However, the mass spectra of the aromatic products (apparently isomers) from the nitroethane–toluene (MS parent peak at *m/e* 165, base peak at *m/e* 119, others at *m/e* 91, 104) were consistent with the expected product structures.

For quantitative yield determinations, an internal standard, *p*-nitrotoluene, was added in known amount to the reaction mixture before workup. After workup, the solutions were analyzed by GC and yields were obtained by comparing the relative peak areas of the products and internal standard (internal standard program of the automatic integrator). Percent yield was based on the stoichiometry of 0.5 mol of product per mol of manganese(III) as the limiting reagent. The average yield of at least duplicate reactions in good agreement are reported in the tables.

Registry No.—**2**, 16787-85-2; α-nitrotoluene, 622-42-4; α-nitroxylene, 64147-35-9; methoxy-α-nitrotoluene, 64147-36-0; chloro-α-nitrotoluene, 64147-37-1.

References and Notes

(1) Presented in part at the 173rd National Meeting of the American Chemical Society, New Orleans, La., March, 1977. A preliminary account of this work has appeared: M. E. Kurz and T. Y. R. Chen, *J. Chem. Soc., Chem Commun.*, 968 (1976); taken from the M.S. Thesis of T. Y. R. Chen, Illinois State University, 1976.
(2) M. E. Kurz, E. M. Steele, and R. L. Vecchio, *J. Org. Chem.*, **39**, 3331 (1974).
(3) M. E. Kurz and M. Pellegrini, *J. Org. Chem.*, **35**, 990 (1970).
(4) M. J. Perkins in "Free Radicals", Vol. II, J. K. Kochi, Ed., Wiley-Interscience, New York, N.Y., 1973, Chapter 16.
(5) E. I. Heiba, R. M. Dessau, and W. J. Koehl, Jr., *J. Am. Chem. Soc.*, **91**, 138 (1969).
(6) M. G. Vinogradov, S. P. Verenchikov, T. M. Fedorova, and G. I. Nikishin, *J. Org. Chem. USSR (Engl. Transl.)*, 937 (1975).
(7) O. T. Christensen, *Z. Anorg. Allg. Chem.*, **27**, 325 (1901).
(8) J. K. Kochi and R. V. Subramanian, *J. Am. Chem. Soc.*, **87**, 4855 (1965); J. K. Kochi, *Science*, **155**, 415 (1967).
(9) J. K. Kochi and D. M. Mog, *J. Am. Chem. Soc.*, **87**, 522 (1965).
(10) B. R. Cowley, R. O. C. Norman, and W. A. Waters, *J. Chem. Soc.*, 1799 (1959).
(11) W. A. Pryor, W. H. Davis, Jr., and J. H. Gleaton, *J. Org. Chem.*, **40**, 2099 (1975).
(12) C. D. Ritchie and W. F. Sager, *Prog. Phys. Org. Chem.*, **2**, 323 (1964).
(13) P. Kovacic, C. G. Reid, and M. E. Kurz, *J. Org. Chem.*, **34**, 3302 (1969).
(14) J. R. Shelton and C. W. Uzlemeir, *J. Am. Chem. Soc.*, **88**, 5222 (1966).
(15) W. A. Pryor and W. H. Davis, Jr., unpublished results.
(16) R. W. Henderson, *J. Am. Chem. Soc.*, **97**, 213 (1975).
(17) R. W. Henderson and R. D. Ward, Jr., *J. Am. Chem. Soc.*, **98**, 7556 (1974).
(18) W. A. Pryor and W. H. Davis, Jr., *J. Am. Chem. Soc.*, **96**, 7557 (1974).
(19) W. A. Pryor, U. Tonellato, D. L. Fuller, and S. Jumonville, *J. Org. Chem.*, **34**, 2018 (1969).
(20) E. S. Huyser, *J. Am. Chem. Soc.*, **82**, 394 (1960).
(21) A. T. Nielsen in "Chemistry of the Nitro and Nitroso Groups", Part 1, H. Fueur, Ed., Wiley-Interscience, New York, N.Y., 1969, p 349.
(22) N. Kornblum, R. A. Smiley, R. K. Blackwood, and D. C. Iffland, *J. Am. Chem. Soc.*, **77**, 6269 (1955).
(23) A. P. Black and F. H. Bakers in "Organic Syntheses", Collect. Vol. II, A. H. Blatt, Ed., Wiley, New York, N.Y., 1943, pp 512, 412.
(24) Some efforts were made to further enhance the preparative aspects of this reaction by trying to generate manganese(III) in situ from the more readily available manganese(II) acetate and by trying to regenerate manganese(III) directly in the reaction medium. However, in all systems studied to date, the oxidants used (oxygen, ozone, and potassium permanganate), in hopes of converting manganese(II) to manganese(III), either occasioned unwanted oxidation of the arene or produced manganese(IV) dioxide, an ineffective promoter.
(25) "The Merck Index", 8th ed, P. G. Stecher, Ed., Merck and Co., Inc., Rahway, N.J., 1968, p 642.

A Study of the Capacity of Group 4 Substituents for Directing the Course of Silver(I)-Catalyzed Tricyclo[4.1.0.0^{2,7}]heptane Rearrangement into the Elusive Type δ Manifold[1]

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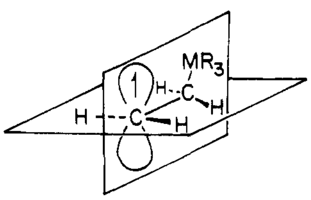
The effect of 1-trimethylsilyl and 1-trimethylgermyl substitution on the course of Ag^+- and H^+-catalyzed rearrangement reactions of the tricyclo[4.1.0.0^{2,7}]heptane ring system has been investigated. When no other substituents are present, as in the case of **12a** and **12b**, exposure to Ag^+ causes ring opening according to the type α mechanism with formation of 2-Me_3M-1,3-cycloheptadienes. When treated with acids or anhydrous ethereal magnesium bromide, these strained molecules were efficiently converted to 2-norcarene **16** and/or its positional isomer **17**. An additional methyl substituent at C_2 resulted in 2-norcarene production irrespective of the catalyst. However, the use of Ag^+ led chiefly to **21**, whereas *p*-TosOH afforded predominantly **22**. By attaching a deuterium atom at C_7 as in **25**, it could be shown that C_2–C_7 bond cleavage proceeded with overall retention of configuration at C_7. The 7-methyl derivatives **28a** and **28b** underwent polymerization in the presence of Ag^+ but smoothly isomerized to **29a** and **29b**, respectively, under conditions of *p*-TosOH catalysis. These results can be fitted to a mechanistic profile in which electrophilic attack at a given edge bicyclobutane bond is dependent upon the locus of the alkyl substituent, the timing of the transition state, and, most importantly, the ability of certain cationic intermediates to become stabilized by virtue of exalted C–Si and C–Ge hyperconjugative and homoconjugative interaction.

The exceptional stabilization provided by group 4 β-(metallomethyl) substituents to neighboring free-radical[3] and carbonium ion centers[4] is a subject which has been accorded considerable attention. Electron spin resonance studies performed on intermediates of type **1** (M = Si, Ge, and Sn) have revealed the sizable hyperconjugative delocalization of the odd electron to the C–M σ bond to be roughly comparable in magnitude to its p–d homoconjugative delocalization onto the metal p orbitals.[5] To permit maximum interaction in **1** (the level of which can approach 5 kcal/mol),[6] that conformational orientation is adopted where the β C–M bond eclipses the half-filled carbon p orbital. In the structurally related carbocations **2**, there is again no doubt that the substituent effect is likewise very sensitive to the relative orientation of the β C–M linkage and the plane of the electron-deficient p orbital. Furthermore, substantial chemical[4,7] and spectroscopic evi-



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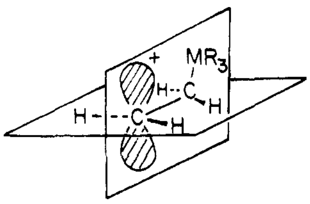

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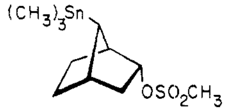
dence[8] is now available to show that the driving force underlying the high reactivity of $R_3MCH_2CH_2X$ compounds in S_N1 solvolysis is derived from vertical σ–π conjugation and not neighboring nucleophilic participation. Since the term "vertical" is intended to have a Franck–Condon connotation, the observed kinetic acceleration has been interpreted as due to σ–π conjugation which operates without significant change in the geometry of the antiplanar β-oriented organometallic center. The observed stereochemical consequences of nucleophilic capture, viz., high levels of configurational retention, are likewise satisfied by this interpretation on microscopic reversibility grounds. As might be expected, such highly exalted hyperconjugative release is also dependent upon the electronegativity of M or, perhaps more appropriately, the C–M bond polarity.

Studies of the solvolytic chemistry of γ-trimethyltin substituted alcohols and sulfonate esters[9] have also played an important role in the development of our understanding of yet more remote C–M interactions with developing cationic centers. These acetolysis experiments involving the conformationally rigid mesylates **3** and **5** have, to this time, provided the greatest level of stereoelectronic insight.[10] Rate measurements and activation parameters reveal that the C–Sn bond in **3** participates strongly to give **4** as the sole product. The syn-endo isomer also gives some **4** but is not accelerated. The importance of W-plan geometry in providing homoconjugative interaction for concerted 1,3-elimination (**6**) or homoconjugative stabilization to the derived cationic intermediate (**7**) is thereby revealed.



