Heteroatom Chemistry
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A Report on the 30th Symposium on Heteroatom Chemistry of the Chemical Society of Japan

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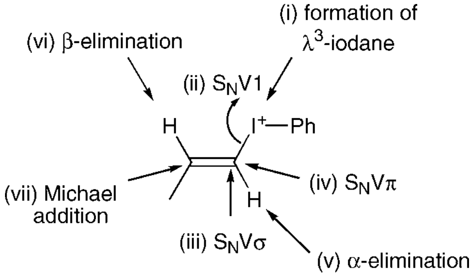
ABSTRACT: *The 30th domestic Chemical Society of Japan Symposium on Heteroatom Chemistry was held at Kuroda Auditorium of Toyama University during the period of December 11–13, 2003, under the management of Prof. Toshiaki Yoshimura and Dr. Takayoshi Fujii. More than 250 chemists from various academic institutes and industries enjoyed 4 plenary lectures, 48 oral presentations, and 62 poster presentations.* © 2004 Wiley Periodicals, Inc. Heteroatom Chem 15:347–361, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20020

PLENARY LECTURES

The first plenary lecture was given by Tadashi Okuyama (Himeji Institute of Technology) on “Diversity in Nucleophilic Substitution and Elimination Reactions of Vinyl Iodonium Salts.” He first surveyed that vinyl iodonium salts **1** undergo a wide variety of types of reactions with nucleophiles/bases due to the highly electron-withdrawing character and high nucleofugacity of the iodonio group, as follows [(i)–(vi), see O06 for (vii)].



1

A nucleophile tends to attach to the iodine atom in **1** to form λ^3-iodane [(i)] in a rapid equilibrium, and the λ^3-iodane can participate in those reactions though less reactive than the free iodonium ion. Unimolecular formation of a vinylic cation occurs only in poorly nucleophilic (and basic) solutions [(ii)] and leads to a secondary system by β-participation to avoid a primary vinyl cation. Solvolysis of cyclohexenyl iodonium salt **2** in a protic solvent took place through an S_N1 type reaction (Scheme 1). A chirality-probe approach using optically active 4-methylcyclohexylidenemethyl iodonium salt **3** showed that the achiral primary vinyl cation can not be an intermediate in solution reactions. The rearranged ring-expanded products, 2-substituted cycloheptenes, always maintained the original chirality of the substrate in solvolysis (Scheme 2).

Poorly basic halides, Cl^-, Br^-, and I^-, induce two modes of bimolecular vinylic nucleophilic substitutions, $S_NV\sigma$ [(iii)] and $S_NV\pi$ [(iv)], with inversion via

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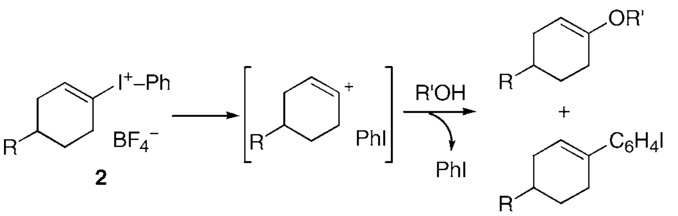


SCHEME 1

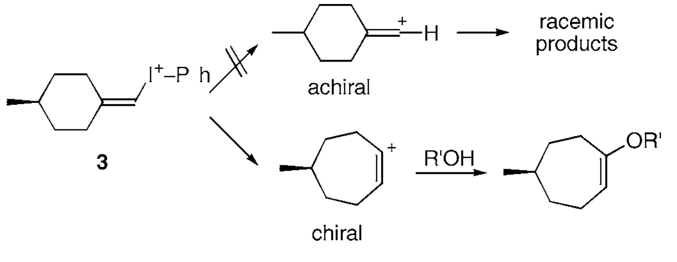
σ* attack and with retention of configuration via π* attack, respectively. The former is a usual reaction with simple 1-alkenyliodonium salts **4**, while the latter occurs with 2-halo-1-alkenyliodonium salts **5** in a ligand coupling manner within a λ^3-haloiodane intermediate (Scheme 3).

The most facile reaction is in general α-elimination (when the α-proton is present) [(v)], and occurs even with a very poor base like dichloroacetate (pK_a 1.35) in methanol. The resulting alkylidenecarbene undergoes 1,2-shift of the hydrogen and phenyl group (**4**: R = Ph) to give alkyne. Even azide and cyanide ions act as a base to the α-proton to lead exclusively to α-elimination. In the case of cyclohexenyliodonium salt **2** lacking the α-proton, β-elimination [(vi)] took place to generate cycloheptyne successfully, which could be trapped with tetraphenylcyclopentadienone or some nucleophiles (Scheme 4).

The second lecture was presented by Koichi Narasaka (The University of Tokyo) on the subject of "Displacement Reactions at Oxime Nitrogen." He discussed two types of C—N bond-forming reactions by displacement of the hydroxy group at the oxime sp^2 nitrogen, that is, unusual S_N2-type substitution and radical cyclization of oxime derivatives induced by one-electron reduction.

Electrophilic amination of aryl and alkyl Grignard reagents by a 2-imidazolidinone *O*-sulfonyloxime proceeded under mild conditions to provide primary or secondary amines after hydrolysis or reduction, respectively (Scheme 5).

