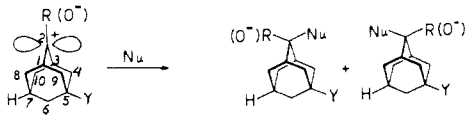
mantan-2-ones under conditions of kinetic control. The important features of these reactions are the following. First, in spite of the near C_{2v} symmetry of the system, the capture ratios depart sig-



nificantly from unity. Secondly, syn approach is favored when Y is a powerful electron acceptor such as fluoro or *p*-nitrophenyl, and anti approach is preferred when Y is *p*-anilino. Finally, since steric effects or solvent-separated ion pairs do not qualify as explanations for these facts, the only alternative available is σ delocalization. Thus, 5-fluoro substitution diminishes the ability of the C_3–C_4 and C_1–C_9 bonds to participate in comparison with the otherwise equivalent bonds C_3–C_{10} and C_1–C_8, resulting in the observed stereochemistry.

In the previous experiments, the range of groups R was not very wide, including only methyl, propargyl, and hydrogen. We now find that nucleophiles capture 5-fluoroadamant-2-yl cations with almost undiminished preference for *Z* approach even with 2-phenyl substitution. Cumyl cations have long occupied a central position in organic chemistry, as the basis of the σ^+ constants;[5] this report is the first instance of stereoselectivity in the capture of such ions in the absence of possible steric influences.

Treatment[6] of either *E* or *Z* para substituted cumyl alcohol (R = Ph, Nu = OH) with tosyl chloride gave a completely equilibrated mixture of *E*- and *Z*-tosylates in every case as judged by ^{13}C NMR. Addition of these mixtures to basic aqueous glyme solutions of sodium borohydride[7] led to reduction products that were separated by means of flash chromatography. The pure hydrocarbons were used to assign[8] the ^{13}C NMR resonances; the crude mixtures were used for analysis, which was based on the C_2 resonances. With *p*-MeO, *p*-Me, and *p*-H the *E*/*Z* ratios were 78/22, 74/26, and 75/25, respectively: the swamping associated with *p*-anisyl was not observed.

The yields with the *p*-Br and *p*-CF_3 analogues were too low to give meaningful information; accordingly, we tried the reaction of HCl with the corresponding alcohols in dry methylene chloride.[9] In this instance, the *Z*/*E* ratios with *p*-CF_3, *p*-Br, *p*-H were 77/23, 76/24, and 73/27, respectively; clearly, increased electron demand did not lead to a significant change in the ratio either (extension to more donating substituents was not feasible because the product chlorides begin to equilibrate).

Possibly even more informative is the borohydride reduction of the 2-methoxy-5-fluoroadamant-2-yl cation, produced from the dimethylketal and BF_3 etherate and isolated as the solid salt. This experiment, reminiscent of one carried out by Traylor and Perrin,[10] gave the *E*- and *Z*-methyl ethers in an 83:17 ratio; thus, not even a methoxy group directly bound to the carbocation center can quench the σ delocalization induced tendency toward syn approach. Finally, when 5-fluoroadamantan-2-one is treated with para-substituted phenylmagnesium bromides, the cumyl alcohols are also once again formed with a uniform and clear prejudice (also about 70/30) for the *E* product (hence, syn approach).[11]

It is concluded that σ delocalization cannot be swamped by means of donating substituents at the electron deficient center. Whether such delocalization should be called σ participation (which is held to produce nonclassical distortions) or hyperconjugation (which Brown[1] *considers* as not doing so), the important point is that the failure of stabilizing 2-substituents in the 2-adamantyl cation to suppress it invalidates the assumption of swamping in the 2-norbornyl ion as well.[12] The recent observations of equilibrating 2,5-dimethyladamant-2-yl cations by Sorensen[13] and Laube's X-ray study[14] of the $SbCl_5$ complex of 5-phenyladamantan-2-one offer powerful indications that at least some distortion of the adamantane structure occurs.[15]

Acknowledgment. W. le Noble thanks the National Science Foundation and the donors of the Petroleum Research Fund for supporting this work and the Japanese Ministry of Education (Mombusho) for the Special Visiting Professorship at Oita, where these lines are written.

