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A Report on the Twenty-Fourth Symposium on Heteroatom Chemistry of the Chemical Society of Japan

Tatsuya Nabeshima,[1] Shigeru Oae[2]

[1]*Department of Chemistry, University of Tsukuba, Tsukuba, Ibaraki 305-8571, Japan*

[2]*Institute of Heteroatom Chemistry, 2509 Hiaro, Mihara-cho, Minamikawachi-gun, Osaka 587-0022, Japan*

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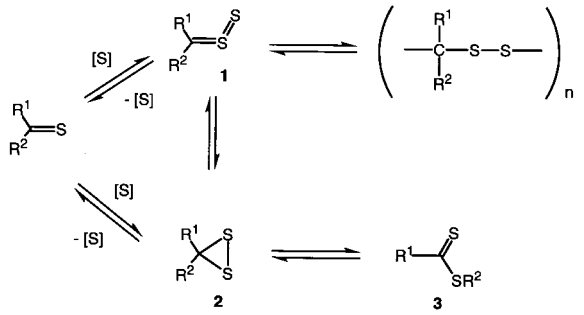
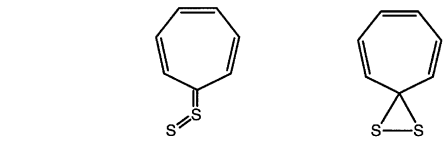
The 24th domestic Chemical Society of Japan Symposium on Heteroatom Chemistry was held in Sendai during the period of December 11 (Thursday) through 13 (Saturday) under the management of Prof. Masaaki Yoshifuji, who introduced for the first time a Poster Session in addition to oral presentations. We had three plenary lectures, namely, by Prof. Alexander Senning of the Technical University of Denmark, Prof. Edgar Niecke of the University of Bonn, and Prof. Kenji Uneyama of Okayama University. The weather treated us nicely, without any very cold days. The first plenary lecture was given by Prof. Alexander Senning on "The Thiosulfine-Dithiirane-Dithioester Manifold $R^1R^2(CS_2)$," and the following is a summary of his lecture. In Scheme 1, which is based on literature data, ($R^1 = R^2 = H$) **3** > **2** > **1** is the order of thermodynamic stability. The isomerization of **1** to **2** is, in most cases, calculated to be exothermic. A notable exception is that of tropothione *S*-sulfide. Calculations show that the *S*-sulfide is roughly isoenergetic with the corresponding spiro compound.



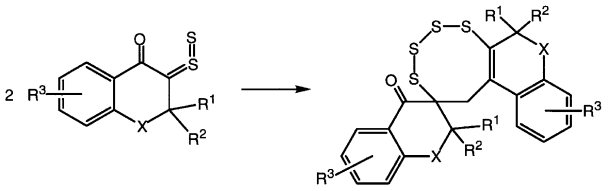
SCHEME 1

Synthetic aspects of the thiosulfine-dithiirane-dithioester manifold were emphasized. Especially intriguing are the many cycloadditions possible with **1**, notably those of the 1,3-dipolar type (Equation 1).



S-sulfide

(1)



The second lecture was presented by Edgar Niecke

Correspondence to: Tatsuya Nabeshima
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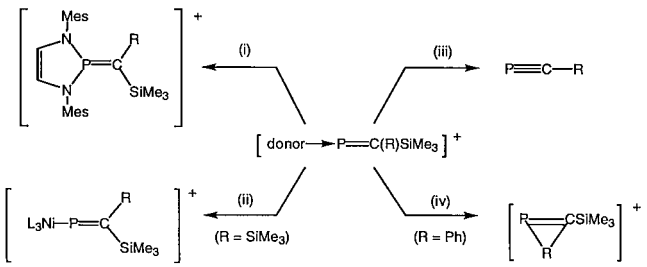
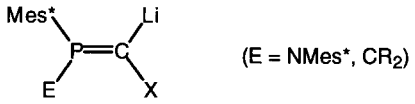
on the subject of "From Reactive Intermediates to Metastable Structures: Cations, Carbenoids and Diradicals Containing P/C–pπ-Bonds." He discussed methylenediylphosphenium cations that undergo the types of reactions shown in Scheme 2 in generalized form.