Various azaheterocycles are prepared from reactions of olefinic *O*-(pentafluorobenzoyl)oximes by amino-Heck reactions. The olefinic oximes are converted to pyrroles, dihydropyrroles, pyridines, isoquinolines (Scheme 6), azaspiro compounds, and azaazulenes by treatment with a Pd(0) catalyst and Et_3N.



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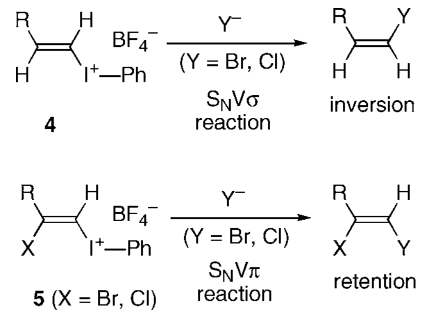
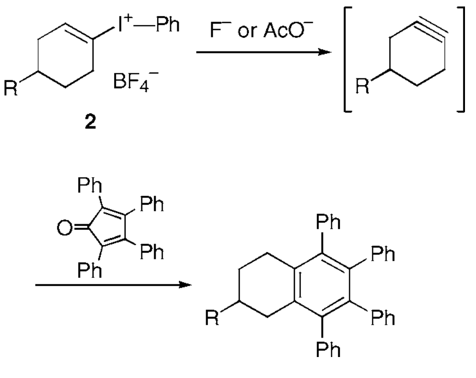


SCHEME 3

While *syn*- and *anti*-isomers of oximes readily isomerize to each other, such isomerization of *O*-alkyl and *O*-acyl derivatives hardly proceeds. He found effective conditions for the isomerization of the *O*-substituted oximes, and examined S_N2-type cyclizations of phenethyl ketone oximes. The treatment of methyl phenethyl ketone oximes with $(CF_3CO)_2O$ and 4-chloranil affords quinolines in good yields (Scheme 7).

He also discussed a catalytic radical cyclization of oxime derivatives. γ,δ-Unsaturated *O*-acetyloximes cyclized by treatment with catalytic amounts of naphthalenediol (or 1,4-dihydroquinone) and 1,4-cyclohexadiene to give pyrroles (Scheme 8).

The third plenary lecture entitled "Recent Advance in Multiple Bonding between Heavy Elements," was delivered by Shigeru Nagase (Institute for Molecular Science). Synthesis and properties of the compounds that have a multiple bond between heavy-main-group elements are a recent topic in the



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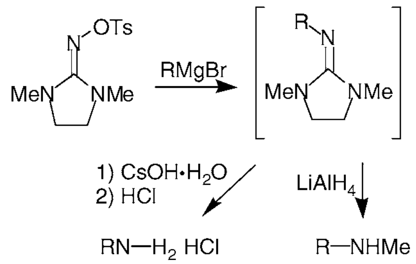

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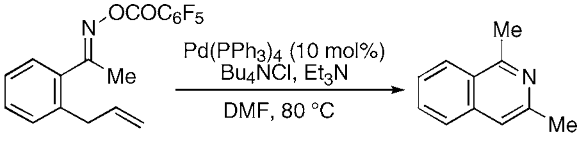

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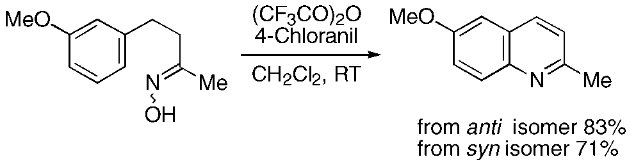

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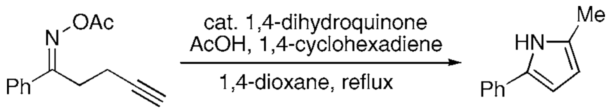


SCHEME 8

area of heteroatom chemistry. He has investigated the nature of the multiple bonding theoretically.

First of all, he explained the properties of heavy elements in terms of the orbital theory for valence electrons. Figure 1 shows the size of valence s and p orbitals in the group-14 elements. An important point is that, when the principal quantum number n is larger than 2, there is a significant size difference in the ns and np orbitals. Thus, it is explained that while the carbon atom, which has almost the same size of valence 2s and 2p orbitals, forms a planar double bond and a linear triple bond in terms of the classical sp^2 and sp hybridizations, respectively, the heavier elements, which have large difference in $r_{\max}$ between the ns and np orbitals, tend to form multiple bonds by using low-valent basic structures, EH and EH_2, rather than by making hybridization. As the result, the trans-bent structures become more stable for both $H_2E{=}EH_2$ and $HE{\equiv}EH$ in the order of Si < Ge < Sn < Pb, and the E=E and E≡E bonds longer than the E—E single bond.

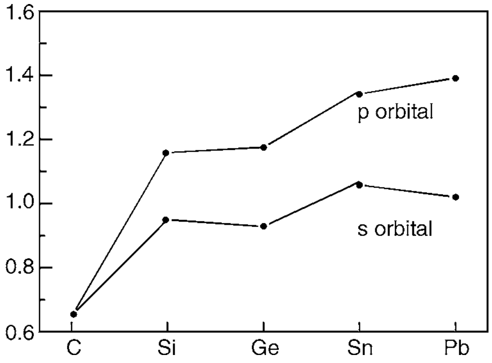


FIGURE 1

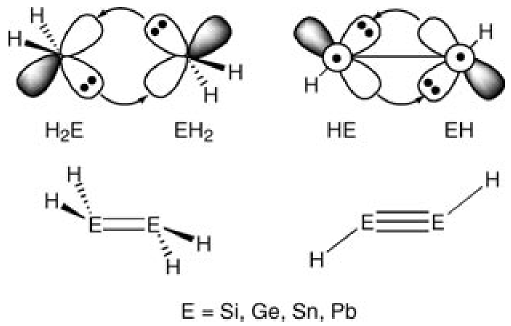


Figure 2 shows the potential energy surface of E_2H_2. Theoretical calculations suggested that the bent HE≡EH isomerizes readily to the bridged and the 1,2-hydrogen-shifted structures. In addition, HE≡EH dimerizes readily to afford compounds having cyclobutadiene and tetrahedrane structures. The results of the theoretical study on steric and electronic effects of substituents predict that fully bulky substituents protect the concerned triple bond from

