}Cl_2$: C, 47.1; H, 6.6; Cl, 46.3. Found: C, 47.2; H, 6.5; Cl, 46.7.

Isobutylene (Phillips reagent grade: >99%) afforded **1,1-dichloro-2,2-dimethylcyclopropane**, b.p. 119.5–120.0° (760 mm.), $n^{25}D$ 1.4465 (reported[1] b.p. 119–120°, $n^{25}D$ 1.4461); sensitivity, 0.79

Vinyl ethyl ether (Matheson practical grade: b.p. 34–36°) afforded **1,1-dichloro-2-ethoxycyclopropane**, b.p. 53.5–53.6° (28 mm.), $n^{25}D$ 1.4444. *Anal.* Calcd. for $C_5H_8OCl_2$: C, 38.7; H, 5.2; Cl, 45.7. Found: C, 39.0; H, 5.2; Cl, 46.1.

(b) Mixtures of Olefins.—Pairs of olefins were treated in the same manner as above, with 10 g. (0.143 mole of a C_5H_{10} olefin corresponding to 5.7 equiv.) of each olefin being used, but after washing the reaction mixtures were immediately analyzed by v.p.c. Analyses were made on a Perkin-Elmer model 154 vapor fractometer, using two columns. The first was a 2-foot column of 1/4″ copper tubing packed with Dow Corning 702 silicone pump oil on Johns–Manville C-22 fire-brick. All analyses were run on this column

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bond angle of 160°. The authors of both papers derive support for their suggestions from the early report of G. Herzberg, *Revs. Mod. Phys.*, **14**, 195 (1942); *Astrophys. J.*, **96**, 314 (1942), that the λ 4050 group of emission bands, first observed in comets, might be due to CH_2 and, in that event, would be accommodated by the assignment of a bond angle of 140° to CH_2. In view of the encouragement which Herzberg himself has given to the later investigations of the λ 4050 group, it is not out of place to point out that the work of A. Monfils and B. Rosen, *Nature*, **164**, 713 (1949), A. E. Douglas, *Astrophys. J.*, **114**, 466 (1951), and K. Clusius and A. E. Douglas, *Can. J. Phys.*, **32**, 319 (1954), has led to the reassignment of the λ 4050 group to the linear molecule, C_3.

(15) P. S. Skell and R. C. Woodworth, This Journal, **78**, 4496 (1956).

(16) All b.p.'s are corrected. Analyses are by the Schwarzkopf Microanalytical Laboratory, Woodside 77, N. Y.

except those on the products from the *cis*- and *trans*-pentene, which were run on a Perkin–Elmer 2-meter "A" column.

The results of the competition experiments are given in Table I. All competitions were run at least in duplicate and were found to be reproducible within ±3%. The competition factors are good to at least 10%.

Reaction of Olefins, Bromoform and Potassium *t*-Butylate. (a) **Pure Olefins.**—The reaction for each olefin was carried out in the same way as for chloroform, except that the amounts of reagent were changed to 17.0 g. of olefin, 6.2 g. (0.055 mole) of potassium *t*-butylate and 12.7 g. (0.050 mole) of bromoform. The work-up was the same as for the reaction with chloroform.

The relative sensitivities for the vapor fractometer were obtained in the same manner as before. All analyses were made on the silicone column at 140° and 10 lb. of helium.

Cyclohexene afforded **1,1-dibromonorcarane**, b.p. 85.5–86.0° (6 mm.), $n^{25}\text{D}$ 1.5568 (reported[1] b.p. 100° (8 mm.), $n^{22}\text{D}$ 1.5578). *Anal.* Calcd. for $C_7H_{10}Br_2$: C, 33.1; H, 4.0; Br, 62.9. Found: C, 33.2; H, 4.0; Br, 62.8.

1-Pentene afforded **1,1-dibromo-2-*n*-propylcyclopropane**, b.p. 63.0–65.0° (10 mm.), $n^{25}\text{D}$ 1.5023; sensitivity, 1.26. *Anal.* Calcd. for $C_6H_{10}Br_2$: C, 29.8; H, 4.2; Br, 66.1. Found: C, 30.0; H, 4.3; Br, 66.2.

2-Methyl-2-butene afforded **1,1-dibromo-2,2,3-trimethylcyclopropane**, b.p. 40–50° (8 mm.), $n^{25}\text{D}$ 1.5140 (reported[3] b.p. 83° (24 mm.), $n^{25}\text{D}$ 1.5134); sensitivity, 0.66. *Anal.* Calcd. for $C_6H_{10}Br_2$: C, 29.8; H, 4.2; Br, 66.1. Found: C, 30.0; H, 4.2; Br, 66.2.