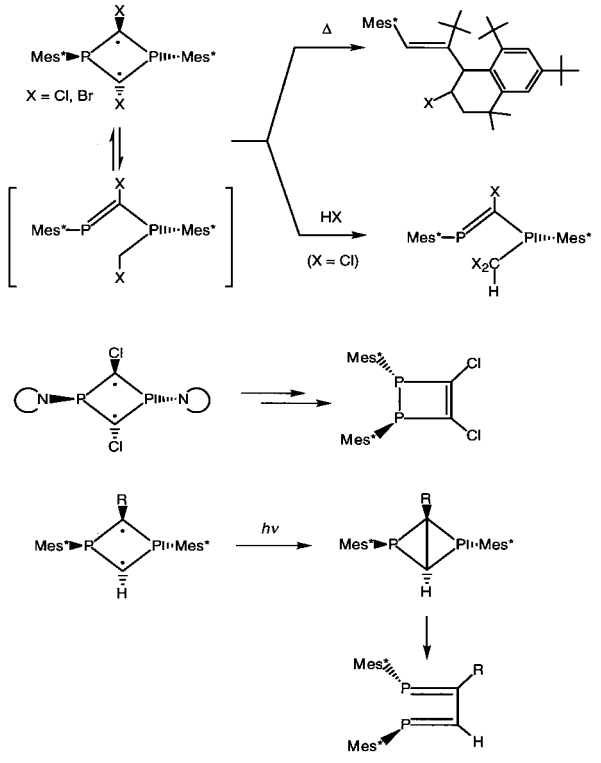


SCHEME 2

He further described the synthesis and behavior of ylene(phosphoranylidene)carbenoids and other unique compounds such as the following:

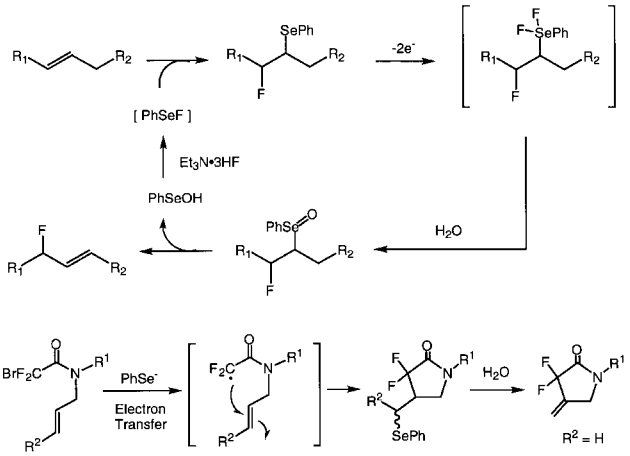


He also pointed out that 1,3-diphosphetane-(2,4)-diyles undergo reactions as shown in Scheme 3.



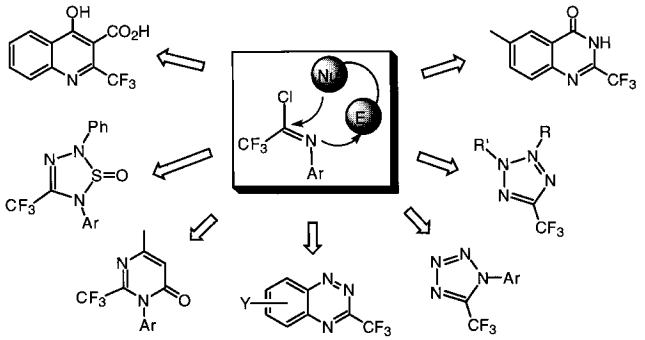
SCHEME 3

The third plenary lecture was given by Prof. Kenji Uneyama on "Fluorofunctionalization by Heteroatom-Mediated Reactions." He described fluoroselenenylation and perfluoroaklyl-selenenylation as shown in Scheme 4.

