

The salts, separated by centrifugation, when decomposed with water and acid produced 2.57 g. (34.5%), b.p. 85–90° (2 mm.), of α -hydroxyisobutyrophenone.

3-*sec*-Butoxy-3-phenyl-2-butanone was converted to the semicarbazone in 69% yield, m.p. 184–185°.

Anal. Calcd. for $C_{15}H_{23}N_3O_2$: C, 64.95; H, 8.36; N, 15.15; O, 11.54. Found: C, 65.08; H, 8.54; N, 15.12; O, 11.62.

The oxime was made from 0.2 g. (0.9 mm.) of ketone. The yield was 0.26 g. (72%) of crude material, m.p. 118–123°. Recrystallization from hexane gave an analytical sample, m.p. 123–125°.

Anal. Calcd. for $C_{20}H_{24}N_2O_2$: C, 59.99; H, 6.04; N, 13.99; O, 19.98. Found: C, 59.92; H, 5.96; N, 13.73; O, 19.68.

Beckmann Rearrangement of 3-*sec*-Butoxy-3-phenyl-2-butanone Oxime.—A mixture of 0.5 g. (2.3 millimoles) of 3-butoxy-3-phenylbutanone, 0.4 g. (5.75 mmoles) of hydroxylamine hydrochloride and 5 ml. of pyridine was allowed to stand overnight at room temperature then heated for two hours on the steam-bath. The pyridine was then removed *via* the vacuum pump and the residue treated with water. The oxime was subjected to the second-order Beckmann re-

action according to the method of Buck and Ide.¹³ The solid oxime from 0.5 g. of ketone was placed in 8 ml. of 10% sodium hydroxide solution and 0.69 ml. of benzenesulfonyl chloride added in two equal portions with shaking. The solid disappeared leaving an oil and when the odor of benzenesulfonyl chloride disappeared (approximately 30 minutes) the basic solution was extracted twice with 15-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate, filtered and evaporated to dryness. The residual oil was converted to the 2,4-dinitrophenylhydrazone derivative and 0.47 g. (68%), m.p. 240–244°, of product was obtained. The material was recrystallized from chloroform, m.p. 244–245°. A mixture melting point with authentic acetophenone 2,4-dinitrophenylhydrazone was not depressed.

Acknowledgment.—The authors wish to thank Dr. J. M. Vandenberg and associates of Parke, Davis and Co. for the spectral data published here and C. E. Childs and associates of the same company for the analytical determinations.

DETROIT 2, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

The Inductive Effects of Alkyl Groups as Determined by Desilylation Reactions

BY ROBERT A. BENKESER, RICHARD A. HICKNER AND DONALD I. HOKE

RECEIVED OCTOBER 7, 1957

It has been found that the rates of desilylation of trimethyl- and triethylphenylsilanes substituted in the *m*-position with alkyl groups increase in the order $H < Me < Et < i\text{-}Pr < t\text{-}Bu$. This is contrary to the decrease in rate for this series which is observed in the solvolysis of *m*-alkylphenyldimethylcarbinyl chlorides. It is rationalized that, at least in this instance, the desilylation reactions more closely approximate conditions realized in true aromatic substitutions. The carbinyl chloride series is apparently complicated in the present instance by unusual hyperconjugative or steric effects.

It is generally accepted that the inductive effect of alkyl groups increases moderately in the order $Me < Et < i\text{-}Pr < t\text{-}Bu$.¹ Likewise these same groups are thought to contribute hyperconjugative effects which tend to increase in the series $t\text{-}Bu < i\text{-}Pr < Et < Me$.^{2a,b}

Recently Professor Brown and co-workers³ have demonstrated that the electrical effects of alkyl groups can be studied conveniently by measuring the solvolysis rates of various alkyl substituted phenyldimethylcarbinyl chlorides in 90% aqueous acetone. Their results generally bear out the sequence shown above for the hyperconjugative series. Rather unexpectedly these authors noted, however, that the rates of solvolysis of the *m*-substituted alkylphenyldimethylcarbinyl chlorides *decrease* in the order $Me > Et > i\text{-}Pr > t\text{-}Bu$ (Fig. 1.) This is just opposite to the gradual *increase* in rate one would predict for this series from a consideration of the inductive effects of the alkyl substituents. They³ explain this anomaly in terms of a hyperconjugative effect in the *o*-position which is relayed to the reaction site by an inductive or field effect.

