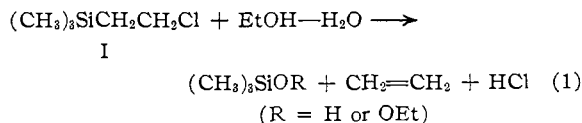tive studies of the kinetics of $\beta$-eliminations involving silicon in which the leaving group is $\beta$-chloroethyl and the silicon bears three organic groups as substituents.

$$(CH_3)_3SiCH_2CH_2Cl + EtOH—H_2O \longrightarrow$$

I

$$(CH_3)_3SiOR + CH_2{=}CH_2 + HCl \quad (1)$$
$$(R = H \text{ or } OEt)$$

Solvolysis of I ($\%$ Si, 20.3; $\%$ Cl, 26.2[4]) in aqueous ethanol at $30.0°$ follows a first-order rate-law with excellent precision (as measured by ethylene evolution); gives excellent correlation of variation in rate constant with variation in solvent composition over the range 50% ethanol to 80% ethanol—20% water by volume, according to the Winstein–Grunwald equation, log $(k/k_0) = mY$[5] and yields a value of $m$, 1.02, which indicates that I and $t$-butyl chloride are about equally susceptible to "ionizing power" of the solvolysis medium: rate constants for I at $30.0°$ vary from $2.9 \times 10^{-3}$-sec.$^{-1}$ in 50% ethanol to $6.1 \times 10^{-5}$ sec.$^{-1}$ in 80% ethanol; at $25°$, the rate constants for $t$-butyl chloride[5] in corresponding solvent compositions are $3.7 \times 10^{-4}$ sec.$^{-1}$ and $9.2 \times 10^{-6}$ sec.$^{-1}$ In formic acid, I reacts more rapidly, by a factor of 2.7, than would be predicted by $m$. For I in formic acid at $30°$, $k_1 = 2.0 \times 10^{-2}$ sec.$^{-1}$; for $t$-butyl chloride[5] in the same solvent at $25°$, $k_1 = 1.1 \times 10^{-3}$ sec.$^{-1}$.

These data clearly show that: (1) solvolysis rates of I are not sensitive to the nucleophilic character of the solvent, but are strongly dependent on its ionizing power—even more so, perhaps, then $t$-butyl chloride solvolyses; (2) approximately equal rate constants in corresponding media for I, a primary chloride, and for $t$-butyl chloride, a tertiary chloride, argue convincingly for strong participation of electron-release from silicon in the rate-controlling transition state, without simultaneous nucleophilic attack by solvent at the silicon atom. On these grounds, and from the rate-retarding effects of electron-withdrawing substituents (e.g., in 70% ethanol at $50.0°$, the rate constant of $C_6H_5(CH_3)_2SiCH_2CH_2Cl$ relative to $m$-$CF_3$-$C_6H_4(CH_3)_2SiCH_2CH_2Cl$ corresponds to $\rho = -2.15$), reaction (1) is properly described as proceeding by a limiting siliconium ion mechanism in the designated solvents in the absence of added lyate ion.

In accord with the current structural hypothesis of limiting carbonium ion reactions,[6] reaction (1) may be formulated as involving structures (2) and (3) as the first and second intermediates (Y is $\beta$-chloroethyl and S is a solvent molecule).[7]
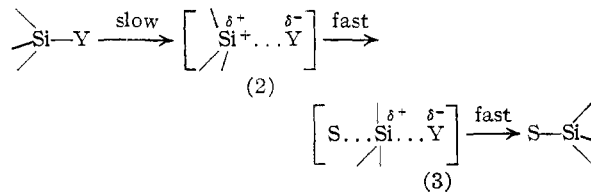
the conclusion that the stability of Me$_3$Si$^+$ relative to Me$_3$SiCl is less than the corresponding difference for Me$_3$C$^+$—they only show that Me$_3$SiCl has a mechanism more favorable than siliconium ion available in the particular reaction studied. This statement and the one in ref. 2 seem necessary, at least in part, because of the classical-historical association of the term "carbonium ion" with tertiary organic halides.

(4) Compound I was prepared by reaction of thionyl chloride with the alcohol furnished by lithium aluminum hydride reduction of ethyl trimethylsilylacetate—J. R. Gold, L. H. Sommer and F. C. Whitmore, J. Am. Chem. Soc., 70, 2874 (1948).

(5) E. Grunwald and S. Winstein, ibid., 70, 846 (1948).