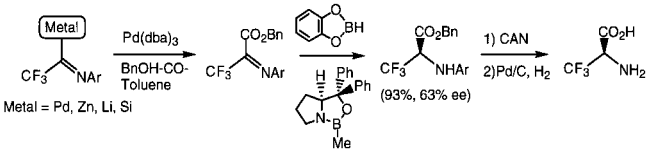


SCHEME 4

He also described the chemistry of trifluoroacetimidoyl halides as depicted in Schemes 5 and 6.

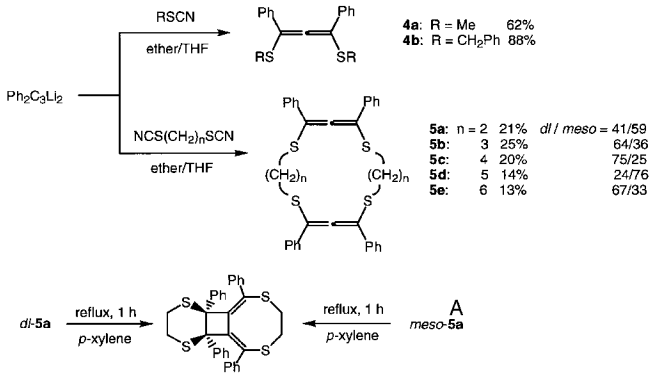


SCHEME 5



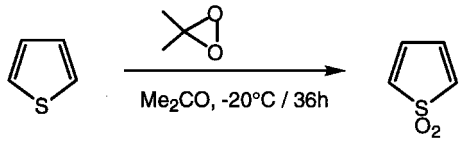
SCHEME 6

Among the 47 regular presentations, some impressive lectures were the following: Professor Nobumasa Kamigata's article was read by Dr. T. Shimizu on the "Synthesis and Reactions of Sulfur-Substituted Allenes." He covered the chemistry summarized in Scheme 7.



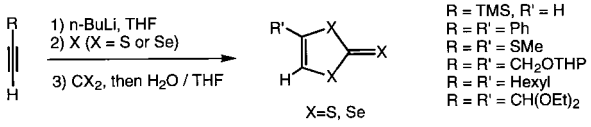
SCHEME 7

Professor Juzo Nakayama and coworkers described the synthesis, isolation, and full characterization of the parent thiophene 1,1-dioxide that is unstable and difficult to characterize. The dioxide was prepared by the reaction of thiophene with dimethyldioxirane (Equation 2).



(2)

Professor Tetsuo Otsubo et al. reported a convenient and high-yield preparation of 1,3-dithiole-2-thiones and 1,3-diselenole-2 selones, key precursors for tetrathiafulvalenes and tetraselenafulvalenes, as shown in Scheme 8.



SCHEME 8

Professor Yoshiaki Yoshimura delivered his article that dealt with the chemistry of the SN triple bond, as shown in Scheme 9: An ORTEP drawing of $Ph_2S(OPr)N$ is presented in Figure 1.

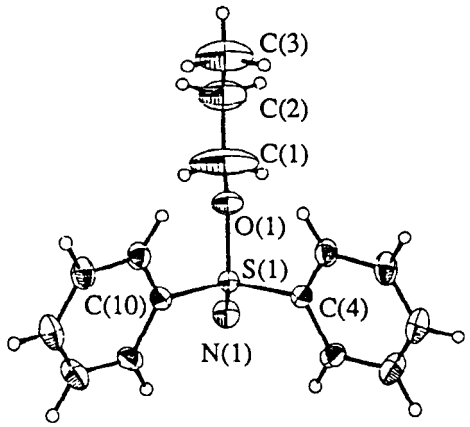
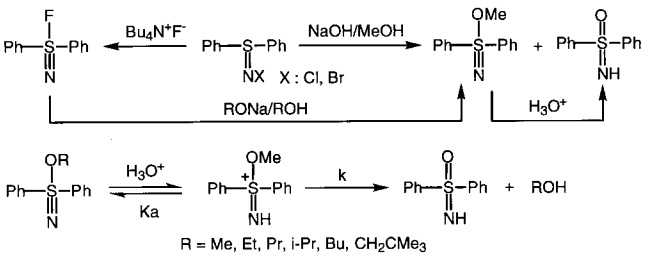
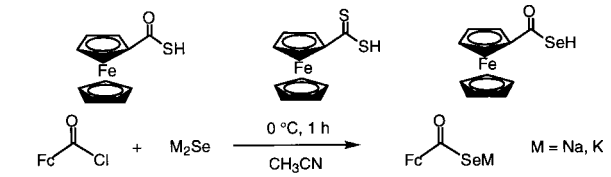


FIGURE 1 ORTEP drawing of $Ph_2S(OPr)N$.

