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]

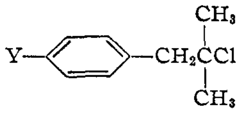
BY ABRAHAM LANDIS AND CALVIN A. VANDERWERF

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.

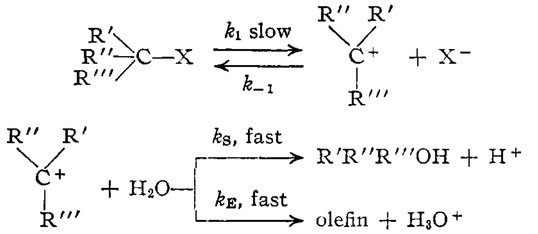
This work was undertaken in an attempt to determine the effect of various alkyl and halogen substituents on the rate of a reaction which proceeds through a carbonium ion intermediate for a system in which the steric effects of the substituents are negligible and in which the electronic effects can be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

TABLE I

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF THE p-SUBSTITUTED BENZYLDIMETHYLCARBINOLS

p-Substituent	B.p. °C.	B.p. Mm.	$n^{30}D$	Yield, %	Analyses, % Calcd. C	Calcd. H	Calcd. Halogen	Found C	Found H	Found Halogen
H	92.5–93[a]	10	1.5105	84	80.0	9.4		80.0	9.5	
Me	86–88	1.0	1.5106	55	80.5	9.8		80.5	9.9	
Et	122–124	15	1.5120	66	80.9	10.2		81.1	10.0	
i-Pr	126.5–127	10	1.5038	64	81.2	10.5		81.2	10.3	
F	87.0–87.5	4	1.4930	58	71.4	7.8	11.3	71.6	7.8	11.0
Cl	126.0–126.2	12	1.5268	63	65.0	7.1		64.9	6.9	
Br	111–115	0.8	1.5499	31	52.4	5.7	34.9	52.6	5.6	34.8

[a] Reported 127–128° (14 mm.),[7a] 109–111° (13 mm.)[7b] and 83–84° (2 mm.).[7b]

TABLE II

PHYSICAL PROPERTIES, YIELDS AND ANALYSES OF THE BENZYLDIMETHYLCARBINYL CHLORIDES

p-Substituent	B.p. °C.	B.p. Mm.	$n^{30}D$	Yield, %	Analyses, % Calcd. C	Calcd. H	Calcd. Cl	Found C	Found H	Found Cl
H	87.0–88.5	10	1.5109	59	71.2	7.8	21.1	71.4	7.9	21.0
Me	104–104.5	10	1.5122	68	72.3	8.3	19.4	72.5	8.3	19.2
Et	89–92	1.1	1.5093	63	73.3	8.7	18.0	73.1	8.5	17.8
i-Pr	86–90	1.0	1.5047	60	74.1	9.1	16.8	74.4	8.9	16.7
F	91–93	10	1.4938	64	64.3	6.5		64.5	6.6	
Cl	95–96	0.8	1.5269	52	59.1	6.0	34.9	59.4	6.1	34.8
Br	99–103	1.0	1.5479	44	48.5	4.9		48.7	4.9	

benzyldimethylcarbinyl chlorides may be considered as vinylogs, have been reported by Brown and Fletcher,[4] and later on the hydrolysis of the homologous alkylphenyldimethylcarbinyl chlorides[5] and halophenyldimethylcarbinyl chlorides[6] by Brown and co-workers.

The rates of hydrolysis of the p-substituted benzyldimethylcarbinyl chlorides were determined in 80% aqueous ethanol at 40.8° from the increase in hydrogen ion concentration as the reaction proceeded. Titration of aliquot portions of the reaction mixture at suitable intervals gives a direct measure of the number of millimoles of chloride hydrolyzed.