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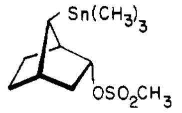

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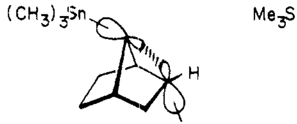

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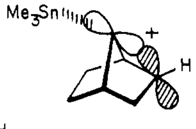

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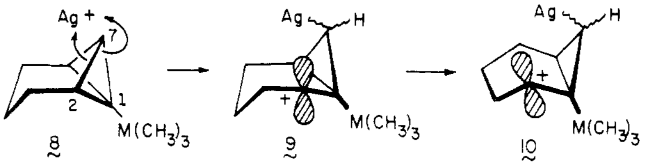
Previous investigations in this laboratory of the varied rearrangement reactions experienced by highly strained molecules under conditions of Ag^+ catalysis have established the principal role of the transition metal ion to be that of a modified Lewis acid.[11] The simplest conceptualization of the mechanistic events which follow upon preliminary substrate–Ag^+ complexation[12] involves the generation of novel covalently bonded Ag-substituted carbocationic structures which generally proceed on to one or more products under the partial control of the metal. It is presently recognized that molecular strain and the attendant exothermicity anticipated upon the release of such energy, although of paramount significance, are not the exclusive controlling factors in determining the directionality and mechanism of ring cleavage. There also exists a striking dependence upon the nature and position of ring substitution, an effect which is perhaps reflected most clearly in the reactivity of the tricyclo[4.1.0.0^{2,7}]heptane ring system.[12a,b,13] These endo,endo-2,4-bridged bicyclobutanes are known to undergo four general types of structural rearrangement. The pathway involving isomerization to 1,3-cycloheptadienes, termed the type α rearrangement,[13c] is believed to proceed by electrophilic Ag^+ attack at one edge bond with subsequent rupture of the diametrically opposite edge bond. This reaction course is followed exclusively by the parent hydrocarbon and is little affected either by "wing" alkyl groups (although kinetic acceleration is evident)[12b] or by a "bridgehead" carbomethoxy substituent (kinetically decelerated).[13a] However, when the bridgehead carbons carry alkyl groups, the type β rearrangement[13c] which defines conversion to alkylidenecyclohexenes gains importance.[12b,13e,f] This mechanistic changeover reflects a facilitation of concurrent (or nearly so) cleavage both of one edge and the central C–C bonds to generate a stabilized (usually secondary) argento carbonium ion. An increase in the effective steric bulk of the 1-substituent simultaneously decreases the tendency for α and β isomerization while promoting bicyclo[3.2.0]hept-6-ene formation (type γ rearrangement).[13a,b,14] This outcome appears to be the necessary consequence of electrophilic edge bond cleavage followed by stereospecific cyclopropylcarbinyl–cyclopropylcarbinyl bond relocation prior to ejection of Ag^+ back to the medium. The fourth (type δ) process which is associated with 2-norcarene production is rarely encountered and its minor role has heretofore not accorded it adequate mechanistic attention. Consequently, it is little understood.

Although a multiplicity of reaction manifolds obviously does exist, it seemingly shares the common parameter of being triggered by Ag^+ attack at one of the four available edge bonds. To the extent that a group 4 metal substituent at C_1 as in **8** might find it possible to direct the approach of Ag^+ to the opposite surface because of steric and electronic factors, and also to substantially stabilize the resultant cyclopropylcarbinyl cation by hyperconjugative interaction, one would expect the subsequent steps leading to product(s) to be appreciably modified from some established norm (the *tert*-butyl derivative,[13c] for example).



8 **9** **10**

We have discussed elsewhere the substantial alteration in hybridization, electronic character, and relative molecular position which can be perceived at C_7 as it becomes covalently bonded to Ag^+.[13a] The present study demands that we now focus attention on the events which occur at C_2. Molecular models of **8** reveal clearly that the strained C_2–C_7 edge bond which is likely to be subject to electrophilic attack by Ag^+ is aligned orthogonally to the C–M bond emanating from C_1. One notes further that ring opening to give **9** does diminish the size of this angle somewhat but decidedly not to the extent required to align the vacant p orbital and the C–M bond sufficiently to permit reasonable σ–π delocalization. In actuality, that degree of eclipsing necessary to achieve full interaction appears attainable uniquely in that boat conformation depicted in **10**. Because movement of the entire structural framework is required to arrive at **10**, the $-M(CH_3)_3$ substituent cannot be expected to provide vertical stabilization to the rate-determining bond rupture. At the experimental level, this particular feature could likely be reflected merely in small deviations in overall kinetic behavior relative to the 1-*tert*-butyltricycloheptane model.

The question at issue is how sensitive the ensuing product-forming steps are to the possibility of substantial energy minimization later in the reaction profile. If we assume, for example, that conformer **10** cannot be arrived at prior to rapid bond cleavage or alternative electronic shift elsewhere within **9**, then the $-M(CH_3)_3$ group should play a less than direct role in the determination of which rearrangement mode is followed. However, under circumstances where the inherent stability of **9** is enhanced to the level such that conformational ring inversion does have time to operate, then the effects of the resultant exalted hyperconjugation available to **10** could prove limiting. Optimistically, if a little observed rearrangement pathway such as the type δ process were to dominate as

Table I. ^{13}C NMR Chemical Shifts of Selected Tricyclo[4.1.0.0^{2,7}]heptanes[a]

Carbon atom	Compd[b] 11[c]	12a	12b	12c	13
1	5.34	3.26	6.26	2.60	28.49[d]
2	39.98	41.38	41.54	42.55	37.66
3	20.53	20.93	21.07	21.06	20.91
4	21.07	21.12	21.07	21.26	21.34
7	5.34	13.46	11.68	11.54	8.71
CH_3		−1.20	−2.72	−10.30	28.79 26.68[d,e]

[a] $CDCl_3$, 22.625 MHz, ppm vs. Me_4Si. [b] Registry no.: **11**, 287-13-8; **12a**, 64036-08-4; **12b**, 64036-09-5; **12c**, 64036-10-8; **13**, 51284-17-4. [c] This spectrum has independently been reported by M. Christl, *Chem. Ber.*, **108**, 2781 (1975). [d] Interchangeable assignments. [e] The quaternary carbon of the *tert*-butyl substituent.

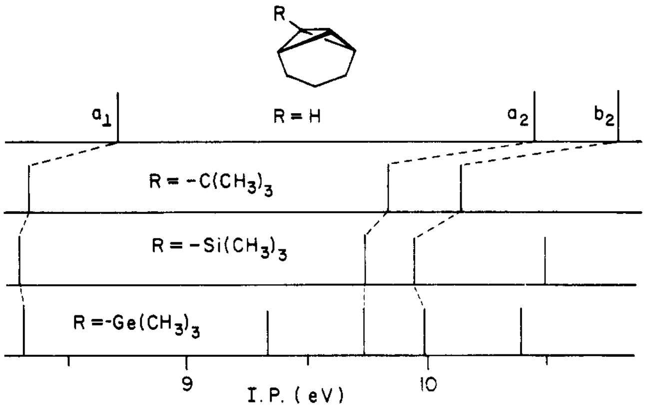
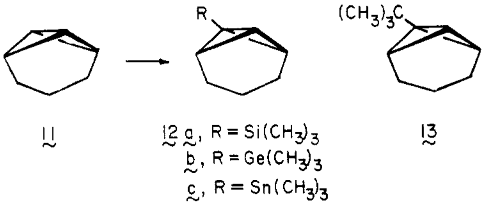


Figure 1. Schematic bar graph of the PE bands of selected 1-substituted tricyclo[4.1.0.0^{2,7}]heptanes.

a result, then an experimental probe for σ–π hyperconjugation might be at hand.

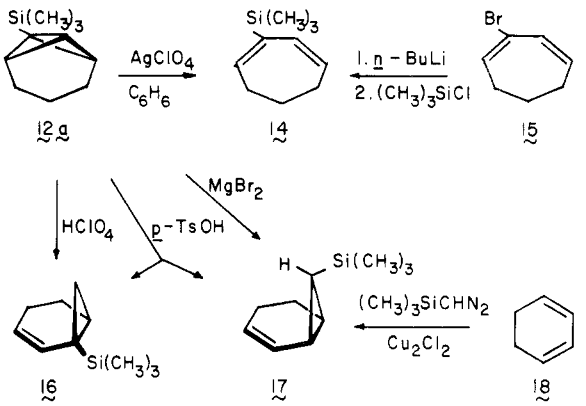
Synthesis and Spectral Properties of the 1-Substituted Derivatives. The desired substrates **12a–c**, conveniently prepared by reaction of 1-lithiotricyclo[4.1.0.0^{2,7}]heptane[15] with $(CH_3)_3MX$, were obtained as colorless stable liquids. Their ^{13}C NMR spectra, the data from which are recorded in Table I together with those for **11** and **13**, reveal certain interesting trends. Although the relative effects of the Si, Ge, and Sn atoms on the attached methyl groups follow the anticipated order of enhanced nuclear shielding with increasing atomic number, the immediately adjacent bridgehead bicyclobutane carbon atom (C_1) appears subject to the fascinating, albeit incompletely understood, irregular variability intrinsic to the chemical behavior of silanes, germanes, and stannanes.[16] The trends reflected in the neighboring bridgehead (C_7) and wing (C_2) carbon shifts are again smoothly progressive but in opposite directions. In both situations, the overall effect is one of deshielding relative to **13**. Inductive polarization is seemingly not uniquely responsible since the shifts differ little, although the electronegativities of Si, Ge, and Sn vary widely. We conclude that yet other undefined factors make substantial contributions as well.



11 12 13

The PE spectra of **11**,[17] **12a**, **12b**, and **13** have also been measured (Figure 1).[18] It is seen that the 1-trimethylsilyl and 1-trimethylgermyl groups, like *tert*-butyl, destabilize the a_1, a_2, and b_2 orbitals of the bicyclobutane ring. This is as expected since PE spectroscopy measures only the energy differences between electronic states. Through application of Koopmans' theorem,[19] these energies can then be associated with factorized molecular orbitals. The perturbation of the latter may be further partitioned into inductive contributions, conjugative interactions, and the like. Qualitatively, the trends observed in Figure 1 are most simply explained on the basis of the donor–acceptor influences of the C_1 substituent.