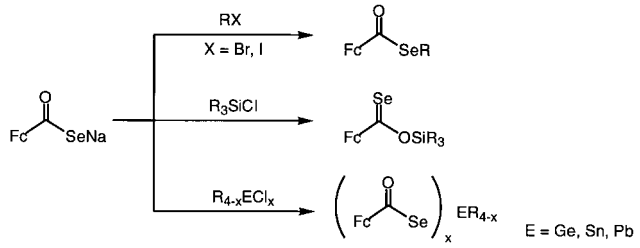


SCHEME 9

Professor Shinzi Kato's article was read by Dr. Toshinori Takahashi, and the chemistry is summarized in Schemes 10 and 11. ORTEP drawings of the key reagents are grown in Figure 2.

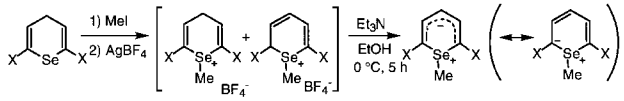


SCHEME 10



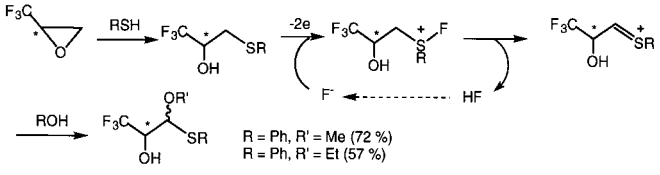
SCHEME 11

Professor Tadashi Kataoka and coworkers reported the synthesis and isolation of selenabenzenes stabilized by the presence of two electron-withdrawing groups, as shown in Scheme 12. Their thermal reactions were also described.



SCHEME 12

Professor Toshio Fuchigami of Tokyo Institute of Technology gave a lecture on "Electrochemical Molecular Conversion of Organofluorine Sulfur Compounds Using Fluoride Ions as a Mediator." In his view, there is much similarity to the Pummerer-type reaction, but one in which fluorine is bonded to the central sulfur atom. This is shown in Scheme 13.



SCHEME 13

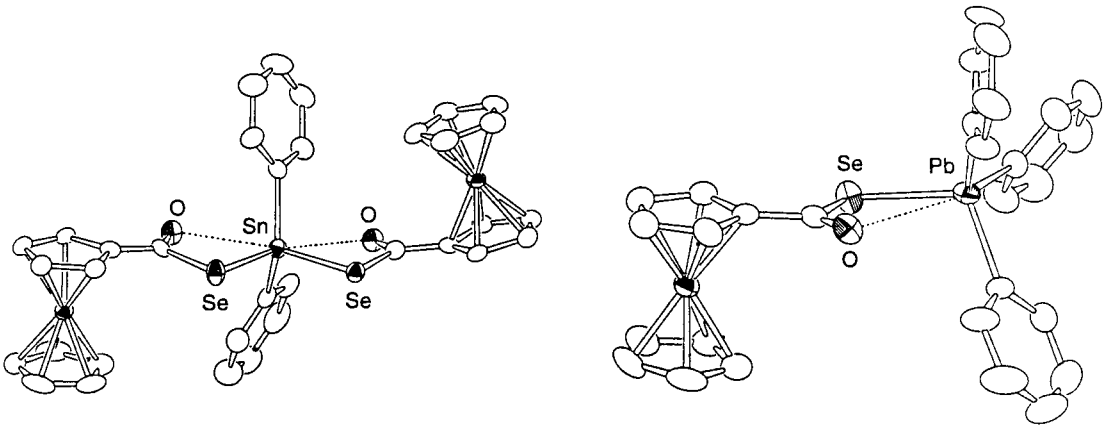
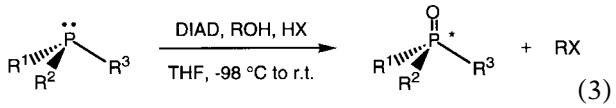


FIGURE 2 ORTEP drawing of key reagents.