(6) Cf., A. Streitwieser, Jr., Chem. Revs., 56, 571 (1956).

In 50% ethanol at $30.0°$, the addition of KOH, making the solution 0.54 $M$ in lyate ion, results in a small $decrease$ in rate (salt effects of KCl, KBr and KNO$_3$ are small; for 0.54 $M$ concentrations, the rate factors, $k_{salt}/k_{no\ salt}$, are 0.8, 1.0 and 1.0); relative rate for the basic solution is 0.95. For 4.0 $M$ KOH, relative rate is still only 1.45.

$$\begin{array}{c}\diagdown \\ \diagup\end{array}Si—Y \xrightarrow{slow} \left[\begin{array}{c}\diagdown \delta^+ \quad \delta^- \\ Si^+ \ldots Y \\ \diagup | \end{array}\right] \xrightarrow{fast}$$
$$(2)$$

$$\left[\begin{array}{c}| \delta^+ \quad \delta^- \\ S \ldots Si \ldots Y \\ \diagup | \end{array}\right] \xrightarrow{fast} S—Si \begin{array}{c}\diagup \\ \diagdown\end{array}$$
$$(3)$$

If the ionizing power of the solvent is decreased, thus decreasing the rate of reaction by a siliconium ion mechanism, and the solvent–reactant is again made 0.54 $M$ in added KOH: at $30.0°$ in 70% ethanol, $k_{base}/k_{neutral} = 4.2$, but the total rate constant, for the neutral and base-catalyzed reactions, is still lower, by a factor of 3, than the rate constant for solvolysis in 50% ethanol.

We conclude that in the present case and also probably in many others, the accessibility of R$_3$Si$^+$ and R$_3$C$^+$ as intermediates is comparable; but that for the former, more favorable reaction paths may prevent a particular reaction from proceeding through a siliconium ion intermediate. For Ar$_3$-Si$^+$ and Ar$_3$C$^+$, it is clear that in equilibria the latter is far more accessible because of the large increase in resonance energy that accompanies ionization[8]; double-bonded silicon using $p_\pi$—$p_\pi$ bonding is still unknown, and the silicon analog of crystal violet is colorless and un-ionized.[9]

We thank Dow Corning Corporation for generous support.

(7) The alternative of a non-classical siliconium ion intermediate in which R$_3$Si$^+$ is $\pi$-bonded to the forming ethylene molecule seems more complex, but cannot be discarded on the basis of the above evidence. However, unlike the mercury case (H. J. Lucas, F. R. Hepner and S. Winstein, J. Am. Chem. Soc., 61, 3102 (1939)), the polar silylation of olefins is unknown. At this moment, it seems necessary to apply "Ocean's Razor" to this situation.

(8) Cf. N. N. Lichtin and P. D. Bartlett, ibid., 73, 5537 (1951); A. Streitwieser, Jr., ibid., 74, 5288 (1952).

(9) U. Wannagat and F. Brandmair, Z. anorg. Chem., 280, 223 (1955); A. B. Thomas and E. G. Rochow, J. Inorg. and Nucl. Chem., 4, 205 (1957).

DEPARTMENT OF CHEMISTRY　　　　　LEO H. SOMMER
THE PENNSYLVANIA STATE UNIVERSITY
UNIVERSITY PARK, PA.　　　　　GLEN A. BAUGHMAN
RECEIVED JUNE 19, 1961

---

## A HOMOALLYLIC HYDRIDE REDUCTION WITH RING CLOSURE

Sir:

Because of its high reactivity, 7-chloronorbornadiene (I)[1,2] seemed a natural precursor, through lithium aluminum deuteride reduction, to 7-deuterionorbornadiene, needed in a mechanism study of another reaction.[3] The reaction using lithium aluminum hydride has been found to yield not only the expected norbornadiene (II) but also,

(1) S. Winstein and C. Ordronneau, J. Am. Chem. Soc., 82, 2084 (1960).

(2) P. R. Story and M. Saunders, ibid., 82, 6199 (1960).

(3) P. R. Story, ibid., 82, 2085 (1960).

quite remarkably, tricyclo[4.1.0.0$^{3,7}$]heptene-4 (III). The tricyclic olefin, which is the unsaturated



Eq. 1

II    III
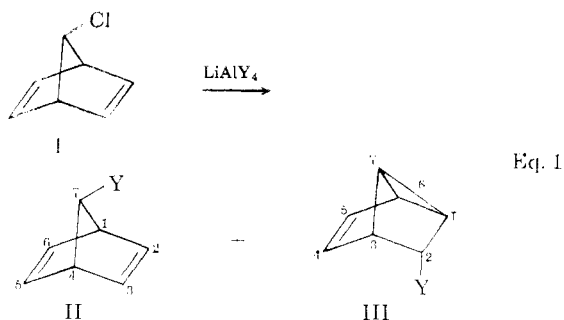
analog of one of the highly strained systems recently reported by Moore, et al.,[4] was obtained in 49% yield and composed 88% of the total product.

