Heteroatom Chemistry
Volume 6, Number 6, 1995

A Report on the 22nd Symposium on Heteroatom Chemistry of the Chemical Society of Japan

Shigeru Oae*

Institute of Heteroatom Chemistry, 2509 Hirao, Miharacho, Minamikawachi-gun, Osaka 587, Japan

Hideo Togo*

Department of Chemistry, Faculty of Science, Chiba University, Yayoi-cho 1-33, Inage-ku, Chiba 263, Japan

Received 16 March 1995

The 22nd Symposium on Heteroatom Chemistry of the Chemical Society of Japan was held at Nagoya and was productive, despite the big earthquake in the Kobe area that disrupted all traffic west of Kobe. The famous super express train, Shinkansen, did not function between Kyoto and Kobe, because of the destruction of the tracks. The meeting was organized by Professor Takashi Toru of Nagoya Institute of Technology, and it took place on the 19th to 21st of January on rather cold days but in a well-heated auditorium of Nagoya University. Amazingly, the symposium attracted nearly 250 people from throughout the country. Many participants came from Fukuoka, Matsuyama, Ube, and other places. Many of the attendees had to spend many extra hours detouring via long routes, but they nevertheless came to the meeting. Unfortunately, nobody in Kobe, which was devastated on the morning of the 17th of January, was able to attend. Kobe University alone suffered the loss of more than 40 people, including many faculty members. Fortunately, the Kintetsu Railway was running to Nagoya, and many came to the meeting from the Osaka area by this railway. Professor T. Toru arranged for four plenary lectures each of fifty minutes duration and for 55 oral presentations each of 20 minutes duration. The schedule from 9 A.M. to 6 P.M. was the same for each of the three days.

The first plenary lecture was given by Professor Ryu Sato of Iwate University in Morioka on the subject of "Synthesis and Reactions of Novel Cyclic Polychalcogenides," and the lecture was a unique and interesting one, since not many people have been working on the chemistry of elemental sulfur or selenium in liquid ammonia. In order to carry out a reaction with sulfur in liquid ammonia, Sato and his colleagues had to use an autoclave made of titanium because of the corrosive nature of the mixture. When Professor Sato spent a year in the mid-seventies at Tsukuba University, many were interested to see the titanium instrument in action. It was apparent that elemental sulfur or selenium could be dissolved in any amount in liquid ammonia to form, finally, S_n–NH_2^- salts, which are very strongly nucleophilic, because the anions are *a*-nucleophiles.

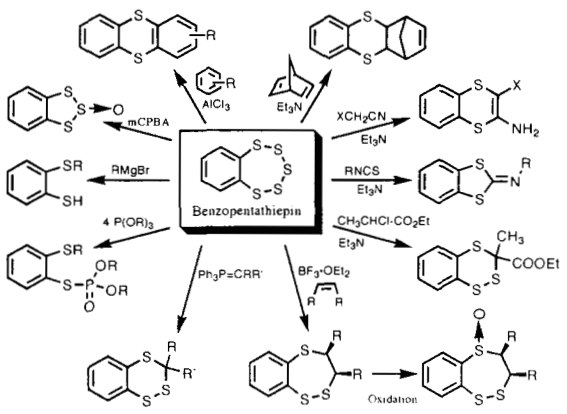
$$S_8 + \text{liq. } NH_3 \rightleftharpoons NH_4^+\ NH_2{-}S_8^- \rightleftharpoons NH_4^+\ NH_2{-}S_n^-$$

$$\rightleftharpoons \rightleftharpoons \rightleftharpoons NH_4^+\ NH_2{-}S_2^-$$

Benzopentathiepin could be prepared by use of those reagents, and the following chart summarizes the interesting reactions that this compound undergoes:

*To whom correspondence should be addressed.

