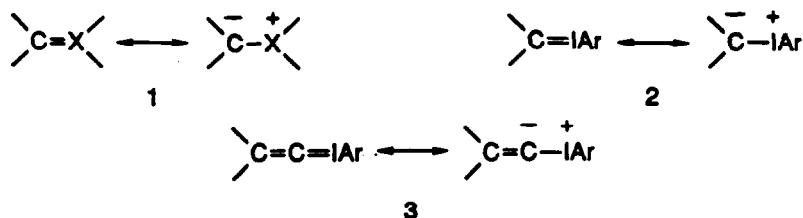# GENERATION, TRAPPING AND FATE OF ALKYLIDENECARBENE-IODONIUM YLIDES
## FROM THE ADDITION OF NaN$_3$ TO ALKYNYLPHENYLIODONIUM TOSYLATES

Tsugio Kitamura and Peter J. Stang*

Chemistry Department, The University of Utah

Salt Lake City, Utah  84112

Summary:  Addition of NaN$_3$ to RC≡CIPh·OTs results in novel alkylidenecarbene-iodonium ylides, 5, R(N$_3$)C=C=IPh, that by either protonation, ylide transfer or insertion of the derived carbene R(N$_3$)C=C: give unique functionalized vinyl azides.

Despite the importance of ylides, 1, in carbene chemistry,[1] until recently[2] there was little known about these species.  In the last few years they have become the object of increasing research effort with particular attention on halonium ylides.[3]  In 1984 Moriarty and co-workers[4] reported the x-ray structure of a stable carbene-iodonium ylide 2.



Even less is known[5] about the homologous alkylidenecarbene ylides.[6]  Hence, we wish to report on the generation, trapping and fate of alkylidenecarbene-iodonium ylides, 3, from alkynylphenyliodonium tosylates, 4.

Reaction of NaN$_3$ with readily available[7,8] 4 results in the addition of the azide ion to the electron deficient β-carbon of 4 giving alkylidenecarbene-iodonium ylides 5.  The subsequent fate of ylide 5 is strongly dependent upon both the nature of R in 4 and the reaction medium as shown in the Scheme.[9]  In methanol the vinyl azide, carbene insertion products, 6 and 10 (and 11 derived from 10 by loss of N$_2$) are formed along with some "protonated" product 9.  In the case of Et$_3$SiH/CH$_2$Cl$_2$ the phenyl substituted ylide 5 (R = Ph) gives only "protonated" product 9 whereas the t-butyl substituted ylide 5 (R = t-Bu) gives only the carbene derived Si-H insertion product 8 both in good yields.  Interestingly in a mixture of Et$_3$SiH/glyme the t-butyl system forms the Si-H insertion product 8 only in minor amounts (9%) the major product being the azidovinyl ether 7 (63%).

Likewise, treatment of the protonated ylide 9 with t-BuOK in glyme results only in the formation of azidovinyl ether 12.  This last result is particularly surprising as this reaction undoubtedly proceeds via the regeneration of 5 and its direct trapping by glyme to give 12.  In other words, we do not believe that the free carbene Ph(N$_3$)C=C: is involved in this reaction as it is well established[5,10] that all β-aryl functionalized alkylidenecarbenes rearrange to the corresponding phenylalkyne and cannot be trapped intermolecularly by trapping agents.