Isobutylene afforded **1,1-dibromo-2,2-dimethylcyclopropane**, b.p. 78–79° (23 mm.), $n^{25}\text{D}$ 1.5114; sensitivity, 0.98. *Anal.* Calcd. for $C_5H_8Br_2$: C, 26.3; H, 3.5; Br, 70.1. Found: C, 26.6; H, 3.8; Br, 70.0.

2,3-Dimethylbutene-2 afforded **1,1-dibromo-2,2,3,3-tetramethylcyclopropane**, m.p. 77.4–78.4° (reported[3] m.p. 77–78°); sensitivity, 0.76. *Anal.* Calcd. for $C_7H_{12}Br_2$: C, 32.8; H, 4.7; Br, 62.4. Found: C, 32.7; H, 4.9; Br, 62.6.

(b) **Mixtures of Olefins.**—Pairs of olefins were treated in the same way as pairs of olefins with chloroform; 1.9 g. (0.017 mole) of potassium *t*-butylate, 3.8 g. (0.015 mole) of bromoform and 8 g. (0.114 mole) of C_5H_{10} (corresponding to 7.6 equiv.) of each olefin being used.

Results are given in Table I. All competitions were run in duplicate and are reproducible within ±5%.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Rates of Solvolysis of *p*-Substituted Benzyldimethylcarbinyl Chlorides[1]

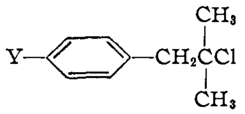
BY ABRAHAM LANDIS AND CALVIN A. VANDERWERF

RECEIVED APRIL 28, 1958

Benzyldimethylcarbinol and its *p*-alkyl (CH_3, Et and *i*-Pr) and *p*-halo (F, Cl and Br) derivatives were synthesized. These carbinols were converted to the corresponding carbinyl chlorides with hydrogen chloride. The first-order rates of hydrolysis of the chlorides were measured in aqueous ethanol at 40.8°. The small increase in rate observed for the *p*-alkyl derivatives (H = 1.00, Me = 1.55, Et = 1.40, *i*-Pr = 1.32) parallels that for the corresponding alkyl substituted *t*-butyl chlorides, both in order and in magnitude, and indicates the importance of a hyperconjugative effect, which can be relayed to the reaction site only by induction, in stabilizing the incipient carbonium ion intermediate. Likewise, the order of rates for the *p*-halo derivatives (H = 1.00, F = 0.80 > Cl = 0.52 < Br = 0.55) strongly suggests the operation of an electron-supplying resonance effect. A Hammett plot for the reaction rates gives a fairly good linear relationship with a reaction constant, ρ, of 1.11.

This work was undertaken in an attempt to determine the effect of various alkyl and halogen substituents on the rate of a reaction which proceeds through a carbonium ion intermediate for a system in which the steric effects of the substituents are negligible and in which the electronic effects can be relayed ultimately to the reaction center only by induction.

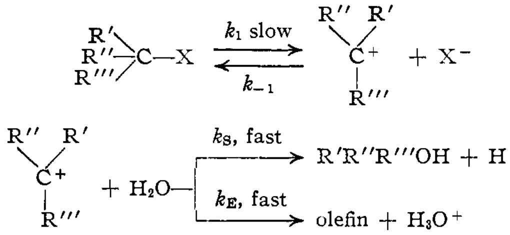
The model compounds selected and synthesized for the study were various heretofore unknown *p*-substituted benzyldimethylcarbinyl chlorides where



$$Y-C_6H_4-CH_2C(CH_3)_2Cl$$

Y = Me, Et, *i*-Pr, F, Cl and Br. In each of these compounds, the *p*-substituted benzyl group is obviously insulated from the reactive carbon center by a methylene group. Thus, with the methylene group serving as an insulator to block the tautomeric transmission of any electronic effect, the *p*-substituent effect can be relayed ultimately to the chlorine-bearing carbon only through an inductive mechanism.

The reaction chosen for the rate study was solvolysis in 80% aqueous ethanol, which for tertiary halides has been shown by Hughes and Ingold and their co-workers[2] to proceed by the mechanism



The rate-determining step is the unimolecular ionization (k_1) of the tertiary halide to yield a carbonium ion intermediate. This ion can then undergo either a fast substitution reaction (k_S) with the solvent to form the corresponding carbinol or ether, or a fast elimination of a proton (k_E) to form the corresponding olefin. Although the transition state probably does not contain a free carbonium ion, it is thought to approach that condition.[3] As a result, the effects of the substituents upon the stability of the transition state and upon the stability of the carbonium ion may be considered as essentially identical.

Corresponding studies, first on the hydrolysis of tertiary aliphatic chlorides, of which our *p*-alkyl-

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[1] Presented in part before the Organic Division at the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 13, 1955.

[2] E. D. Hughes and B. J. MacNulty, *J. Chem. Soc.*, 1283 (1937); E. D. Hughes and C. K. Ingold, *Trans. Faraday Soc.*, **37**, 657 (1941).

[3] G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).