Results

A series of p-substituted benzyldimethylcarbinols in which the p-substituents are H, Me, Et, i-Pr, F, Cl and Br, respectively, were synthesized by reaction of the Grignard reagent of the appropriately p-substituted benzyl chloride with acetone and isolated in pure form in yields of 30–80%. Benzyldimethylcarbinol, itself, and p-fluorodimethylbenzylcarbinol also were prepared by reaction of the corresponding phenylacetone with methylmagnesium iodide. With the exception of the parent tertiary carbinol,[7] the compounds are new. Their physical properties, yields and analyses are reported in Table I.

The corresponding benzyldimethylcarbinyl chlorides were synthesized by the action of gaseous hydrogen chloride on the appropriate pure tertiary carbinol. The utmost precautions were required in order to obtain the chlorides in pure form. The procedure which ultimately proved successful involved washing of the product with concentrated sulfuric acid in the cold, immediate separation of layers by means of centrifugation, treatment of the organic layer with calcium carbonate and distillation of the chloride under reduced pressure. The physical properties, yields and analyses of the benzyldimethylcarbinyl chlorides, all new compounds, are reported in Table II.

Hydrolysis of each of the benzyldimethylcarbinyl chlorides in 80% ethanol at 40.8° proceeded by clear-cut first-order kinetics. Both the absolute and relative rate constants are shown in Table III.

TABLE III

RATE DATA FOR THE FIRST-ORDER HYDROLYSIS OF p-SUBSTITUTED BENZYLDIMETHYLCARBINYL CHLORIDES AT 40.8° IN 80% AQUEOUS ETHANOL

p-Substituent	k_1, sec.$^{-1}$ × 10^5	Relative rate
H	1.236	1.00
Me	1.913	1.55
Et	1.727	1.40
i-Pr	1.637	1.32
F	0.992	0.803
Cl	.642	.519
Br	.675	.546

Discussion of Results

First of all, it is noteworthy that the rates of hydrolysis of all of the benzyldimethylcarbinyl chlorides are significantly lower than that of t-butyl chloride. The rate constants for the hydrolysis of t-butyl chloride in 80% ethanol over a range of temperatures[8] indicate that at 40.8° t-butyl chloride is hydrolyzed about six times as rapidly as is benzyldimethylcarbinyl chloride, for example. This is in keeping with the positive Hammett σ-constant for m-C_6H_5 and with the generalization of the English school that the inductive effect of the phenyl group is one of electron

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(4) H. C. Brown and R. S. Fletcher, THIS JOURNAL, **71**, 1845 (1949).

(5) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *ibid.*, **79**, 1897 (1957).

(6) H. C. Brown, Y. Okamoto and G. Ham, *ibid.*, **79**, 1906 (1957).

(7) (a) A. Klages and H. Haehn, *Ber.*, **37**, 1723 (1904); (b) T. A. Zalesskaya, *J. Gen. Chem. (U.S.S.R.)*, **17**, 489 (1947).

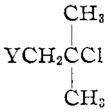
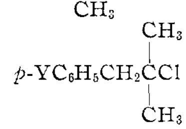
(8) E. D. Hughes, *J. Chem. Soc.*, 255 (1935).

withdrawal.[9] It also indicates that neighboring aryl group participation is not an important contributing factor in this tertiary halide system, as already has been suggested for C_α-tertiary systems in general by the work of Winstein and co-workers.[10] Rigorous studies designed to reveal any possibility of aryl participation in this system are now in progress in these laboratories.

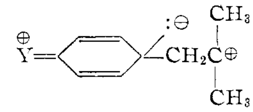
A comparison of the relative rates of hydrolysis of the *p*-alkylbenzyldimethylcarbinyl chloride with those of the simple vinylogous alkyl-substituted *t*-butyl chlorides[4] is striking. As is shown in Table IV, not only are the relative orders of reactivity the same in the two series, but the relative magnitudes as well. The differences in the *p*-alkylbenzyldimethylcarbinyl chloride series are almost certainly attributable to electronic, and not to steric, factors. The data would suggest strongly that the same is true for the corresponding alkyl-substituted *t*-butyl chlorides, which, for the simple compounds under consideration, the original authors[4] had implied to be the case.

