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.

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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

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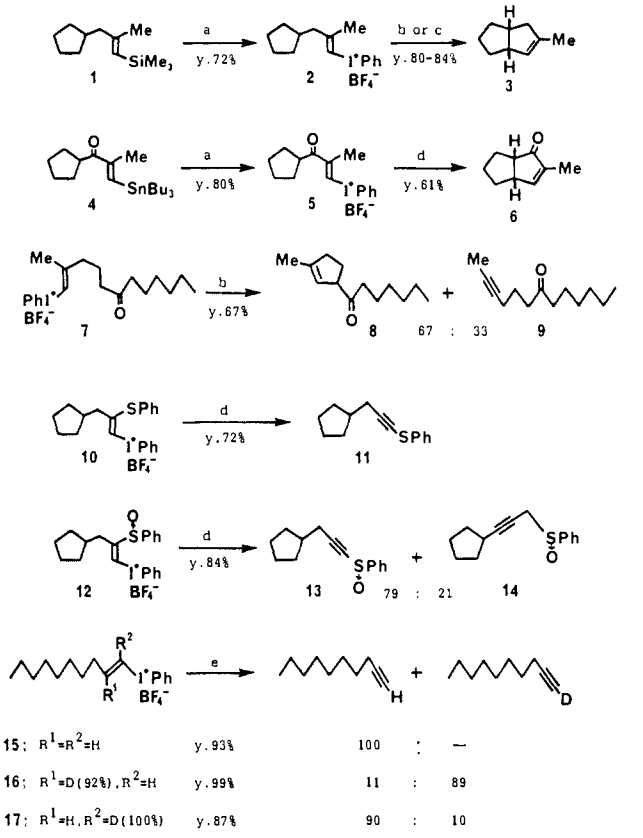
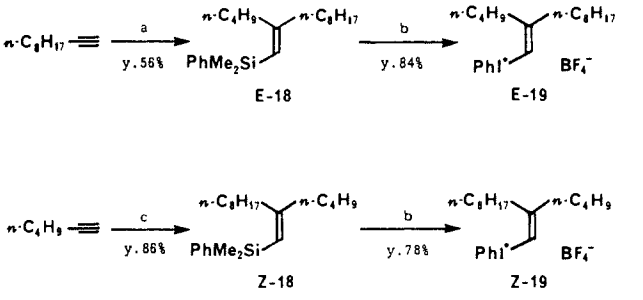
In spite of extensive studies on the chemistry of diaryliodonium[1] and alkynyl(aryl)iodonium salts,[2] little is known about alkenyl(aryl)iodonium salts, mostly due to the considerable difficulty of their synthesis.[1,2c,3] Recently, we reported the highly stereoselective synthesis of alkenyl(phenyl)iodonium 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.

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.

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-

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(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.

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Table I. Stereoselectivity for Carbene Insertion

19	reactn condtns[a]	% yield	ratio (20:21)
(*E*)-**19**	*t*-BuOK, −78, 15 min	60	51:49
(*E*)-**19**	*t*-BuOK, −78, 15 min[b]	51	51:49
(*E*)-**19**	*t*-BuOK, 0, 10 min	63	49:51
(*Z*)-**19**	*t*-BuOK, −78, 20 min	60	52:48
(*Z*)-**19**	*t*-BuOK, 0, 10 min	65	51:49
(*Z*)-**19**	Et_3N, 25, 1.5 h	63	49:51

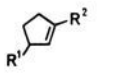
[a] Reactions were carried out in THF; temperatures are in °C. [b] The reaction was carried out in the presence of 18-crown-6 (1.3 equiv).

Elimination of alkenyliodonium salts by base treatment yielding the corresponding alkylidenecarbenes, followed by regioselective 1,5-C–H insertion, probably can explain the formation of these bicyclic compounds.[9,10]

Alkylidenecarbenes are electrophilic, as are most carbenes,[11] and hence the rate of insertion of carbenes to C–H bonds bearing electron-withdrawing substituents such as carbonyl groups on the carbon atoms should decrease considerably. In the reaction of **7** with triethylamine, in fact, competitive 1,2-rearrangement of a β-alkyl group of the resulting carbene occurred, and the insertion product, β,γ-enone **8**, and the rearranged alkyne **9** were obtained in a ratio of 67:33. Alkenyliodonium salts with β-heteroatom substituents exclusively undergo intramolecular 1,2-migration: the only isolated product from the reaction of vinyl sulfide **10** was the alkynyl sulfide **11** (72% yield). Similarly, the vinyl sulfoxide **12** produced a mixture of acetylenic sulfoxides **13** and **14** in a ratio of 79:21 (84% yield). This is presumably a result of 1,2-migration to give **13**, followed by isomerization.[12] The absence of insertion products in the reaction mixture of **10** and **12** is probably due to high migratory aptitude of phenylsulfenyl and phenylsulfinyl groups.[14]

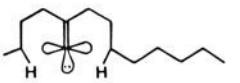
Reaction of (*E*)-vinyliodonium salt **15**[4] with triethylamine afforded 1-decyne in high yield. Since the much faster rate of cis-β-elimination compared to that of α-elimination in the dehydrohalogenation of vinyl halides yielding alkynes has been well documented,[15] both α- and β-deuteriovinyliodonium salts, **16** and **17**, were treated with triethylamine to investigate the possible reaction pathway. Surprisingly, the results shown in Scheme I clearly suggest that the alkyne-forming reaction proceeds predominantly via α-elimination affording carbenes followed by an intramolecular 1,2-hydrogen shift.

