[CONTRIBUTION FROM THE CHEMICAL DEPARTMENT OF PURDUE UNIVERSITY, LAFAYETTE, IND.]

The Electrical Effects of Alkyl Groups. The Acid Cleavage of *m*-Alkylphenyltriisopropylsilanes

BY ROBERT A. BENKESER AND FRANK S. CLARK

RECEIVED FEBRUARY 1, 1960

The rates of cleavage by acid of the triisopropylsilyl group from a series of *m*-alkylphenyltriisopropylsilanes [m-$RC_6H_4Si(i\text{-}C_3H_7)_3$] were measured. The rates were found to increase gradually, and in a regular fashion, as the *m*-alkyl group was made to vary from methyl, to ethyl, isopropyl and *t*-butyl. This is explained in terms of an increasing inductive effect of the alkyl group. Solvation effects in the detriisopropylsilylation reaction are shown to be relatively unimportant. The rate relationships which exist in the desilylations of trimethyl-, triethyl- and triisopropylsilyl compounds are explained in terms of a variation in transition states in this series. Since the *m*-alkyl groups have a greater influence on the rates of cleavage in the triisopropylsilyl series, the "selectivity" of these three reactions is shown to decrease in the order $(i\text{-}C_3H_7)_3Si- > (C_2H_5)_3Si- > (CH_3)_3Si-$. Hence, the recently developed concept of Selectivity Factors is shown to depend, not only on the activity of the attacking species, but upon the nature of the leaving group as well.

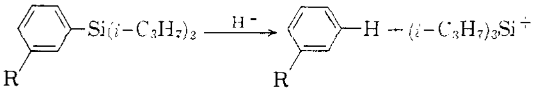
There are contradictory views regarding the electrical effects of alkyl groups on an aromatic ring. Data on the electronic transitions of *p*-alkylnitrobenzenes and *p*-alkylacetophenones in the gas phase have been presented as evidence that stabilization of the electron-demanding excited state takes an inductive order: *t*-Bu > Et > CH_3.[1] In contrast, spectral data on alkyl and chloroalkyl groups have been quantitatively correlated with enhanced resonance interactions in the excited state.[2]

Likewise, anomalies have occurred in kinetic results. *m*-Alkyl substituents give a hyperconjugative order in the solvolysis of phenyldimethylcarbinyl chlorides in 90% acetone,[3] but an inductive order is observed in the desilylation of trimethyl- and triethylsilanes.[4]

Explanations which have been advanced to explain these divergent results include: (1) the greater electrical demands of the carbinyl ion necessitating hyperconjugative stabilization from the *m*-substituents in the system[3]; (2) buttressing effects by the *m*-alkyl groups[4]; (3) the existence of a "bulk effect"[5] or steric hindrance to solvation in the proximity of the alkyl substituents in the carbinyl system[1,6]; (4) other solvent effects, such as solvent enhancement of hyperconjugation.[7]

Important solvent effects undoubtedly do occur in the carbinyl chloride system, since the *m*-alkyl hyperconjugative order can be inverted to the inductive order by a change in solvent from 90% acetone to ethanol.[8]

In an attempt to ascertain which of these explanations was correct, the detriisopropylsilylation of *m*-alkylphenylsilanes was studied (see equation 1). Unfortunately, because of their insolubility, these compounds could not be cleaved in the hydrochloric acid–acetic acid media used on the trimethyl- and triethylsilanes. A sulfuric acid–acetic acid cleaving system was employed. The kinetic results are shown in Table I and a plot of the rate constant *versus* the *m*-substituent is shown in Fig. 1.



(I)

R = Me, Et, *i*-Pr, *t*-Bu

TABLE I

RATE CONSTANTS FOR THE ACID CLEAVAGE OF *m*-ALKYLPHENYLTRIISOPROPYLSILANES

m-Alkyl group R	[m-$RC_6H_4Si(i\text{-}C_3H_7)_3$] Rate constant × 10^3, min.$^{-1}$ (25°)	Average rate[a] constant
H	0.176; 0.122; 0.134; 0.183	0.154
CH_3	0.856; 0.784; 0.861	.834
C_2H_5	1.01; 0.97	.99
i-C_3H_7	1.21; 1.23	1.22
t-C_4H_9	1.42; 1.43	1.43

[a] The cleaving medium was glacial acetic acid which was 1.78 molar in hydrogen sulfate and 0.44 molar in water. The rates are pseudo first order in silane. Approximately 0.3-g. samples of the silane were used in each determination.

