as intense as the other, and two quartets centered at 6.28 and 5.59, the quartet at 6.28 being twice as intense as the other.

The Reaction of 1,2,3-trichloro-3-ethoxy-4,4-difluorocyclobutene (XVI) with ethoxide ion was carried out according to the previously described procedure to yield 2.0 g. (49% of theory) of pure XXVII, $n^{25}\text{D}$ 1.4289, whose infrared spectrum and g.l.c. retention time were identical with an authentic sample, and 0.8 g. (20% of theory) of pure XXVIII, m.p. 22.0°, $n^{25}\text{D}$ 1.4295, and infrared spectrum and g.l.c. retention time identical with an authentic sample.

The reaction was repeated at −10° and was worked up after a 1-hr. reaction time in an attempt to isolate the proposed intermediate XXXII. G.l.c. analysis showed 60% starting material, trace of a new peak, 28% XXVII, and 12% XXVIII. The infrared spectrum of each compound indicated no impurities.

Acknowledgment.—The authors wish to express their appreciation to Professor Melvin Hanna of this Chemistry Department for assistance in the interpretation of the n.m.r. spectra, and to the Minnesota Mining and Manufacturing Company, St. Paul, Minnesota, for their partial support of this work.

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

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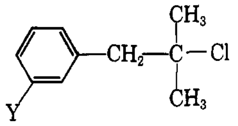
Received January 6, 1964

The rates of solvolysis in 80% ethanol of benzyldimethylcarbinyl chloride and the *meta*-methyl-, -ethyl-, -isopropyl-, -fluoro-, -chloro-, and -bromo-substituted carbinyl chlorides have been measured at 40.5, 50.0, and 61.1°. The unusual relative rate sequence was explained by means of solvent and dipole–dipole interactions on the transition state.

This work was undertaken in an attempt to evaluate the effect of inductance on the stability of tertiary carbonium ions in a system where resonance and steric effects are negligible.

The model compounds selected for the study were the heretofore unknown *meta*-substituted benzyldimethylcarbinyl chlorides, where Y = Me, Et, *i*-Pr, F, Cl, and Br.



With the substituent being in the *meta* position to minimize resonance effects and the methylene group serving as an insulator to block the transmission of any resonance effect, the *meta* substituent should influence the chlorine-bearing carbon only by an inductive mechanism.

The reaction chosen for study was solvolysis in 80% aqueous ethanol. It has been well established that tertiary halides hydrolyze in this solvent by the S_N1 mechanism.[3,4] The transition state is probably not a free carbonium ion, but it is thought to approach this condition.[5] Since the rate of the reaction is a measure of the formation of a carbonium ion, the effects of substituents upon the stability of the transition state and upon the stability of the carbonium ion can be considered as essentially identical.

Studies on the hydrolysis of the homologous alkylphenyldimethylcarbinyl chlorides,[6] and the halophenyldimethylcarbinyl chlorides[7] have been reported by Bown and co-workers. The analogous *para*-substituted benzyldimethylcarbinyl chlorides have been shown to be stabilized in a hyperconjugative order by alkyl groups and destabilized through the inductive effect by the halogen groups, although there was also evidence for the operation of a resonance effect with the halogens.[8] The elimination reactions of the unsubstituted benzyldimethylcarbinyl chloride have also been investigated.[9]

Results

The series of *meta*-substituted benzyldimethyl carbinols was synthesized by the reaction of the appropriate *meta*-substituted benzylmagnesium halide with acetone. These compounds are oily liquids which are stable at room temperature. With the exception of the unsubstituted carbinol,[8-10] the compounds are new. Their physical properties and analyses are reported in Table I.

The *meta*-substituted benzyldimethylcarbinyl chlorides were synthesized by mixing the pure carbinols with concentrated hydrochloric acid and simultaneously bubbling through hydrogen chloride gas. The resulting tertiary chlorides were contaminated with trace amounts of olefin and unreacted carbinol. These impurities were removed by washing the chloride with cold concentrated sulfuric acid, immediate separation of the layers by means of centrifugation, treatment of the organic layer with a mixture of calcium chloride and calcium carbonate, and distillation of the chloride under reduced pressure. The resulting purified chloride was, in each case, a colorless oil which decomposed upon standing for several weeks. With the exception of the unsubstituted carbinyl chloride,[8,9] all of the compounds

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(1) Taken from the thesis submitted by M. M. Tessler to the Graduate School at the University of Kansas, in partial fulfillment of the requirements for the Ph.D. degree, July 1962.

