

"Electroanalytical Principles", Interscience, New York, N.Y., 1963.

- (14) Values of n , where n is the total number of electrons transferred in exhaustive electrolysis at constant potential, were calculated after measuring the total area under current vs. time curves for the complete reaction. Reactions were judged to be complete when the current had fallen to 1% of its initial value.
- (15) E means an electrochemical reaction, either an oxidation or a reduction, while C means a chemical reaction. Thus an EC reaction would be an electrode process followed by a chemical reaction.
- (16) Yields of $\text{Re}_2\text{Cl}_6(\text{PR}_3)_2$ are in the range of 60–70%.
- (17) A benzene solution of $\text{Re}_2\text{Cl}_4(\text{PEt}_3)_4$ when exposed to O_2 produces $\text{Re}_2\text{Cl}_6(\text{PEt}_3)_3$ together with small quantities of ReO_4^- and phosphine oxide; see C. A. Hertzler, M.S. Thesis, Purdue University, 1977.
- (18) J. Chatt, C. M. Elson, N. E. Hooper, and G. J. Leigh, *J. Chem. Soc., Dalton Trans.*, 2392 (1975).
- (19) D. J. Salmon and R. A. Walton, unpublished observations.
- (20) When a solid sample of $\text{Re}_2\text{Cl}_4(\text{PPr}_3)_4$ is exposed to the air, the major oxidation product is $\text{Re}_2\text{Cl}_6(\text{PPr}_3)_3$ together with a small amount of perchlorate. The presence of the latter species was confirmed by infrared spectroscopy ($\nu_{\text{Re-O}}$ at 900 cm^{-1}) and ESCA measurements. $\text{Re } 4f_{5/2,7/2}$ binding energies at 47.9 and 45.9 eV are typical of the ReO_4^- anion.²¹
- (21) D. G. Tisley and R. A. Walton, *J. Mol. Struct.*, **17**, 401 (1973).
- (22) 0.05 M tetraethylammonium chloride.
- (23) R. N. Adams, "Electrochemistry at Solid Electrodes", Marcel Dekker, New York, N.Y., 1969.
- (24) R. E. Dessy and L. A. Bares, *Acc. Chem. Res.*, **5**, 415 (1972), and references therein.
- (25) F. R. Keene, D. J. Salmon, and T. J. Meyer, *J. Am. Chem. Soc.*, **99**, 4821 (1977).
- (26) F. A. Cotton, *Chem. Soc. Rev.*, 27 (1975).

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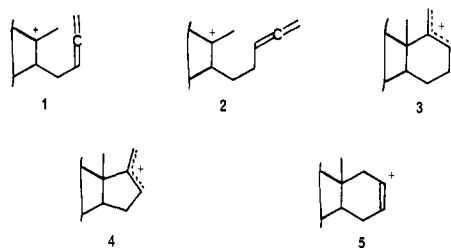
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Cationic Cyclization of Allenes. Preferential Cyclization via Vinyl Cations

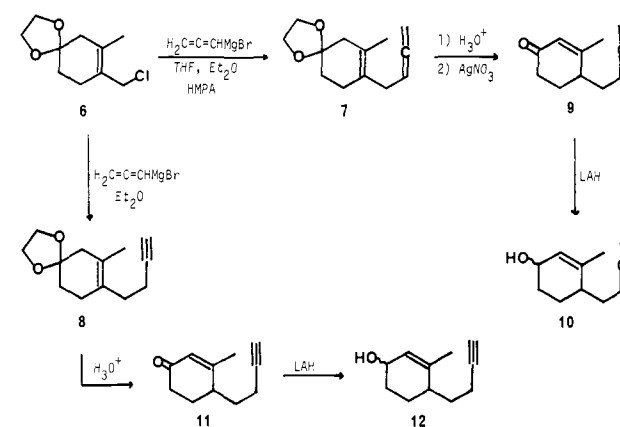
Sir:

An area of continuing interest in the development of cationic olefin cyclizations as a method for generating carbocyclic ring systems involves study of variations in the π moiety participating in these cyclizations.¹ We report herein the results of cyclization studies involving γ -allenyl cation systems (**1**) which differ markedly from results reported previously³ with δ -allenyl cation systems (**2**).