Rearrangements of the 1-Substituted Derivatives. When **12a** was treated with an anhydrous benzene solution of $AgClO_4$ in the temperature range 40–50 °C, rearrangement proceeded quite slowly with initial formation only of the 1,3-cycloheptadiene **14**, the structure of which was established conclusively by independent synthesis from bromide **15**. At longer reaction times, there appeared a subsidiary product whose ^{1}H NMR spectrum (see Experimental Section) gave a concrete indication[20] that it was the 1-substituted 2-norcarene **16**. Since rigid control experiments proved beyond doubt that **16** was a transition metal promoted rearrangement product neither of **12a** nor of **14**, our suspicions were aroused that its formation might result from the presence of perchloric acid which is gradually produced[21] during the extended periods required to achieve complete consumption of **12a**. Indeed, when a solution of **12a** in benzene was treated with a drop of 70% aqueous perchloric acid, an instantaneous rearrangement leading exclusively to **16** was observed.

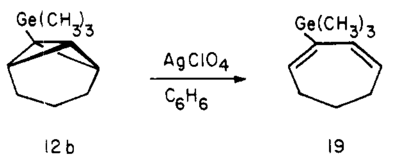


12a 14 15 16 17 18

A brief investigation of the reactivity of **12a** toward other Brønsted and Lewis acids revealed some fascinating alterations in product distribution. For example, exposure to catalytic quantities of *p*-toluenesulfonic acid led to a mixture of **16** and **17**, while ethereal solutions of anhydrous magnesium bromide provided **17** exclusively. Although the ^{1}H NMR spectrum provided diagnostic structural information on **17**, this silane was prepared in an alternative manner by cuprous ion-catalyzed decomposition of trimethylsilyldiazomethane in 1,3-cyclohexadiene.

These observations indicate that the response of **12a** to Ag^+ attack (exclusive type α isomerization) parallels that observed for parent hydrocarbon **11** rather than the sterically more related congener **13** (4% α; 92% γ; 2% δ).[13c] Furthermore, the behavior of **12a** toward other catalysts is more widely divergent than that exhibited by these other tricycloheptanes. Such relevant points will be discussed later.

Following the same procedure, $AgClO_4$-promoted rearrangement of **12b** proceeded smoothly and quantitatively to give **19**. Upon comparable treatment of the trimethylstannyl derivative **12c**, however, a silver mirror was observed to form rapidly, and ^{1}H NMR analysis of the supernatant solution revealed the formation of a very complex mixture. Since this behavior was traced to the high susceptibility of the Sn–C



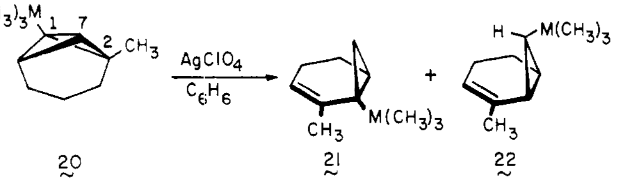
12b **19**

bond for cleavage under such conditions, the further study of stannyl compounds was not pursued.

The initial rates of disappearance of **12a** and **12b** at 40.0 °C were determined to proceed with catalytic constants (k_{Ag}) of 1.17 (±0.13) × 10^{-5} and 2.82 (±0.27) × 10^{-5} M^{-1} s^{-1}, respectively. Although the overall isomerization of the *tert*-butyl derivative **13** at the same temperature proceeds with a tenfold faster pseudo-first-order rate constant (1.31 × 10^{-4} M^{-1} s^{-1}),[13c] factoring of this value to exclude all but the type-α pathway gives evidence of a slower kinetic profile for this hydrocarbon (k_α = 3.93 × 10^{-6} M^{-1} s^{-1}) in this specific reaction channel. As a group, this trio of tricycloheptanes is seen to uniformly rearrange more slowly than **11** (k_{Ag} = 2.27 × 10^{-3} M^{-1} s^{-1}).

Impact of 2-Methyl Substitution. With recognition of the fact that **12a** and **12b** undergo type α rearrangement when exposed to Ag^+, attention was next turned to enhancing the stability of the hypothetical cationic intermediates **9** and **10** by positioning a methyl group at C_2. Should cleavage of the C_2–C_7 bond in **20** not be sterically impeded, then the electron-deficient center in the resultant cation would now be tertiary in nature. Should greater levels of C–M bond hyperconjugation now be made possible, we remained optimistic that unprecedented reactivity patterns would be seen.

To test this idea, the preparation of **20a** and **20b** was effected by functionalization of 2-methyltricyclo[4.1.0.0^{2,7}]heptane as before. The results of their $AgClO_4$-promoted rearrangement gave immediate recognition of the fact that the type α pathway was no longer followed. During reaction periods of 1.5–2 h at 40 °C, **20a** was transformed into an inseparable mixture of **21a** and **22a** in the approximate relative proportions of 90:10. As the time of reaction was extended, the concentrations of these silanes were seen to decay (^{1}H NMR) as three further transformation products made their appearance. One of these was 1-methyl-1,3-cycloheptadiene (**23**).[12b] Since **21a** and **22a** were converted to the identical three products under the original reaction conditions, it is obvious that the latter are not primary products.



20 **21** **22**

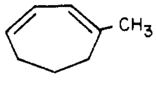
a, M = Si ; **b**, M = Ge

The germane **20b** likewise underwent isomerization initially to a 90:10 mixture of **21b** and **22b**, respectively. These 2-norcarenes are similarly unstable to the reaction medium and experience further chemical change to **23** and other unidentified products.

Silane **20a** also underwent rearrangement in the presence of *p*-toluenesulfonic acid, but the product distribution was now heavily in favor of **22a** (85%) rather than **21a** (15%). When **20b** was treated with an anhydrous ethereal solution of magnesium bromide, somewhat slower rearrangement occurred to give predominantly **22b** (95%). The second product proved to be **21b** (5%).

The gross structures of the four 2-norcarenes are consistent with the spectral evidence and their formation upon alternative ring opening of **20**. Compounds **21a** and **21b**, for example, are characterized by an olefinic proton resonance of area 1 in the δ 5.60–5.35 region, an sp^2-bound methyl group at 1.85–1.87, and three individually well-resolved cyclopropyl absorptions. For **22a** and **22b**, the olefinic and methyl signals were again in evidence, but because the exo group 4 substituent at C_7 induces a shielding effect on $H_{7(endo)}$ while deshielding H_1 and H_6 the cyclopropyl protons now appear as a pair of multiplets at δ 1.50–0.70 (2 H) and 0.50–0.00 (1 H) (compare **17**).

The particularly striking aspects of these findings are the total dominance by type δ processes and the particular efficacy of Ag^+ in promoting high levels of C_2–C_7 bond cleavage contrary to the other catalysts. It should be recognized that the exclusivity of 2-norcarene production constitutes an unprecedented mechanistic changeover which proceeds when a silicon or germanium atom is present at C_1. In the case of 1,2-dimethyltricyclo[4.1.0.0^{2,7}]heptane (**24**), for example, exposure to catalytic amounts of Ag^+ leads to the following partitioning: 12% α, 28% β, 52% γ, and only 8% δ. In view of the quite small δ fractionation factor shown by this hydrocarbon, C_1–C_2 disubstitution alone is not a sufficient condition for incursion of this isomerization route.



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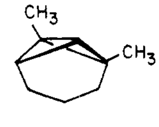

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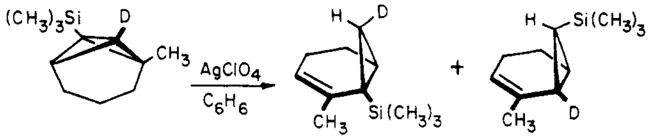
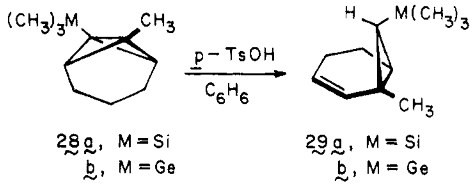
A further stereochemical aspect of the **20a** → **21a** reaction was investigated by the incorporation of a deuterium atom at C_7. Treatment of **25** with the identical silver perchlorate–benzene solution under comparable conditions resulted again in conversion to a 90:10 mixture of 2-norcarenes, in this case **26** and **27**. Since the ^{1}H NMR spectrum of **26** showed loss of the δ 0.90 multiplet and simplification of the former triplet at 0.40 to a doublet, the deuterium atom must be exo oriented at C_7. The difference in chemical shift between $H_{7(exo)}$ and $H_{7(endo)}$ in **21a** and **21b** appears to be due chiefly to anisotropic shielding by the C–M single bond. If it is recognized that the diamagnetic susceptibility of C–M bonds should be greatest in a transverse direction,[22] then the deshielding zone which extends out along the bond direction will cause $H_{7(endo)}$ to shift upfield of $H_{7(exo)}$. In this context, it is interesting that a comparable effect has been encountered earlier in 1-*tert*-butyl-2-methyl-2-norcarene.[13c] However, 1,2-dimethyl-2-norcarene which possesses an identical substitution plan exhibits overlapping signals for this pair of protons at δ 0.60.[20] Although a change in molecular geometry may be responsible for a portion of this effect, we are inclined to believe that the electron-donating capabilities of the three methyl groups attached to the atom bonded to C_1 also make an important anisotropy contribution.