Among 32 poster presentations, Prof. Tsuneo Imamoto's poster was of particular interest. He carried out a stereospecific Mitsunobu reaction on a chiral phosphine (Equation 3).



(3)

We look forward to the 25th Heteroatom Symposium to be held in Kyoto at about this time of year. We look forward to viewing the impressive temples, shrines, and gardens at this location as well as to the presentation of new research results.

ORAL PRESENTATIONS

1. "Synthesis and Reactions of Sulfur-substituted Allenes" by T. Shimizu, K. Sakamaki, and N. Kamigata (Tokyo Metropolitan University).
2. "Synthesis, Isolation, and Full Characterization of the Parent Thiophene 1,1-Dioxide" by H. Nagasawa, Y. Sugihara, A. Ishii, and J. Nakayama (Saitama University).
3. "First Isolation and Molecular Structure of the Bis(2,2′-biphenylylene)sulfuranyl Dication Species [8-S-4(C4)]$^{2+}$" by S. Sato, H. Ameta, H. Tsutsui, E. Horn, and N. Furukawa (University of Tsukuba).
4. "Synthesis, Structure and Redox Reactions of Chalcogenanthrenes Containing Bulky Substituents at Adjacent Positions" by S. Ogawa, M. Sugawara, Y. Kawai, T. Kimura, and R. Sato (Iwate University and Kyoto University).
5. "Aklylidene- and Imino-Bridged Cobalta Dithiolene Complexes" by C. Takayama, K. Takeuchi, T. Yagisawa, T. Sugiyama, M. Kajitani, and A. Sugimori (Sophia University).
6. "A Novel Route to Optically Active Heterohelicenes by Intramolecular Transfer of Axial Chirality into Helicity" by H. Osuga and K. Tanaka (Kyoto University).
7. "New Syntheses of Polycyclic Thiophenes and Cyclic Polythiophenes" by S. M. H. Kabir, Y. Kuwatani, M. Yoshida, and M. Iyoda (Tokyo Metropolitan University).
8. "A Convenient Preparation of 1,3-Dithiole-2-thiones and 1,3-Diselenole-2-selones Starting from Various Terminal Acetylenes, and Its Applications" by A. Morikami, K. Takimiya, Y. Aso, and T. Otsubo (Hiroshima University).
9. "A Serial One-Pot Synthesis of Homooxacalix[n]heteroarenes" by A. Taniguchi, N. Komatsu, and H. Suzuki (Kyoto University).
10. "Reactions of Bis(trimethylsilyl)thioketene with Miscellaneous N,N-disubstituted Amides" by T. Tsuchiya, M. Tanaka, and K. Honda (National Institute of Materials and Chemical Research).
11. "Synthesis and Characterization of Macrocyclic Compounds Using 10-S-3 Tetraazapentalene Derivatives" by N. Matsumura, T. Konishi, H. Hayashi, and K. Mizuno (Osaka Prefecture University).
12. "Synthesis of 2-Thiacumulenes from Thiiranes and the Study of Their Properties Including ZINDO MO Calculations" by T. Yamamoto, M. Ohba, and M. Muraoka (Josai University).
13. "Mechanism for the Hydrolysis of S,S-Di-

phenyl-S-alkoxythiazynes" by T. Yoshimura, T. Dong, M. Ohkubo, T. Fujii, S. Ono, H. Morita, C. Shimasaki and E. Horn (Toyama University and University of Tsukuba).