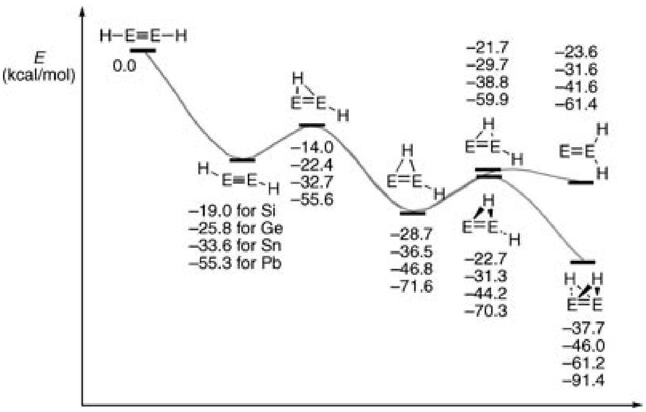
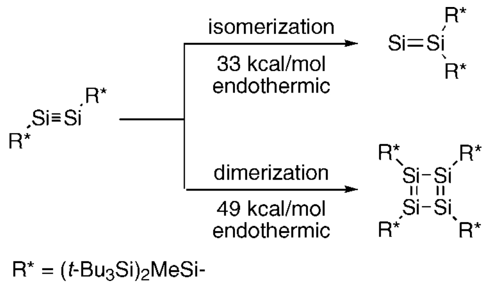


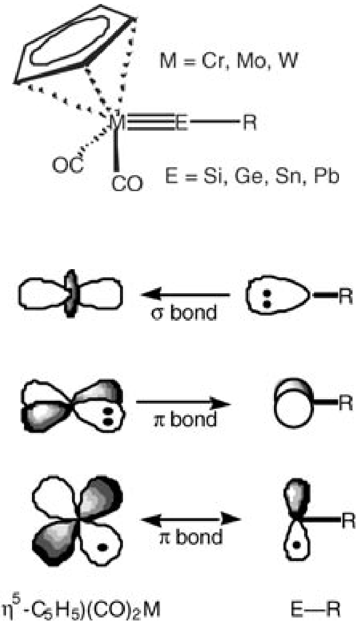
FIGURE 2



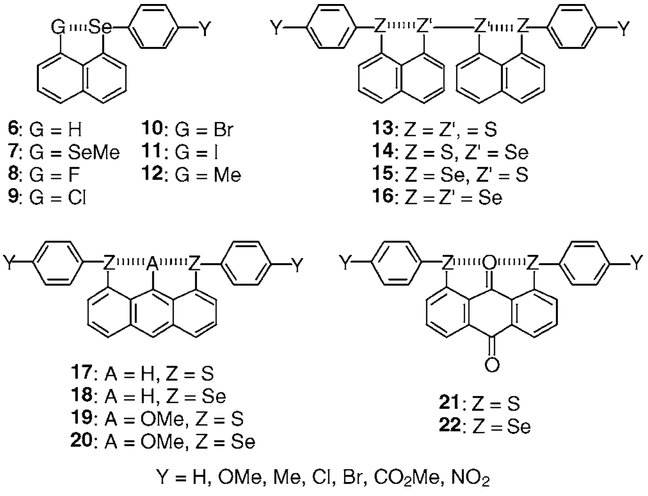
SCHEME 9

isomerization and dimerization. Because electron-donating substituents decrease the difference in the size of *n*s and *n*p orbitals of the element attached, bulky and electron-donating silyl groups like $(t\text{-}\mathrm{Bu_3Si})_2\mathrm{MeSi}$- stabilize the triple bonds both sterically and electronically. Calculations showed that $\mathrm{R^*{-}Si{\equiv}Si{-}R^*}$ [$\mathrm{R^*} = (t\text{-}\mathrm{Bu_3Si})_2\mathrm{MeSi}$-] has a trans-bent structure with an obtuse $\mathrm{R^*{-}Si{\equiv}Si}$ bond angle with almost same Si≡Si bond length (2.07 Å) as the ideal one (2.03 Å), and its isomerization and dimerization are largely endothermic (Scheme 9).

The last topic of his lecture was triple bonds between transition-metal elements and heavier group-14 elements. Transition-metal elements that can utilize d orbitals to form one σ bond and two π bonds form the linear triple bond ($\mathrm{L_XM{\equiv}E{-}R}$) with heavier group-14 elements. The M≡E bond energies increase in the order of Cr < Mo < W and in the order of Pb < Sn < Ge < Si. Thus the triple bond between W and Si atoms must be the strongest in the series.