1042-7163/96/060507-06

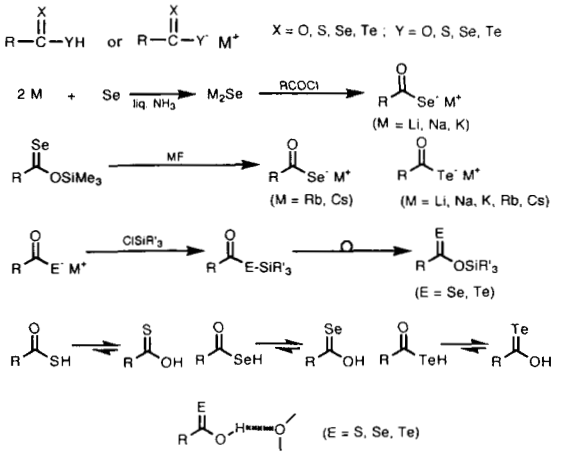


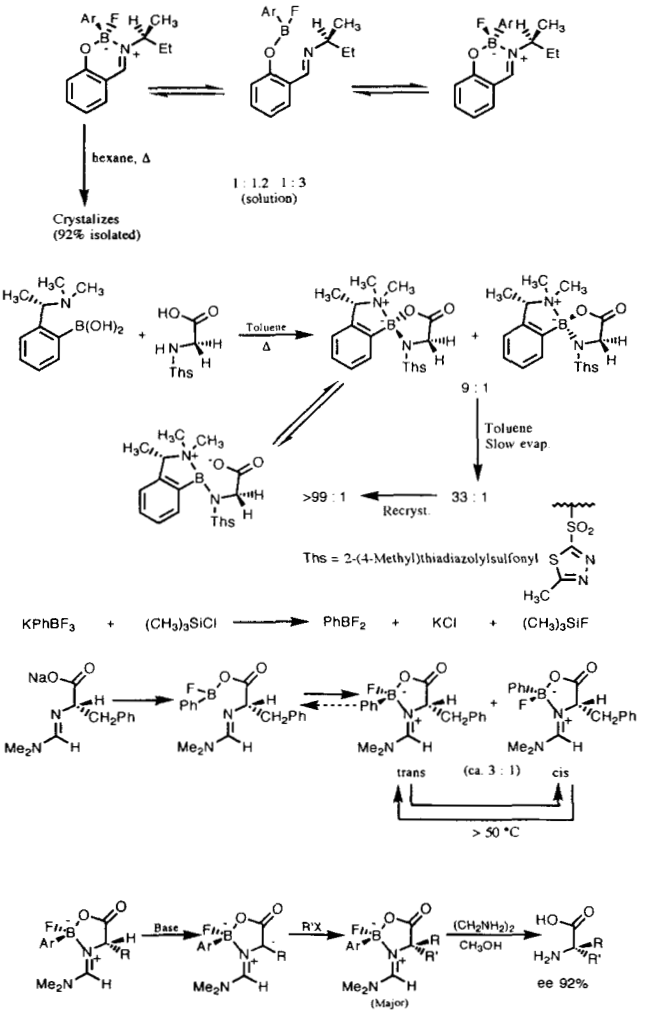
Professor Sato also showed that an intramolecular oxygen migration of a complex sulfoxide derivative can take place as shown in the following example. The α-sulfoxide does not undergo oxygen migration. By use of an ^{18}O isotope study, the intramolecular nature of the migration was proved.

The second lecture was delivered by Professor Edwin Vedejs of the University of Wisconsin on the subject of "Asymmetric Transformation: A Method to Control Heteroelement Stereochemistry." It covered an interesting concept, that of using crystallization of an equilibrating mixture of diastereomers to drive the equilibrium towards the least soluble isomer, and this is designated as asymmetric transformation (AT). This is methodology based on phase rule concepts. We know that solubilities of isomers of boron-aminoacid complexes differ. A good example is shown subsequently. Thus, the high recovery of one isomer is possible. Many more examples are also shown here. One drawback is the corrosive nature of $PhBF_2$. This could be avoided by other approaches.

This concept of AT is quite useful in organic preparations since many of the isomers have different solubilities. Professor Vedejs was born in Riga, Latvia, and migrated to the United States in 1950 when he was 9 years old. He obtained his B.S. degree from the University of Michigan and his Ph.D. from the University of Wisconsin under German Professor, H. Muxfeldt. After one year with Prof. E. J. Corey in 1966, he returned to the University of Wisconsin.