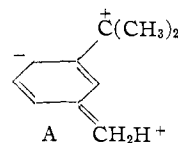
It should be noted that these results also can be explained in terms of a "normal inductive effect"

(1) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

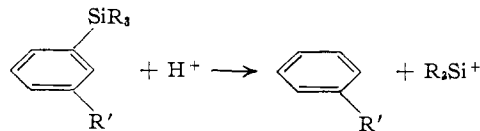
(2) (a) E. D. Hughes, C. K. Ingold and N. Taher, *J. Chem. Soc.*, 949 (1940); (b) J. W. Baker, "Hyperconjugation," Oxford University Press, New York, N. Y., 1952.

(3) H. C. Brown, J. D. Brady, M. Grayson and W. H. Bonner, *THIS JOURNAL*, **79**, 1897 (1957).

counterbalanced by steric hindrance to solvation of the ring *ortho* to the alkyl substituents as suggested by Schubert and co-workers.⁴



Recently⁵ it was demonstrated in this Laboratory that the removal of a trimethylsilyl group (desilylation) from an aromatic ring by acid is a reliable and convenient tool for studying electrical effects at a particular position in a benzene ring.



It was decided therefore, to study the rate of removal of the trimethylsilyl group from various *m*-substituted alkylphenyltrimethylsilanes to determine whether the same unexpected decreases in rate would be obtained as were found in the carbinyl chloride series. As an added check on the method, the rates of cleavage of the triethylsilyl series were also determined.

(4) W. A. Sweeney and W. M. Schubert, *ibid.*, **76**, 4625 (1954); **79**, 910 (1957); see also *J. Org. Chem.*, **21**, 119 (1956).

(5) R. A. Benkeser and H. R. Krysiak, *THIS JOURNAL*, **76**, 6353 (1954); see also C. Eaborn, *J. Chem. Soc.*, 4858 (1956).

TABLE I

Compound (R = Me ₃ Si-)	<i>m</i> -ALKYLPHENYLTRIMETHYLSILANES							
	<i>n</i> ²⁰ _D	<i>d</i> ²⁰ ₄	°C. B.p., Mm.	<i>MR</i> ^a	Carbon, ^a %	Hydrogen, ^a %	Yield, %	
R-Benzene	1.4910 ^b	169 ^b	65	
<i>m</i> -R-Toluene	1.4924 ^c	190 ^c	55	
<i>m</i> -R-Ethylbenzene	1.4924	0.8645	206-207	59.88 (60.36)	73.96 (74.08)	9.96 (10.17)	50	
<i>m</i> -R- <i>i</i> -Propylbenzene	1.4894	.8597	94	14 64.62 (64.03)	74.80 (74.89)	10.58 (10.48)	75	
<i>m</i> -R- <i>t</i> -Butylbenzene	1.4884	.8617	82	6 69.05 (68.66)	75.47 (75.63)	10.66 (10.75)	55	

^a The value in parentheses is the calculated value. ^b Reported b.p. 169°, *n*²⁰_D 1.4908; R. A. Benkeser and P. E. Brumfield, *THIS JOURNAL*, **73**, 4770 (1951). ^c Reported b.p. 189°, *n*²⁰_D 1.4922; H. A. Clark, A. F. Gordon, C. W. Young and M. J. Hunter, *THIS JOURNAL*, **73**, 3798 (1951).