The last plenary lecture was given by Waro Nakanishi (Wakayama University). The title of his presentation was "Full Elucidation of Nonbonded Interactions between Heteroatoms and Its Application to Construct the Extended Hypervalent System." In order to elucidate nonbonded interactions between heteroatoms, suitable heteroatom substituents were introduced at the 1- and 8-positions of naphthalene (**6–16**), 1-, 8-, and 9-positions of anthracene (**17–20**), 1- and 8-positions of anthraquinone (**21** and **22**), and 5- and 10-positions of selenanthrene (**23–25**). He investigated the compounds **6–25** by X-ray single crystal analyses and theoretical calculations.



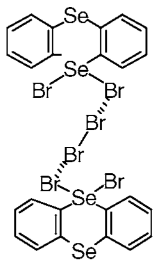
6: G = H
7: G = SeMe
8: G = F
9: G = Cl
10: G = Br
11: G = I
12: G = Me

13: Z = Z', = S
14: Z = S, Z' = Se
15: Z = Se, Z' = S
16: Z = Z' = Se

17: A = H, Z = S
18: A = H, Z = Se
19: A = OMe, Z = S
20: A = OMe, Z = Se

21: Z = S
22: Z = Se

Y = H, OMe, Me, Cl, Br, $\mathrm{CO_2Me}$, $\mathrm{NO_2}$



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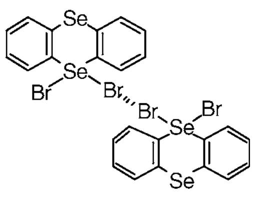

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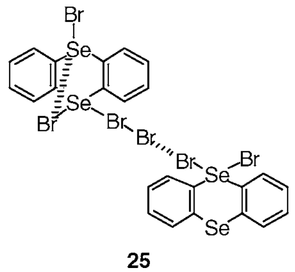

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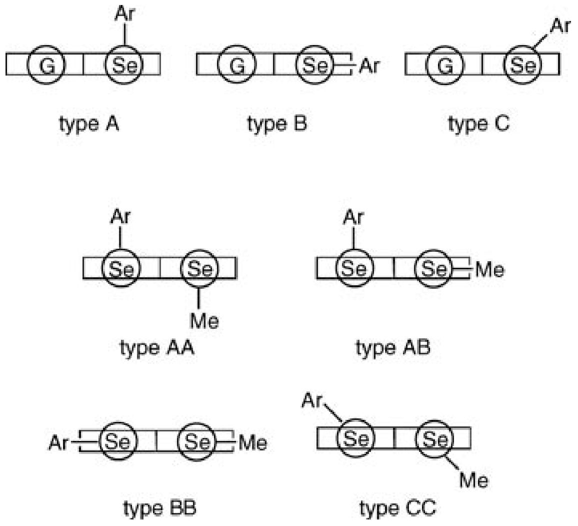
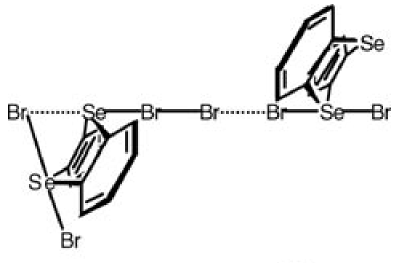
He showed that the structure of the naphthalenes **6–12** varies from types A to C in the solid state depending upon the substituents G and Y. Compound **7** is possible to take one of the four conformations; types AA, AB, BB, and CC. For the type AA the conformation is controlled by nonbonded interactions such as σ(Se$\cdots$Se), for the type AB by charge transfer (CT) from n(Se) to σ^*(Se—C), for the type BB by p-π conjugation, and for the type CC by π^*(Se$\cdots$Se). While the stable conformers of **6** (Y = Cl) and **6** (Y = OMe) are of type A and type B, respectively, those of **9** (Y = Cl) and **10** (Y = Cl) are of type B. Compound **7** (Y = Cl) takes the type AB conformation. The alignment of G$\cdots$Se—C atoms in the type B [**9** (Y = Cl) and **10** (Y = Cl)] and the type AB [**7** (Y = Cl)] conformations are brought about by energy-lowering effect of the hypervalent three-center four-electron (3*c*-4*e*) type interactions, where the CT occurs from n_p(Cl, Br, or Se) to σ^*(Se—C).



The factor that results in the extended hypervalent 4*c*-6*e* interaction of Z$\cdots$Z′—Z′$\cdots$Z (Z, Z′ = S, Se) in **13–16** and Br$\cdots$Br—Br$\cdots$Br in **23** is due to the CT from their outside n_p(Z or Br) to the central σ^*(Z′—Z′ or Br-Br). In the C—Z$\cdots$A$\cdots$Z—C part of **19–22** (A = O, Z = S, Se), CT occurs from their central n_p(O) to the outside two σ^*(Z—C) to form a 5*c*-6*e* system. The linear alignment was not observed between the corresponding five atoms of **17** and **18** (A = H, Z = S, Se). In cases of the 6*c*-8*e* system of Br—Se—Br$\cdots$Br—Se—Br in **24** and the 7*c*-10*e* system of Br—Se—Br$\cdots$Br—Br—Se$\cdots$Br in **25**, HOMO and LUMO of the 3*c*-4*e* system of Br—Se—Br in the selenurane part act as an electron donor and an acceptor, respectively.