(5) Brown, H. C.; Okamoto, Y. *J. Am. Chem. Soc.* **1957**, *79*, 1913.
(6) Kabalka, G. W.; Varma, M.; Varma, R. S.; Srivastava, R. C.; Knapp, F. F. *J. Org. Chem.* **1986**, *51*, 2386.
(7) Bell, H. M.; Brown, H. C. *J. Am. Chem. Soc.* **1966**, *88*, 1473.
(8) Srivastava, S.; Cheung, C. K.; le Noble, W. J. *Magn. Reson. Chem.* **1985**, *23*, 232.
(9) Brown, H. C.; Rei, M.-H. *J. Org. Chem.* **1966**, *31*, 1090.
(10) Traylor, T. G.; Perrin, C. L. *J. Am. Chem. Soc.* **1966**, *88*, 4934.
(11) Lin, M.-H.; Silver, J. S.; le Noble, W. J. *J. Org. Chem.*, in press.
(12) For an authoritative review of this cation, see: Lenoir, D.; Apeloig, Y.; Arad, D.; Schleyer, P. von R. *J. Org. Chem.* **1988**, *53*, 661.
(13) Finne, E. S.; Gunn, J. R.; Sorensen, T. S. *J. Am. Chem. Soc.* **1987**, *109*, 7816.
(14) Laube, T.; Stilz, H. U. *J. Am. Chem. Soc.* **1987**, *109*, 5876.
(15) We take note here of the fact that Grob has confirmed our observations[4a] of the unexpectedly powerful 5-substituent effect on the rates of formation and capture of the 2-adamantyl cation; however, he writes that our conclusion of σ delocalization or hyperconjugation "conflicts with the observed lower inductivity of the γ carbon C_4 compared to that of the δ carbon C_5". Apparently Grob overlooked the fact that C_5 substituents deactive *both* C_1–C_9 *and* C_3–C_4 bonds, whereas a C_4 substituent leaves the C_1–C_9 bond essentially unaffected (see: Grob, C. A.; Wang, G.; Yang, X. *Tetrahedron Lett.* **1987**, *28*, 1247).

Unbridged and Bridged Isomers of $W_2(PCy_2)_2(NMe_2)_4$: Preparations, Characterizations, and Comments on Thermodynamic and Activation Parameters for the Closing of Phosphido Bridges in d^3–d^3 Dinuclear Compounds

William E. Buhro,[1] Malcolm H. Chisholm,* Kirsten Folting, John C. Huffman, James D. Martin, and William E. Streib

Department of Chemistry and Molecular Structure Center Indiana University, Bloomington, Indiana 47405

Received February 22, 1988

We describe herein the preparation and structural characterization of unbridged and bridged isomers of formula $W_2(PCy_2)_2(NMe_2)_4$ where Cy = cyclohexyl.[2] This is the first isolated example of both unbridged and bridged *isomers* of a phosphido metal complex,[3] and the first example of unbridged and bridged *isomers* of $M_2Y_2X_4$ d^3–d^3 dimers.[2] Dinuclear phosphido complexes having PR_2 groups in terminal positions are rare and typically very reactive.[3,4] Our terminal isomers are likely stabilized kinetically by steric congestion and thermodynamically by strong M–M triple bonds. Phosphido ligands are ubiquitous bridging groups, and our results provide the first information regarding the energetics of phosphido bridge formation.

The reaction between 1,2-$W_2Cl_2(NMe_2)_4$[5] and $LiPCy_2$ (2 equiv) proceeds in tetrahydrofuran (−78 to 0 °C) to give 1,2-$W_2(PCy_2)_2(NMe_2)_4$. The orange crystalline compound *gauche*-1,2-$W_2(PCy_2)_2(NMe_2)_4$ was obtained by crystallization from

(1) Chester Davis Fellow, 1985/1986. Present address: Department of Chemistry, Washington University, St. Louis, MO 63130.
(2) (a) Unbridged compounds of the type $X_2YM{\equiv}MX_2Y$ where M = Mo and W are now well known: Chisholm, M. H. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 21. (b) The first example of a bridged $X_4M_2(\mu\text{-}Y)_2$ compound, $(t\text{-BuO})_4W_2(\mu\text{-}PPh_2)_2$, was recently reported: Buhro, W. E.; Chisholm, M. H.; Folting, K.; Eichhorn, B. W.; Huffmann, J. C. *J. Chem. Soc., Chem. Commun.* **1987**, 845.
(3) The most closely related examples are the isomers $[(CO)_3Fe(\mu\text{-}CO)(\mu\text{-}PR_2)Fe(CO)_2(PR_2)]^{2-}$ and $[(CO)_3Fe(\mu\text{-}PR_2)_2Fe(CO)_3]^{2-}$, see: Wojcicki, A. *Inorg. Chim. Acta* **1985**, *100*, 125 and references therein.
(4) Buhro, W. E.; Chisholm, M. H.; Folting, K.; Huffman, J. C. *J. Am. Chem. Soc.* **1987**, *109*, 905.
(5) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407. Dry and oxygen free atmospheres (N_2) and solvents were used throughout.