TABLE II

Compound (R = Et ₃ Si-)	<i>m</i> -ALKYLPHENYLTRIETHYLSILANES							
	<i>n</i> ²⁰ _D	<i>d</i> ²⁰ ₄	°C. B.p., Mm.	<i>MR</i> ^a	Carbon, ^a %	Hydrogen, ^a %	Yield, %	
<i>m</i> -R-Toluene	1.5022 ^b	123	11	24	
<i>m</i> -R-Ethylbenzene	1.5015	0.8833	125	9	73.58 (73.29)	76.12 (76.28)	10.95 (10.97)	
<i>m</i> -R- <i>i</i> -Propylbenzene	1.4972	.8902	131	9	78.03 (78.02)	76.80 (76.84)	11.02 (11.18)	
<i>m</i> -R- <i>t</i> -Butylbenzene	1.4956	.8747	145	11	82.93 (82.55)	77.27 (77.33)	11.02 (11.36)	

^a The value in the parentheses is the calculated value. ^b Reported *n*²⁰_D 1.5030; R. A. Benkeser and H. Landesman, *THIS JOURNAL*, **76**, 904 (1954).

The desilylation reactions were accomplished in a cleaving medium of glacial acetic acid which was 2.35 molar in hydrogen chloride and 7.23 molar in

rate of cleavage *increases* as the inductive effect (+I) of the alkyl group increases.

It is not unexpected that the rates of cleavage of the triethylsilyl group are generally slower than

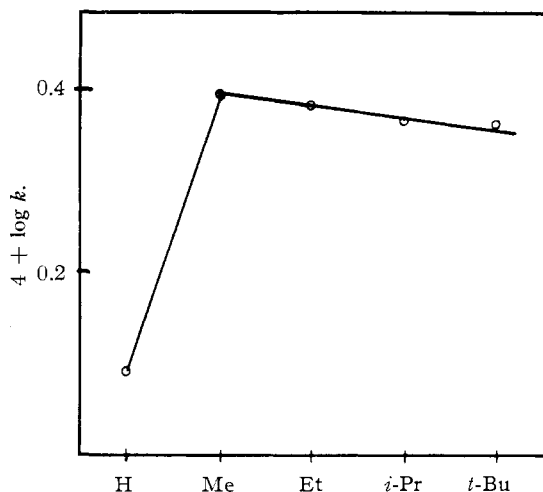


Fig. 1.—Effect of alkyl substituents upon the rates of solvolysis of the alkylphenyldimethylcarbinyl chlorides in 90% aqueous acetone at 25°.

water at 25°. The rates were followed by volume expansion employing dilatometers.⁵ The results are listed in Tables III and IV and are plotted in Fig. 2.

Results and Discussion

It is apparent from Fig. 2 that, contrary to the results obtained in the solvolysis of the tertiary carbinyl chlorides, the rates of cleavage of the trialkylsilyl groups *increase* in a fashion which is completely predictable in terms of the inductive effects of the substituent alkyl group. Thus, the

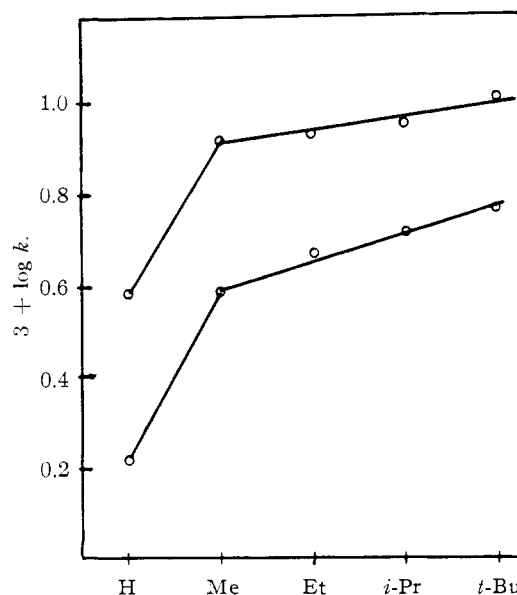


Fig. 2.—Effect of alkyl substituents upon the rates of acid-catalyzed cleavage of trialkylsilylalkylbenzenes by 2.35 *M* hydrochloric acid in glacial acetic acid containing 7.23 *M* water at 25°: top curve, Me₃Si-series; lower curve, Et₃Si-series.

