Heteroatom Chemistry
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A Report on the 19th Symposium on Heteroatom Chemistry of the Chemical Society of Japan

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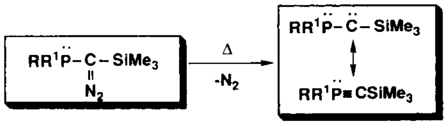
The 19th domestic Chem. Soc. Japan Symposium on Heteroatom Chemistry was held at a new auditorium of the Osaka Institute of Technology on January 16–18, 1992, and all the participants (about 250) enjoyed 50 oral presentations and four plenary lectures. The organizer, Professor Atsuyoshi Ohno of Kyoto University, and his staff-members, as well as Professor Yuzuru Uchida of Osaka Institute of Technology, did a wonderful job of organization. We had three foreign plenary lectures, that is, Prof. William E. McEwen of the Univ. of Mass., Amherst, U.S., Editor-in-Chief of *Heteroatom Chemistry,* Prof. Yuri G. Gololobov of the Nesmeyanov Institute of Organo-Element Compounds of Moscow, and Dr. Guy Bertrand of CNRS in Toulouse, France. There was also one domestic plenary lecturer, Prof. Masaru Hojo of Kobe University. The first plenary lecture was presented by Dr. Bertrand on "Use of Heteroatoms for Stabilizing Highly Reactive Organic Species." He has been able to synthesize stable carbenes bearing phosphorus and silyl substituents (**1**) and nitrilimines bearing phosphorus (**2**) as well as silyl or boryl substituents. The carbenes (**1**) show typical reactivities of both carbenes and the P ═ C bond.



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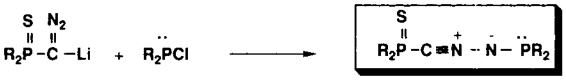

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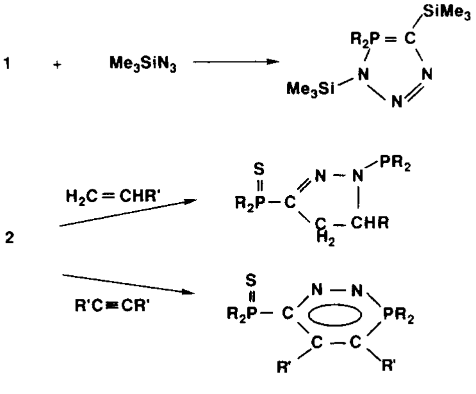
The nitrilimines (**2**) are useful in heterocyclic synthesis since the phosphorus atom can function as a second functional group in addition to the 1,3-dipolar reactivity.



Stable diazomethylenephosphoranes (**3**) and distillable diazoboranes (**4**) have also been prepared. The former is an excellent "naked" carbon generator as well as powerful building block in heterocyclic synthesis, and the latter is a precursor of a new type of diazocumulene.

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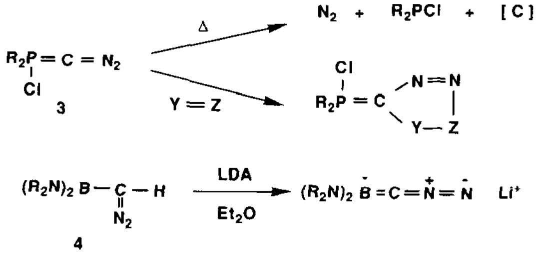
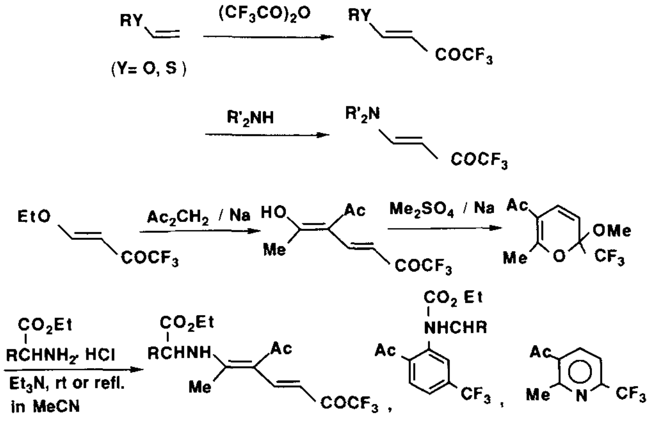
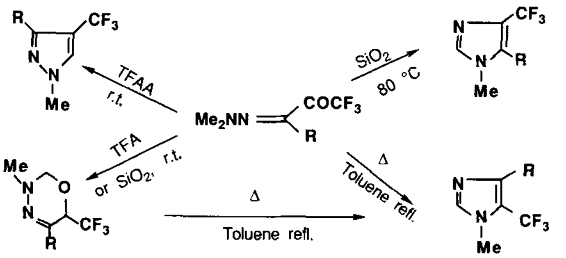