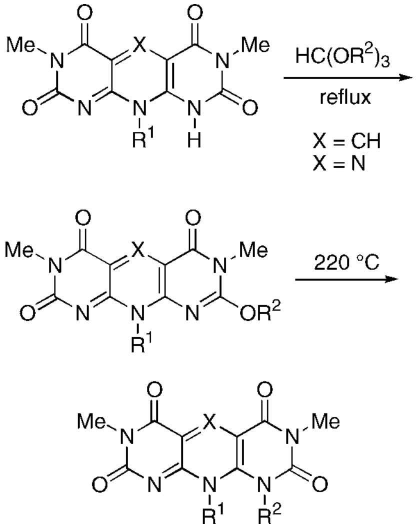


7*c*-10*e* system in **25**

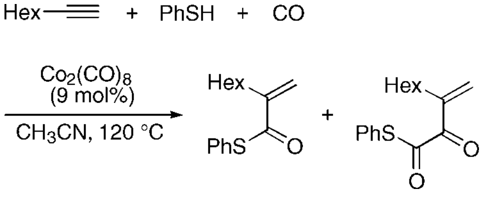
In addition to these plenary lectures, 48 oral and 62 poster presentations were given. Here are given graphical abstracts of oral presentations.

ORAL PRESENTATIONS

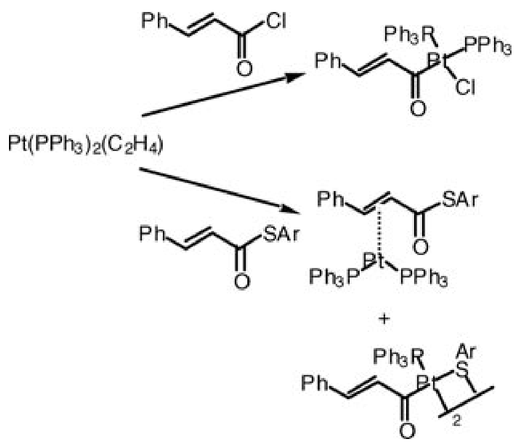
O01. "Synthesis of Pyridodipyrimidines and Pyrimidopteridines as Organic Catalysts for Redox Reaction and Their Intermolecular Transalkylation" by T. Nagamatsu (Okayama University).



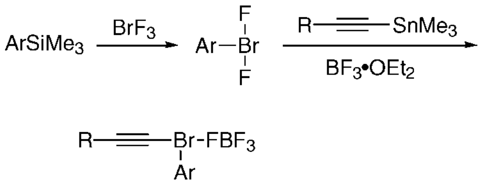
O02. "The Development of Novel Catalytic Carbonylation Systems with Highly Selective Introduction of Heteroatom Functions" by M. Tanaka, I. Kamiya, and A. Ogawa (Nara Women's University).



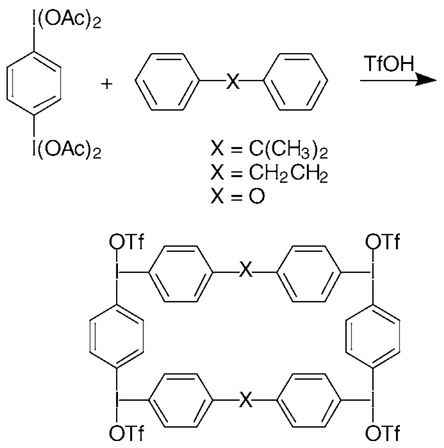
O03. “Mechanistic Study on the Oxidative Addition of Acid Halides and Its Derivatives to Pt(0)” by T. Kato, H. Kuniyasu, and N. Kambe (Osaka University).



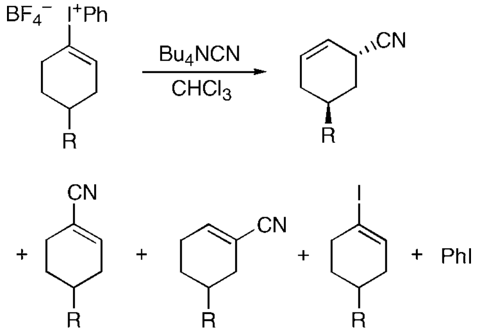
O04. “Synthesis and Reactions of 1-Alkynyl(aryl)-λ^3-bromanes” by Y. Nishi and M. Ochiai (Tokushima University).



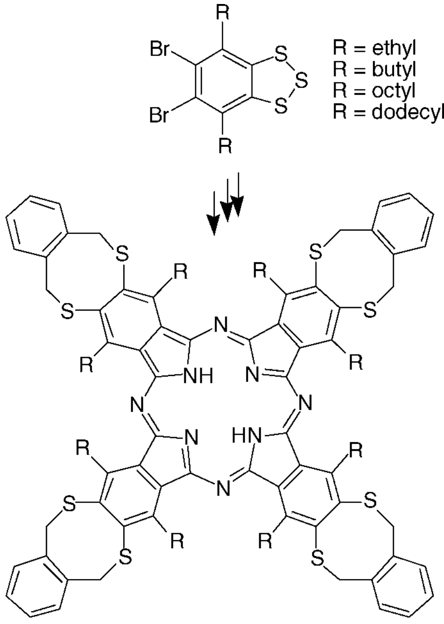
O05. “Synthesis of Hypervalent Iodine Macrocycles” by T. Kitamura, D. Inoue, and H. Morita (Saga University; Kusyu University).