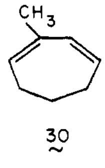
25 **26** **27**

Consequence of Bridgehead Methyl Substitution. Prepared by trimethylsilylation of the 1-methyltricyclo[4.1.0.0^{2,7}]heptyl anion, **28a** was found to be isomerized exceedingly slowly by Ag^+. This lack of reactivity is perhaps best reflected in our finding that considerable amounts of **28a**



28a, M = Si
b, M = Ge

29a, M = Si
b, M = Ge



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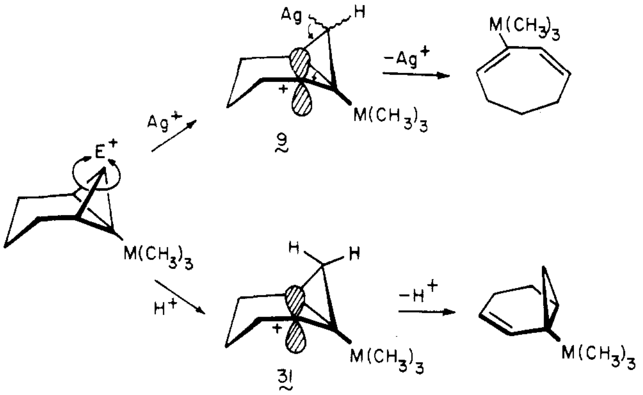
could be recovered after heating with silver perchlorate in benzene at 40 °C for 14 days! As expected, the small quantities of adventitious acid produced during such prolonged treatment did cause partial decomposition of the silane. Although the majority of these by-products appeared to be polymeric, the one volatile constituent was identified as 2-methyl-1,3-cycloheptadiene (**30**).[12b]

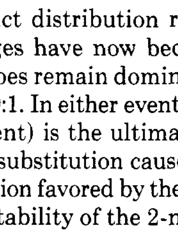
Methyl-substituted germane **28b** was conveniently synthesized by methylation of the anion generated upon treatment of **12b** with *n*-butyllithium and EDA. This substance also demonstrated a low reactivity toward Ag^+ and a comparable susceptibility for conversion to polymer and **30**. Independent treatment of **28b** in benzene with a drop of 70% aqueous perchloric acid caused entirely similar degradation. This was not the case with *p*-toluenesulfonic acid in benzene where efficient ring opening to **29b** was observed. The conversion of **28a** to **29a** was satisfactorily accomplished in a comparable manner.

Discussion

Our results indicate that **12a** and **12b** react with Ag^+ and H^+ (as $HClO_4$) by initial C_2C_7 bond cleavage. According to Wiberg and Szeimies,[23] approach of an electrophile along the bisector of the $C_1C_2C_7$ angle is the minimum energy pathway for the ring opening of bicyclobutanes, particularly when retention of configuration occurs. If inversion of configuration at C_7 is operational, then that working hypothesis featuring approach of the electrophile unsymmetrically from above the flap is most likely.[13a] Irrespective of which assumption is made, the first formed 2-norcaranyl cations will be **9** and **31**. Despite the obvious structural similarity of these intermediates, **9** proceeds to deliver 1,3-cycloheptadiene products (e.g., **14** and **19**) while **32** gives rise to 2-norcarenes (e.g., **16**). This mechanistic dichotomy must be intimately tied to the nature of the C_7 substituent just introduced and can best be understood in the following terms. As a consequence of the weakness of C–Ag bonds, molecules containing such entities manifest a particular sensitivity to those homolytic or heterolytic processes which cause loss of the transition metal.[24] In **9**, the existing positive charge at C_2 will certainly cause the silver atom to be ejected as Ag^+ and there apparently exists an overwhelming preference for that particular electronic change within this cation which introduces the diene unit (see arrows) to occur more rapidly and effectively than other possible conformational or chemical changes. In **31**, the proton just appended is not as likely a leaving group and this cation possesses no intrinsic driving force to do other than the chemistry customarily associated with 2-norcaranyl cations. Under the conditions of the present experiments, this would appear to be simple proton loss from C_3.



Anhydrous magnesium bromide, in contrast, is found to attack the C_1–C_2 bond of **12a** exclusively. The ability of this catalyst to promote 2-norcarene formation has previously been recognized.[25] Free cyclopropylcarbinyl cations have not been implicated as intermediates in these isomerizations. Rather, the main pathway is believed to involve proton transfer to a bicyclobutane edge bond within a complex, followed by proton loss from C_3 to an external base such as bromide ion.[25] We do not wish to address mechanistic issues in this particular instance but emphasize only the uniqueness of site selectivity for $MgBr_2$ attack. It is particularly tempting to invoke the possible involvement of long-range contributions by the C–M bond as in **32**, despite the fact that little evidence is available to substantiate this hypothesis.[26]



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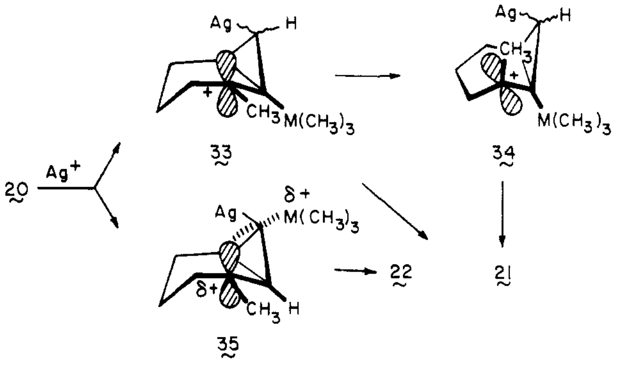
A further significant comparison emerges from analysis of the product distributions which arise from the $HClO_4$- and *p*-TosOH-promoted rearrangements of **12a**. The production of **17** under the latter conditions is the likely result of the differing acid strengths of these catalysts and the dissimilarities in solvent polarity. In the case of *p*-TosOH, catalytic quantities of the hydrated form were added to an otherwise anhydrous benzene solution of the silane. On the other hand, the $HClO_4$ was dissolved in water (commercial 70% solution). These apparently small changes are not negligible and exert a pronounced effect on the kinetically controlled bond cleavages in **12a**. It may well be that yet different acids or solvent systems could promote higher levels of C_1–C_2 attack than observed with *p*-TosOH.

The response of **20a** and **20b** to isomerization provides an interesting contrast to the above. Under conditions of Ag^+ catalysis, the product distribution reveals that C_1–C_2 and C_2–C_7 bond cleavages have now become competitive. The latter process still does remain dominant, however, being favored by a factor of 9:1. In either event, 2-norcarene formation (type δ rearrangement) is the ultimate result. The findings that "wing" methyl substitution causes total inoperability of the type α isomerization favored by the parent systems suggest that the enhanced stability of the 2-norcaranyl cation intermediates is very much a key factor in these reactions. To the extent that the tertiary nature of **33** and **35** reflects an enhanced degree of charge localization at C_2 and lesser intimate interaction with the adjoining cyclopropane ring, kinetically controlled proton loss from C_3 appears to gain kinetic importance. Although there exists no direct evidence that **33** experiences conformational inversion to boat form **34** prior to conversion to **21**, the exceptional chemical behavior of **33** provides some measure of support for this theory. It should be recognized that this structural modification, the energetics of which remain unknown, necessitates that the thermodynamically favored bisected alignment of the vacant p–π orbit with the three-membered ring[27] be substantially altered to enjoy C–M hyperconjugative effects. The prevailing dihedral angle relationships are such that these two stabilizing influ-



ences cannot be operative to their maximum level at the same time. Under normal circumstances, therefore, the ring inversion leading from **33** to **34** would have little reason to operate. We have previously found that 1,2-dimethyltricyclo[4.1.0.0^{2,7}]heptane reacts with Ag^+ to give a transient cation related to **33** but with $M(CH_3)_3$ equal to CH_3.[12b] In the absence of an opportunity for exalted hyperconjugative interaction, this species experiences only 8% conversion to type δ (2-norcarene) product. Consequently, the possibility exists that the availability of stabilizing C–M interaction in **34** facilitates passage to this conformer.

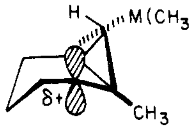
Perhaps a more revealing aspect of this study is the finding that attack by Ag^+ at the most highly substituted edge bond (C_1–C_2) in **20** has gained a certain amount of kinetic importance. The additional experimental evidence indicates that interaction with *p*-TosOH causes cleavage of this same bond with a still higher preference than observed earlier with **12a.** We view this contrasting behavior to be a possible reflection of the timing at which the rate-determining transition states are reached. Qualitative rate measurements have shown that these tricycloheptane rearrangements proceed more rapidly under conditions of acid (*p*-TosOH) catalysis than with Ag^+. Logically, those reactions promoted by H^+ could pass through earlier transition states relative to when Ag^+ is the electrophile, their structures resembling starting material more closely than intermediate. Those pathways involving the highest attainable levels of internal stabilization will therefore be especially favored kinetically under acidic conditions.

We might on this basis ascribe the preference for *p*-TosOH-promoted cleavage in **12a, 20a,** and **20b** to the involvement of long-range homoconjugative interaction (cf. **35** with and without the 2-methyl substituent) of the same type encountered during the solvolysis of **3.** Molecular models reveal that rupture of the C_1–C_2 bond with retention of configuration progresses through an intermediate stage (possibly that of maximum σ-bond stretching) where the C–M bond and the developing p orbital at C_2 adopt a well-defined W-plan orientation.

Such contributions need not be of comparable importance when Ag^+ is involved not only for the reasons discussed above but also because an endo-oriented silver atom in **9, 31,** or **33** could further stabilize the cation by d orbital interactions of its own (not illustrated). Also, if the methyl group in **33** and **35** does provide enough added stability to the electron-deficient center to relieve it of a strong dependency on the proximate cyclopropane ring, then the dominant role which cyclopropylcarbinyl interaction plays in **31** could be diminished sufficiently to allow for observation of other usually less influential stabilizing effects. Although such "secondary" influences as C–M hyperconjugative interaction are likely to have their greatest impact on early transition states (see above), they appear to be capable of influencing Ag^+-promoted isomerizations as well (10% **22a;** 10% **22b**).

Our approach to determining whether the C–Ag bond in **33** is oriented exo or endo at C_7 was to examine the stereochemical outcome of the $AgClO_4$-catalyzed rearrangement of **25.** Although **26** was shown to be the exo-7-*d* isomer, it has remained unclear whether protonolysis of the C–Ag bond occurs with retention or inversion of configuration, and alternative attempts to establish this point have not yielded positive information. This particular question remains unsolved. The locus of the deuterium atom in **26** and **27** does, however, unequivocally define the isomerization as the result of C_2–C_7 cleavage.