To gain some insight into the freeness of the carbenic species generated from alkenyliodonium salts, both stereoisomers of phenyl(2-butyl-1-decenyl)iodonium tetrafluoroborates ((*E*)- and (*Z*)-**19**) were synthesized in a highly stereoselective manner as shown in Scheme II. Both (*E*)- and (*Z*)-**19** were treated with *t*-BuOK or triethylamine in THF, and the ratio of the insertion products, 3-methyl-1-octylcyclopentene (**20**) and 1-butyl-3-pentylcyclopentene (**21**), was determined from the 400 MHz NMR spectra of the crude reaction mixtures (Table I).[16] The structures of these isomeric cyclopentenes were determined from their mass spectra, which showed relatively abundant fragments derived from a cleavage of allylic and vinylic carbon–carbon bonds. It seems reasonable to assume that if there is any association with the leaving group, that is, iodobenzene in the transition state for 1,5-C–H insertions such as **23**,[9e] there should be a memory effect that reflects the stereochemistry of alkenyliodonium salts (*E*)- and (*Z*)-**19** in the product ratios.[9e,11] Table I clearly indicates that the product ratios of **20** and **21** were equally about 1:1

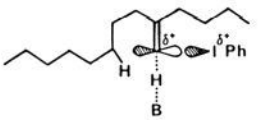


20; R^1 = Me, R^2 = n-C_8H_{17}

21; R^1 = n-C_5H_{11}, R^2 = n-C_4H_9



22



23; B = base

irrespective of the stereochemistry of the alkenyliodonium salts and the reaction conditions used. The complete lack of regioselectivity for the intramolecular insertion of carbenes derived from the vinyliodonium salts clearly indicates that the loss of stereochemistry of the vinyliodonium salts precedes the intramolecular insertion. Thus, these results suggest the involvement of the free carbene **22** rather than the carbenoid **23**.

Strong bases like alkyllithiums or drastic reaction conditions are required to generate carbenic species from vinyl halides, thus precluding the presence of many functional groups in the substrate. Our new method produces alkylidenecarbenes under mild conditions, making the reaction compatible with a variety of functional groups.

Supplementary Material Available: Synthetic procedure for **4**, **7**, **10**, **12**, **16**, and **17** and spectral data for **1**, **2**, **4**, **5**, **7**, **10**, **12**, **18**, **19**, **20**, and **21** (4 pages). Ordering information is given on any current masthead page.

(9) For generation of carbenoids from α-elimination of vinyl halides, see: (a) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142. (b) Walsh, R. A.; Bottini, A. T. *J. Org. Chem.* **1970**, *35*, 1086. (c) Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* **1976**, *41*, 745. (d) Fischer, R. H.; Baumann, M.; Köbrich, G. *Tetrahedron Lett.* **1974**, 1207. (e) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035. (f) Harada, T.; Nozaki, Y.; Yamaura, Y.; Oku, A. *J. Am. Chem. Soc.* **1985**, *107*, 2189.

(10) For generation of RCOCH=C: from gas-phase thermolysis of α-alkynones, see: (a) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 852. (b) Karpf, M.; Huguet, J.; Dreiding, A. S. *Helv. Chim. Acta* **1982**, *65*, 13.

(11) For excellent reviews of alkylidenecarbenes, see: (a) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (b) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.

(12) Reaction of **13** with *t*-BuOK in THF at −78 °C for 10 min gave the sulfoxide **14** in 82% yield.[13]

(13) Cf. O'Connor, D. E.; Lyness, W. I. *J. Am. Chem. Soc.* **1964**, *86*, 3840.

(14) The facile 1,2-migration of acyloxy groups of alkylidenecarbenes yielding alkynyl carboxylates has been proposed.[6]

(15) Cristol, S. J.; Whittemore, C. A. *J. Org. Chem.* **1969**, *34*, 705.

(16) Isomerization of **19** was not observed under the reaction conditions employed.

Experimental Support for Asp-52's Importance in Lysozyme Using a Carbohydrate-Based Enzyme Model. Acetal Hydrolysis Catalyzed by a "Stereoelectronically Correct" Carboxylate Group

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Theories concerning the mechanism of action of lysozyme and the testing of those theories by enzyme modelling efforts are amongst the most thoroughly documented in the bioorganic literature. The function of lysozyme's Glu-35 as a general acid catalyst has been extensively modelled; rate enhancements of acetal hydrolysis as high as 10^6 have been observed.[1] By comparison, much smaller (2–100-fold) accelerations have been attributed to the presence of an adjacent ionized carboxylate group;[2,3] a large acceleration would provide support for the proposed role of lysozyme's Asp-52 residue as either an electrostatic or nucleophilic catalyst. These small rate effects have prompted more than one author to conclude that Asp-52 contributes little or nothing to

(1) For a summary of work by several labs on g.a.c. in acetal hydrolysis, see: Sinnott, M. I. In *The Chemistry of Enzyme Action*; Page, M. I., Ed.; Elsevier: Amsterdam, 1984; pp 417–420.

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