TABLE IV

RELATIVE RATES OF HYDROLYSIS OF ALKYL-SUBSTITUTED *t*-BUTYL CHLORIDES AT 25° AND OF *p*-ALKYLBENZYLDIMETHYLCARBINYL CHLORIDES AT 40.8°

Y =	H	Me	Et
 $YCH_2C(CH_3)_2Cl$	1.00	1.67	1.58
 $p\text{-}YC_6H_5CH_2C(CH_3)_2Cl$	1.00	1.55	1.40

The data in Table III afford a convincing argument in favor of the importance of the contribution to the incipient carbonium ion intermediate of resonance structures of the type



Such structures emphasize the effect of Y in bringing about an increase in the electron density at the *p*-position, whence it can be relayed to the reaction site only by induction.[11]

For the *p*-alkylbenzyldimethylcarbinyl chlorides, in which Y = an alkyl group, this effect is, of course, that of hyperconjugation, and the order of relative rates of hydrolysis for these compounds can be explained best on the basis that hyperconjugation is the controlling factor. For series of compounds in which the hyperconjugative effect of the alkyl group can be relayed directly to the reaction center through resonance, the relative order of rates is exactly the same, although, as expected, the magnitudes of the effect are considerably greater. Thus for the hydrolysis of the *p*-alkylbenzhydryl chlorides in 80% aqueous acetone at 25° the relative rates are H (1.00) $<$ Me (21.4) $>$ Et (17.3) $>$ *i*-Pr (13.8).[12] Similarly, for the hydrolysis of the *p*-alkylphenyldimethylcarbinyl chlorides in 80% aqueous acetone at 25°, the relative rates are H (1.00) $<$ Me (26.0) $>$ Et (22.0) $>$ *i*-Pr (18.8).[5] In both cases, the observed order is attributed to hyperconjugative stabilization of the incipient carbonium ion.

For the *p*-halobenzyldimethylcarbinyl chlorides, the rates of hydrolysis are reduced over that of the parent compound, as would be predicted from the inductive effect of the halogens. But once again, the order of rates, this time an irregular one, for the various halogen substituents [H (1.00) $>$ F (0.80) $>$ Cl (0.52) $<$ Br (0.55)], suggests the operation of a small electron-supplying resonance component which here opposes the inductive effect. A similar explanation appears necessary to account for the comparative data dealing with the solvolysis of *p*-chlorobenzyldimethylcarbinyl chloride and chloromethyldimethylcarbinyl chloride (1,2-dichloro-2-methylpropane). As can be seen from Table III, the rate of hydrolysis of *p*-chlorobenzyldimethylcarbinyl chloride, where the resonance effect of the chlorine, which tends to stabilize the incipient carbonium ion, can oppose the destabilizing $-I$ effect, is reduced over that of the unsubstituted compound (Y = H) by less than 50%. On the other hand, for chloromethyldimethylcarbinyl chloride, where only the $-I$ and not the resonance, effect of the chlorine can be operative, the chlorine substituent reduced the rate of hydrolysis to a value 2.53×10^{-4} that of the unsubstituted compound (*t*-butyl chloride).[13]

A plot of the logarithms of the relative rates of hydrolysis of the *p*-substituted benzyldimethylcarbinyl chlorides against the substituent constants (σ-values) of Jaffé[14] gives a fairly good linear relationship (Fig. 1), with a reaction constant, ρ, of 1.11.