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TABLE I

meta-SUBSTITUTED BENZYLDIMETHYL CARBINOLS

meta substituent	B.p., °C. (mm.)	n_D (t, °C.)	Calcd., %			Found, %[a]		
			C	H	X	C	H	X
CH_3	84–87 (0.5)	1.5112 (25.7)	80.4	9.7		80.6	9.5	
C_2H_5	92–98 (1.1)	1.5089 (24.8)	80.9	10.2		80.6	10.2	
i-C_3H_7	85–90 (0.9–1.1)	1.4992 (31.2)	81.2	10.5		81.0	10.5	
F	75–76 (0.4)	1.4945 (25.7)	71.4	7.8	F, 11.2	71.7	7.9	F, 11.0
Cl	104–108 (1.1–1.3)	1.5290 (25.2)	65.0	7.1	Cl, 19.2	65.2	7.2	Cl, 19.2
Br	97–100 (0.6–0.7)	1.5483 (25.7)	52.4	5.7	Br, 34.9	52.6	5.7	Br, 35.0

[a] Analyses were done by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, N. Y.

TABLE II

meta-SUBSTITUTED BENZYLDIMETHYLCARBINYL CHLORIDES

meta substituent	B.p., °C. (mm.)	n_D (t, °C.)	Calcd., %			Found, %[a]		
			C	H	X	C	H	X
CH_3	59–59.5 (0.9)	1.5080 (32.0)	72.3	8.3	Cl, 19.4	72.5	8.2	Cl, 19.1
C_2H_5	62–65 (0.7)	1.5012 (32.0)	73.3	8.7	Cl, 18.0	73.2	8.6	Cl, 18.5
i-C_3H_7	67–69 (0.6)	1.4980 (30.1)	74.1	9.1	Cl, 16.8	74.5	9.1	Cl, 16.7
F	46–47 (0.6)	1.4932 (30.3)	64.3	6.5		64.5	6.5	
Cl	67–68.5 (0.7)	1.5274 (29.0)	59.1	6.0	Cl, 34.9	59.4	6.1	Cl, 34.7
Br	78.3–79.6 (0.4)	1.5471 (25.7)	48.5	4.9		48.6	5.0	

[a] The analyses were done by Schwarzkopf Microanalytical Laboratory, 56-19 37th Avenue, Woodside 77, N. Y.

TABLE III

RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE HYDROLYSIS OF *meta*-SUBSTITUTED BENZYLDIMETHYLCARBINYL CHLORIDES IN 80% AQUEOUS ETHANOL

meta substituent	k, sec.$^{-1}$ × 10^5[a]			ΔH,[b,c] kcal. mole^{-1}	ΔS,[b,c] e.u.
	40.5°	50.0°	61.1°		
Br	0.457 ± 0.004	1.36 ± 0.01	5.24 ± 0.05	24.1 ± 0.6	−6.3 ± 1.8
Cl	0.443 ± 0.004	1.55 ± 0.04	5.41 ± 0.02	24.6 ± 0.5	−4.5 ± 1.5
F	0.596 ± 0.011	1.85 ± 0.02	6.41 ± 0.24	23.3 ± 0.1	−8.2 ± 0.1
H	1.35 ± 0.02	3.95 ± 0.09	13.8 ± 0.04	22.9 ± 0.3	−8.1 ± 0.9
Me	1.56 ± 0.04	4.29 ± 0.07	15.9 ± 0.04	22.8 ± 0.8	−8.0 ± 2.4
Et	1.17 ± 0.04	3.03 ± 0.03	10.0 ± 0.02	21.1 ± 0.6	−14.2 ± 1.8
i-Pr	1.26 ± 0.04	3.70 ± 0.03	12.0 ± 0.02	22.2 ± 0.1	−10.4 ± 0.1

[a] Average deviation. [b] Probable error. [c] A. G. Worthing and J. Geffner, "Treatment of Experimental Data," John Wiley and Sons, Inc., New York, N. Y., 1959, Chapter XI.

are new. Their physical properties and analyses are reported in Table II.