for the trimethylsilyl group. From a steric standpoint it would be predicted that both the proton attack on the carbon atom holding the silicon, as well as the attack of water molecules on the silicon

TABLE III

RATE CONSTANTS AND HALF-LIVES FOR THE ACID-CATALYZED CLEAVAGE OF SOME *m*-TRIMETHYLSILYLALKYLBENZENES IN A GLACIAL ACETIC ACID SOLUTION (2.35 MOLAR IN HYDROGEN CHLORIDE AND 7.23 MOLAR IN WATER AT 25°)

Me ₃ SiC ₆ H ₄ R- (<i>m</i>) R group	Rate constant × 10 ³ , min. ⁻¹	Average	Half-life, min.
H	3.80, 3.85, 3.86	3.84	181
CH ₃	8.48, 8.10, 8.35	8.31	83
C ₂ H ₅	8.56, 8.40, 8.67	8.54	81
<i>i</i> -C ₃ H ₇	9.07, 9.36, 8.83	9.08	71
<i>t</i> -C ₄ H ₉	11.0, 10.6	10.8	64

TABLE IV

RATE CONSTANTS AND HALF-LIVES FOR THE ACID-CATALYZED CLEAVAGE OF SOME *m*-TRIETHYLSILYLALKYLBENZENES IN A GLACIAL ACETIC ACID SOLUTION (2.35 MOLAR IN HYDROGEN CHLORIDE AND 7.23 MOLAR IN WATER AT 25°)

Et ₃ SiC ₆ H ₄ R(<i>m</i>) R group	Rate constant × 10 ³ , min. ⁻¹	Average	Half-life, min.
H	1.66, 1.62	1.64	422
CH ₃	3.82, 3.91	3.87	179
C ₂ H ₅	4.73, 4.65	4.69	148
<i>i</i> -C ₃ H ₇	5.18, 5.09	5.14	135
<i>t</i> -C ₄ H ₉	5.84, 5.95	5.90	117

atom⁶ would be rendered slower by the bulkier ethyl groups. Further evidence bearing on this point will be offered in a forthcoming paper.

It is interesting to speculate on the reason for the opposite trends shown in Figs. 1 and 2. This is especially true since both desilylation and carbonyl chloride solvolysis have been put forth^{3,5} as reliable methods for determining electrical effects in a ring position.

Considerable work has been accumulated to date which shows that hyperconjugative effects of alkyl groups become most apparent in electron deficient systems, *i.e.*, those systems which involve carbonium ions. Thus Norris and Banta⁷ observed that the rate of solvolysis of *p*-methylbenzhydryl chloride is eight times faster than that of the *m*-isomer. Likewise *p*-methylphenyldimethylcarbinyl chloride is solvolyzed thirteen times faster than the *m*-isomer. Obviously the *p*-methyl group in these cases is very effective in stabilizing the carbonium ion transition state through hyperconjugation. On the other hand, the hyperconjugative effects



are scarcely detectable in systems not electronically deficient. Thus the ionization constants for *m*- and *p*-methylanilines and benzoic acids are not greatly different.⁸

The mechanism of both the carbonyl chloride solvolysis and the desilylation reaction involves the generation of a positive charge. However, it is conceivable that the electronic demands of the carbonium ion in the former case (S_N1 mechanism) may be so great as to call into play the hyperconjugative effects of the alkyl groups, even though the latter are in a *m*-position to the reaction site (for-

mula A). On the other hand, the electronic demands of the desilylation system may never attain this intensity, and hence hyperconjugative effects of the alkyl groups are not called into play. In these cases the reaction rate would be governed only by the inductive effect of the alkyl group.