Cyclizations involving δ -allenyl cations (or their equivalent) have been shown to result in attack on the central carbon of the allene to form products resulting from an allylic cation (**2** \rightarrow **3**). Since the formation of five-membered rings in a similar fashion would be useful synthetically, we decided to examine some γ -allenyl cation systems to determine if reaction would lead to the allylic system **4** or the vinyl system **5**.^{2,7}



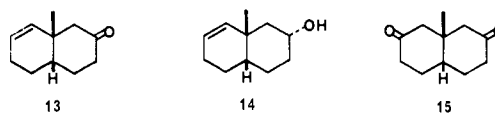
Scheme 1



gave pure ketone **9**. Reduction then gave alcohol **10**. Hydrolysis and reduction of acetylene **8** led to the related acetylenic compounds **11** and **12**.

Treatment of alcohol **10** with anhydrous formic acid gave, after hydrolysis, a single (NMR, GC, TLC) product in 70% yield. The product was shown to be the *cis*-octalone **13** by comparison (IR, NMR) with an authentic sample prepared by oxidation of alcohol **14**.¹⁴ No evidence was obtained for an allylic alcohol product. The same ketone **13** was obtained (70% yield) from cyclization of acetylenic alcohol **12**.¹⁵ Alcohol **10** did not undergo cyclization with trifluoroacetic acid under conditions used by Johnson and Hall.^{3a}

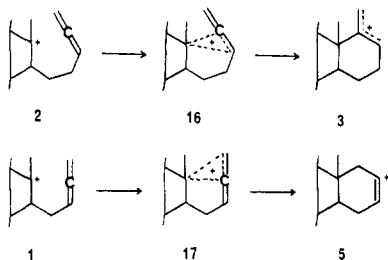
Preferential formation of a six-membered ring was also observed in the cyclization of ketone **9**. Treatment of **9** with either acetic anhydride in acetic acid with perchloric acid catalysis (66% yield)¹⁶ or with trifluoroacetic anhydride in trifluoroacetic acid (74% yield)¹⁷ gave, after hydrolysis, the crystalline (mp 115–116 °C) *cis* diketone **15**. This material was identical (melting point, IR, NMR) with material prepared by cyclization of 4-(3-butenyl)-3-methyl-2-cyclohexenone^{12,14} with TFAA/TFA, followed by hydrolysis and Jones oxidation. Diketone **15** was also obtained in a 90% yield by TFAA/TFA cyclization of acetylenic ketone **11**.



Thus these cyclizations of γ -allenyl systems gave only products derived from cationic attack on the terminus of the allene. No evidence for five-membered ring products was obtained. This divergence from previous results with δ -allenyl cation systems³ where attack only on the central carbon of the allene was observed demonstrates that additional studies are necessary to define the factors controlling the course of cationic cyclizations involving an allene as the π moiety. One potentially important difference between the γ - and δ -allenyl systems can be discerned by examination of molecular models. A δ -allenyl cation **2** readily interacts with the C-2,C-3 π bond of the allene (**2** \rightarrow **16**). The orbital overlap in **16** is exactly analogous to the overlap found in cyclization of δ -alkenyl systems to form six-membered rings. It has been demonstrated that, although electrophilic attack on an unsubstituted allene takes place preferentially at the terminal carbon, substitution with alkyl groups leads to increased attack at the central carbon.^{6,18} Thus the reaction of **2** through **16** to give **3** may be a result of alkyl substitution at C-3 of the allene. However, examination of a model of cation **1** shows that overlap with the C-2,C-3 π bond of the allene is much less favorable. In fact the orthogonal C-1,C-2 π bond appears to overlap very favorably (**1** \rightarrow **17**). Thus, a fundamental difference exists between **16** and **17**. In