**Scheme:** Alkylidene-Iodonium Ylides 5 via Addition of NaN₃ to Alkynylphenyliodonium Tosylates 4.⁹

Hence, it is evident that the fate and chemistry of alkylidenecarbene-iodonium ylides 5 is distinct from that of the free carbenes. Specifically, these intermediates may be a) protonated, resulting in 9; b) undergo some sort of ylide-transfer process resulting in 6, 7, 10 and 12 or c) loose PhI giving the free carbene 13 that then gets trapped via insertion into Si-H resulting in 8. Further evidence for the uniqueness of 5 is provided by the fact that in mixtures of $Et_3SiH$/glyme it (5: R = t-Bu) prefers to undergo ylide transfer resulting in 7 and only a small amount of the free carbene is formed to give 8 (via loss of PhI and Si-H insertion). Free alkylidenecarbenes do not interact with glyme itself, which in fact is the solvent of choice for the generation and subsequent reaction of unsaturated carbenes.[5] Further evidence for the involvement of the free carbene 13 is the formation of cyclic vinyl azide 14 via the insertion of 13 into the secondary C-H bond of the n-hexyl group. Such C-H insertion with preferential formation of cyclopentenes is well precedented for alkylidenecarbenes.[11] An alkylidenecarbene ylide, similar to 5, (but with an enolate as nucleophile instead of $^{-}N_3$) was recently postulated by Ochiai and co-workers[12] in a novel cyclopentene annulation reaction via tandem Michael-carbene insertion reactions of related alkynyliodonium salts 4.

All products 6-12 and 14 were identified by infrared and ^{1}H and ^{13}C NMR spectra.[13] Specifically, with the exception of 11 all products showed a strong IR-absorption around 2100 $cm^{-1}$, (very characteristic of vinylazides)[14] along with absorption in the range of 1570 - 1660 $cm^{-1}$ due to the olefinic double bond. In the proton NMR they all showed a singlet between 5.9 - 6.6 ppm, (characteristic of the vinylic proton), except for 8 that has two singals at 4.76 and 4.86 ppm corresponding to the E and Z isomers. In the ^{13}C NMR the olefinic signals were at 118 - 128 ppm and 134 - 138 ppm for the alkoxyvinylazides, at 149.97 and 85.79 ppm for 9, and at 103.18, 162.01, 108.79 and 160.27 ppm for 8 (mixture of E and Z isomers).

Finally, these reactions represent not only further evidence for novel alkylidenecarbene-iodonium ylides, 5, but also a new way of preparing unique functionalized vinyl azides[14] (albeit only in modest yields) via alkynyliodonium salts 4.

## References and Notes

1. A.W. Johnson, "Ylide Chemistry", Academic Press, New York, 1964. W. Kirmse, "Carbene Chemistry", 2nd Ed., Academic Press, New York, 1971.

2. P. deMarch and R. Huisgen, J. Am. Chem. Soc., 104, 4952, 4953 (1982). R.P. L'Esperance, T.M. Ford and M. Jones, Jr., J. Am. Chem. Soc., 110, 209 (1988).

3. G.F. Koser, in "The Chemistry of Functional Groups, Supplement D", S. Patai, Ed., Wiley-Interscience, Chapt. 18, pp. 774-806, 1983.

4. R.M. Moriarty, I. Prakash, O. Prakash and W.A. Freeman, J. Am. Chem. Soc., 106, 6082 (1984). R.M. Moriarty, B.R. Bailey, III, O. Prakash and I. Prakash, ibid., 107, 1375 (1985).

5. P.J. Stang, Chem. Rev., 78, 383 (1978).

6. P.J. Stang, H. Wingert and A.M. Arif, J. Am. Chem. Soc., 109, 7235 (1987).

7. P.J. Stang, B.W. Surber, Z.-C. Chen, K.A. Roberts and A.G. Anderson, J. Am. Chem. Soc., 109, 228 (1987). P.J. Stang, B.W. Surber, ibid., 107, 1452 (1985).

8. L. Rebrovic and G.F. Koser, J. Org. Chem., 49, 4700 (1984). G.F. Koser, L. Rebrovic and R.H. Wettach, ibid., 46, 4324 (1981).

9. All reactions were carried out as follows: At -70°C to a solution of $NaN_3$ (8-16 mmol) in methanol (50 mL) was added 4 (4 mmol) and the mixture was warmed to room temperature with stirring. In the reactions with $Et_3SiH/CH_2Cl_2$ and $Et_3SiH$/glyme, 18-crown-6 (8 mmol) was