The third plenary lecture covered the syntheses of all of the chalcogen acids of the following structures and was entitled "New Chalcogenocarboxylic Acids and Their Alkali Metal Salts: Synthesis and Reactions," and was presented by Professor Shinji Kato





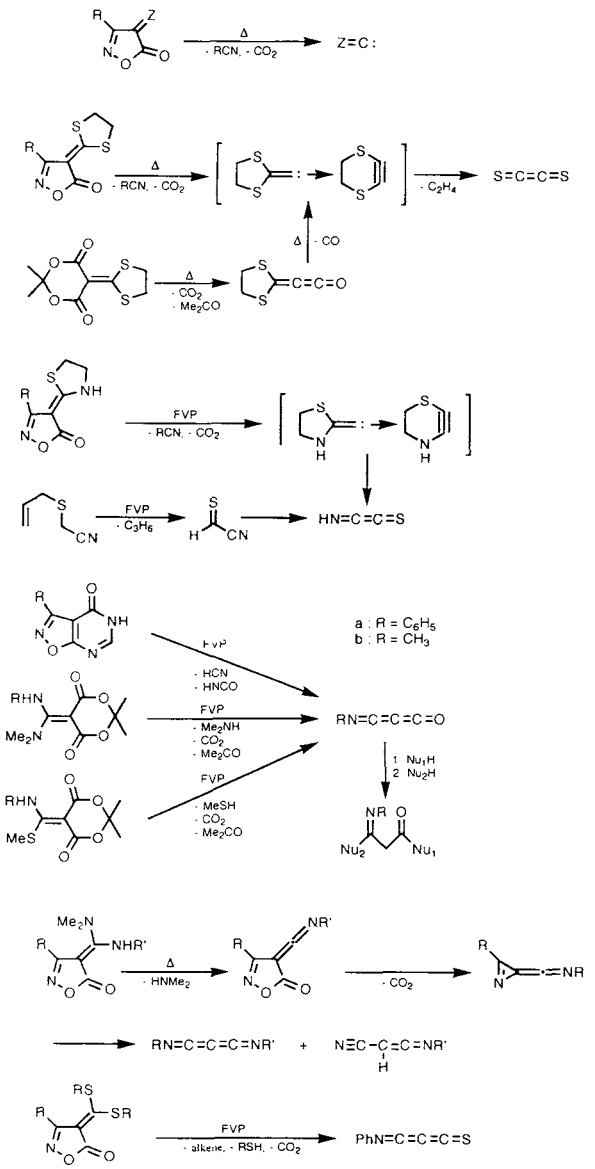
of Gifu University. It covers his lifework of more than 30 years since he joined Gifu University. He stated that, contrary to the common knowledge, both the selenoxo forms (RCSeOH) and telluroxo forms (RCTeOH) of these acids mainly exist in THF or MeOH solutions. He had to synthesized many of the acids, some of which are shown in the chart. Not

only the Li and sodium salts but also all kinds of alkali metal salts were prepared; for example, tellurocarboxylate salts were obtained as shown on the previous page.

He found that triorganosilyl esters rearrange to the O-silyl derivatives as shown.

The most striking finding is that of the equilibria shown. One speculation is that of hydrogen bonding in THF at a low temperature.

The last plenary lecture was presented by Professor Curt Wentrup of the University of Queensland, Brisbane, Australia, on the subject of "Novel Heterocumulenes, X=C=C=Y and RN=C=C=C=X." Using flash vacuum pyrolysis, he could make useful precursors of vinylidenes as shown in the following.



An extension of this research involved the synthesis of C_2S_2.

The formation of HN=C=C=S was detected by mass spectrometry. The extended cumulene, RN=C=C=C=O, was detected in the same way.

The bisimines, RN=C=C=C=NR', and C-cyanoketenimines, NC-CH=C=CNR', have been found to be generated in the manner shown below.