We chose allylic alcohol **10** as a substrate for our cyclization studies because of its ready availability and its expected ease of cyclization. The cyclization of the corresponding allenyl ketone **9** was also investigated. The substrates for cyclization were prepared as shown in Scheme 1.⁸ Reaction of propargylmagnesium bromide⁹ with the allylic halide **6**¹⁰ in ether gave the acetylene **8** in good yield.¹¹ However, reaction in THF with added HMPA gave the allene **11** containing only ~20% acetylene.¹³ Hydrolysis of the mixture and removal of acetylenic material by precipitation with silver nitrate in methanol

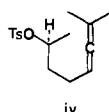
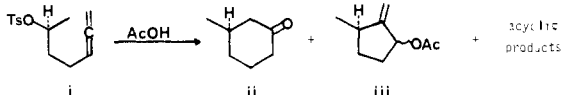
the case of **17** the terminal carbon is unsubstituted⁵ and thus conversion to the vinyl cation **5** is favored by electronic factors (and possibly geometric factors). This rationale is useful in that it suggests that substitution of a single methyl group at C-1 in the allenyl cation **1** might lead to preferential formation of five-membered-ring products.¹⁹ Studies to examine this hypothesis are in progress.²⁰



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References and Notes

- Examples include acetylenes,² allenes,³ and silyl enol ethers.⁴
- (a) W. S. Johnson, *Bioorg. Chem.*, **5**, 51 (1976); (b) S. W. Baldwin and J. C. Tomesch, *Synth. Commun.*, **5**, 445 (1975); (c) Tj. Boer-Terpstra, J. Dijkink, H. E. Shoemaker, and W. N. Speckamp, *Tetrahedron Lett.*, 939 (1977), and references cited therein.
- (a) H. T. Hall, Ph.D. Dissertation, Stanford University, 1973. See ref 2a. (b) M. H. Sekera, B.-A. Weissman, and R. G. Bergman, *J. Chem. Soc., Chem. Commun.*, 679 (1973).
- S. Hashimoto, A. Itoh, Y. Kitagawa, H. Yamamoto, and H. Nozaki, *J. Am. Chem. Soc.*, **99**, 4193 (1977).
- It has been pointed out that, although attack of an electrophile on the central carbon of an allene gives an allyl cation, little of this potential stabilization is realized in the transition state.^{3,6}
- P. J. Stang, *Prog. Phys. Org. Chem.*, **10**, 205 (1973).
- In one previous study on this type of system acetolysis of tosylate **i** gave predominantly uncyclized products, but both ketone **ii** (6% yield) and allylic acetate **iii** (15% yield) were formed: B. Ragonnet, M. Santelli, and M. Bertrand, *Helv. Chim. Acta*, **57**, 557 (1974).
- The new compounds prepared in this study were characterized by their spectra (IR, ¹H and ¹³C NMR) and by elemental composition (combustion analysis or high resolution MS) on the stable compounds.
- Cf. M. Gaudemar, *Ann. Chim. (Paris)*, **1**, 161 (1956).
- K. E. Harding and K. A. Parker, *Tetrahedron Lett.*, 1633 (1971).
- Only a trace of allenic material could be detected from this reaction although previous preparations of **8** have been reported to contain significant amounts of allene.¹²
- K. A. Parker and W. S. Johnson, *J. Am. Chem. Soc.*, **96**, 2556 (1974).
- The predominant formation of allenes in the coupling of propargylmagnesium bromide with allyl bromide in THF has been previously noted: L. Miginiac-Groizeleau, *Bull. Chem. Soc. Fr.*, 1449 (1963).
- W. S. Johnson and K. E. Harding, *J. Org. Chem.*, **32**, 478 (1967); W. S. Johnson, P. J. Neustaedter, and K. K. Schmiegel, *J. Am. Chem. Soc.*, **87**, 5148 (1965).
- The NMR spectra of the enol formates from cyclization of alcohols **14** and **16** showed that they were isomeric as expected on mechanistic considerations. Thus these procedures could be useful as a means for regio-specific generation of enolates.
- The use of Ac₂O/AcOH/HClO₄ for cyclizations involving a cyclohexenone functionality as the initiating group was developed in our laboratories: J. L. Cooper and K. E. Harding, *Tetrahedron Lett.*, 3321 (1977).
- We recently found that, in some cases, cyclization of cyclohexenones with TFAA/TFA proceeds in higher yields than with Ac₂O/AcOH/HClO₄.¹⁶
- G. Modena and U. Tonallato, *Adv. Phys. Org. Chem.*, **9**, 215-225 (1971).
- Bertrand and coworkers⁷ have reported that the system with two methyl groups on the terminal carbon (iv) did give good yields of five-membered-ring products.