The pair of molecules **28a** and **28b** likewise is converted to 2-norcarenes upon treatment with *p*-TosOH. Both of these rearrangements are strikingly regiospecific, giving rise uniquely to 2-methyl-*exo*-7-trimethylsilyl- and -germyl-2-norcarenes (**29a** and **29b**). The intermediacy of **36** but not **37** is thereby implicated in agreement with the preceding mechanistic analysis. Both **28a** and **28b** polymerized when treated with catalytic quantities of $HClO_4$, thus pointing up again the rather different nature of this proton source.



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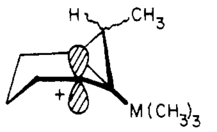

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In summary, it is our conclusion that the ability of certain cationic intermediates to gain stabilization by means of hyperconjugative interaction with C–M bonds is the major determinant underlying the propensity for several of the 1-trimethylsilyl- and 1-trimethylgermyl-substituted tricycloheptanes studied herein to undergo clean type δ rearrangement.

Experimental Section

All boiling points are uncorrected. Melting points were obtained on a Thomas-Hoover capillary apparatus. Infrared spectra were recorded on a Perkin-Elmer Model 467 instrument. ^1H NMR spectra were recorded on Varian A-60A, T-60, and HA-100 instruments as well as a Joelco MH-100 spectrometer. Fourier spectra (both carbon and proton) were obtained on a Bruker HX-90 instrument. Apparent splittings are given. Combustion analyses were performed by the Scandinavian Microanalytical Laboratory, Herlev, Denmark. Preparative VPC work was carried out with the aid of a Varian Aerograph A-90P3 chromatograph equipped with a thermal conductivity detector, while analytical determinations were performed on a Hewlett-Packard HP5750 research gas chromatograph equipped with a flame ionization detector and Model HP3370A electronic integrator.

1-Trimethylsilyltricyclo[4.1.0.0^{2,7}]heptane (12a). To a solution containing 10 mL of 2.4 M *n*-butyllithium in hexane, 2.3 mL of tetramethylethylenediamine (TMEDA), and 10 mL of pentane was added under nitrogen 2.0 g (0.02 mol) of tricyclo[4.1.0.0^{2,7}]heptane (**11**) at 5 °C. The yellow solution was diluted with 15 mL of pentane, allowed to warm to room temperature, and stirred for 12 h prior to treatment at 5 °C with 2.40 g (0.022 mol) of trimethylchlorosilane dissolved in 5 mL of pentane. The resultant mixture was stirred for 1 h and 15 mL of water was slowly added. The organic layer was washed with saturated curpic sulfate solution (2 × 50 mL), dried, and concentrated. Flash distillation afforded 1.19 g (34%) of an oil which VPC analysis (2 ft × 0.25 in. 5% SE-30 on Chromosorb W, 80 °C) indicated was uncontaminated: $\delta_{Me_4Si}{}^{C_6D_6}$ 2.22 (m, 2), 1.68–1.20 (m, 7), and 0.14 (s, 9); *m/e* 166.1179 (calcd 166.1178). Anal. Calcd for $C_{10}H_{18}Si$: C, 72.22; H, 10.93. Found: C, 72.22; H, 11.11.

1-Trimethylgermyltricyclo[4.1.0.0^{2,7}]heptane (12b). In the predescribed manner, 940 mg (10 mmol) of **11** dissolved in 20 mL of pentane was treated with 6 mL of 2.2 M *n*-butyllithium in hexane and 1.8 mL of TMEDA. After 12 h the anion was similarly treated with 2.0 g (10 mmol) of bromotrimethylgermane. The usual workup afforded 1.05 g (49%) of **12b,** further purification of which was accomplished by VPC methods (5.5 ft × 0.25 in. 12% OV-11 on Chromosorb W, 100 °C): $\delta_{Me_4Si}{}^{C_6D_6}$ 2.30–2.05 (m, 2), 1.65–1.30 (m, 7), and 0.14 (s, 9); *m/e* 212.0624 (calcd 212.0620). Anal. Calcd for $C_{10}H_{18}Ge$: C, 56.95; H, 8.62. Found: C, 56.90; H, 8.91.

1-Trimethylstannyltricyclo[4.1.0.0^{2,7}]heptane (12c). In the same manner, 940 mg (10 mmol) of **11** was lithiated by addition to a pentane solution (50 mL) containing 6 mL of 2.2 M *n*-butyllithium and 1.8 mL of TMEDA. Subsequent to addition of chlorotrimethylstannane (2.0 g, 10 mmol) and the usual workup, there was isolated 2.13 g (80%) of **12c.** Isolation by VPC (5.5 ft × 0.25 in. 12% OV-11, 115 °C) afforded an analytically pure sample: $\delta_{Me_4Si}{}^{C_6D_6}$ 2.17 (m, 2), 1.78 (m, 1), 1.45 (m, 6), and 0.10 (s, 9); *m/e* 258.0435 (calcd 258.0429). Anal. Calcd for $C_{10}H_{18}Sn$: C, 46.73; H, 7.07. Found: C, 47.14; H, 7.10.

Ag(I)-Catalyzed Rearrangement of 12a. Into a thin-walled NMR tube was dissolved 152.5 mg of **12a** in 3 mL of a 0.2204 M solution of silver perchlorate in benzene. The tube was sealed and heated in a constant temperature bath at 40.0 °C. The ^1H NMR spectrum of the solution no longer contained starting material. The tube was opened and the solution was added to saturated brine. VPC analysis (5.5 ft × 0.25 in. 12% OV-11, 100 °C) indicated the presence of two components which proved to be 1-trimethylsilylbicyclo[4.1.0]hept-2-ene (**16**) and 2-trimethylsilyl-1,3-cycloheptadiene (**14**). Quantitative analysis of several runs of this reaction revealed the ratio of these two products to vary from 80:20 to 30:70, respectively. Careful NMR observation and VPC examination of the solutions employed in the kinetic experiments (vide infra) at various time intervals showed **14** to be the only product formed initially. In contrast, the 2-norcarene **16** arose very rapidly at longer reaction times, usually coinciding with the formation of a dark, finely divided precipitate.

2-Trimethylsilyl-1,3-cycloheptadiene (14). A stirred solution of 2.73 g (0.016 mol) of 2-bromo-1,3-cycloheptadiene (**15**)[28] in 20 mL of dry ether was cooled to 5 °C under a nitrogen atmosphere. *n*-Butyllithium in hexane (10 mL of 2.2 M) was added. The resulting solution was stirred at room temperature for 12 h, recooled to 5 °C, and treated with 2.50 g (0.023 mmol) of chlorotrimethylsilane. After 60 min at room temperature, water (50 mL) was introduced and the separated organic layer was washed with water, dried, and concentrated. VPC analysis (5.5 ft × 0.25 in. 12% OV-11, 100 °C) yielded a single product which was identical in all respects with **14** isolated earlier: $\delta_{Me_4Si}^{C_6D_6}$ 6.35–5.90 (m, 3), 2.40–2.00 (m, 4), 2.00–1.70 (m, 2), and 0.16 (s, 9); *m/e* 166.1179 (calcd 166.1178). Anal. Calcd for $C_{10}H_{18}Si$: C, 72.22; H, 10.93. Found: C, 72.19; H, 10.93.

Perchloric Acid Catalyzed Rearrangement of 12a. 1-Trimethylsilylbicyclo[4.1.0]hept-2-ene (16). Into a solution of 30 mg of **12a** in 110 μL of C_6D_6 was added 1 drop of 70% aqueous perchloric acid. ^{1}H NMR analysis indicated an instantaneous reaction. The solution was extracted with dilute sodium bicarbonate solution. VPC analysis (12 ft × 0.25 in. 5% XF-1150, 90 °C) indicated quantitative isomerization to a single product whose isolation afforded pure **16**: $\delta_{Me_4Si}^{C_6D_6}$ 6.04–5.92 (d, ½ of AB, J = 13 Hz, 1), 5.60–5.40 (m, 1), 1.96–1.60 (m, 4), 1.30–1.00 (m, 1), 0.88–0.60 (m, 2), and 0.40 (s, 9); *m/e* 166.1179 (calcd 166.1178). Anal. Calcd for $C_{10}H_{18}Si$: C, 72.22; H, 10.93. Found: C, 72.34; H, 10.93.

Magnesium Bromide Promoted Rearrangement of 12a. *exo*-7-Trimethylsilylbicyclo[4.1.0]hept-2-ene (17). Into 1.0 mL of 1.0 M magnesium bromide in anhydrous ether was injected 45 μL of **12a** via syringe. The solution was shaken in a 2-dram vial and kept at room temperature for 24 h. Water (1.0 mL) was added. VPC ANALYSIS (12 ft × 0.25 in 5% XF-1150, 90 °C) of the organic layer indicated quantitative conversion to **17**: $\delta_{Me_4Si}^{C_6D_6}$ 6.10 (m, 1), 5.50 (m, 1), 1.75 (m, 4), 1.16 (m, 2), 0.13 (t, J = 6 Hz, 1), and 0.00 (s, 9); *m/e* 166.1179 (calcd 166.1178). Anal. Calcd for $C_{10}H_{18}Si$: C, 72.22; H, 10.93. Found: C, 72.55; H, 11.02.

***p*-Toluenesulfonic Acid Catalyzed Rearrangement of 12a.** A few crystals of *p*-toluenesulfonic acid monohydrate were added to a solution containing 20 g of **12a** in 300 μL of C_6D_6. After heating at 40.0 °C for 24 h, the solution was added to water. VPC analysis (12 ft 5% XF-1150, 90 °C, 60 mL/min) of the organic phase showed a single broad peak, which ^{1}H NMR analysis indicated to consist of an approximately 50:50 mixture of **16** and **17** (from careful integration of the olefinic region).