The sulfur analog, phenyliminopropadienethione, PhN=C=C=C=S, was prepared by flash vacuum pyrolysis (FVP) of isoxazolone in the preceeding column.

Some of the cumulenes, for example RN=C=C=C=O, are quite stable and can be trapped at below −50°C and allowed to react with a nucleophile as shown in the preceding. Apparently Professor Curt Wentrup is a world traveler. He was born in Denmark, but stayed in Germany many years before migrating to Australia. He frequently visits this country and includes skiing among his activities here.

In addition to the plenary lectures, many oral presentations were given. The topics and authors were as follows.

1. "Stereoselective Synthesis of α,β-Unsaturated Carbonyl Compounds from α-Seleno Carbonyl Compounds" by T. Hayakawa, T. Nishi, Y. Watanabe, Y. Ueno, and T. Toru (Nagoya Institute of Technology).
2. "Synthesis of Optically Pure Selenonium Ylides Bearing an Efficient Ligand, the 2-exo-Hydroxy-10-bornyl Group" by N. Kurose, S. Kawanami, T. Takahashi, Y. Arai, T. Koizumi, and M. Shiro (Toyama Medical and Pharmaceutical University, Rigaku Corporation).
3. "Synthesis and Reactions of Alkynylselenonium Salts" by T. Kataoka, Y. Banno, T. Iwamura, and H. Shimizu (Gifu Pharmaceutical University).
4. "Synthesis and Sterochemistry of Optically Active Telluronium Salts" by T. Urakubo, T. Shimizu, and N. Kamigata (Tokyo Metropolitan University).
5. "Selective Thioselenation of Isocyanides by Using a Disulfide-Diselenide Mixed System" by A. Ogawa, Y. Tsuboi, R. Obayashi, N. Kambe, and N. Sonoda (Osaka University).
6. "Highly Efficient 1,2-Asymmetric Induction in Intermolecular Radical Addition to γ-Oxy α,β-Unsaturated Sulfones" by K. Ogura, A. Kayano, M. Akazome, and M. Fujita (Chiba University).
7. "Radical Substitution on Sulfur in the Presence of Cobalt(II) Complexes" by M. Tada, K. Sugano, and T. Yoshihara (Waseda University).
8. "Radical Substitution Reactions of Metalladithiolene Rings" by K. Kobayashi, M. Ta-

mada, G. Hagino, M. Kajitani, T. Akiyama, and A. Sugimori (Sophia University).