The second plenary lecture by Professor Masaru Hojo was entitled "Electrophilic and Nucleophilic Substitution at Olefinic Carbon Atoms. Facile Synthetic Methods for Fluorine-Containing Heterocyclic Compounds." Professor Hojo showed that vinyl ethers and vinyl sulfides react easily with trifluoroacetic anhydride at room temperature to give the corresponding β-trifluoroacetylated vinyl compounds in almost quantitative yields, and these products can undergo O — N, O — S, N — O, N — N, and N — C exchange reactions on treatment with various nucleophilic reagents.



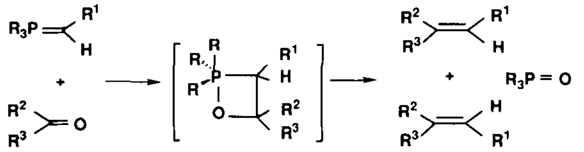
Bifunctional nucleophiles lead to fluorine-containing heterocycles such as pyrazoles, isoxazoles, and pyrimidines. The trifluooacetylation can successfully be extended to various hydrazones which are converted to many heterocyclic compounds bearing a trifluoromethyl group.

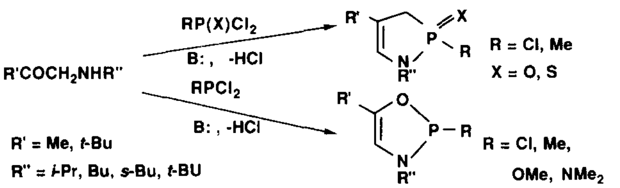


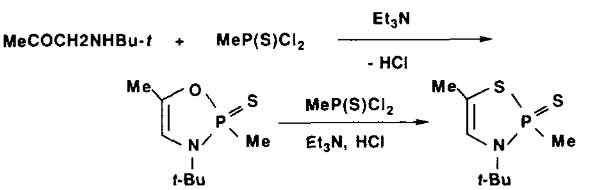
The third plenary lecture was given by professor William E. McEwen of The University of Massachusetts (U.S.A.) and the title of his lecture was "Mechanisms of Wittig Reactions."