 © 1988 American Chemical Society

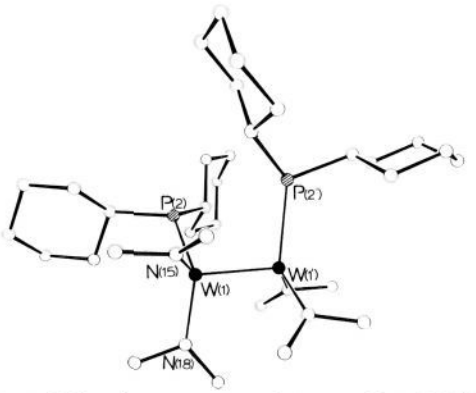


Figure 1. A ball-and-stick drawing of the *gauche*-1,2-$W_2(PCy_2)_2(NMe_2)_4$ molecule. Pertinent distances (Å) and angles (deg) are as follows: W–W = 2.294 (2), W–P = 2.401 (6), W–N = 1.98 (2) (av); W–W–P = 99.9 (1)°, W–W–N = 103 (1) (av). The molecule has crystallographically imposed C_2 symmetry. The sum of the angles at P are 347°.

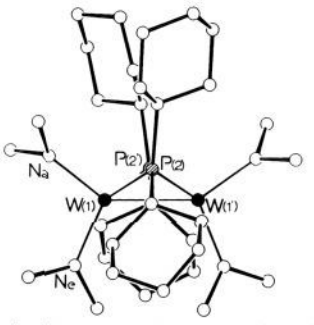
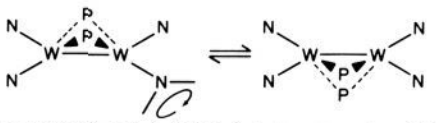


Figure 2. A ball-and-stick drawing of the $(Me_2N)_4W_2(\mu\text{-}PCy_2)_2$ molecule. Selected distances (Å) and bond angles (deg) are as follows: W–W = 2.5701 (8), W(1)–P(2) = 2.359 (3), W(1)–P(2)′ = 2.405 (3), W(1)′–P(2) = 2.393 (3), W(1)′–P(2)′ = 2.354 (3), W(1)–N_a = 2.004 (10), W(1)–N_c = 1.983 (10), W(1)′–N_a = 1.996 (10), W(1)′–N_c = 1.972 (10), W–W–P = 57 (av), W–P–W = 65.4 (1).

hexane (−25 °C).[6] A view of the molecular structure found in the solid state is shown in Figure 1.[7] The W≡W bond distance of 2.294 (2) Å and the W–P and W–N distances of 2.401 (6) Å and 1.976 (10) Å (av) are similar to those seen in related ethane-like 1,2-$W_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ molecules.[4]

In solution (toluene-d_8) 1,2-$W_2(PCy_2)_2(NMe_2)_4$ exists as a mixture of anti and gauche rotamers with the equilibrium favoring the gauche;[8] however, above 0 °C isomerization occurs to give the bis-μ-phosphido isomer, $(NMe_2)_4W_2(\mu\text{-}PCy_2)_2$.[6] In the solid state the molecular structure contains[7] a puckered central $W_2(\mu\text{-}P)_2$ moiety having a dihedral angle of 129.6° (defined as the angle between the tow W_2P planes) with W–W = 2.5701 (8) Å and W–P spanning the range 2.354 (3) to 2.405 (3) Å. The W–P distances in the bridging isomer are equal to or slightly shorter than those in the terminal isomer. See Figure 2.