9. "Some Reactions of 5-Membered Cyclic Xanthates and Episulfides with the Tributyltin Radical" by J. Uenishi and Y. Kubo (Okayama University of Science).
10. "Reaction of Thionyl Chloride with Organolithium Compounds" by S. Oae, Y. Inubushi, H. Ishihara, and M. Yoshihara (Institute of Heteroatom Chemistry, Kinki University).
11. "New Method for Generation of β-Oxido Carbenoids via Ligand Exchange Reactions of Sulfoxides and Its Application to a Procedure for One-Carbon Homologation of Carbonyl Compounds" by T. Satoh, N. Itoh, Y. Hayashi, Y. Mizu, and K. Yamakawa (Science University of Tokyo).
12. "Synthesis and Reactions of 2-Thianaphthalenes Carrying an Electron-withdrawing Group at the 3-Position" by H. Shimizu, T. Yonezawa, T. Watanabe, S. Miyazaki, and T. Kataoka (Gifu Pharmaceutical University).
13. "All-or-none Type Regulation of Selective Ag^+ Binding by Redox Reactions Between Thiol and Disulfide" by T. Nabeshima, T. Shinnai, T. Haruyama, T. Aoki, and Y. Yano (Gunma University).
14. "Carbon-Carbon Bond Formation via a Chiral Episelenonium Ion Bearing a Bulky Arylseleno Group as a Protective Auxiliary" by A. Toshimitsu, K. Nakano, T. Mukai, and K. Tamao (Kyoto University).
15. "Highly Selective Remote Asymmetric Induction: Asymmetric Reduction of α,β-Unsaturated Ketones with a 1,7-Hydride Shift" by K. Nishide, K. Obata, M. Yukawa, and M. Node (Kyoto Pharmaceutical University).
16. "Electrochemical Activation of Organochalcogens for Synthetic Organofluorine Chemistry" by K. Uneyama, Y. Dan-oh, and H. Asai (Okayama University).
17. "Reaction of Selenobenzophenones with Tetracyanoethylene" by K. Okuma, K. Miyazaki, K. Kojima, H. Ohta, Y. Yokomori, and T. Machiguchi (Fukuoka University, National Defense Academy, Saitama University).
18. "The Reaction of Aromatic Thioaldehyde Pentacarbonyltungsten(O) Complexes with Diazoalkanes: Synthesis of Thioketone Complexes and Formation of Alkenes via Thiirane Complexes" by M. Muraoka, T. Yamamoto, H. Okabe, and K. Sakurada (Josai University).
19. "Reaction of Thiolates with Carbon Monoxide" by T. Mizuno, I. Nishiguchi, T. Daigaku, and A. Nishinaga (Osaka Municipal Technical Research Institute, Osaka Institute of Technology).
20. "Potassium, Rubidium, and Cesium Dithiocarboxylates: A Facile Preparation and X-Ray Crystallography" by N. Kitaoka, T. Kanda, M. Ebihara, T. Murai, and S. Kato (Gifu University).
21. "Reactions of Carbonyl Selenide and Carbonyl Sulfide with Carbon Nucleophiles" by A. Asai, S. Fujiwara, T. Shin-ike, N. Kambe, and N. Sonoda (Osaka University, Osaka Dental University).
22. "Synthesis of the Framework of β-Amino Acids Utilizing Optically Active Vinyl Sulfoxides" by N. Itoh, H. Matsuyama, M. Yoshida, and M. Iyoda (Tokyo Metropolitan University).
23. "High Enantioselective Protonation of Prochiral Lithium Enolates Using Enantiomerically Pure β-Hydroxy Sulfoxides and Its Synthetic Utilities" by H. Kosugi, K. Hoshino, H. Kohno, R. Hatsuda, and H. Uda (Tohoku University).
24. "Diastereoselective Addition to Furfurals and Thienylaldehydes Using a p-Tolylsulfinyl Group as a Chiral Auxiliary" by Y. Arai, T. Matsuda, A. Suzuki, and Y. Masaki (Gifu Pharmaceutical University).
25. "Reaction of Sulfinyl-activated Methylene Compounds and Its Synthetic Application" by J. Nokami, Y. Ogawa, A. Ichikawa, Y. Maesaka, M. Mitsuoka, and M. Honda (Okayama University of Science).
26. "Synthesis and Reactivity of Chiral Allylic Ferrocenyl Chalcogenides" by T. Chiba, Y. Nishibayashi, K. Ohe, and S. Uemura (Kyoto University).
27. "Stereospecific Redox Reactions Directed by a Sulfinyl Group" by N. Yamazaki, A. Tsutsumi, Y. Mikata, M. Okamura, and A. Ohno (Kyoto University, Nara Women's University, Niigata University).
28. "Optical Resolution of a Dithiirane Oxide and Asymmetric Oxidation of a Dithiirane" by A. Ishii, T. Yamada, S. Nakamura, K. Hiyoshi, M. Hoshino, and J. Nakayama (Saitanma University).
29. "Polycoordinated Iodine(III) Reagent Prepared from o-Iodosylbenzoic Acid and TfOH. Reaction with Aromatics and Alkynylsilanes" by K. Nagata, K. Kitamura, and H. Taniguchi (Kyushu University).
30. "Electrosynthesis of Hypervalent Iodobenzene Difluoride Derivatives and Its Application to gem-Difluorination" by T. Fuchi-

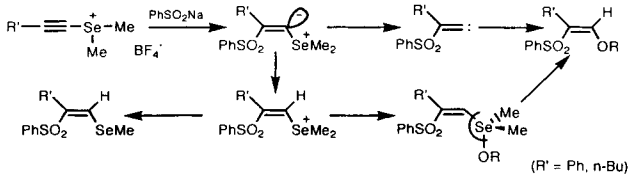
gami, T, Fujita, A. Konno, and T. Nonaka (Tokyo Institute of Technology).