Independent Synthesis of 17. To a solution of 1,3-cyclohexadiene (300 mg, 3.75 mmol) in 3 mL of benzene was added 100 mg of cuprous chloride and 570 mg (5.0 mmol) of trimethylsilyldiazomethane.[29] The slurry was stirred at room temperature for 2 h and added to 10 mL of water. The organic layer was washed with brine, dried, and concentrated. Preparative VPC isolation (5.5 ft × 0.25 in. 10% OV-11, 125 °C) afforded 50 mL (~10%) of **17** as the only observable adduct. Its spectral properties proved identical with those of the silane isolated above.

Kinetic Study of the Ag(I)-Catalyzed Rearrangement of 12a. Into each of 18 dry previously base-washed ampules was added 100 μL of 0.1898 M silver perchlorate in benzene and 3 μL of **12a**. The ampules were heated in a constant temperature bath at 40.0 ± 0.1 °C. As aliquots were periodically removed, the progress of reaction was arrested by addition to saturated brine and determined quantitatively by VPC analysis of the organic phases (18 ft × 0.125 in. UC-W-98, 120 °C). Measurements were made for periods up to 48 h. Only those ampules in which rearrangement to the diene was the exclusive reaction were included in the analysis. Six ampules in which some amount of the norcarene **16** was observed were discarded. A plot of ln [([**12a**] + [**14**])/[**12a**]] vs. time was linear. Least-squares regression analysis gave a pseudo-first-order rate constant, division of which by the concentration of silver perchlorate yielded k_{Ag} = 1.17 ± 0.13 × 10^{-5} M^{-1} s^{-1}.

Ag(I)-Catalyzed Rearrangement of 12b. Into an NMR tube was placed 30 mg of **12b** and 100 μL of a 0.2204 M solution of silver perchlorate in benzene. The tube was sealed and heated at 40.0 °C while the extent of rearrangement was monitored. After 90 h, less than 10% of the starting material remained, while conversion to a single rearrangement product had occurred. The solution was treated with brine and the organic layer was subjected to VPC analysis (5.5 ft × 0.25 in. 12% OV-11, 100 °C). Quantitative rearrangement to a single component identified as 2-trimethylgermyl-1,3-cycloheptadiene (**19**) was observed: $\delta_{Me_4Si}^{C_6D_6}$ 6.16–5.64 (m, 3), 2.28–1.96 (m, 4), 1.88–1.60 (m, 2), and 0.24 (s, 9); *m/e* 212.0624 (calcd 212.0620). Anal. Calcd for $C_{10}H_{18}Ge$: C, 56.95; H, 8.62. Found: C, 57.06; H, 8.71.

Kinetics of the Ag(I)-Catalyzed Rearrangement of 12b. As before, 15 ampules containing 100 μL of 0.1898 M silver perchlorate in benzene and 2.5 μL of **12b** were sealed and heated at 40.0 ± 0.1 °C. The ampules were periodically removed, treated with brine, and analyzed by VPC (18 ft × 0.125 in. UC-W-98, 120 °C). A plot of ln [([**12b**] + [**19**])/[**12b**]] vs. time was linear and least-squares analysis produced the pseudo-first-order rate constant. When divided by [$AgClO_4$], the k_{Ag} value of 2.82 ± 0.27 × 10^{-5} M^{-1} s^{-1} was obtained.

Ag(I)-Promoted Decomposition of 12c. To 100 μL of 0.1898 M silver perchlorate in benzene was added 20 μL of **12c**. Within minutes, the solution darkened and a silver mirror was formed. After addition to brine, the organic layer was analyzed by VPC (5.5 ft × 0.25 in. 12% OV-11, 115 °C). The disappearance of starting material and total absence of any volatile products were thereby indicated.

1-Trimethylsilyl-2-methyltricyclo[4.1.0.0^{2,7}]heptane (20a). In the predescribed manner, 430 mg (4.0 mmol) of 2-methyltricyclo[4.1.0.0^{2,7}]heptane was subjected to the action of 2.0 mL of 2.4 M *n*-butyllithium and 0.5 mL of TMEDA dissolved in 10 mL of pentane. The anion was treated with 0.5 g (4.6 mmol) of chlorotrimethylsilane and the product isolated by preparative VPC (12 ft × 0.125 in. 5% XF-1150, 105 °C). There was obtained 200 mg (28%) of **20a**: $\delta_{Me_4Si}^{C_6D_6}$ 2.02 (m, 1), 1.70 (m, 1), 1.32 (m, 6), 1.00 (s, 3), and 0.07 (s, 9); *m/e* 180.1336 (calcd 180.1334). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.04; H, 11.31.

1-Trimethylgermyl-2-methyltricyclo[4.1.0.0^{2,7}]heptane (20b). In an identical manner, 430 mg (4.0 mmol) of 2-methyltricyclo[4.1.0.0^{2,7}]heptane was lithiated by addition to 2.0 mL of 2.4 M *n*-butyllithium and 0.5 mL of TMEDA in 10 mL of pentane. The resulting anion was treated with 900 mg (4.5 mmol) of bromotrimethylgermane. After the usual workup, VPC isolation (5.5 ft × 0.25 in. 12% OV-11, 120 °C) afforded 300 mg (30%) of **20b**: $\delta_{Me_4Si}^{C_6D_6}$ 2.05 (m, 1), 1.65 (m, 1), 1.40 (m, 6), 1.00 (s, 3), and 0.22 (s, 9); *m/e* 226.0781 (calcd 226.0777). Anal. Calcd for $C_{11}H_{20}Ge$: C, 58.75; H, 8.97. Found: C, 58.85; H, 9.10.

Ag(I)-Catalyzed Rearrangement of 20a. Into an NMR tube was placed 300 μL of a 0.1898 M solution of silver perchlorate in anhydrous benzene. A 60-μL sample of **20a** was injected and the solution was heated to 40.0 ± 0.1 °C with constant monitoring of the ^{1}H NMR spectrum. As reaction proceeded, one product was seen to predominate but proved in turn to be subject to further rearrangement leading to several other products. After 1.5 h when the integral associated with the first formed isomer was at a maximum, the solution was poured into saturated brine. VPC analysis (12 ft × 0.25 in. 5% XF-1150, 100 °C) revealed the presence of several peaks, one of which did predominate. Collection of this component permitted its identification as 1-trimethylsilyl-2-methylbicyclo[4.1.0]hept-2-ene (**21a**): $\delta_{Me_4Si}^{C_6D_6}$ 5.50 (m, 1), 1.88 (pseudo s, 7), 1.60–1.00 (m, 1), 0.90 (m, 1), 0.40 (t, J = 3 Hz, 1), and 0.07 (s, 9); *m/e* 180.1336 (calcd 180.1334). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.17; H, 11.45.

Careful analysis of the ^{1}H NMR spectrum of this norcarene indicated the presence of ca. 10% of **22a** as prepared below.

Resubmission of **21a** to the original reaction conditions or extension of the isomerization of **20a** to 12 h gave rise to identical product mixtures. VPC analysis (12 ft × 0.25 in. 5% XF-1150, 100 °C) of these solutions showed three components to be present in the ratio of 1: 3.3:4.

The smallest constituent proved identical with authentic 1-methyl-1,3-cycloheptadiene (**23**).[12b]

The middle peak remains as yet unidentified: $\delta_{Me_4Si}^{C_6D_6}$ 6.40–5.90 (m, 2), 2.40–1.85 (m, 5), 1.80 (br s, 4), and 0.16 (s, 9); *m/e* 180.1336 (calcd for $C_{11}H_{20}Si$ 180.1334).

The largest peak has likewise eluded positive structural assignment: $\delta_{Me_4Si}^{C_6D_6}$ 6.12 (m, 1), 5.50 (m, 1), 2.90 (m, 2), 2.28 (m, 4), 1.80 (br s, 3), and 0.20 (s, 9); *m/e* 180.1336 (calcd for $C_{11}H_{20}Si$ 180.1334).

Acid-Promoted Rearrangement of 20a. *exo*-7-Trimethylsilyl-2-methylbicyclo[4.1.0]hept-2-ene (22a). Into a solution containing 45 mg of **20a** in 300 μL of C_6D_6 was added a few crystals of *p*-toluenesulfonic acid monohydrate. After being heated at 40 °C for 3 h, the solution was added to water. Preparative VPC purification of the product contained in the organic layer afforded 20 mg (45%) of **22a**: $\delta_{Me_4Si}^{C_6D_6}$ 5.20 (m, 1), 1.83 (br s, 7), 1.50–0.80 (m, 2), 0.30–0.00 (m, 1), and 0.00 (s, 9); *m/e* 180.1336 (calcd 180.1334). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.48; H, 11.60.

Careful integration of the ^{1}H NMR spectrum indicated the presence of ca. 15% of **21a**.

Ag(I)-Catalyzed Rearrangement of 20b. In the previously described manner, a solution of **20b** (80 mg) in 250 μL of 0.1898 M silver perchlorate in anhydrous benzene was heated at 40.0 °C for 2 h and then added to saturated brine. VPC isolation of the predominant peak (12 ft × 0.25 in. 5% XF-1150, 100 °C) afforded 30 mg (38%) of 1-trimethylgermyl-2-methylbicyclo[4.1.0]hept-2-ene (**21b**): $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 5.60–5.35 (m, 1), 1.85 (pseudo s, 7), 1.00–0.80 (m, 1), 0.80–0.50 (m, 1), 0.50–0.20 (m, 1), and 0.15 (s, 9); *m/e* 226.0781 (calcd 226.0777). Anal. Calcd for $C_{11}H_{20}Ge$: C, 58.75; H, 8.97. Found: C, 59.06; H, 9.08.

Careful ^1H NMR analysis indicated the presence of ca. 10% of **22b** (as prepared below) to be present.

Further reaction of **20b** or **21b** with the silver perchlorate solution for 12 h produced identical reaction mixtures, VPC analysis of which (12 ft × 0.25 in. 5% XF-1150, 100 °C) showed three components to be present in the ratio of 1:3:3.