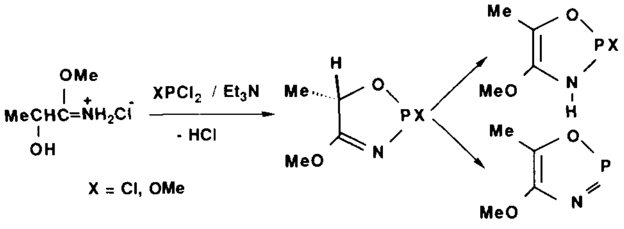
Mari, Lahti and McEwen have previously reported [F. Mari, P. M. Lahti, W. E. McEwen, *Heteroatom Chem.* 2, 1991, 225] that the MNDO-PM3 molecular modeling method reproduces the geometric and thermodynamic parameters calculated by others via a more elaborate *ab-initio* molecular orbital treatment of the "mythical Wittig half reaction" ($H_3P = CH_2 + CH_2O_2 \rightarrow$ the oxaphosphetane). MNDO-PM3 calculations and subsequent analyses of bond orders and localized molecular orbitals indicated that the transition state has an important ionic character in which the C — C bond is about 40% formed, but there is essentially no P — O bond formation. In new calculations, they have now found that the same types of transition states are formed in the reactions of unstabilized ylides with acetaldehyde. These transition states are best described as "syn" pseudo betaine types in which the syn geometry is a consequence of a strong interaction of the positively charged phosphorus atom and negatively charged oxygen atom. The reactions can be described as very asynchronous cycloadditions (borderline two-step mechanisms). The reactions of stabilized and semistabilized ylides with acetaldehyde have also been modeled by the PM3 approach, and indications of both partial P — O bonding (5–10%) and partial C — C bonding (30–40%) are provided. Thus, these reactions are less asynchronous than those of unstabilized ylides. In all cases of the present molecular modeling, E stereoselectivity is predicted for any hypothetical gas phase syn approach of the reactants. For real Wittig reactions carried out in salt-free tetrahydrofuran solutions, however, unstabilized ylides are known to give Z stereoselective products; stabilized ylides, E stereoselective products; and semistabilized ylides, mixtures of Z and E products. The only apparently reasonable rationalization for Z stereoselectivity would be the result of an "anti" approach of the reactants. The formation of an anti transition state with the same pseudo betaine characteristics described by the use of the MNDO-PM3 SCF calculations is conceivable for the reactions of unstabilized ylides in the presence of metal salts or sufficiently polar solvents through polarization by these external elements.

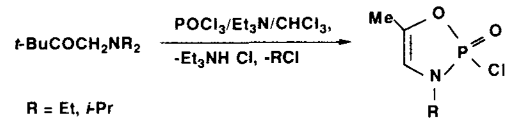
The last plenary lecture, "Formation of P-Heterocycles via the Cleavage of C ═ O and P ═ O Groups," was presented by Professor Yuri G. Gololobov of the A. N. Nesmeyanov Institute of Organo-Element Compounds of the Russian Academy of Sciences (Russia). He mentioned the synthesis of many heterocycles containing a phos-

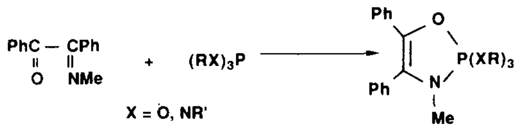


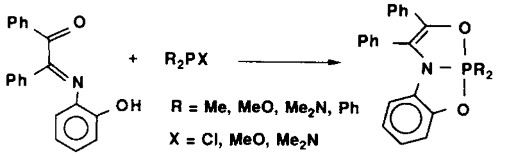


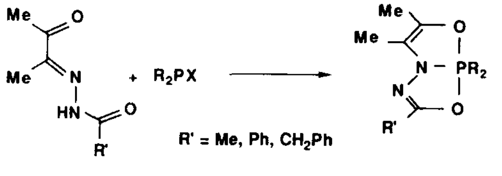












phorus atom by the cleavage of C = O and P = O bonding, such as shown below. He also reported that an 8-membered heterocycle containing a P — N linkage has a staggered conformation. In addition to these plenary lectures, many oral presentation were given as follows:

1. Reactions of Triarylphosphines with Organolithium Reagents by Y. Uchida, M. Kawai (Osaka Institute of Technology), and S. Oae (Institute of Heteroatom Chemistry)
2. Reactions of Diphenylphosphinites with N-Methylacridinium Ion by S. Yasui (Tezukayama College), K. Shioji and M. Yoshihara (Kinki University), and A. Ohno (Kyoto University)
3. Reaction of Tertiary Phosphine with Some Monophenylthallium(III) Crown Ether Complexes by J. Tomioka and Y. Kawasaki (Osaka Institute of Technology)
4. Synthesis of Muscone of Very High Enantiomeric Purity by Conjugate Addition of Chiral Dimethylheterocuprate to (E)-2-Cyclopentadecene-1-one by K. Tanaka, J. Matsui, and H. Suzuki (Kyoto University)
5. Chemistry of Silylketenes: Preparation of α-Silyl-α-stannylacetates of Their Stereoselective and Reformasky-type Reaction with Aldehydes or Imines by S. Akai, Y. Tsuzuki, S. Matsuda, S. Kitagaki, and Y. Kita (Osaka University)
6. Novel Generation of 1,3-Dipoles by Thermal Silicon Shift and Its Application to Heterocyclic Synthesis by M. Ohno, M. Komatsu, and Y. Ohshiro (Osaka University)
7. Reaction of 2-Thienyl Sulfoxide with Organometallic Reagents by S. Oae (Institute of Heteroatom Chemistry), Y. Inubushi, and M. Yoshihara (Kinki University)
8. Carbonylation and Thiocarbonylation of Aromatic Amides Using Carbon Monoxide and Sulfur, or Carbon Disulfide by Y. Mizuno, I. Nishiguchi, and T. Hirashima (Osaka Municipal Research Institute)
9. Reactions of 2-Methyl-2-Propanesulfenic Acid in Aqueous Solution by T. Okuyama, K. Miyake, and T. Fueno (Osaka University)
10. Palladium-Catalyzed Addition of Benzenethiol and Benzeneselenol to Acetylenes by K. Sato, H. Kuniyasu, A. Ogawa, I. Ryu, N. Kambe, and N. Sonnoda (Osaka University)
11. Reactions of Cyclic Selenonium Salts with Nucleophiles by T. Kataoka, H. Tsutsui, T. Iwamura, H. Shimizu, and M. Hori (Gifu Pharmaceutical University)
12. Reaction of o-Trimethylsilyl Selenocarboxylates with Bisphosphine Plalldium and Platinum Dichloride by Y. Kawahara, T. Kanda (Gifu University), K. Miki (Tokyo Institute of Technology), T. Murai, H. Ishihara, and S. Katoh (Gifu University)
13. Synthesis and Reactions of Heterocyclic Bismuth (III) and (V) Compounds by T. Murafuji, Y. Matano, and H. Suzuki (Kyoto University)
14. Synthesis of an Optically Active Tellurium Compound Containing 1,1′-Binaphthyl Group and Its Application to Asymmetric

Reactions by Y. Doi, M. Osuka, M. Irie, Y. Aso, T. Otsubo, and F. Ogura (Hiroshima University)