In solution the bridged isomer undergoes two dynamic processes. (1) The W_2P_2 "butterfly" flaps its wings, i.e., the puckered W_2P_2 moiety passes through a planar transition state. This process is monitored by ^1H NMR spectroscopy from examination of the coalescence behavior of the diastereotopic *P-Cy-α* protons: $\Delta G^{\ddagger}_{252K}$ = 12.1 (1) kcal mol^{-1}. (2) The amido ligands are averaged and also show restricted rotations about their respective M–N bonds. The averaging of the amido ligands is coincident with the $W_2(\mu\text{-}P)_2$ flapping process, while the rotational barriers have lower $\Delta G^{\ddagger}$ values: $\Delta G^{\ddagger}_{211K}$ = 9.5 (1) kcal mol^{-1} for one NMe_2 group; the other NMe_2 group shows only initial line broadening at −87 °C, and its rotation has not been frozen out.[9] These combined operations are shown diagramatically in eq 1 below.



(1)

While 1,2-$W_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ is inert to phosphido bridge closure, the related dicyclohexyl phosphido compound reported here shows a thermodynamic preference for the μ-phosphido isomer. Reversion to the unbridged isomer has not been observed either upon heating (25–90 °C) or cooling (25 to −87 °C). We have determined the activation parameters for phosphido bridge closure 1,2-$W_2(PCy_2)_2(NMe_2)_4$ → $(Me_2N)_4W_2(\mu\text{-}PCy_2)_2$ by following the first-order reaction as a function of temperature (26–49 °C) in toluene-d_8 employing ^1H NMR spectroscopy: $\Delta H^{\ddagger}$ = 18.8 (5) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −12.4 (20) eu. These values are very similar to those found for anti ⇄ gauche interconversion of 1,2-$W_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$, namely for anti → gauche, $\Delta H^{\ddagger}$ = 18.8 (6) and $\Delta S^{\ddagger}$ = −10.6 (19) eu and for gauche → anti, $\Delta H^{\ddagger}$ = 19.4 (6) kcal mol^{-1} and $\Delta S^{\ddagger}$ = −10.1 (20) eu.[10] We cannot state whether phosphido bridge closure occurs from *anti*- or *gauche*-1,2-$W_2(PCy_2)_2(NMe_2)_4$, but we do know that neither gauche → anti nor anti → gauche interconversion is the rate-determining step. The similarity in the activation parameters for bridge closure in 1,2-$W_2(PCy_2)_2(NMe_2)_4$, and for anti ⇄ gauche interconversion in 1,2-$W_2(P(t\text{-}Bu)_2)_2(NMe_2)_4$ raises the possibility that the transition states for each may have common features.

It is interesting to consider what factors favor the bridged versus the terminal isomers. Since phosphido ligands are relatively inefficient π donors,[4] the M–P bonding is not maximized in the terminal phosphido isomer, but this is compensated by the presence of the strong $(M{\equiv}M)^{6+}$ bond. In the bridged isomer two new M–P σ bonds are formed, but at the expense of M–M bonding—note M–M increases by ca. 0.3 Å upon bridge formation. Decreasing the size of the alkyl/aryl substituent on P favors the bridged isomer, e.g., for 1,2-$W_2(PR_2)_2(NMe_2)_4$ thermal stability follows the order R = Et < Ph < Cy ≪ *t*-Bu (in the latter case closure has not been observed).[11]

Two questions can be posed from the above. (1) Does an equilibrium exist between bridged and terminal isomers and (2) does bridge closing (and opening) occur in a pair-wise concerted or in a stepwise, one-at-a-time process? In an attempt to interrogate the system further we have prepared compounds of formula 1,2-$W_2(PR_2)(PR_2')(NMe_2)_4$ by successive additions of $LiP(t\text{-}Bu)_2$ (1 equiv) followed by $LiPR_2'$ where R′ = Cy,[10] Ph, and Et.[11] The identity of $W_2(P(t\text{-}Bu)_2)(PR_2')(NMe_2)_4$ compounds can be reliably established by NMR spectroscopy. In particular the $^{31}P(^1H)$ spectra can distinguish, by the nature of the satellite spectra due

(6) Satisfactory elemental analyses have been obtained.