The minor constituent was again identical with an authentic sample of 1-methyl-1,3-cycloheptadiene (**23**).[12b]

The first of the larger peaks was not identified: $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 6.20–5.80 (m, 2), 2.40–1.80 (m, 6), 1.70 (br s, 3), and 0.24 (s, 9); *m/e* 226.0781 (calcd for $C_{11}H_{20}Ge$ 226.0787).

The final component likewise remains unidentified: $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 6.00 (m, 1), 5.50 (m, 1), 2.92 (m, 2), 2.25 (m, 4), 1.72 (br s, 3), and 0.24 (s, 9); *m/e* 226.0781 (calcd for $C_{11}H_{20}Ge$ 226.0787).

***exo*-7-Trimethylgermyl-2-methylbicyclo[4.1.0]hept-2-ene (22b).** To 450 μL of a 1.0 M ethereal solution of magnesium bromide was added 15 mg of **20b.** The solution was sealed in an ampule and heated at 40.0 °C for 14 h and then added to water. VPC isolation of the volatile product afforded 8 mg (53%) (12 ft × 0.25 in. 5% XF-1150, 100 °C) of **22b:** $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 5.24 (m, 1), 1.90 (br s, 7), 1.40–0.70 (m, 2), 0.50–0.20 (m, 1), and 0.14 (s, 9).

Careful integration of the ^1H NMR spectrum indicated contamination by approximately 5% of **21b.**

1-Trimethylsilyl-2-methyltricyclo[4.1.0.$0^{2,7}$]heptane-*7-d* (25). Into a solution containing 3 mL of 2.5 M *n*-butyllithium in hexane, 1.0 mL of TMEDA, and 10 mL of pentane was added 168 mg (0.9 mmol) of **20a** at 0 °C under nitrogen. After being stirred at room temperature for 12 h, the solution was cooled and 1.0 mL of 99.8% deuterium oxide was added. After the usual workup, the organic phase was concentrated and then flash distilled. The oil thus obtained was resubmitted to the above conditions and the process repeated for a total of four lithiations. Preparative VPC purification (12 ft × 0.25 in. 5% XF-1150, 100 °C) yielded 50 mg (30%) of **25:** *m/e* 181.1400 (calcd 181.1397). Deuterium incorporation was calculated to be 97%. The ^1H NMR spectrum showed loss of the signal at δ 1.70.

Ag(I)-Catalyzed Rearrangement of 25. Into a solution of 150 μL of 0.1898 M silver perchlorate in anhydrous benzene was added 40 mg of **25.** Following 12 h of heating at 40.0 °C, the solution was added to saturated brine. VPC purification on the XF-1150 column allowed isolation of the major peak, which was identified as *exo*-7-deuterio-1-trimethylsilyl-2-methylbicyclo[4.1.0]hept-2-ene (**26**) (20 mg, 50%): *m/e* 181.1400 (calcd 181.1397). Deuterium incorporation was estimated at 97%. The ^1H NMR spectrum indicated loss of the signal at δ 0.90 and simplification of the triplet at δ 0.40 to a doublet (*J* = 4 Hz). Careful integration of this spectrum showed approximately 10% of **27** to also be present.

1-Trimethylsilyl-7-methyltricyclo[4.1.0.$0^{2,7}$]heptane (28a). In the usual manner, 200 mg (1.85 mmol) of 1-methyltricyclo[4.1.0.$0^{2,7}$]heptane was added to 1.0 mL of 2.5 M *n*-butyllithium and 0.2 mL of TMEDA in 10 mL of pentane. The resulting anion was silylated with 220 mg (2.0 mmol) of chloromethylsilane and the reaction mixture processed in the usual manner. Preparative VPC isolation (12 ft × 0.25 in. 5% XF-1150, 90 °C) provided 300 mg (70%) of **28a:** $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 2.03 (m, 2), 1.53 (s, 3), 1.40 (m, 6), and 0.13 (s, 9); *m/e* 180.1336 (calcd 180.1334). Anal. Calcd for $C_{11}H_{20}Si$: C, 73.25; H, 11.18. Found: C, 73.14; H, 11.34.

1-Trimethylgermyl-7-methyltricyclo[4.1.0.$0^{2,7}$]heptane (28b). To a solution of 2 mL of 2.2 M *n*-butyllithium and 0.5 mL of TMEDA in 20 mL of pentane was added 533 mg (3.2 mmol) of **12b.** The resulting anion was methylated through addition of 570 mg (4.0 mmol) of methyl iodide. The usual workup and preparative VPC purification (5.5 ft × 0.25 in. 12% OV-11, 120 °C) afforded a nearly quantitative yield of **28b:** $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 2.00 (m, 2), 1.45 (s, 3), 1.35 (m, 6), and 0.17 (s, 9); *m/e* 226.0781 (calcd 226.0777). Anal. Calcd for $C_{11}H_{20}Ge$: C, 58.75; H, 8.97. Found: C, 58.55; H, 9.19.

***exo*-7-Trimethylsilyl-1-methylbicyclo[4.1.0]hept-2-ene (29a).** To a solution of 30 mg of **28a** in 300 μL of C_6D_6 was added a few crystals of *p*-toluenesulfonic acid monohydrate. The solution was heated at 40.0 °C for 5 h at which time ^1H NMR analysis showed nearly quantitative conversion to a single product. The solution was added to water. VPC isolation (12 ft × 0.25 in. 5% XF-1150, 100 °C) afforded 15 mg (50%) of **29a;** $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 5.90 (d, ½ of AB, *J* = 10 Hz, 1), 5.70–5.10 (m, 1), 1.80 (m, 4), 1.30 (s, 3), 1.29–1.00 (m, 1), 0.20–0.10 (m, 1), and 0.10 (s, 9); *m/e* 180.1336 (calcd 180.1334).

***exo*-7-Trimethylgermyl-1-methylbicyclo[4.1.0]hept-2-ene (29b).** In the same manner, 40 mg of **28b** in 300 μL of C_6D_6 was admixed with *p*-toluenesulfonic acid and heated at 40.0 °C for 2 h, at which time ^1H NMR analysis revealed total reaction. After the usual workup, VPC isolation (12 ft × 0.25 in. 5% XF-1150, 110 °C) afforded 30 mg (75%) of **29b:** $\delta_{\mathrm{Me_4Si}}^{\mathrm{C_6D_6}}$ 6.00 (d, ½ of AB, *J* = 10 Hz, 1), 5.40 (m, 1), 1.80 (m, 4), 1.20 (s, 3), 1.10 (m, 1), 0.40 (d, *J* = 7 Hz, 1), and 0.20 (s, 9); *m/e* 222.0781 (calcd 222.0777). Anal. Calcd for $C_{11}H_{20}Ge$: C, 58.75; H, 8.97. Found: C, 58.54; H, 9.40.

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Registry No.—**14,** 64036-11-9; **15,** 3045-85-0; **16,** 64036-12-0; **17,** 64036-13-1; **19,** 64036-14-2; **20a,** 64036-15-3; **20b,** 64036-16-4; **21a,** 64036-17-5; **21b,** 64036-18-6; **22a,** 64036-19-7; **22b,** 64036-20-0; **25,** 64036-21-1; **28a,** 64036-22-2; **28b,** 64036-23-3; **29a,** 64036-24-4; **29b,** 64036-25-5; trimethylchlorosilane, 75-77-4; bromotrimethylgermane, 1066-37-1; chlorotrimethylstannane, 1066-45-1; 2-methyltricyclo[4.1.0.$0^{2,7}$]heptane, 40391-49-9; 1-methyltricyclo[4.1.0.$0^{2,7}$]heptane, 32348-63-3; methyl iodide, 74-884.

References and Notes

(1) Silver(I) Ion Catalyzed Rearrangements of Strained σ Bonds. 34. For the preceding paper in this series, see L. A. Paquette, T. G. Wallis, T. Kempe, G. G. Christoph, J. P. Springer, and J. Clardy, *J. Am. Chem. Soc.*, **99,** 6946 (1977).

(2) The Ohio State University Dissertation Fellow, 1975–1976.

(3) (a) P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, **91,** 6161 (1969); *ibid.*, **93,** 846 (1971); (b) F. R. Jensen and B. F. Smart, *ibid.*, **91,** 5686 (1969); (c) F. R. Jensen and H. E. Guard, *ibid.*, **90,** 3250 (1968); (d) H. Sakurai, A. Hosomi, and M. Kumada, *J. Org. Chem.*, **34,** 1764 (1969); (e) T. G. Traylor and J. C. Ware, *J. Am. Chem. Soc.*, **89,** 2304 (1967); (f) N. S. Vyazankin, E. N. Gladyshev, and G. A. Razuvaev, *Dokl. Akad. Nauk SSSR*, **153,** 104 (1963).

(4) T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *J. Am. Chem. Soc.*, **93,** 5715 (1971), and relevant references cited therein.

(5) T. Kawamura and J. Kochi, *J. Am. Chem. Soc.*, **94,** 648 (1972).

(6) T. Kawamura and J. Kochi, *J. Organometal. Chem.*, **30,** C8 (1971).

(7) (a) T. G. Traylor, H. J. Berwin, J. Jerkunica, and M. L. Hall, *Pure Appl. Chem.*, **30,** 599 (1972); (b) J. C. Ware and T. G. Traylor, *Tetrahedron Lett.*, 1295 (1965); (c) Yu. G. Bundel, N.-D. Antonova, and A. O. Reutov, *Dokl. Akad. Nauk. SSSR*, **166,** 1103 (1966); (d) A. N. Nesmeyanov and I. I. Kritskaya, *ibid.*, **121,** 447 (1958).

(8) (a) W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Am. Chem. Soc.*, **92,** 829, 7476 (1970); (b) T. G. Traylor and J. C. Ware, *ibid.*, **89,** 2304 (1967).

(9) H. G. Kuivila and N. M. Scarpa, *J. Am. Chem. Soc.*, **92,** 6990 (1970); D. D. Davis, R. L. Chambers, and H. T. Johnson, *J. Organometal. Chem.*, **25,** C13 (1970).

(10) D. D. Davis and H. T. Johnson, *J. Am. Chem. Soc.*, **96,** 7576 (1974).