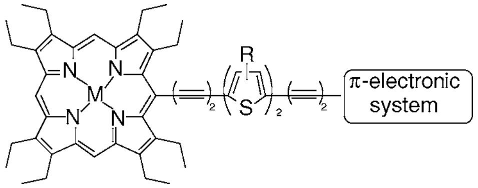
O06. “Michael Addition–Elimination Reactions of Cycloalkenyl Iodonium Salts: Comparison with Elimination–Addition Reaction” by M. Fujita, K. Fujiwara, W. H. Kim, and T. Okuyama (Himeji Institute of Technology).



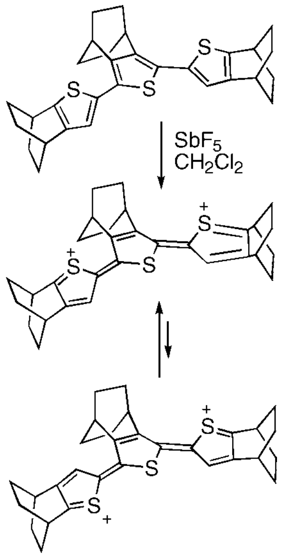
O07. “Preparation and Electrochemical Properties of *o*-Xylylenedithiophthalocyanine Derivatives from 4,7-Dialkyl-5,6-dibromobenzotrithioles” by T. Kimura, T. Suzuki, I. Tanaka, and K. Matsui (Iwate University).



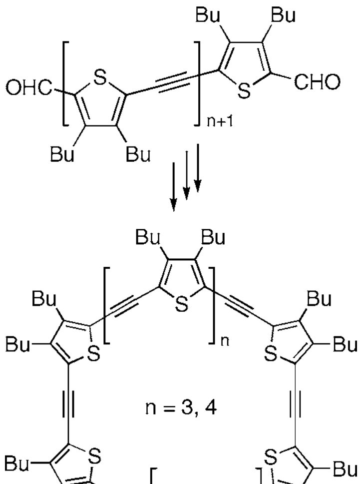
O08. “Synthesis and Properties of the Extended Porphyrin Derivatives Combined with Various π-Electronic Systems” by Y. Yamakawa, A. Matsuda, E. Chikamatsu, N. Hayashi, and H. Higuchi (Toyama University).



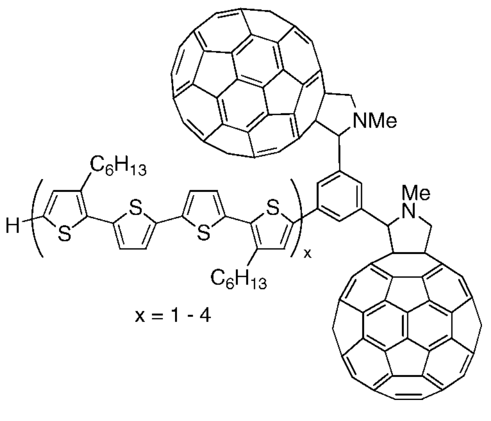
O09. "Properties of Oligothiophene Dications Annelated with Rigid σ-Frameworks" by T. Nishinaga, D. Yamazaki, A. Wakamiya, and K. Komatsu (Kyoto University).



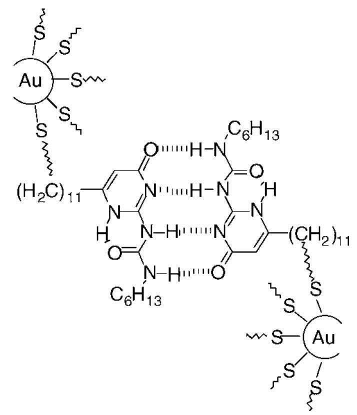
O10. "Synthesis and Properties of Macrocyclic Compounds Based on Oligo(thiophene-ethynylene)" by K. Nakao, K. Okimura, Y. Miyake, Y. Kuwatani, and M. Iyoda (Tokyo Metropolitan University).



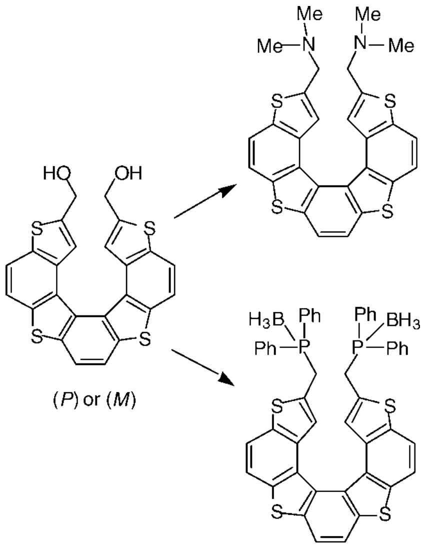
O11. "Preparation and Photochemical Properties of Oligothiophene/Fullerene-Dimer Linkage Molecules as High Performance Photovoltaic Materials" by N. Negishi, K. Takimiya, T. Otsubo, Y. Harima, and Y. Aso (Hiroshima University; Osaka University; CREST).



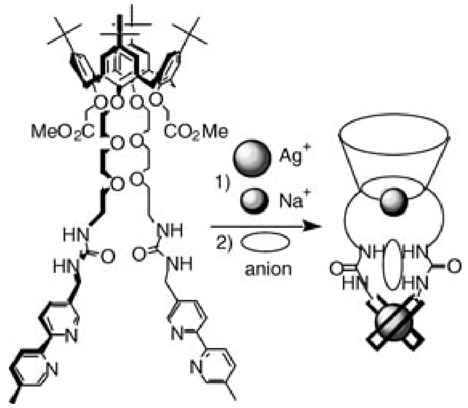
O12. "Multiple Hydrogen Bonding Mediated Self-Assembly of Chalcogenide-Protected Metal Nanoclusters" by Y. Kido, T. Dei, and H. Fujihara (Kinki University).