In a typical reduction the chloride (I) was treated with a two mole excess of lithium aluminum hydride in refluxing ether and stirred for 16 to 24 hours. Water and wet sodium sulfate then were added and the ether solution was decanted and dried. All apparatus in contact with the product was pre-washed with dilute ammonium hydroxide because of the extreme acid sensitivity of III. After removal of most of the ether, the crude product was separated and purified by gas phase chromatography utilizing a 10 ft. × $^5/_8$ in. 20% N,N,-N',N'-tetrakis-(2-hydroxyethyl)-ethylenediamine (THEED) on Celite column at room temperature. Further analysis of the crude product with a 20 ft. × $^1/_4$ in. 25% THEED column showed the presence of only two compounds. Silicone and Apiezon columns were found to be too acidic or to require excessively high temperatures.

Collection of the second peak in the preparative scale chromatograph gave a volatile, colorless, vile-smelling liquid identified as tricyclo[4.1.0.0$^{3,7}$]-heptene-4 (III) in 49% yield. Anal. Calcd. for C$_7$H$_8$: C, 91.25; H, 8.75. Found: C, 91.15; H, 8.87; $\lambda_{max}^{hex.}$ 215 m$\mu$ (250); infrared (CCl$_4$, $\mu$): 3.2(m), 6.3(w), 10.0(m), 11.5(s), 13.7(s), 14.3(s). The n.m.r. in CCl$_4$ showed the two olefinic hydrogens as a multiplet at 4.4 ppm. relative to tetramethylsilane as 10.0 ppm. A two hydrogen multiplet appeared at 7.4 and one hydrogen each in complex multiplets at 7.6, 8.0 and 8.4. A quadruplet appearing at 9.5 was assigned to the endo C.2 hydrogen on the basis of its predictably simpler multiplicity[5] and chemical shift. The n.m.r. spectrum of the lithium aluminum deuteride reduction product (IIIb) showed the deuterium to be exclusively in the endo C.2 position.

The tricyclic olefin (III) absorbed 1.92 moles of hydrogen (5% Pd/C in ethanol) to give norbornane (82%) and three other products, one of which ac-

counted for 13% of the total product.[6] These three products were not identified. The norbornane was identified by melting point, n.m.r. and infrared.

Collection of the first peak in the preparative scale chromatographic separation gave norbornadiene in 8% yield, identified by retention time, n.m.r. and infrared. The n.m.r. spectrum of the corresponding lithium aluminum deuteride reduction product (IIb) showed the deuterium to be at C.7 exclusively.

This reaction, in addition to yielding labeled norbornadiene, thus provides a very convenient synthesis of a novel and interesting tricyclic system. Of even greater interest, however, is the question of the mechanism of the reduction. Examples of hydride reduction of carbon–carbon double bonds are rare and most, or all, cases are considered to occur in an intramolecular fashion.[7,8]

Winstein[1] has demonstrated that 7-chloronorbornadiene solvolyzes ca. 10$^{14}$ faster than the corresponding saturated chloride in aqueous acetone, probably proceeding through a stable non-classical cation to give 7-norbornadienol exclusively. The first direct physical evidence for the existence and structure of such a non-classical ion recently was provided by the n.m.r. spectrum of 7-norbornadienyl fluoroborate.[2] It now appears likely that the hydride reduction of 7-chloronorbornadiene constitutes the first direct chemical evidence of the interaction of a double bond and a developing carbonium ion at C.7 in the 7-norbornadienyl molecule.

The structure of the reduction product (III) correlates well with the structure proposed for the 7-norbornadienyl carbonium ion in which an apparent coupling constant of 5 cps. was observed between the hydrogen at C.7 and the olefinic hydrogens at C.2 and C.3, thus indicating considerable bond formation from C.7 to the olefinic carbons.[2]

All previous reactions of 7-substituted norbornadienes (or norbornenes) have been, by their very nature, equilibrium processes.[1,2,8] In no case was a rearrangement product observed. Certainly, the tricyclic structure (III) would not have been obtained since the equilibrium, because of the enormous strain involved in III, would be shifted quite far in the direction of the bicyclic structure. The cholesteryl and 2-norbornenyl systems provide examples in which the equilibrium, under certain conditions, is in favor of the rearranged molecule.[9] A hydride reduction, however, is essentially irreversible and a reaction at any carbon other than C.7 will necessarily result in a rearranged product.