(7) Crystal data for (i) gauche 1,2-$W_2(PCy_2)_2(NMe_2)_4$ at −156 °C: a = 23.249 (15) Å, b = 15.979 (9) Å, c = 10.119 (4) Å, Z = 4, d_{calcd} = 1.658 g cm^{-3}, and space group *Pnna*. Of 2877 reflections collected, Mo Kα, 6° < 2θ < 45°, 2475 were unique, and the 1710 having $F > 3.0\sigma(F)$ were used in the full least-squares refinement: $R(F)$ = 0.067 and $R_w(F)$ = 0.060; (ii) $(Me_2N)_4W_2(\mu\text{-}PCy_2)_2$ at −135 °C: a = 18.793 (5) Å, b = 10.824 (2) Å, c = 19.631 (4) Å, β = 110.49 (1)°, Z = 4, d_{calcd} = 1.667 g cm^{-3}, and space group $P2_1/c$. Of 5517 reflections collected, Mo Kα, 6° < 2θ < 45°, 4911 were unique, and 4123 having $F > 3\sigma(F)$ were used in the least-squares refinement: $R(F)$ = 0.047 and $R_w(F)$ = 0.043.

(8) Pertinent $^{31}P\{^1H\}$ NMR data (ppm, toluene-d_8 or benzene-d_6 25 °C): *gauche*-1,2-$W_2(NMe_2)_4(PCy_2)_2$ 156 (s, $^1J_{^{31}P-^{183}W}$ = 341 Hz, 14%), *anti*-1,2-$W_2(NMe_2)_4(PCy_2)_2$ 133 (s, $^1J_{^{31}P-^{183}W}$ = 312 Hz, 14%), $W_2(NMe_2)_4(\mu\text{-}PCy_2)_2$ 229 (s, $^1J_{^{31}P-^{183}W}$ = 304 Hz, 24%). 1,2-$W_2(NMe_2)_4(P\text{-}t\text{-}Bu_2)(PCy_2)$ 161 (s, $^1J_{^{31}P-^{183}W}$ = 360 Hz, 14%, PCy_2), 188 (s, $^1J_{^{31}P-^{183}W}$ = 311 Hz, *P-t*-Bu_2) and 129 (s, $^1J^{31}_{P-^{183}W}$ = 289 Hz, 14%, PCy_2), 187 (s, $^1J_{^{31}P-^{183}W}$ = 308 Hz, *P-t*-Bu_2). $W_2(NMe_2)_4(\mu\text{-}PCy_2)(\mu\text{-}P\text{-}t\text{-}Bu_2)$ 228.1 (d, $J_{P-P'}$ = 9.2 Hz, $^1J_{^{31}P-^{183}W}$ = 313 Hz, 24%, PCy_2), 272.4 (d, $J_{P-P'}$ = 7.6 Hz, $^1J_{^{31}P-^{183}W}$ = 269 Hz, 24%, *P-t*-Bu_2), average $J_{P-P'}$ = 8.4 Hz.

(9) $\Delta G^{\ddagger}$ values quoted are calculated from coalescence temperatures, K, according to the equation given

$$k = \frac{\pi(\Delta\nu)}{\sqrt{2}}; \qquad \Delta G^{\ddagger} = -\left[\ln\frac{kh}{kT_c}\right]RT_c$$

(10) Buhro, W. E.; Chisholm, M. H., manuscript in preparation.

(11) Characterization data of the compounds R = Et and Ph will be presented elsewhere: Buhro, W. E.; Chisholm, M. H.; Martin, J. D., results to be published.

(12) The compound 1,2-$W_2(P(t\text{-}Bu)_2)Cl(NMe_2)_4$ can be isolated as an oil, ref 10.

to ^{183}W ($I = 1/2$, 14.5% natural abundance), the bridged and unbridged isomers. The preliminary results indicate an equilibrium exists for the mixed $P(t\text{-Bu})_2/PCy_2$ compound that favors the unbridged form by ca. 4:1, while the $P(t\text{-Bu})_2/PPh_2$ compound closes completely to the bridged isomer, $t_{1/2}$ ca. 45 h, 22 °C. The $P(t\text{-Bu})_2/PCy_2$ compound reaches equilibrium in ca. 8 h at 22 °C. No monobridged species have been observed.

Further studies are in progress aimed at elucidating the mechanism(s) of bridge opening and closing in dinuclear d^3–d^3 compounds of the type described above.

Acknowledgment. We thank the National Science Foundation for support.

Supplementary Material Available: Tables of atomic positional parameters for the two isomers of $W_2(PCy_2)_2(NMe_2)_4$ (5 pages). Ordering information is given on current masthead page.