14. "Formation of Disulfide Bonds and Protein Folding" by M. Iwaoka and H. A. Scheraga (Cornell University).
15. "Palladium-Catalyzed Asymmetric Reactions of Olefinic Cyclopropane Systems with Organosulfur Functionality" by Y. Yoshida, Y. Kaneko, F. Kato, and K. Hiroi (Tohoku College of Pharmacy).
16. "Synthesis of α,β-Unsaturated Sulfones Using Methylthiomethyl *p*-Tolyl Sulfone (MT-sulfone)" by K. Ogura, T. Arai, A. Kayano, and M. Akazome (Chiba University).
17. "Asymmetric Polyene Cyclization via an Episulfonium Ion" by H. Kosugi, H. Tanaka, K. Hoshino, H. Uda, and M. Kato (Tohoku University).
18. "Stereoselective Radical Reactions of β-Hydroxyvinylsulfones or Sulfoxides by Use of Intramolecular Hydrogen Bonding" by N. Mase, Y. Watanabe, Y. Ueno, and T. Toru (Nagoya Institute of Technology).
19. "New C–C Bond Formation Reactions of Silylacetylenes Activated by $GaCl_3$" by Y. Kido, T. Tsukagoshi, T. Sugihara, and M. Yamaguchi (Tohoku University).
20. "Synthesis and Structure of Ferroceneselenocarboxylic Acid and Its Derivatives" by T. Takahashi, O. Niyomura, T. Kanda, T. Murai, and S. Kato (Gifu University).
21. "Synthesis and Thermal Reactions of Selenabenzenes Stabilized by Two Electron-Withdrawing Groups" by T. Kataoka, E. Honda, T. Iwama, T. Iwamura, and S. Watanabe (Gifu Pharmaceutical University).
22. "Time-Delayed, Two-Color Laser Photolysis of 1,2-Bis[(phenylsereno)methyl]benzene" by A. Ouchi and Y. Koga (National Institute of Materials and Chemical Research).
23. "Photoinduced Reduction of Group 16 Heteroatom Compounds with Samarium Diiodide" by A. Ogawa, S. Ohya, and T. Hirao (Osaka University).
24. "Imination of Fluorene Derivatives with Selenium and Isocyanides" by S. Fujiwara, H. Maeda, T. Shin-ike, N. Kambe, and N. Sonoda (Osaka Dental University, Osaka University, and Kansai University).
25. "Reactions of Vinylic Cuprates Having Phenylseleno Group Generated via Hydrozirconation with Electrophiles" by M. Suzuki, M. Segi, and T. Nakajima (Kanazawa University).
26. "Highly Selective Asymmetric Intramolecular Selenocyclisation" by H. Takada, Y. Nishibayashi, S. K. Srivastava, K. Ohe, and S. Uemura (Kyoto University).
27. "Generation of Organolithium Compounds by Te-Li Exchange" by M. Iwasaki, T. Inoue, H. Kumaoka, N. Kambe, and N. Sonoda (Osaka University and Kansai University).
28. "Asymmetric Synthesis of Optically Pure Telluronium Salts by the Reaction of Chiral Halooxatelluranes with Lithium or Grignard Reagents" by J. Zhang, S. Saito, K. Tanida, and T. Koizumi (Toyama Medical & Pharmaceutical University).
29. "Hexaaryltellurium($TeAr_6$): A Novel Neutral Hypervalent Organotellurium Compound" by M. Minoura, T. Sagami, M. Miyasato, and K. Akiba (Hiroshima University).
30. "Group 14 Element-Based Dendrimers" by M. Nanjo, A. Sekiguchi, C. Kabuto, and H. Sakurai (University of Tsukuba, Tohoku University, and Science University of Tokyo).
31. "Structure and Reactions of Double-Decker Cage Compounds with Group 14-Group 16 Elements" by M. Unno, D. Ishii, Y. Kawai, and H. Matsumoto (Gunma University).
32. "X-Ray Crystallographic Analysis of 3-Silacyclopropene with Electronegative Substituents on Silicon" by S. Tsutsui, K. Sakamoto, C. Kabuto, and M. Kira (Tohoku University).
33. "Synthesis and Reactions of a Stable 1-Germaallene" by K. Kishikawa, N. Tokitoh, and R. Okazaki (The University of Tokyo).
34. "Insertion of Germanium Divalent Species into Carbon–Halogen Bonds" by H. Ohgaki and W. Ando (University of Tsukuba).
35. "Dimerization and Intramolecular Reaction of Sterically Protected 1-Halo-2-phosphaethenyllithium" by S. Ito, K. Toyota, and M. Yoshifuji (Tohoku University).
36. "Reaction of Iron Phosphite Complexes Containing an Alkyl Group with a Lewis Acid-Formation of a Phosphenium Complex-" by H. Nakazawa, Y. Yamaguchi, and K. Miyoshi (Hiroshima University).
37. "Energetics of Single-Electron Transfer from Trivalent Phosphorus Compounds to