15. Thermal Rearrangement of Oxime O-Vinyl Ether by M. Yokoyama, M. Irie, K. Sujino, H. Togo, and T. Imamoto (Chiba University)
16. Structure and Bonding Nature of Propellane Type Modecule, 2,4,5-Triselena-1,3-Disilatricyclo[1.1.1.0^{1,3}] Pentane by H. Yoshida and W. Ando (Tsukuba University)
17. Formation of Dication and Hypervalent Bonds from Cyclic Componds Containing Selenium Atoms by H. Fujihara, H. Mima, and N. Furukawa (Tsukuba University)
18. Novel Catalytic Reactions Using Organoselenium Compounds by M. Iwaoka and S. Tomoda (Tokyo University)
19. N-Carbonylation of Nitrogen-containing Compounds with Selenium and Carbon Monoxide and Its Synthetic Application by K. Okada, S. Fujiwara, T. Shin-ike, N. Kambe, and N. Sonoda (Osaka University)
20. Synthesis and Stereochemistry of Optically Active Selenonium Ylide by N. Kamigata, Y. Nakamura, H. Matsuyama, and T. Shimizu (Tokyo Metropolitan University)
21. Synthesis of Enantiomerically Pure Selenoxides Bearing Efficient Ligand, 2-Exo-Hydroxy-10-Bornyl Group by Y. Arai, S. Kawanami, and T. Koizumi (Toyama Medical and Pharmaceutical University)
22. Synthesis of β-Halovinyliodonium Salts and Generation of α-Haloalkylidenecarbenes by M. Ochiai, K. Uemura, K. Oshima, and Y. Masaki (Gifu Pharmaceutical Unviersity)
23. Activation of Iodosylbenzene with One Equivalent Triflic Anhydride and the Reactions by T. Kitamura, R. Furuki, and H. Taniguchi (Kyushu University)
24. Preparation and Reactions of Electron Rich Organylbismuth Compounds by T. Ogawa, T. Hikasa, T. Ikegami, N. Ono (Ehime University), and H. Suzuki (Kyoto University)
25. Cationic Ring-Opening Living Polymerization of Six-membered Cyclic Phosphonite Initiated with a New Catalyst Using a Halobenzene/ Nickel Bromide System by J. Kadokawa and S. Kobayashi (Tohoku University)
26. Photochemical Reaction of Methoxyphenyl Phosphates by Y. Okamoto, M. Nakamura, K. Sawasaki, Y. Osako, and S. Takamuku (Osaka University)
27 Formation Reaction of Pentavalent Pent-Coordinated Phosphorus Compounds Containing an Iron Fragment as a Substituent by H. Nakazawa, K. Kubo, C. Kai, and K. Miyoshi (Hiroshima University)
28. Asymmetric Transfer of Chiral Sulfinates by Transition Metal Catalysts by K. Hiroi, N. Kawamoto, and M. Umemura (Tohoku College of Pharmacy)
29. Absolute Structure of Some Sulfoxides and Their Reaction Products with Grignard Reagents by F. Iwasaki, N. Yamazaki, M. Hirota, and M. Yasui (The University of Electro Communications)
30. Preparation of Chiral Aziridines from Chiral Oxiranes with Retention of Configuration by A. Toshimitsu, H. Abe, C. Hirosawa, and S. Tanimoto (Kyoto University)
31. Synthesis and Reactions of Sterically Crowded, Novel Tin-Chalcogen Compounds by Y. Matsuhashi, M. Saito, N. Tokitoh, and R. Okazaki (Tokyo University), M. Goto (National Chemical Laboratory for Industry)
32. Formation and Reactions of the Novel Chalcogen-Containing Bicyclic Compounds by M.-X. Ding, K. Maeda, A. Ishii, J. Nakayama, and M. Hoshino (Saitama University)
33. Preparation and Reactions of Highly Coordinated Organoantimony Compounds by H. Nakata, Y. Doi, S. Kojima, Y. Yamomoto, and K. Akiba (Hiroshima University)
34. Ion Selective Macrocyclic Compounds with a Redox Gate by T. Nabeshima, H. Furusawa, and Y. Yano (Gunma University)
35. Synthesis of Trithiocarbonates and Development of C-C Bond Formation Using These Compounds by A. Sugawara, T. Segawa (Tsuruoka National College of Technology), and R. Sato (Iwate University)
36. Generation and Reaction of o-Methylthiomethyldiphenylcarbene. Direct Observation of Sulfonium Ylide Intermediate by K. Hirai and H. Tomioka (Mie University)
37. C-Se Bond Cleavage in Selenides with Iodine. Examination of the Scope and the Mechanism of the Reaction by W. Nakanishi, A. Kusumi, K. Isaka, and S. Hayashi (Wakayama University)
38. Isolation and Reaction of Selenobenzophenones by K. Kojima, I. Kaneko, K. Okuma, and H. Ohta (Fukuoka University)
39. A new Carbon-Carbon Bond Formation Using α-(Phenylseleno)ketones by T. Wakayama, Y. Watanabe. Y. Ueno, and T. Toru (Nagoya Insititute of Technology)
40. Synthesis of Phosphorus Sugar Derivatives from Phospholenes by M. Yamashita, A. Iida, K. Ikai, H. Mizuno, Y. Miyamoto, T. Morishita, M. Uchimura, T. Oshikawa (Shizuoka University), H. Yamamoto, T. Hanaya (Okayama University), L. Parkanayi, and J. Clardy (Cornell University)
41. Intramolecular Rearrangement of Dichlorophosphiranes Having Exocyclic Double Bonds and Their Synthesis Applications to Phospha-

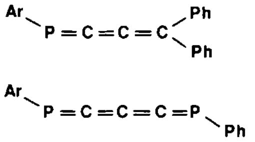
cumulenes by K. Toyota, H. Yoshimura, and M. Yoshifuji (Tohoku University)