Hypervalent Alkenyliodonium Tetrafluoroborates. Evidence for Generation of Alkylidenecarbenes via Base-Induced α-Elimination

Masahito Ochiai,* Yoshikazu Takaoka, and Yoshimitsu Nagao*

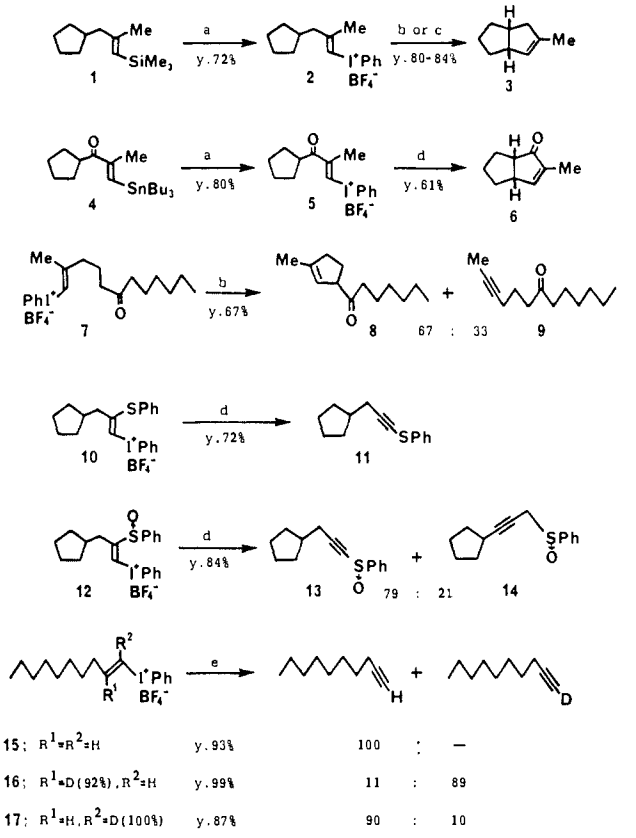
Institute for Chemical Research, Kyoto University Uji, Kyoto 611, Japan

Received April 11, 1988

In spite of extensive studies on the chemistry of diaryliodonium[1] and alkynyl(aryl)iodonium salts,[2] little is known about alkenyl(aryl)iodonium salts, mostly due to the considerable difficulty of their synthesis.[1,2c,3] Recently, we reported the highly stereoselective synthesis of alkenyl(phenyl)iodonium tetrafluoroborates by the reaction of alkenyltrimethylsilanes with iodosylbenzene activated with Lewis acids.[4] Kitamura and Stang reported that the reaction of β-azidovinyliodonium salt with *t*-BuOK in glyme undergoes some sort of ylide-transfer process via the generation of iodonium ylides, and free alkylidenecarbenes are not involved in this reaction.[5] Iodonium ylides generated from alkynyliodonium salts can lose iodobenzene giving free carbenes.[2i,6] We report herein evidence for the generation of alkylidenecarbenes, which undergo subsequent 1,5-carbon–hydrogen insertions yielding cyclopentenes and/or rearrangements to the corresponding alkynes, from α-elimination of the alkenyl(phenyl)iodonium tetrafluoroborates.

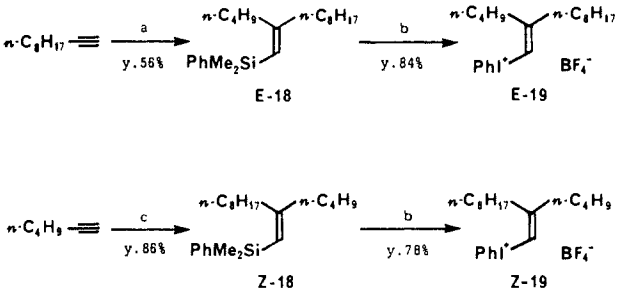
Exposure of (*E*)-phenyl(3-cyclopentyl-2-methyl-1-propenyl)iodonium tetrafluoroborate (**2**),[7] prepared stereoselectively from (*E*)-vinyltrimethylsilane **1**[8] by the reaction with BF_3-activated iodosylbenzene (72% yield), to 1.2 equiv of triethylamine in THF at room temperature resulted in the formation of bicyclo[3.3.0]octene **3** in 84% yield. Similarly, *t*-BuOK (1.1 equiv) in THF at room temperature afforded **3** in 80% yield. Treatment of (*E*)-**5**, prepared from the (*E*)-vinyltributylstannane **4**, with *t*-BuOK at −78 °C produced the bicyclic α-enone **6** (61%). α-