It will be noted that the triisopropylsilyl group is cleaved considerably more slowly than the triethylsilyl group,[4] which in turn is cleaved more slowly than the trimethylsilyl group.[9] This trend is completely predictable in terms of steric hindrance to the attack of a hydronium ion on the ring carbon atom to which the silicon is attached. It should also be noted that the slope of the plot in Fig. 1 is greater than the slope of the corresponding plots for the trimethyl- and triethylphenylsilanes (compare Fig. 2).

The rate data in Table I rather clearly indicate that there can be little significant steric hindrance to solvation in the deisopropylsilylation reaction (eq. I). If such steric hindrance did exist, one would predict a non-linearity for the cleavage rates. At least the rate for the *m*-*t*-butyl group should be slower than that predicted by a straight line relationship. One might even be led to predict an inversion of rates for the alkyl groups (*i.e.*, a hyperconjugative order) which obviously is not the case. For these two reasons there seems to be little likelihood of important "solvation effects" in this system.

---

(1) W. M. Schubert, J. M. Craven, R. G. Minton and R. B. Murphy, *Tetrahedron*, **5**, 194 (1959).

(2) (a) R. W. Taft, Jr., and I. C. Lewis, *ibid.*, **5**, 226 (1959), and references cited therein; (b) F. A. Matsen, W. W. Robertson and R. L. Chuoke, *Chem. Revs.*, **41**, 273 (1947); (c) W. F. Hamner and F. A. Matsen, THIS JOURNAL, **70**, 2482 (1948).

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

(4) R. A. Benkeser, R. A. Hickner and D. I. Hoke, *ibid.*, **80**, 2279 (1958).

(5) C. C. Price and D. C. Lincoln, *ibid.*, **73**, 5836 (1951).

(6) R. A. Clement and J. N. Naghizadeh, *ibid.*, **81**, 3154 (1959).

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

(8) Y. Okamoto, T. Inukai and H. C. Brown, *ibid.*, **80**, 4972 (1958).

(9) This becomes particularly apparent when one considers that the sulfuric acid–acetic acid cleaving medium used in the present study is "faster" than the hydrochloric acid system used previously (see ref. 4). The ratio of cleavage rates of the two systems ($k_{HCl}/k_{H_2SO_4}$) for phenyltrimethylsilane is 0.56.

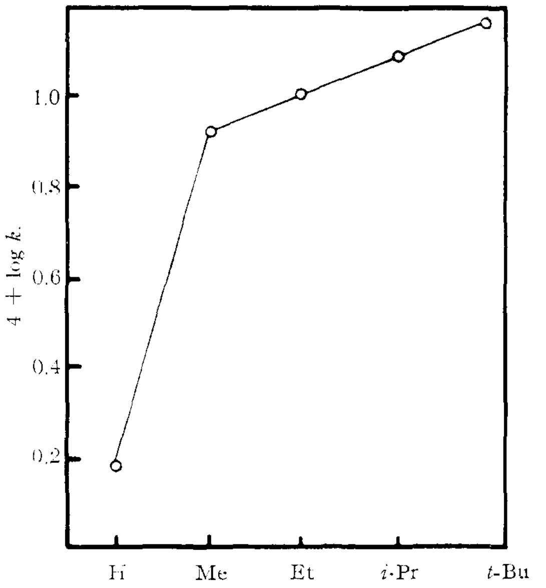


Fig. 1.—Effect of *m*-alkyl substituents on the rates of acid cleavage of triisopropylsilylalkylbenzenes. Cleaving medium was glacial acetic acid (1.78 molar in hydrogen sulfate and 0.44 molar in water at 25°).