31. "Mechanistic Analysis of Hypervalent Interaction between a Divalent Selenium and Nitrogen" by M. Iwaoka and S. Tomoda (Tokyo University).
32. "Formation and Reactions of New Hypervalent Triaryl Chalcogen Ate Complexes" by Y. Masutomi and N. Furukawa (Tsukuba University).
33. "Synthesis and Structures of Phosphorus(V) Octaethylporphyrins That Contain a σ-Bonded Element-Carbon Bond" by Y. Yamamoto, R. Nadano, and K. Akiba (Hiroshima University).
34. "Structures of Metal Complexes Derived from Tetraazathiapentalene Derivatives 2: Effect of Side Groups" by M. Yasui, N. Manabe, H. Nishiyama, F. Iwasaki, N. Matsumura, and H. Inoue (Electro-Communication University, University of Osaka Prefecture).
35. "Synthesis, Structure and Reactivity of Stable Germanium-Chalcogen Double-Bond Compounds" by T. Matsumoto, N. Tokitoh, and R. Okazaki (Tokyo University).
36. "Synthesis and Reactions of Metallacycles Containing Group 14 Elements" by N. Choi, S. Sugi, S. Morino, and W. Ando (Tsukuba University).
37. "Effect of Adjacent Substituents for Formation of Cyclic Benzopolychalcogenides" by S. Ogawa, A. Sasaki, and R. Sato (Iwate University).
38. "Synthesis of Optically Active Functionalized [7] Heterohelicenes" by K. Tanaka, K. Koyama, H. Osuga, Y. Shogase, and H. Suzuki (Kyoto University).
39. "Syntheses and Properties of Dimeric and Trimeric Tellurophenes" by S. Inoue, H. Nozoe, T. Jigami, T. Otsubo, and F. Ogura (Hiroshima University).
40. "Synthesis and Properties of New Twin-Donor Compounds Containing Tetrathiafulvalenes as Units" by U. Kux, M. Miura, M. Fukuda, S. Sasaki, and M. Iyoda (Tokyo Metropolitan University).
41. "Synthesis and Properties of Pyrroles and Pyrimidines Annulated with Hetero-aromatic Compounds" by T. Murashima, K. Fujita, T. Kaneko, and N. Ono (Ehime University).
42. "The Reaction of the Cyclopropenium Salts Having Sulfur Substituents" by H. Yoshida (Shizuoka University).
43. "Synthesis of Sugar Tetrazoles" by M. Yokoyama, M. Matsushita, S. Hirano, M. Kubo, H. Togo, and H. Seki (Chiba University).
44. "Synthesis and Reactions of an Intermediate of the Boron-Wittig Reaction" by N. Yamashita, T. Kawashima, and R. Okazaki (Tokyo University).
45. "Bismuthine Oxides: Synthesis and Reactions" by T. Ikegami and H. Suzuki (Kyoto University).
46. "Use of Chiral Quaternary Salts in Asymmetric Synthesis" by M. Higashiyama, A. Bohsako, A. Ando, and T. Shioiri (Nagoya City University).
47. "Synthesis and Synthetic Applications of Highly-Substituted Vinylphosphorus Compounds" by M. Nakamura, T. Sakuda, T. Fukamachi, H. Matsuki, J. Ichikawa, and T. Minami (Kyushu Institute of Technology).
48. "Reactions of Sterically Protected 3,4-Diphosphinidenecyclobutenes" by K. Toyota, A. Maack, K. Tashiro, K. Masaki, T. Abe, H. Matsuzawa, and M. Yoshifuji (Tohoku University).
49. "Synthesis of Novel Phospholane Derivatives" by M. Yamashita, K. Suzuki, A. Yabui, and T. Oshikawa (Shizuoka University).
50. "Reaction of Regioselective Phosphonylation of Sugar Derivatives Using Phosphenium Cation" by T. Kasaka, M. Kyoda, T. Fujimoto, K. Ohta, and I. Yamamoto (Shinshu University).
51. "Synthesis and Reactions of Boranophosphoric Acid Dialkyl Ester Monopotassium Salts and Boranopyrophosphoric Acid Tetramethyl Ester" by T. Imamoto, E. Nagato, Y. Wada, T. Uchimaru, K. Yamaguchi, and H. Masuda (Chiba University).
52. "Reaction of Trivalent-Phosphorus Compounds with Methylviologen as a Electron Acceptor" by S. Yasui, M. Tsujimoto, K. Shioji, and A. Ohno (Tezukayama College, Kyoto University).
53. "Intra- and Intermolecular Photochemical Reactions of Aryl Phosphates" by Y. Okamoto, T. Tatsuno, and S. Takamuku (Osaka University).
54. "Synthetic Organic Reactions Based on the Redox Reactions Between $TeCl_4$ and Trialkyl Phosphites" by Y. Watanabe, T. Yamamoto, S. Inoue, and S. Ozaki (Ehime University).
55. "Synthesis and Reactivity of Group 6 Transition Metal Phosphenium Complexes: Dou-