Scheme I[a]



[a] (a) (PhIO)*n*, BF_3–Et_2O, CH_2Cl_2 then $NaBF_4$, H_2O; (b) Et_3N, THF or CH_2Cl_2, 25 °C; (c) *t*-BuOK, THF, 25 °C; (d) *t*-BuOK, THF, −78 °C; (e) Et_3N, THF, 0 °C.

Scheme II[a]



[a] (a) $PhMe_2SiLi$, CuCN, THF then butyl iodide, HMPT; (b) (PhIO)*n*, BF_3–Et_2O, CH_2Cl_2 then $NaBF_4$, H_2O; (c) $PhMe_2SiLi$, CuCN, THF then octyl iodide, HMPT.

(1) For an excellent review of diaryliodonium salts, see: Koser, G. F. *The Chemistry of Functional Groups, Supplement D*; Wiley: New York, 1983; Chapter 25.

(2) (a) Beringer, F. M.; Galton, S. A. *J. Org. Chem.* **1965**, *30*, 1930. (b) Merkushev, E. B.; Karpitskaya, L. G.; Novosel'tseva, G. I. *Dokl. Akad. Nauk SSSR* **1979**, *245*, 607. (c) Koser, G. F.; Rebrovic, L.; Wettach, R. H. *J. Org. Chem.* **1981**, *46*, 4324. (d) Rebrovic, L.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4700. (e) Margida, A. J.; Koser, G. F. *J. Org. Chem.* **1984**, *49*, 4703. (f) Ochiai, M.; Kunishima, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 4501. (g) Stang, P. J.; Surber, B. W. *J. Am. Chem. Soc.* **1985**, *107*, 1452. (h) Stang, P. J.; Boehshar, M.; Lin, J. *J. Am. Chem. Soc.* **1986**, *108*, 7832. (i) Ochiai, M.; Kunishima, M.; Nagao, Y.; Fuji, K.; Shiro, M.; Fujita, E. *J. Am. Chem. Soc.* **1986**, *108*, 8281. (j) Stang, P. J.; Surber, B. W.; Chen, Z. C.; Roberts, K. A.; Anderson, A. G. *J. Am. Chem. Soc.* **1987**, *109*, 228. (k) Stang, P. J.; Kitamura, T. *J. Am. Chem. Soc.* **1987**, *109*, 7561. (l) Moriarty, R. M.; Vaid, R. K.; Duncan, M. P.; Vaid, B. K. *Tetrahedron Lett.* **1987**, *28*, 2845.

(3) (a) Freidlina, R. Kh.; Brainina, E. M.; Nesmeyanov, A. N. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1945**, 647. (b) Brainina, E. M.; Freidlina, R. Kh. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1947**, 623. (c) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V. *Dokl. Akad. Nauk. SSSR* **1971**, 1337. (d) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Goltsev, A. N. *Dokl. Akad. Nauk SSSR* **1977**, *235*, 591. (e) Nesmeyanov, A. N.; Tolstaya, T. P.; Petrakov, A. V.; Leshcheva, I. F. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 1109. (f) Stang, P. J.; Wingert, H.; Arif, A. M. *J. Am. Chem. Soc.* **1987**, *109*, 7235.

(4) (a) Ochiai, M.; Sumi, K.; Nagao, Y.; Fujita, E. *Tetrahedron Lett.* **1985**, *26*, 2351. (b) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron Symposium-in-Print*, in press.

(5) Kitamura, T.; Stang, P. *J. Tetrahedron Lett.* **1988**, *29*, 1877.

(6) Stang, P. J.; Boehshar, M.; Wingert, H.; Kitamura, T. *J. Am. Chem. Soc.*, in press.

(7) All new compounds exhibited compatible infrared, proton magnetic resonance, and mass spectrometric data.

(8) This compound was prepared by the carbo-silylation of 3-cyclopentyl-1-propyne in 66% yield, according to the procedure developed by Fleming and his co-workers: Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1805.

0002-7863/88/1510-6565$01.50/0 © 1988 American Chemical Society