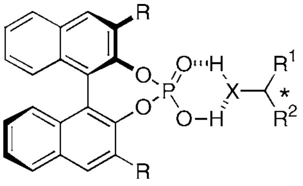
O13. "Synthesis and Properties of Optically Active [7] Heterohelicenes Bearing Functional Groups" by M. Nakazawa, H. Osuga, and K. Tanaka (Wakayama University).



O14. "Synthesis of Novel Calix[4]arene Bearing Two Urea Moieties and Multi-Step Regulation of the Guest Recognition Ability" by T. Saiki, J. Iwabuchi, and T. Nabeshima (University of Tsukuba).

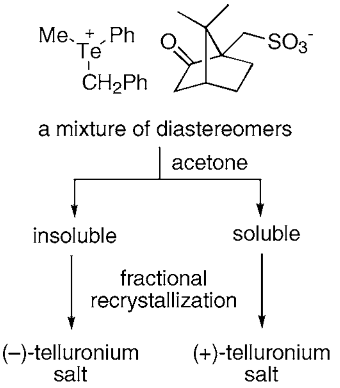


O15. "Synthesis and Dynamic Chiral Recognition Ability of Novel Hydrogen Cyclic Diphosphates with Axially Chiral Cleft Structure" by R. Nishida, H. Ito, H. Furuno, J. Inanaga (Kusyu University).

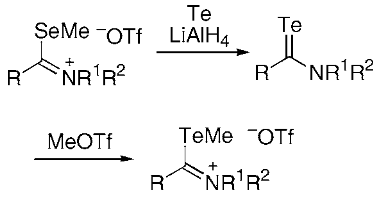


R = *m*-terphenyl, 9-anthryl, 9-anthrylethynyl

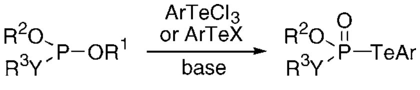
O16. "Synthesis, Structure, and Properties of Optically Active Benzylmethylphenyl Telluronium Salts" by R. Sakurai, Y. Azami, T. Shimizu, K. Hirabayashi, and N. Kamigata (Tokyo Metropolitan University).



O17. "Telluroiminium Salts: Synthesis, Structure, and Reactivities" by Y. Mutoh and T. Murai (Gifu University).

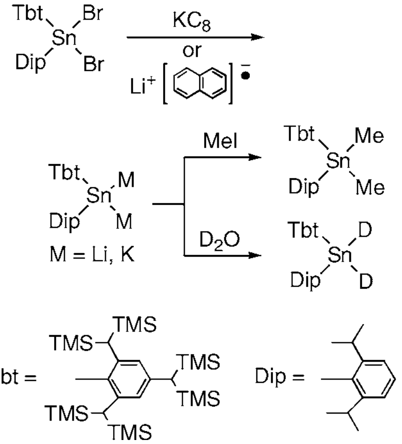


O18. "Synthesis of Te-Aryl Phosphorotelluroates from Phosphites and Organotellurium Compounds" by M. Hayashi, K. Matsuchika, T. Miura, M. Nishizawa, T. Inoue, and Y. Watanabe (Ehime University).

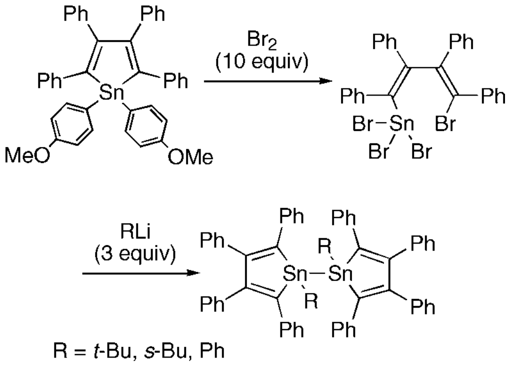


Y = O, C, N

O19. "Properties of Novel Tin Dianions Bearing Bulky Substituents and Their Application to the Syntheses of New Type of Tin Compounds" by T. Tajima, T. Sasamori, N. Takeda, and N. Tokitoh (Kyoto University).

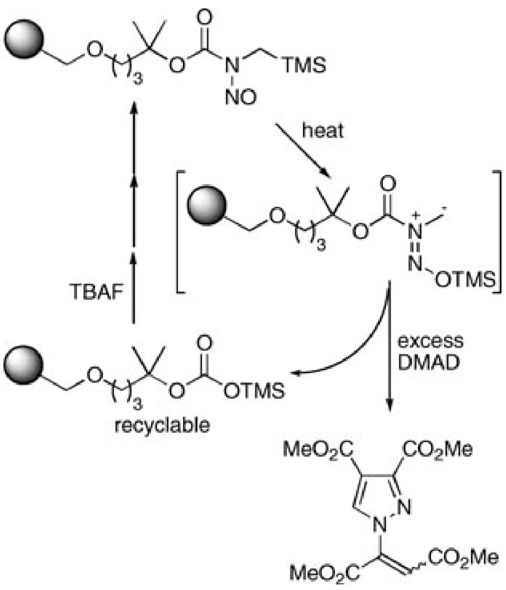


O20. "Synthesis, Structure, and Properties of Some Bi(1,1-stannole)s" by R. Haga, M. Saito, and M. Yoshioka (Saitama University).