Electron Acceptors" by S. Yasui, M. Tsujimoto, and A. Ohno (Tezukayama College and Kyoto University).

38. "New Approach to the Stereoselective Horner-Wadsworth-Emmons Reaction" by S. Sano, K. Yokoyama, T. Ando, and Y. Nagao (The University of Tokushima).
39. "Synthesis of Novel Glycoside and Nucleoside Derivatives of Phospha Sugar Analogs with Substituents" by M. Yamashita, Y. Kato, T. Oshikawa, S. Koketsu, and J. Onogawa (Shizuoka University).
40. "Synthesis of Macrolides by Using Enantiomerically Pure (R)-(-)-5-Methyl-2,2,2-triphenyl-1,2λ^5-oxaphospholane" by S. Hirabayashi, K. Shioji, and K. Okuma (Fukuoka University).
41. "Synthesis and Synthetic Application of α-Functionalized Vinylphosphonates" by R. Kouno, T. Tsubota, T. Okauchi, J. Ichikawa, and T. Minami (Kyushu Institute of Technology).
42. "Allylation of Aldehydes by Allyl Group Transfer of Homoallylic Alcohols" by J. Nokami, S. Sumida, H. Matsuura, H. Tonaka, and S. Torii (Okayama University of Science and Okayama University).
43. "Synthesis and Cycloaddition of Mesomeric Betaines; Bicyclotriaziniumolates and Thiolates" by M. Komatsu, M. Funabashi, N. Sakai, S. Minakata, I. Ryu, and Y. Ohshiro (Osaka University and Kinki University).
44. "Comments on a Boiling Point of Fluorinated Compounds" by T. Katagiri and K. Uneyama (Okayama University).
45. "Electrochemical Molecular Conversion of Organofluorine Sulfur Compounds Using Fluoride Ions as a Mediator" by T. Fuchigami (Tokyo Institute of Technology).
46. "Ligand-Coupling Mechanism in Nucleophilic Substitution of Vinyliodonium Salts" by T. Okuyama and M. Ochiai (Osaka University and University of Tokushima).
47. "Synthesis and Reactions of Hypervalent Iodine Aryne Precursors" by T. Kitamura, M. Todaka, N. Fukatsu, and Y. Fujiwara (Kyushu University).