Each of the benzyldimethylcarbinyl chlorides hydrolyzed in 80% aqueous ethanol at 40.5, 50.0 and 61.1° by clear-cut first-order kinetics. The chlorides used in these kinetic experiments were prepared and purified immediately before use so that the possibility of their decomposition was eliminated. The absolute rate constants and the activation parameters are shown in Table III.

Discussion

The rates of hydrolysis of all of the benzyldimethylcarbinyl chlorides are significantly lower than that of *t*-butyl chloride. The rate constants of the hydrolysis of *t*-butyl chloride in 80% ethanol over a range of temperatures[11] indicates that at 40.5° *t*-butyl chloride is hydrolyzed about six times as rapidly as benzyldimethylcarbinyl chloride. This is consistent with the positive Hammett σ-constant for m-C_6H_5 and with the generalization that the inductive effect of the phenyl group is one of electron withdrawal.[12] This is also evidence that neighboring aryl group participation is not an important contributing factor in this tertiary halide system. The absence of B-aryl participation was expected on the basis of work of Winstein and coworkers[13] and has been observed experimentally in the solvolysis of the unsubstituted compound[8,9] and the *para*-substituted compounds.[8]

The specific rate constants for the various compounds were reproducible in all cases to within 5% and in most cases to within 2%.

The values of ΔH^* and ΔS^* for the solvolysis of the fluorine, methyl, and unsubstituted compounds are within experimental error of each other. Although the experimental errors is large, the differences in ΔH^* and ΔS^* for the other substituted compounds are much greater and the direction of change of ΔH^* and ΔS^* becomes apparent.

The influence of the inductive effect can be seen by a study of the values of ΔH^*. The compounds with electron-donating ethyl and isopropyl groups should react faster and the compounds with electron-withdrawing bromine and chlorine groups should react slower than the unsubstituted compound. The intervention of a large entropy effect causes a scrambling of the experimental order and produces the unexpected results.

The unusual order of reactivity of the alkyl substituted compounds probably indicates that a steric

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(12) C. K. Ingold, *Chem. Rev.*, **15**, 225 (1934).

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or solvent effect is operating. Arnett and co-workers[14] have recently studied the solvolysis of *t*-butyl chloride in aqueous ethanol and found significant changes in the ground state solvation. As activation parameters for reactions in solution are defined as the differences in enthalpy or entropy between the solvated ground state and solvated transition state, it is difficult to decide how much of the variation of ΔH^* or ΔS^* is caused by changing solvation in the ground state *vs.* changing solvation in the transition state.

One possible explanation for these results is obtained by studying Stuart and Briegleb models of these compounds. The large *meta* substituents come very close to the tertiary chlorine atoms and there might be a dipole–dipole interaction. As solvolysis of the alkyl substituted compounds begins, the favorable dipole–dipole interaction is replaced by a stronger dipole–ion attraction which would lead to a greater restriction to rotation in the transition state and a more negative ΔS^* relative to the unsubstituted compound. The nearness of the alkyl substituent to the leaving chloride ion may produce some steric hindrance to solvation. The greater the extent of steric hindrance to solvation, the higher will be ΔH^* (solvent is not able to stabilize transition state) and ΔS^* (more randomness in solvent due to lack of solvation).[15] The low value of ΔS^*, because of the greater restriction of free rotation in the transition state, will cause the *meta*-ethyl and -isopropyl compounds to react slower than the unsubstituted compound while the solvent effect, which should raise the value of ΔS^* for the isopropyl compound above that of the ethyl, causes the isopropyl compound to react faster than the ethyl compound. This explanation considers only changes in solvation and rotation of the transition state. It should be emphasized that there may be differences in ground state solvation as the structure changes which would greatly complicate the interpretation of the data.

Experimental

***meta*-Substituted Benzyldimethyl Carbinols.**—The *m*-alkyl- and the *m*-halobenzyldimethyl carbinols were all prepared by the general procedure described in detail for *m*-methylbenzyldimethyl carbinol.