(11) (a) For relevant reviews of this subject, consult L. A. Paquette, *Acc. Chem. Res.*, **4,** 280 (1971); (b) L. A. Paquette, *MTP Int. Rev. Sci.: Org. Chem., Ser. One, 1973,* **5,** 127 (1973); (c) L. A. Paquette, *Synthesis*, 347 (1975).

(12) (a) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *J. Am. Chem. Soc.*, **93,** 1288 (1971); (b) L. A. Paquette, S. E. Wilson, R. P. Henzel, and G. R. Allen, Jr., *ibid.*, **94,** 7761 (1972); (c) L. A. Paquette and J. S. Ward, *Tetrahedron Lett.*, 4909 (1972); (d) L. A. Paquette, R. S. Beckley, and W. B. Farnham, *J. Am. Chem. Soc.*, **97,** 1089 (1975).

(13) (a) L. A. Paquette and G. Zon, *J. Am. Chem. Soc.*, **96,** 224 (1974); (b) G. Zon and L. A. Paquette, *ibid.*, **96,** 215 (1974); (c) L. A. Paquette and G. Zon, *ibid.*, **96,** 203 (1974); (d) G. Zon and L. A. Paquette, *ibid*, **95, 4456** (1973); (e) L. A. Paquette, S. E. Wilson, and R. P. Henzel, *ibid.*, **94,** 7771 (1972); (f) L. A. Paquette and S. E. Wilson, *ibid.*, **93,** 5934 (1971); (g) L. A. Paquette, G. R. Allen, Jr., and R. P. Henzel, *ibid.*, **92,** 7002 (1970); (h) M. Sakai and S. Masamune, *ibid.*, **93,** 4610 (1971); (i) W. G. Dauben and A. J. Kielbania, Jr., *ibid.*, **94,** 3669 (1972).

(14) L. A. Paquette and R. T. Taylor, *J. Am. Chem. Soc.*, **99,** 5708 (1977).

(15) G. L. Closs and L. E. Closs, *J. Am. Chem. Soc.*, **85,** 2022 (1963).

(16) (a) The chemistry of the Si–C bond has been reviewed: A. G. MacDiarmid, "Organometallic Compounds of the Group IV Elements", Vol. 1, Part 1, C. Eaborn and R. W. Bott, Ed., Marcel Dekker, New York, N.Y., 1968, Chapter 2. (b) For a discussion of the properties of the Ge–C bond, consult F. Glocking and K. A. Hooton.

(17) P. Bischof, R. Gleiter, and E. Müller, *Tetrahedron*, **32,** 2769 (1976).

(18) These determinations were made in the laboratory of Professor Rolf Gleiter (Darmstadt, West Germany), whose willingness to assist is most appreciated.

(19) T. Koopmans, *Physica*, **1,** 104 (1934).

(20) L. A. Paquette and S. E. Wilson, *J. Org. Chem.*, **37,** 3849 (1972).

(21) For similar events in another context, see L. A. Paquette, S. E. Wilson, G. Zon, and J. A. Schwartz, *J. Am. Chem. Soc.*, **94,** 9222 (1972).

(22) This most useful empirical correlation has seen wide application. For leading references, see F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy", Academic Press, New York, N.Y., 1969, p 77.

(23) K. B. Wiberg and G. Szeimies, *J. Am. Chem. Soc.*, **92**, 571 (1970).
(24) For a review of organosilver chemistry, consult C. D. M. Beverivizk, G. J. M. vander Kerk, A. J. Lensink, and J. G. Noltes, *Organometal. Chem. Rev., Sect. A*, **5**, 218 (1970).
(25) W. R. Moore and B. J. King, *J. Org. Chem.*, **36**, 1882 (1971).
(26) P. G. Gassman and T. J. Atkins [*J. Am. Chem. Soc.*, **94**, 7749 (1972)] have examined the $SnCl_2 \cdot 2H_2O$ catalyzed rearrangement of 1-methyltricyclo[4.1.0.0^{2,7}]heptane and determined the exclusive ring opened product to be 1-methyl-2-norcarene. Evidently, the bridgehead methyl group directs catalyst attack only to those edge bonds *most remote* from the substituent in this instance.
(27) (a) K. B. Wiberg, B. A. Hess, Jr., and A. J. Ashe, III, in "Carbonium Ions", Vol. 3, G. A. Olah and P. v. R. Schleyer, Ed., Wiley, New York, N.Y., 1972, p 1295; (b) J. Haywood-Farmer, *Chem. Rev.*, **74**, 315 (1974); (c) for a recent leading reference, see L. A. Paquette and M. R. Detty, *J. Am. Chem. Soc.*, **99**, 828 (1977).
(28) O. G. Lindsay and C. B. Reese, *Tetrahedron*, **21**, 1673 (1965).
(29) U. Schöllkopf and H.-U. Scholz, *Synthesis*, 271 (1976).

Reaction of Thiophenoxides with Nitro- and Halo-Substituted Phthalimide Derivatives

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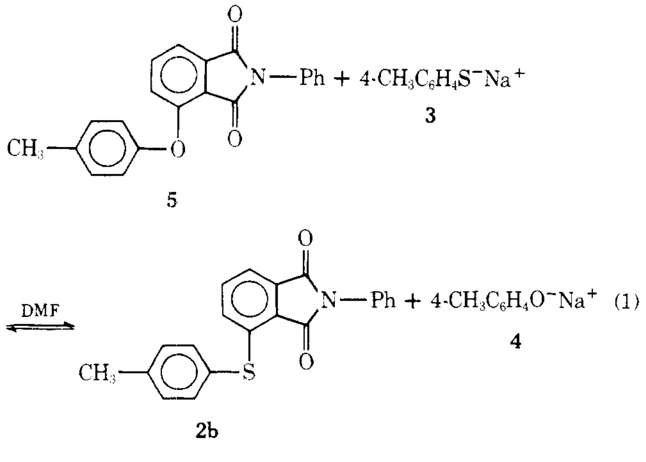
The reaction of thiophenoxides 3 with nitro- and halo-substituted phthalimide derivatives 1 was studied. In contrast to the reaction of 1 with phenoxides, a variety of inorganic bases, organic amines, and solvents such as THF, EtOH, and CH_2Cl_2 were used successfully in the thiophenol reactions. Using these procedures, a series of previously unknown thioether imides 2 were synthesized and identified with the assistance of ^{13}C NMR analysis. The relative rates of reaction of the different imides with thiophenoxide were measured and the differences in rate between the thiophenoxide and phenoxide nucleophiles are discussed in detail. The 3-substituted nitro derivatives were much more reactive toward thiophenoxide than any of the other systems which were studied. An examination of the formation of disulfides as side products was also made.

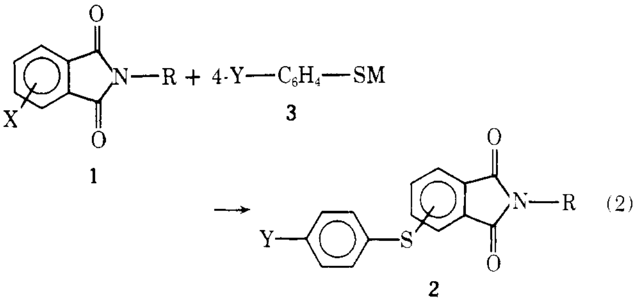
Recent studies by these authors have dealt with the reaction of phenoxide nucleophiles with nitro and halo groups activated by derivatives of phthalic acid. These studies have covered reactions with N-substituted phthalimides,[1] phthalate esters,[2] and phthalic anhydrides.[3] The tremendous nucleophilicity of sulfur in aromatic nucleophilic displacement reactions is well documented.[4] According to Parker,[5] "the thiophenoxide ion is the most powerful nucleophile which has been thoroughly studied in bimolecular SnAr reactions".

Preliminary work[1] has demonstrated that, indeed, in displacement reactions involving the phthalimide moiety as an activating group, thiophenoxide is vastly superior to phenoxide as a nucleophile. For example, in the displacement of the nitro group from 3-nitro-*N*-phenylphthalimide (**1**, X = 3-NO_2; R = Ph) in DMF, sodium 4-methylthiophenoxide (**3**) was found to react >100 times faster than sodium 4-methylphenoxide (**4**). In addition, if a mixture of **3** and 3-(4-methylphenoxy)-*N*-phenylphthalimide (**5**) or **4** and 3-(4-methylthiophenoxy)-*N*-phenylphthalimide (**2b**) was allowed to react in DMF at 120 °C for 1 h, the ratio of **2b** to **5** from either starting mixture was 97 to 3 (eq 1). These experiments suggested that the enhanced reactivity of sulfur might allow us to explore new base and solvent systems with thiophenol derivatives in these displacements.



Results and Discussion[6]

Studies of Base System. Initial work was carried out with the preformed sodium salt of thiophenol (**3**, Y = H; M = Na) or 4-methylthiophenol (**3**, Y = CH_3; M = Na). Reaction of these salts with 3- or 4-substituted nitro, chloro, or fluoro derivatives of **1** (R = alkyl or aryl) in DMF gave essentially quantitative yields of **2** (eq 2). Reactions involving an in situ formation of the anion of 4-methylthiophenol using potassium carbonate or sodium hydroxide as a base gave good yields of **2**. Apparently, the displacement is so rapid with the sulfur nucleophile that the reaction is complete before the base can enter into the hydrolysis reactions with **1** that are seen in the phenol derivatives.[7]



Amine bases were also used in these reactions of **1** where X = NO_2, and essentially quantitative yields of **2** were obtained. These results are in direct contrast to reactions involving 4-methylphenol in which amine bases gave no displacement with any derivatives of **1**. Particularly interesting was the reaction of 4-hydroxythiophenol (**3**, Y = OH; M = H) in which only displacement by sulfur was seen. If amine bases were used with fluoro and chloro derivatives of **1**, only 50% yields of **2** were obtained, even at temperatures of 80 °C. In addition to