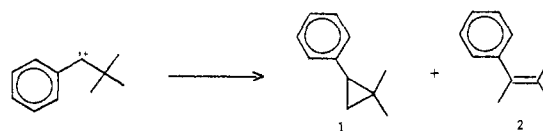
(20) This research constitutes a portion of the Ph.D. requirements for J.L.C. and P.M.P.

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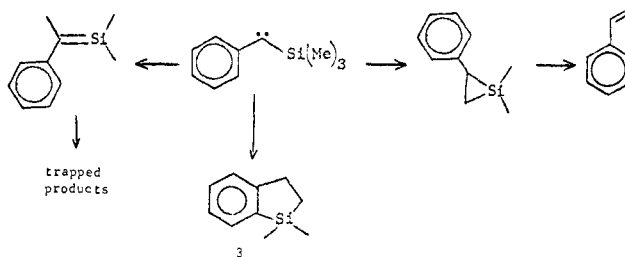
Gas-Phase Reactions of Phenyltrimethylgermylcarbene. Evidence for Transient Formation of 1,1-Dimethyl-2-phenylgermirane¹

Sir:

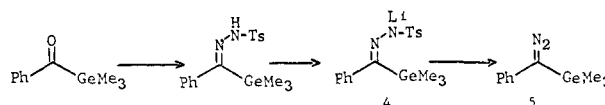
The gas-phase chemistry of phenyl-*tert*-butylcarbene and phenyltrimethylsilylcarbene is now reasonably well worked out.² In the *tert*-butylcarbene the normal 1,3-insertion reaction to give the major product, 1,1-dimethyl-2-phenylcyclopropane (**1**) is accompanied by ~15% carbon-carbon insertion to produce trimethylstyrene (**2**).² In the silicon case the carbene es-



chews the usual reactions in favor of addition to the benzene ring to give, ultimately, the silaindan **3**. Minor amounts of products analogous to **1** and **2** can be detected by trapping experiments in the case of the silene and through formation of styrene by extrusion of dimethylsilene from the silirane.² Here we provide a preliminary account of the properties of the analogous germanium-containing carbene and evidence for the formation of a germirane.



Phenyltrimethylgermyl ketone³ was converted to its tosylhydrazone in good yield by standard procedures. Treatment with butyllithium gave a salt **4** that could be converted on gentle heating under vacuum into the orange diazo compound **5**.



Flash vacuum pyrolysis of **4** or gas-phase decomposition of **5** in either a vertical quartz tube packed with aged quartz chips or in a conventional Pyrex flow system led to the same set of products, although in slightly different ratios depending upon the method. The best yields were obtained from **4** pyrolyzed at 450 °C under high vacuum. Under these conditions the major product was germaindan **6** (45%) and significant minor products were styrene (15%) and α -methylstyrene (7.5%). Traces of benzyltrimethylgermane and other unidentified products were also found.