POSTER PRESENTATIONS

1. "Syntheses of 1,2-Oxaboretanides and Effects of the Substituents at 3,4-Positions on Their Reactivity and Structures" by T. Kannabe, T. Kawashima, and R. Okazaki (The University of Tokyo).
2. "Synthesis and Reactions of a Thionitroso Compound by Taking Advantage of a Substituent of a Reaction Bowl Type" by B. Tan, K. Goto, and R. Okazaki (The University of Tokyo).
3. "Remote Pummerer Reaction of the Monoxides of Bis(methylthio)-Aromatics" by K. Kobayashi, K. Namatame, T. Kitaura, E. Koyama, and N. Furukawa (University of Tsukuba).
4. "Synthesis of a Pseudocryptand from Allosteric Control of Ion Recognition" by T. Nabeshima, Y. Yoshihira, and D. Nishida (University of Tsukuba).
5. "Chiral Bis(oxazoline)-Copper(I)-Catalyzed Asymmetric Sulfimidation of 1,3-Dithianes" by Y. Miyake, H. Takada, K. Ohe, and S. Uemura (Kyoto University).
6. "Synthesis of Heterocyclic Compounds by Use of Cyclopropenethione Derivatives" by N. Matsumura, M. Itoh, Y. Yagyu, and K. Mizuno (Osaka Prefecture University).
7. "Generation and Trapping of Cyclobutenethiones via Thermal Reaction of Alkynyl Propargyl Sulfides" by S. Aoyagi, K. Sugimura, N. Kanno, K. Shimada, and Y. Takikawa (Iwate University).
8. "Formation and Reactions of Cobaltadithiazole Rings" by T. Noguchi, T. Sugiyama, M. Kajitani, and A. Sugimori (Sophia University).
9. "Synthesis and Properties of Ethylenedithio Modified Acenaphthylene as a π-Electron Donor" by K. Miyauchi, H. Tani, N. Azuma, and N. Ono (Ehime University).
10. "Development of a New Synthetic Method of Unsymmetrical Ketones from Selenoamides" by T. Murai, T. Ezaka, and S. Kato (Gifu University).
11. "Se—X (X = N, O, F) Non-bonded Intramolecular Interaction" by H. Komatsu, M. Iwaoka, and S. Tomoda (The University of Tokyo).
12. "Syntheses and Reactivity of Hexacoordinate Pertelluranes [12-Te-6(C4X2)](X = Cl, F)" by S. Sato, T. Yamashita, E. Horn, and N. Furukawa (University of Tsukuba).
13. "Synthesis and Structure of New Dicationic Pertellurane Species [12-Te-6(C2O2S2)]$^{2+}$"

by S. Sato, Y. Nakajima, and N. Furukawa (University of Tsukuba).

14. "Strategic Approach to C-Nucleosides via Sugar Anomeric Radical, Cation, and Anion with Sugar Tellurides" by W. He, H. Togo, Y. Waki, and M. Yokoyama (Chiba University).
15. "Structure and Characterization of Highly Coordinate Telluronium Salts Having Intramolecular N-Te Coordination" by K. Sarushashi, M. Minoura, and K. Akiba (Hiroshima University).
16. "1,3-Dipolar Cycloaddition Behavior of Pyrazole-4-one N,N-Dioxides" by Y. Yoshitake, M. Eto, and K. Harano (Kumamoto University).
17. "Stereochemistry at the Chiral Phosphorus Atom in the Mitsunobu Reaction" by T. Imamoto, T. Watanabe, and H. Tsuruta Chiba University).
18. "Synthesis of Chiral Trivalent Pnictogen Compounds from the Corresponding Ethynyl Derivatives" by J. Kurita, T. Ikeda, N. Kakusawa, and T. Tsuchiya (Hokuriku University).
19. "Positional Isomerization of Hypervalent Antimony Compounds Bearing a Transition Metal Ligand" by K. Toyota, Y. Wakisaka, Y. Yamamoto, and K. Akiba (Hiroshima University).
20. "Synthesis and Properties of TTF-Organosilicon Compounds" by H. Fukui and M. Takahashi (Ibaraki University).
21. "Synthesis, Structure, and Isomerization of *E* and *Z* Isomers of Tetrasilyldisilene" by S. Ohya, T. Iwamoto, M. Ichinohe, C. Kabuto, and M. Kira (Tohoku University).
22. "Physical Properties and Reactivity of Alkyl-Substituted Digermenes Photo-Generated from 7,8-Digermabicyclo[2.2.2]octa-2,5-dienes" by T. Kayamori, K. Mochida, M. Fujituka, A. Watanabe, and O. Ito (Gakushuin University and Tohoku University).
23. "The Diels–Alder Reaction of a Trimethylsilylethynyliodonium Salt and Reactions of the Cycloadducts" by M. Kotani, T. Yokoyama, T. Kitamura, and Y. Fujiwara (Kyushu University).
24. "Preparation and the Reactions of Hypervalent Iodine(V) Reagents with Aromatics" by K. Nagata, T. Kitamura, and Y. Fujiwara (Kyushu University).
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