Experimental[15]

***p*-Substituted Benzyldimethylcarbinols.**—The *p*-alkyl- and *p*-halobenzyldimethylcarbinols were all prepared by the general procedure described in detail for *p*-isopropylbenzyldimethylcarbinol:

A mixture of 50 ml. of dry ether, 8.6 g. (0.34 mole) of magnesium and 5 g. of *p*-isopropylbenzyl chloride was added to a round-bottomed flask. As soon as a vigorous reaction had begun, 1000 ml. of dry ether was added and 55 additional g. (total of 0.35 mole) of *p*-isopropylbenzyl chloride was added dropwise with vigorous stirring under a nitrogen atmosphere. The mixture was hydrolyzed at ice temperature by the dropwise addition of an ice-cold solution of 17 g. of concentrated sulfuric acid in 300 ml. of water. The organic layer was removed, dried for 12 hr. over anhydrous magnesium sulfate, filtered, the ether removed and the residue distilled under reduced pressure through a 25-cm. Vigreux column to yield 44 g. (64%) of analytically pure *p*-isopropylbenzyldimethylcarbinol, b.p. 126–128° (10 mm.), m.p. 24.4–25.6° (reported[7a] 24°).

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[9] See C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934); and C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 72–73.

[10] S. Winstein and B. K. Morse, THIS JOURNAL, **74**, 1133 (1952); S. Winstein, B. K. Morse, E. Grunwald, K. C. Schreiber and J. Corse, *ibid.*, **74**, 1113 (1952).

[11] A comparable effect was reported for the *m*-alkylphenyldimethylcarbinyl chlorides[5] and the *m*-halophenyldimethylcarbinyl chlorides.[6]

[12] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940); see also the interesting work of V. J. Shiner, Jr., and C. J. Verbanic, THIS JOURNAL, **79**, 369 (1957).

[13] H. C. Brown, M. S. Kharasch and T. H. Chao, THIS JOURNAL, **62**, 3435 (1940).

[14] H. H. Jaffé, *Chem. Revs.*, **53**, 191 (1953).

[15] Boiling points uncorrected. Analyses by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

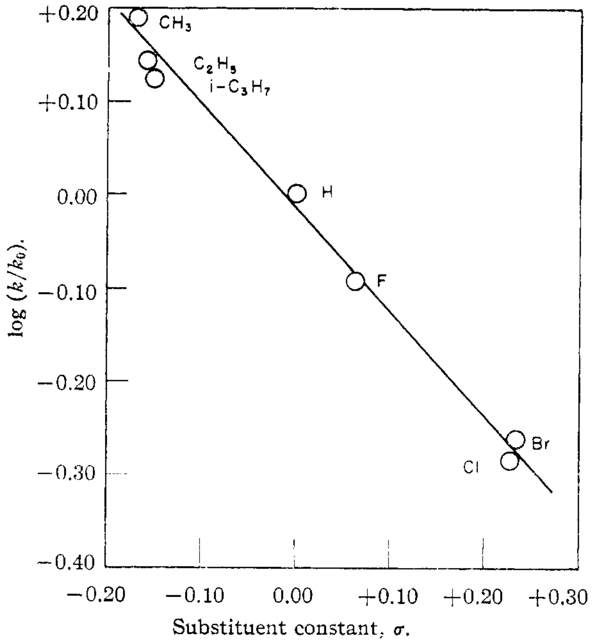

Fig. 1.—Hydrolysis of *p*-substituted benzyldimethylcarbinyl chlorides at 40.8°.

Benzyldimethylcarbinol and *p*-fluorobenzyldimethylcarbinol also were prepared by reaction of the appropriately substituted phenylacetone with methylmagnesium iodide, as described in detail for the former compound.

Approximately 250 ml. of dry ether, 30.7 g. (1.26 moles) of magnesium and 10 g. of methyl iodide were placed in a dry flask. After a vigorous reaction had begun, 750 ml. of ether was first added and then 169.2 g. (total of 1.26 moles) of methyl iodide was added dropwise with vigorous stirring under a nitrogen atmosphere. After all the methyl iodide had been added, the mixture was stirred for 2.5 hr. Then 154 g. (1.15 moles) of phenylacetone was added dropwise and the mixture stirred for an additional 30 minutes. Hydrolysis was effected by the addition of an ice-cold solution containing 58 g. of concentrated sulfuric acid in 500 ml. of water. The organic layer was separated, washed with 100 ml. of 5% sodium thiosulfate solution to remove free iodine, and dried over magnesium sulfate. The ether was removed and the residue distilled under reduced pressure through a 25-cm. Vigreux column to afford 145 g. (84.0%) of benzyldimethylcarbinol, b.p. 94–96° (10 mm.), $n^{30}\text{D}$ 1.5102.