The observed results also may be explained in terms of a buttressing effect.⁹ A large group substituted on the benzene ring probably distorts the C-H bonds of the *o*-hydrogens. Another large group *meta* to the first would increase the distortion of the C-H bond between the two large groups. Thus, the larger the *m*-substituents the greater would be the strain due to this buttressing effect. Such an effect would account for the difference in slope of the trimethylsilyl- and triethylsilylalkylbenzenes illustrated in Fig. 2 since the relief of strain in the triethyl series would be greater than for the trimethyl case and hence the rate of cleavage would be more rapid in the former. This same effect would tend to hinder the formation of a coplanar system in the solvolysis of the aryldimethylcarbinyl chlorides. Coplanarity of this system is required for resonance stabilization of the carbonium ion. The attainment of this requirement would be increasingly more difficult as the size of the group in the *m*-position increased, and thus the rates of solvolysis would decrease in the order Me > Et > *i*-Pr > *t*-Bu as observed by Brown and co-workers.^{3,9}

Another possible explanation for the opposite trends of these two reactions is that solvation is more important in the solvolysis of the carbonyl chlorides than in the desilylation reactions. According to the qualitative theory of solvent effects of Hughes and Ingold¹⁰ an increase in the ion solvating power of the medium will accelerate the formation, and inhibit the destruction of charges. Thus a reaction incapable of forming a charged species should be little affected by the solvent. If one envisions the desilylation reaction to be a concerted process, a charge such as that present in a carbonium ion is not developed. In the case of the carbonyl chlorides solvation becomes very important in the formation and stabilization of the carbonium ion. Any factor which interferes with this solvation probably would cause a decrease in the rate of reaction. Conceivably an increase in the size of the groups in the *m*-position could hinder the solvation of the carbonium ion and thus give rise to the "bulk effect" suggested by Price and Lincoln.¹¹

An additional factor which should be given consideration is the nature of the solvent. Shiner and Verbanic¹² have shown recently that the solvolysis of *m*-alkylbenzhydryl chlorides shows a marked dependence upon the composition of the solvent. A change in solvent from "80%" acetone to "90%" alcohol resulted in a reversal of reactivity of the *m*-methyl and *m*-*t*-butyl compound. This effect may be due, as suggested by Shiner and Verbanic, to solvent enhancement of hyperconjugation in the

(6) See C. Eaborn, *J. Chem. Soc.*, 3148 (1953), where a proposed mechanism for these acid cleavages is put forth.

(7) J. F. Norris and C. Banta, *THIS JOURNAL*, **50**, 1804 (1928).

(8) *pK_a*, 25°: *m*-toluic acid, 4.28; *p*-toluic acid, 4.35; *pK_b*, 25°: *m*-methylaniline, 9.30; *p*-methylaniline, 9.70.

(9) Professor H. C. Brown, in a private communication, suggested this explanation to us.

(10) E. D. Hughes and C. K. Ingold, *J. Chem. Soc.*, 244 (1935).

(11) C. C. Price and D. C. Lincoln, *THIS JOURNAL*, **73**, 5836 (1951).

(12) V. J. Shiner and C. J. Verbanic, *ibid.*, **79**, 369 (1957).

less hindered groups or to steric inhibition of solvation in the transition state.

It would not seem unlikely that other instances will be found in which there are discrepancies in the results obtained from two such vastly different approaches to electrical effects in an aromatic system. In the present instance, at least, the desilylation reaction more closely approximates conditions which maintain during aromatic substitution than do the solvolysis reactions.

Experimental

Triethylphenylsilane was prepared according to the directions of Bygden^{13a}; a yield of 51% was obtained, b.p. 105° (9 mm.), n_D^{20} 1.5024 (reported^{13b} n_D^{20} 1.5024).