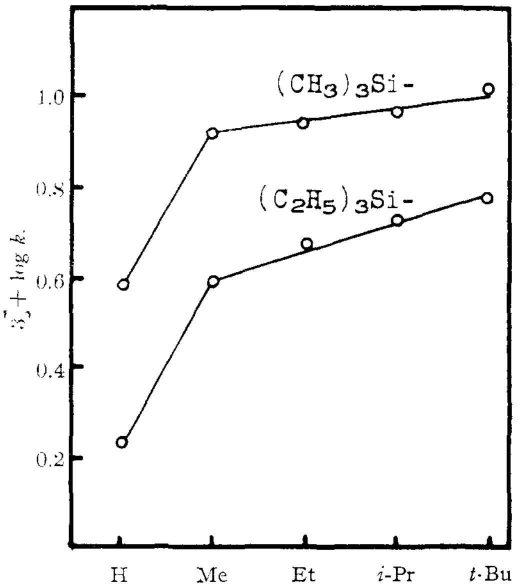


Fig. 2.—Effect of *m*-alkyl substituents on the rates of acid cleavage of trimethyl- (top curve) and triethylsilyl-alkylbenzenes (lower curve).[4] Cleaving medium was glacial acetic acid (2.35 molar in hydrogen chloride and 7.23 molar in water at 25°).

Although the concept of a buttressing effect between the *m*-alkyl group and the R-groups attached to the silicon was disproved earlier,[10] the present data also argue against this view. For again, if alkyl rotational effects[11] were occurring, the rate of cleavage of the *m*-*t*-butylphenyl triisopropylsilane would not be linearly related to the other *m*-alkyl substituents. The observed trend in rates in Fig. 1 can be best, and most simply, explained in terms of an increase in inductive effect (+I) of the *m*-alkyl substituent.

Of particular interest is the gradual increase in the slope of the lines shown in Figs. 1 and 2. It is apparent that the slopes are in the sequence Me_3Si– < Et_3Si– < $(i\text{-}Pr)_3Si$–. It would seem that the best explanation for this trend lies in a consideration of the three transition states involved in these desilylations. There can be no doubt that detrimethylsilylation is the most vigorous of the three reactions, and hence the geometry of the transition state for this reaction should more closely resemble the structure of the starting silane.[12] Stated another way, the breaking of the carbon–silicon bond in the transition state of detrimethylsilylations has not progressed as far as in detriethylsilylation, which, in turn, has not progressed as far as in detriisopropylsilylation. Hence, the *positive nature* of the ring in the transition state is *greatest* in detriisopropylsilylation and *least* in detrimethylsilylation. As a result of this variation in positive character, there is a greater electron demand on the *m*-alkyl substituent in the case of deisopropylsilylation than in detrimethylsilylation, and hence one observes a greater spread in rates in proceeding from a *m*-methyl to a *m*-*t*-butyl group. Where the electronic demands on the *m*-alkyl substituent are small in the transition state (detrimethylsilylation), one observes only a slight increase in the rate from *m*-methyl to *m*-*t*-butyl.[13] This becomes much more apparent by comparing the relative rates of these three reactions (Table II).

TABLE II

RELATIVE RATES OF CLEAVAGE OF THE *m*-ALKYL SUBSTITUTED TRIALKYLPHENYLSILANES [*m*-RC_6H_4R']

m-Alkyl Group R	Relative rates[a] R' = MeS_3i–	Et_3Si–	$(i\text{-}Pr)_3Si$–
H	1	1	1
CH_3	2.1	2.4	5.4
C_2H_5	2.2	2.9	6.4
i-C_3H_7	2.4	3.1	7.9
t-C_4H_9	2.8	3.6	9.3

[a] It must be noted that the cleaving medium for the triisopropylsilyl series was different from that used in the case of trimethyl- and triethylsilyl compounds. Hence, quantitative comparisons of rates *between* the triisopropylsilyl series and the other two are not valid.

It is obvious that the *m*-alkyl substituents have a greater influence in increasing the cleavage rate in the triisopropylsilyl series than in the other two series. Thus, $K_{t\text{-Bu}}/K_H$ in the triisopropylsilyl series is 9.3, while in the trimethylsilyl series it is 2.8. Stated another way, detrimethylsilylation is the least selective[14] of the three reactions, and detriisopropylsilylation is the most selective.[14] These results lead to the very interesting corollary that the Selectivity Factor of Brown and co-workers[14] is influenced, not only by the activity of the attacking species, but by differences in the leaving group as well.