The most likely mechanism is illustrated in Equation 2. Aluminum hydride (or perhaps an aluminum oxide formed by a trace of moisture)

(4) W. R. Moore, H. R. Ward and R. F. Merritt, J. Am. Chem. Soc., **83**, 2019 (1961).

(5) The endo C.2 hydrogen will not couple with the bridgehead hydrogen at C.3, hence it appears as a quadruplet through coupling with hydrogens at exo C.2 and C.1. All other hydrogens would be expected to be more complex through coupling with at least three other hydrogens: F. A. L. Anet, Canad. J. Chem., **39**, 789 (1961); E. J. Corey, M. Ohno, S. W. Chow and R. A. Scherrer, J. Am. Chem. Soc., **81**, 6305 (1959); M. Karplus, J. Chem. Phys., **30**, 11 (1959).

(6) This compares favorably with the hydrogenation of tricyclo-[4.1.0.0$^{8,7}$]heptane which gave 92% norbornane and three other unidentified products (ref. 4).

(7) F. A. Hochstein and W. G. Brown, J. Am. Chem. Soc., **70**, 3484 (1948).

(8) P. R. Story, J. Org. Chem., **26**, 287 (1961). Recent work, to be published later, has shown that lithium aluminum deuteride reduction of 7-norbornadienol and of 7-norbornadienyl acetate leads to anti-7-norbornenol with a single deuterium in the exo 2 position.

(9) S. Winstein and R. Adams, J. Am. Chem. Soc., **70**, 838 (1948); S. Winstein, H. M. Walborsky and K. Schreiber, ibid., **72**, 5795 (1950).

coördinates with the chlorine thereby providing impetus to ionization which is strongly assisted by the proper double bond to give a non-classical intermediate. Probably, ionization does not proceed to a great extent before reduction occurs.
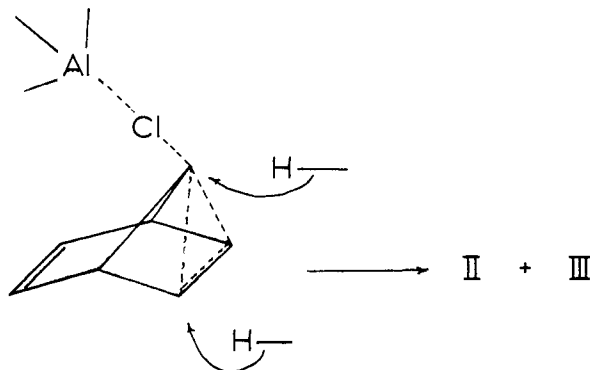


The intermediate might be considered as a very tight ion pair. It seems highly unlikely that the reaction proceeds by simple nucleophilic attack on the double bond without some prior ionization, especially since the attack cannot be intramolecular. Support for this position is gained by the preliminary observation that the addition of water increases the rate of reduction but does not change the product ratio. This observation is consistent with that of Eliel[10] who found that yields were materially improved in the lithium aluminum hydride reduction of a chlorohydrin, involving a tertiary chloride, by the addition of water or alcohols. This was attributed to the greater acidity of the oxygen substituted aluminum which was presumed to coördinate with the chlorine.

The chemistry of the tricyclic olefin (III) and the mechanism and scope of the reaction are presently under further investigation.

(10) E. L. Eliel and T. J. Prosser. J. Am. Chem. Soc., **78**, 4045 (1956).

BELL TELEPHONE LABORATORIES, INC.
MURRAY HILL, NEW JERSEY                    PAUL R. STORY
RECEIVED JUNE 29, 1961

---

## REGARDING ENHANCED RESONANCE EFFECTS FROM META POSITION IN RADICAL REACTIVITIES[1]

*Sir:*

A valuable tool for the characterization of the transition state of a radical reaction is provided by a measure of enhanced resonance effects of *meta*-substituents.

The Ar–Y inductive effects of a *meta* methoxy substituent in reactivities of benzene derivatives (in the general formula for such compounds, X–Ar–Y, X refers to the substituent and Y to the reaction center) are precisely described (to a standard error of $\pm$ 0.03 sigma unit) by the modified Hammett equation[2]: $\log (k/k_0) = \sigma^0 \rho$. Included are

(1) This work was supported in part by the Office of Naval Research.