Triethylchlorosilane.—Ethylmagnesium bromide was prepared from 109 g. (1 mole) of ethyl bromide and 26 g. (1.1 g. atoms) of magnesium turnings in 250 ml. of anhydrous ether under an atmosphere of dry nitrogen. The mixture was filtered and added, with stirring, to a solution of 157 g. (1 mole) of diethyldichlorosilane (redistilled, b. 128°) in 250 ml. of anhydrous ether. When Color Test I¹⁴ was negative, the solid which had formed was filtered and washed with anhydrous ether. The filtrate was distilled through a Widmer column. There was obtained 89 g. (59%) of material boiling continuously from 137 to 149°. All the fractions in this range had the same refractive index (n_D^{20} 1.4340) (reported¹⁵ n_D^{20} 1.4320).

***m*-Bromoacetophenone** was prepared according to the directions of Pearson and Popel¹⁶; yield 79%, b.p. 96–97° (4 mm.), n_D^{20} 1.5759 (reported¹⁶ n_D^{20} 1.5740).

***m*-Bromoethylbenzene** was prepared according to the directions of Pope and Bogert¹⁷; yield 61%, b.p. 91° (20 mm.) (reported¹⁷ b.p. 88–90° (20 mm.)).

***m*-Chlorophenyldimethylcarbinol**.—*m*-Chlorophenylmagnesium bromide was prepared from 7.3 g. (0.3 g. atom) of magnesium turnings in 50 ml. of ether and 57.5 g. (0.3 mole) of 1-bromo-3-chlorobenzene (Eastman Kodak Co.) in 150 ml. of anhydrous ether. Acetone (17.4 g., 0.3 mole) was added at such a rate as to maintain gentle reflux. The mixture was stirred for an additional 15 minutes at room temperature. It was then hydrolyzed by pouring onto clipped ice. The ether layer was separated, dried with magnesium sulfate, and distilled through a Vigreux column. There was obtained 34.8 g. (68%) of carbinol boiling at 86–88° (2.5 mm.), n_D^{20} 1.5380.

Anal. Calcd. for C₉H₁₁ClO: C, 63.40; H, 6.46. Found: C, 63.68; H, 6.49.

α -Methyl-*m*-chlorostyrene.—*m*-Chlorophenyldimethylcarbinol (51 g., 0.3 mole), 2 g. of fused potassium bisulfate and 0.5 g. of hydroquinone were heated in a Claisen flask fitted for distillation. The product distilled from the reaction mixture at 125–130° (95 mm.) over about a 40-minute period. The distillate was dissolved in ether and the ether solution washed twice with 5% sodium hydroxide and twice with water. It was then dried over anhydrous magnesium sulfate and distilled through a 12-inch Vigreux column to give 29 g. (72%) of material boiling at 60–62° (4 mm.), n_D^{20} 1.5536, and 6.4 g. of crude starting material.

Anal. Calcd. for C₉H₉Cl: C, 70.83; H, 5.95. Found: C, 70.94; H, 6.35.

***m*-Chloroisopropylbenzene**.—A Parr hydrogenator was charged with 35.8 g. (0.24 mole) of α -methyl-*m*-chlorostyrene, 50 ml. of absolute ethanol and 0.3 g. of 10% platinum-

on-charcoal. The theoretical amount of hydrogen was absorbed in about two hours from an initial pressure of 55 p.s.i. The catalyst was filtered off and the ethanol distilled. Distillation of the product through a 12-inch Vigreux column gave 24.8 g. (70%) of product boiling at 66–68° (8 mm.), n_D^{20} 1.5136.

Anal. Calcd. for C₉H₁₁Cl: C, 69.92; H, 7.17. Found: C, 69.62; H, 7.35.