---

(10) R. A. Benkeser, R. A. Hickner, D. I. Hoke and O. H. Thomas, THIS JOURNAL, **80**, 5289 (1958).

(11) H. C. Brown and A. Cahn, *ibid.*, **77**, 1721 (1955); H. C. Brown *J. Chem. Ed.*, **36**, 427 (1959).

(12) G. S. Hammond, THIS JOURNAL, **77**, 334 (1955).

(13) These three desilylations present a unique case in which the same reaction carried out on three *different* compounds, yields the *same* product.

(14) L. M. Stock and H. C. Brown, THIS JOURNAL, **81**, 5621 (1959).

It is to be understood that an assumption basic to the present work is that the variations in rate observed are a true reflection of differences in ΔH^* (or ΔF^*) alone, and hence are solely dependent on potential energy differences. This implies that the entropies of activation for the various detriisopropylsilylations studied are essentially constant, or at least exhibit *no definite trends* as the *m*-alkyl group is made to vary from methyl to *t*-butyl. While this supposition may at first be an uncomfortable one in view of the small rate differences observed, there is definite evidence that it is valid. Thus in the mercuration of *t*-butylbenzene[15] and toluene,[16] the ΔS^* values for *m*- and *p*-substitution have been calculated and found to be constant within experimental error. This same constancy has been noted as well in recent nitration studies of ethyl benzoate.[17] In fact, wherever ΔS^* values have been determined for reactions of *m*- and *p*-substituted benzene derivatives, they provide little assurance of being anything but random.[18]

Experimental

***m*-Alkylbromobenzenes.**—The *m*-bromotoluene used was a commercial product. *m*-Bromoethylbenzene was prepared by a Clemmensen reduction of *m*-bromoacetophenone.[19]

m-Bromoacetophenone also was used as an intermediate in the synthesis of *m*-bromocumene. Treatment of this haloketone with the methyl Grignard reagent produced *m*-bromophenyldimethylcarbinol in 71% yield. This carbinol was dehydrated (60–70%) by vacuum distillation (twice) in the presence of iodine catalyst. The resulting olefin, 2-(*m*-bromophenyl)-propylene was reduced in ethanol in a Parr hydrogenator with platinum oxide catalysis. *m*-Bromocumene was obtained in 85% yield. The physical constants of these compounds were in good agreement with those previously reported.[20]

m-Bromo-*t*-butylbenzene was obtained by a procedure already described in the literature[21].

Aryltriisopropylsilanes.—Previous directions were used to synthesize phenyltriisopropylsilane.[22]

The *m*-substituted arylsilanes were all prepared by the reaction of the appropriate aryllithium derivative with triisopropylchlorosilane.[23] The directions which follow for the preparation of *m*-*t*-butylphenyltriisopropylsilane may be considered as typical of all of these preparations.

***m*-*t*-Butylphenyltriisopropylsilane.**—To 0.84 g. (0.12 g. atom) of freshly cut lithium ribbon in 75 ml. of ether under nitrogen was added, dropwise, 11.4 g. (0.0535 mole) of *m*-bromo-*t*-butylbenzene. The refluxing which started during this addition was continued for 90 minutes, whereupon triisopropylchlorosilane (10.3 g., 0.0535 mole) was added. The refluxing was continued for 26 hours. After the mixture was poured onto ice, the organic layer was separated and dried over Drierite. Distillation through an 18-inch Vigreux column gave a low boiling fraction (b.p. 30–39° (2 mm.)) and a high boiling fraction. The latter fraction was redistilled through a glass spiral Todd column and yielded 2.4 g. (15%) of the silane (b.p. 118.5–119.5° (1 mm.), $n^{21}D$ 1.5019).

Experimental variables for the preparation of the other *m*-substituted silanes as well as some physical constants of these compounds are summarized in Table III.