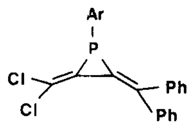
42. Development of a New Type of Chiral Diphosphinocarboxylic Acids and Synthetic Application of β-Ketophosphonates in the Presence of Transition Metal Catalyst by Y. Okada, U. Nakayama, J. Ichikawa, and T. Minami (Kyushu Institute of Technology)
43. Synthesis and Reactions of 2-Silatetralin Derivatives by O. Hoshino, A. Hirokawa, K. Miyauchi, A. Tatsuno, and T. Miura (Science University of Tokyo)
44. Stabilization of Intermediates of Wittig and Peterson Reactions Utilizing Characteristics of Martin Ligand by T. Kawashima, K. Kato, N. Iwama, and R. Okazaki (Tokyo University)
45 Boron-Dianion Species: Generation and Reactivities by T. Imamoto, T. Hikosaka, H. Togo, and M. Yokoyama (Chiba University)
46. Oxidation of Thiophene 1,1-Dioxides with *m*-Chloroperbenzoic Acid. Formation of the Corresponding Epoxides and Their Acid-Catalyzed Rearrangement to Thiete 1,1-Dioxides by H. Kamiyama, R. Hasemi, and J. Nakayama (Saitama University)
47. Oxidation of Benzotrithioles and Oxygen Migration of Benzobistrithiole 2-Oxide by R. Sato, N. Yomoji, and S. Satoh (Iwate University)
48. Radical Substitution on Sulfur by M. Tada, H. Nakagiri, and T. Uetake (Waseda University)
49 Oxidation Reaction of Cyclic Allyl Selenides by M. Ito, M. Segi, and T. Nakajima (Kanazawa University)
50. Photooxygenation of Organic Selenium Compounds by M. Abe, T. Akasaka, and W. Ando (Tsukuba University)

Most of these oral presentations were suitable for lengthy presentations. However, due to the limited time schedule, they had to be shortened. Among these, the work of Dr. Kawaski (No 3) on the reaction of monoarythallium(III), shown below, was the first

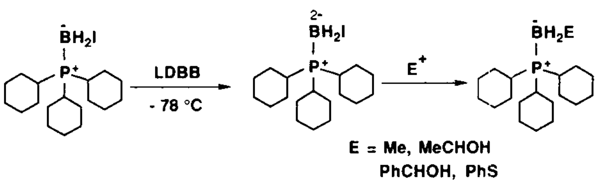
$$\mathrm{ArTl(OCOR)_2 + Nu \rightarrow Ar\text{-}Nu + TlOCOR}$$

example of ligand coupling within a hypervalent Tl compound. The concept of ligand coupling within hypervalent species has apparently become well-accepted, and a few more examples were shown, for example, No. 1, 7, 11, 27, 29, 31, 33, 44, etc. The work on phosphacumulenes as well as on a three membered heterocycle containing phosphorus, by Yoshifuji (No. 41) was of significance.

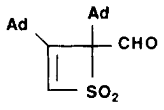




The chemistry of boron-dianion species presented by Imamoto (No. 45) is unique.



Also unique is the synthesis of the thiete dioxide shown next, carried out by Nakayama (No 42).



There were 14 papers on compounds containing sulfur, selenium and phosphorus atoms and a few involving Si, Bi, I, and others. Many more will appear within the domain of heteroatom chemistry. Boron, Fluorine, and Copper are included among these. This trend is indeed a healthy one. The change of the name of the Symposium from Sulfur and Phosphorus to the present one three years ago has gradually uplifted the quality of the Symposium to the present high level.

We look forward to the 20th Symposium on Heteroatom Chemistry in January of 1993 to be held in Tokyo. The 20th Symposium will be organized by Professor Nobumasa Kamigata of Tokyo Metropolitan University at their new campus, to the west of Tokyo where Mt. Fuji is clearly seen at this time of the year. We hope that many more people will participate in the next Symposium.