***m*-Chloro-*t*-butylbenzene**.—*p*-*t*-Butylacetanilide was prepared according to the directions of Herstein.¹⁸ This was converted to *m*-chloro-*t*-butylbenzene by the method of Capon and Chapman.¹⁹ The over-all yield based on acetanilide was 20%. The product, when distilled through a Todd continuous wire spiral column, boiled at 88° (11 mm.), n_D^{20} 1.5127 (n_D^{20} 1.5125 after distillation through a Podbielniak column²⁰).

***m*-Trialkylsilylalkylbenzenes** were prepared by the following general method. A solution of 0.1 mole of *m*-chloro- or *m*-bromoalkylbenzene and 0.1 mole of trimethylchlorosilane or triethylchlorosilane in 50 ml. of anhydrous ether was added over a 15-minute period to a well-stirred suspension of 6.5 g. (0.28 g. atom) of sodium sand in 50 ml. of anhydrous ether under dry nitrogen. The mixture was stirred and refluxed until most of the sodium had reacted. The mixtures were various shades of blue at this point. Hydrolysis was accomplished by cooling the mixture in an ice-bath and adding 100 ml. of cold water dropwise. The ether layer was separated, dried with Drierite, and distilled through a Todd continuous wire spiral column.

The data for the preparation of the *m*-trimethylsilylalkylbenzenes are summarized in Table I. The data for the preparation of the *m*-triethylsilylalkylbenzenes are summarized in Table II.

Purification of Materials.—Glacial acetic acid was purified by distillation from a mixture of glacial acetic acid, the calculated amount of acetic anhydride and a small amount of potassium permanganate.

The hydrochloric acid was the Baker and Adamson C.P. product, 37–38% HCl, used without further purification since the listed impurities were negligible.

Thermostat and dilatometers in this study were described in a previous paper from this Laboratory.⁵

General Kinetic Procedure.—A stock solution of aqueous hydrochloric acid in glacial acetic acid was made to such a concentration that a 15-ml. aliquot when diluted to 50 ml. would give a cleaving medium of the desired concentration.

For the rate determinations an aliquot of stock solution was diluted to about 35 ml. and allowed to stand overnight. At zero time this solution was added to the silane (0.3 g.-0.5 g.) contained in a 50-ml. volumetric flask suspended in the constant temperature bath. The volume was made up to the mark with glacial acetic acid. The flask was removed from the bath, stoppered, and shaken vigorously. The solution was transferred rapidly by suction to the dilatometer. Readings of meniscus height were recorded with the aid of a cathetometer which could be read to 0.01 cm. All runs exhibited an expansion in volume on cleavage, the increase in meniscus height amounting to 1–2 cm.

Rate constants (pseudo first order) were determined graphically from a plot of constant + log ($l_\infty - l_t$) against time, t , in minutes (l is the meniscus height). The slope of this plot is $-k/2.303$ where k is the pseudo first order-rate constant. The rate constants and half-lives are given in Tables III and IV.

Acknowledgment.—The authors are grateful to the National Science Foundation whose financial assistance made this research possible.

LAFAYETTE, IND.

(13) (a) A. Bygden, *Ber.*, **45**, 711 (1912); (b) H. Gilman, R. K. Ingham and A. G. Smith, *J. Org. Chem.*, **18**, 1743 (1953).

(14) H. Gilman and F. Schultz, *THIS JOURNAL*, **47**, 2002 (1925).

(15) J. W. Jenkins and H. W. Post, *J. Org. Chem.*, **15**, 556 (1950).

(16) D. E. Pearson and H. W. Pope, *ibid.*, **21**, 381 (1956).

(17) G. W. Pope and M. T. Bogert, *ibid.*, **2**, 276 (1937).

(18) B. Herstein, U. S. Patent 2,092,972 (1936).

(19) B. Capon and N. B. Chapman, *J. Chem. Soc.*, 601 (1957).

(20) H. C. Brown and L. Stock, unpublished work.