A mixture of 100 ml. of dry ether, 13.0 g. (0.535 mole) of magnesium, a crystal of iodine, and 5.0 g. of *m*-methylbenzyl bromide was placed in a flask. After the reaction had begun, 150 ml. of dry ether was added and a solution of 95.0 g. (total of 0.535 mole) of *m*-methylbenzyl bromide in 200 ml. of ether was then added dropwise with vigorous stirring. The solution was then stirred and refluxed for 1.75 hr. and 31.0 g. (0.535 mole) of acetone added dropwise. The mixture was stirred for 3 hr., cooled in an ice bath, and decomposed by the dropwise addition of a saturated ammonium chloride solution. The ether layer was decanted, the ether was removed by distillation, and the organic residue was distilled through a Vigreux column at reduced pressure to yield 56.0 g. (64%) of analytically pure *m*-methylbenzyldimethyl carbinol, b.p. 84–87° (0.5 mm.), $n^{25.7}\text{D}$ 1.5112.

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.4; H, 9.7. Found: C, 80.6; H, 9.5.

***meta*-Substituted Benzyldimethylcarbinyl Chlorides.**—The *m*-alkyl- and *m*-halobenzyldimethylcarbinyl chlorides were prepared by the reaction of the carbinols with hydrogen chloride. The detailed procedure given below for the preparation of *m*-bromobenzyldimethylcarbinyl chloride was used to prepare all of the carbinyl chlorides.

A mixture of 18.4 g. (0.080 mole) of *m*-bromobenzyldimethyl carbinol and 10 ml. of concentrated hydrochloric acid was placed in a flask. Hydrogen chloride gas was bubbled through the mixture for 1 hr. while the material was stirred with a magnetic stirrer. The organic layer was separated and treated for 12 hr. with a mixture of calcium chloride and calcium carbonate. The organic material was filtered and distilled under reduced pressure to yield 13.7 g. (69%) of *m*-bromobenzyldimethylcarbinyl chloride, b.p. 78–82° (0.5–0.6 mm.), $n^{25.7}\text{D}$ 1.5500. In order to remove traces of olefin and carbinol, the carbinyl chloride was washed with several milliliters of ice-cold concentrated sulfuric acid, immediately separated by centrifugation, and placed in a flask containing calcium chloride and calcium carbonate. After drying for 8 hr., it was filtered twice and distilled under reduced pressure to yield 10.4 g. of analytically pure *m*-bromobenzyldimethylcarbinyl chloride, b.p. 78.3–79.6° (0.4 mm.), $n^{25.7}\text{D}$ 1.5471.

Anal. Calcd. for $C_{10}H_{12}BrCl$: C, 48.5; H, 4.9. Found: C, 48.6; H, 5.0.

Kinetic Measurements.—The solvent was prepared by adding distilled water to 1600 ml. of absolute alcohol in a 2-l. volumetric flask at 25.0° until the total volume was 2000 ml. The rate measurements were made by an adoption of the method of Brown and Fletcher.[3] Exactly 100 ml. of solvent was placed in a 250-ml. flask in a constant-temperature bath and kept at the reaction temperature for 1 hr. Then 0.1–1.0 ml. of the *meta*-substituted benzyldimethylcarbinyl chloride was added and the contents of the flask thoroughly mixed. The solvolysis was run at temperatures of 40.5, 50.0 and 61.1°. At given time intervals, 5-ml. aliquot portions of the solution were added to 50 ml. of ice-cold absolute ethanol to quench the solvolysis. The hydrochloric acid produced during the solvolysis was titrated with 0.0136 *N* sodium hydroxide with methyl red as the indicator. The amount of hydrochloric acid produced after the solvolysis was completed was taken as a direct measure of the initial concentration of carbinyl chloride. Each compound was run in triplicate at each temperature as a check of the precision of the results.

Acknowledgment.—We are pleased to acknowledge the generous support of this work by E. I. du Pont de Nemours and Company in the form of a predoctoral teaching fellowship to M. M. T. and also by the University of Kansas General Research Fund. This study was supported in part through an unrestricted grant from the Petroleum Research Fund to the senior author (C. V. W.)

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