TABLE III

PREPARATION OF *m*-SUBSTITUTED ARYLTRIISOPROPYLSILANES

m-$RC_6H_4Si(i\text{-}C_3H_7)_3$

R groups	Reflux time, hr.	Boiling Pt. °C.	Mm.	n^tD	t, °C.	Yield, %
CH_3[a,d]	66	[b]		[b]		31
C_2H_5[c,e]	70.5	106.5–107.5	0.5	1.5072	24	49
i-C_3H_7[f]	26	111–112	1	1.5004	25	18
t-C_4H_9[g]	26	118.5–119.5	1	1.5019	21	15

[a] Excess triisopropylchlorosilane employed (0.104 mole to 0.073 mole of *m*-bromotoluene). [b] Solid, m.p. 53°, after recrystallization from methanol. [c] Excess triisopropylchlorosilane employed (0.104 mole to 0.068 mole of *m*-bromoethylbenzene). [d] *Anal.* Calcd. for $C_{16}H_{28}Si$: C, 77.4; H, 11.3. Found: C, 77.13; H, 11.1. [e] *Anal.* Calcd. for $C_{17}H_{30}Si$: C, 77.8; H, 11.45. Found: C, 77.54; H, 11.43. [f] *Anal.* Calcd. for $C_{18}H_{32}Si$: C, 78.3; H, 11.6. Found: C, 78.20; H, 11.91. [g] *Anal.* Calcd. for $C_{19}H_{34}Si$: C, 78.6; H, 11.7. Found: C, 78.35; H, 11.78.

The cleavage rates were measured by dilatometric techniques which were described previously.[24]

Acknowledgments.—The authors are grateful to the Monsanto Chemical Co. and the National Science Foundation for fellowship aid which made this work possible.

---

[15] H. C. Brown and M. Dubeck, THIS JOURNAL, **81**, 5608 (1959).

[16] H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2306, 2310 (1955).

[17] W. J. le Noble and G. W. Wheland, *ibid.*, **80**, 5397 (1958).

[18] L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, p. 121.

[19] D. E. Pearson and H. W. Pope, *J. Org. Chem.*, **21**, 381 (1956).

[20] W. E. Parham, E. L. Wheeler, R. M. Dodson and S. W. Fenton, THIS JOURNAL, **76**, 5380 (1954).

[21] B. W. Larner and A. T. Peters, *J. Chem. Soc.*, 680 (1952).

[22] R. A. Benkeser, W. Schroeder and O. H. Thomas, THIS JOURNAL, **80**, 2283 (1958).

[23] H. Gilman and R. N. Clark, *ibid.*, **69**, 1499 (1947).

[24] R. A. Benkeser and H. Krysiak, *ibid.*, **76**, 6353 (1954).

[CONTRIBUTION FROM THE SHELL DEVELOPMENT CO., EMERYVILLE, CALIF.]

Chemistry of Glycidaldehyde[1]

BY PAUL H. WILLIAMS, GEORGE B. PAYNE, WILLIAM J. SULLIVAN AND PAUL R. VAN ESS

RECEIVED FEBRUARY 5, 1960

Glycidaldehyde condenses with acetylacetone and ethyl acetoacetate to form furan derivatives. It combines through its carbonyl group with cyanoacetic and malonic esters, primary amines, ethyl chloroacetate, ethyl orthoformate, ketene and hydrogen cyanide to yield products in which the oxirane ring is retained. It is reduced to glycidol with metal hydride reducing agents. The addition of active hydrogen compounds under acidic conditions yields β-substituted lactaldehydes and their derivatives.

The synthesis of glycidaldehyde (I) by the reaction of acrolein with alkaline hydrogen peroxide, and its isolation and characterization as a pure substance were reported recently.[2] Some of the carbonyl and epoxide reactions of glycidaldehyde are described in this paper.

The reactions of glycidaldehyde with reagents which attack the carbonyl group are given in the diagram. In most of these the epoxide group remains

---

[1] Presented in part before the Division of Organic Chemistry at the 135th National Meeting of the American Chemical Society, April, 1959.

[2] G. B. Payne, THIS JOURNAL, **80**, 6461 (1958); **81**, 4901, (1959).