***p*-Substituted Benzyldimethylcarbinyl Chlorides.**—The *p*-alkyl- and halobenzyldimethylcarbinyl chlorides were prepared by treatment of the corresponding carbinol with hydrogen chloride according to a procedure of which the synthesis of benzyldimethylcarbinyl chloride is typical.

Gaseous hydrogen chloride was bubbled into an ice-cooled mixture of 82 g. of benzyldimethylcarbinol and 25 ml. of concentrated hydrochloric acid at 0° for 15 minutes and finally for 30 minutes at room temperature. The lower aqueous layer was removed and the crude chloride was treated for 12 hr. with a mixture of powdered calcium carbonate and anhydrous sodium sulfate. Distillation of the decantate through a 25-cm. Vigreux column under reduced pressure afforded 54 g. (59%) of benzyldimethylcarbinyl chloride, b.p. 88–92° (10 mm.). The product was further purified by washing with cold concentrated sulfuric acid, the acid layer separated by centrifugation and the organic layer immediately treated with powdered calcium carbonate for 12 hr. The decantate was distilled under reduced pressure to yield 49 g. of analytically pure benzyldimethylcarbinyl chloride, b.p. 88–90° (10 mm.).

Kinetic Measurements.—The rate measurements were made by an adaptation of the method of Brown and Fletcher.[4] The solvent was prepared by the addition of sufficient water to 800 ml. of absolute ethanol at 25° to bring the total volume to 1000 ml. The solvent, 100 ml., was placed in a long necked flask and brought to reaction temperature (40.8 ± 0.02°) in a constant temperature bath. Approximately 3 ml. of the benzyldimethylcarbinyl chloride was added with thorough mixing. At definite time intervals, 5-ml. aliquot portions of the solution were added to 50 ml. of absolute ethanol at 0° in order to quench the solvolysis. The hydrochloric acid formed was determined by titration against 0.04 *N* sodium hydroxide solution with methyl red as the indicator. The original concentration of the halide was determined by allowing the reaction mixture to stand for at least ten times the measured half-life of the chloride being solvolyzed to provide an aliquot for the infinity titer. Each determination was run at least four times as a check of the precision of the results.

Determination of the Rate Data.—The first-order rate constants were obtained by a plot of lot $(a - x)$ *vs.* t, where a is the original concentration of the alkyl chloride and $(a - x)$ is the concentration of the unhydrolyzed chloride at time t, in hours. For a first-order reaction of this type, the concentrations may be expressed conveniently in terms of the ml. of the standard sodium hydroxide solution required for the titration of the 5-ml. aliquots of the reaction mixture. In all cases, the hydrolyses of the benzyldimethylcarbinyl chlorides showed excellent first-order kinetics. The specific rate constant in all cases agreed to within 4% and in most cases to within 2%. Experimental data for a typical run are shown in Table V.

TABLE V

RATE DATA FOR THE HYDROLYSIS OF *p*-FLUOROBENZYLDIMETHYLCARBINYL CHLORIDE IN 80% ETHANOL AT 40.8°

Time, hr.	x, ml.	$(a - x)$, ml.	log $(a - x)$
0.00	0.00	21.06	1.323
2.00	1.53	19.53	1.291
5.00	3.52	17.54	1.244
8.32	5.48	13.61	1.134
12.32	7.45	13.61	1.134
16.18	9.22	11.84	1.073
25.47	12.45	8.61	0.935
26.63	13.00	8.06	0.906

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LAWRENCE, KANSAS