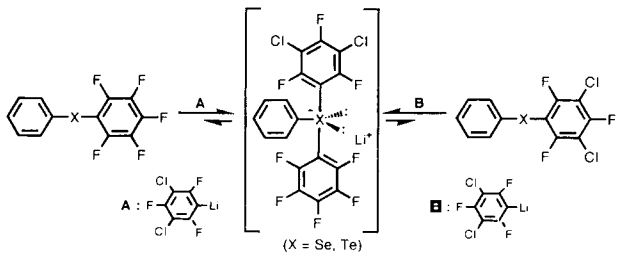
ble Bond Character of a Metal-Phosphorus Bond" by H. Nakazawa, Y. Yamaguchi, and K. Miyoshi (Institute of Molecular Science, Hiroshima University).

Although there were many good oral presentations, only a few interesting works can be shown here.

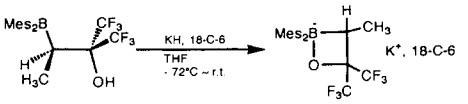
The work of Professor Kataoka's group at Gifu Pharmaceutical College on "Synthesis and Reactions of Alkynylselenium Salts (No. 3)" was interesting. They presented the following scheme but did not discriminate between the involvement of ligand coupling and other possible processes, as shown below.



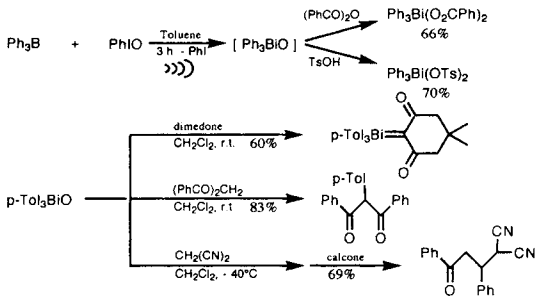
Professor Furukawa's oral presentation on "Formation and Reactions of New Hypervalent Triaryl Chalcogen Ate Complexes (No. 32)" included the following example, among many others.



Professors Okazaki and Kawashima's group (No. 44) reported on the discovery of a new boron-Wittig reaction, as shown below, actually isolating the four-membered ring intermediate, which was found to give the olefin.



Professor Suzuki's group of Kyoto University reported on bismuthine oxides that were easily made and quite reactive. The synthesis was carried out by the following method, and the resulting triphenylbismuthine oxide could be caused to react in the following manner (No. 45).



Since there will be an ICHAC-4 meeting in the coming summer, a Pan Pacific Meeting in Honolulu that will have a conference on Heteroatom Chemistry, and there will be an ISCOS meeting next year in Tsukuba, Professor Kenji Uneyama of Okayama University announced that the next Heteroatom Chemistry Symposium, 23rd, will be held in Okayama in December of 1996. By then, we hope, our railroads will be repaired and running again in their usual efficient manner.