(2) (a) R. W. Taft, Jr., and I. C. Lewis, J. Am. Chem. Soc., **81**, 5343 (1959); (b) R. W. Taft, Jr., S. Ehrenson, I. C. Lewis, and R. E. Glick, *ibid.*, **81**, 5352 (1959); (c) R. W. Taft, Jr., J. Phys. Chem., **12**, 1805 (1960).

such pronounced electrophilic reactivities as the rates of solvolysis of *t*-cumyl chlorides, rates of protonolysis of phenyltrimethylsilanes, and rates of bromination of mesitylenes and durenes, as well as such strongly nucleophilic reactivities as the ionization of phenols and thiophenols (for listings of reactions *cf.* Table II, ref. 2a).[3]

In contrast, in three radical reaction series (for which data are available) the $m$-$OCH_3$ substituent shows enhanced reactivity over that predicted $(\sigma^0\rho)$ for the Ar–Y inductive effect (benzoyl peroxide reaction series F-1, F-3, and F-4 of Table II, ref. 2a), the enhancement (Ar–Y resonance effect) amounting in each case to *0.3 kcal./mole*. While this figure is not impressive in magnitude, it comes from reactions with relatively small $\rho$ values and consequently is clearly discernible in the $\bar{\sigma}$ value.[4] In the radical reactivities listed in Table II of reference 2a, small apparent Ar–Y resonance enhancements in rate are also noted for $m$-alkyl and phenyl substituents.

A much more impressive enhancement (Ar–Y resonance effect) is obtained for the $m$-$OCH_3$ substituent in the formation of the radical ion by polarographic oxidation of $m$- and $p$-substituted anilines.[5] Here the effect on oxidation potential over that estimated by $\sigma^0\rho$ amounts to a free energy decrease of *1.1 kcal./mole*. It is further to be noted that an extensive investigation of $m$-substituents has been made and substantial Ar–Y resonance effects are noted for other –R meta substituents (*e.g.*, $-NH_2$, $-NHCOCH_3$ and $-CH_3$). The resonance enhanced effects reach a maximum free energy decrease of *3.0 kcal./mole* for the $m$-$NH_2$ substituent.

The enhancement of the resonance effect of *meta* substituents may be accounted for in terms of acceptable quinoid isovalent structures,[5a] *e.g.*
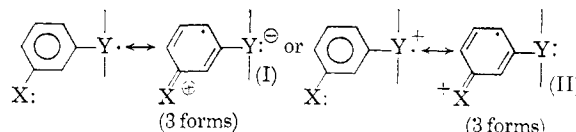


It is well known that the analog interaction structures for $-Y:^-$ or $-Y^+$ (systems with an even number of $\pi$ electrons) are not acceptable, in accord with the applicability (noted above) of the modified Hammett equation to such systems. The

(3) Not all -R *meta* substituents are as well behaved as $m$-$OCH_3$. Effective $\bar{\sigma}$ values for $m$-$SCH_3$, $NH_2$ and $N(CH_3)_2$ are appreciably affected by the polarization from a change in formal charge at the first atom of the side-chain reaction center. In reactivities in which the latter factor is not involved, however, these substituents appear generally to follow the $\sigma^0$ scale (*cf.* references 5a and b).

(4) This type of rate enhancement for *para* -R substituents has been well recognized and documented in terms of correlations employing $\sigma^+$ values; *cf.* P. D. Bartlett and C. Rüchardt, J. Am. Chem. Soc., **82**, 1756 (1960). However, Bartlett and Rüchardt have given an additional reason (besides that considered here for *meta* substituents) for such rate enhancements with *para* substituents. See also, G. A. Russell, J. Org. Chem., **23**, 1407 (1958); E. S. Hayser, J. Am. Chem. Soc., **82**, 394 (1960).

(5) I. R. Fox, R. W. Taft, Jr., and J. M. Schempf, Abst. of Papers, Am. Chem. Soc. Meeting, Atlantic City, N. J., Sept., 1959.

(5a) NOTE ADDED IN PROOF.--W. N. White, C. D. Slater, and W. K. Fife, J. Org. Chem., **26**, 627 (1961) have similarly noted that enhanced resonance effects of $m$-substituents in the rate of the Claisen rearrangement can be accounted for by the contribution of such structures to the reaction transition state.