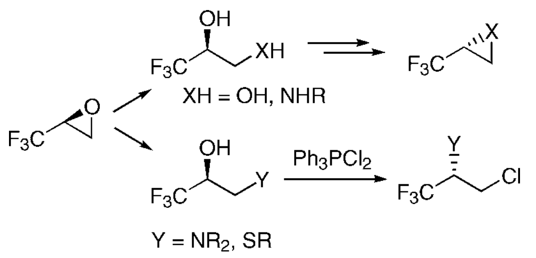


R = *t*-Bu, *s*-Bu, Ph

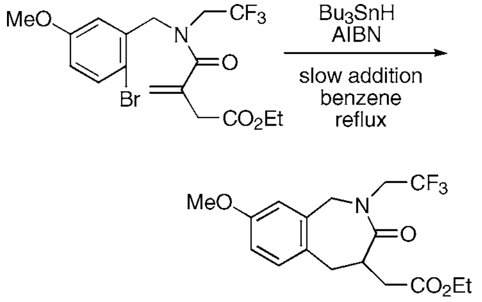
O21. “Efficient Generation and Cycloaddition of Polymer-Supported Azomethine Imines via 1,4-Silatropy” by M. Komatsu, E. Go, Y. Oderaotoshi, and S. Minakata (Osaka University).



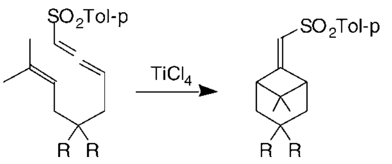
O22. “Preparations of Hetero-Three Membered Rings with 2-Trifluoromethyl Group” by T. Katagiri, S. Takahashi, S. Mishima, T. Kawate, Y. Yamauchi, H. Itahashi, and K. Uneyama (Okayama University).



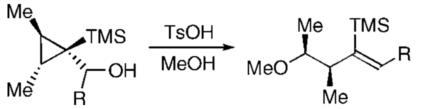
O23. “Construction of 2-Benzazepines with Radical Cyclization Strategy: The Use of Heteroatoms as a Temporary Element to Control the Regioselectivity” by A. Kamimura and Y. Taguchi (Yamaguchi University).



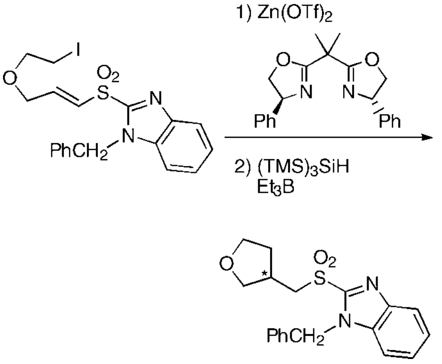
O24. “Metal-Catalyzed Cycloadditions in Allene-Ene Systems” by S. Watanabe and K. Hiroi (Tohoku Pharmaceutical University).



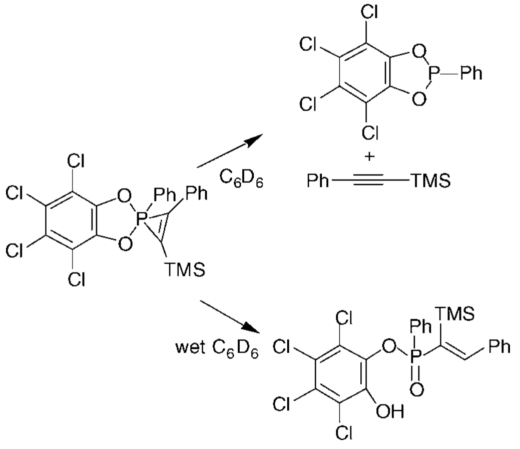
O25. “Acid-Catalyzed Reaction Behavior of 1-Silyl or 1-Phenylselenocyclopropylcarbinols” by M. Honda, T. Nishizawa, and M. Segi (Kanazawa University).



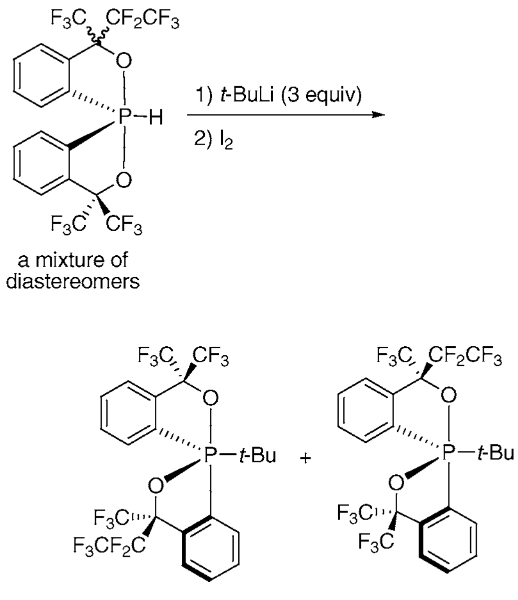
O26. “Enantioselective Radical Reactions of Vinyl Sulfones: Selective Coordination of Chiral Lewis Acid to an Enantiotopic Sulfonyl Oxygen” by H. Sugimoto, S. Nakamura, and T. Toru (Nagoya Institute of Technology).



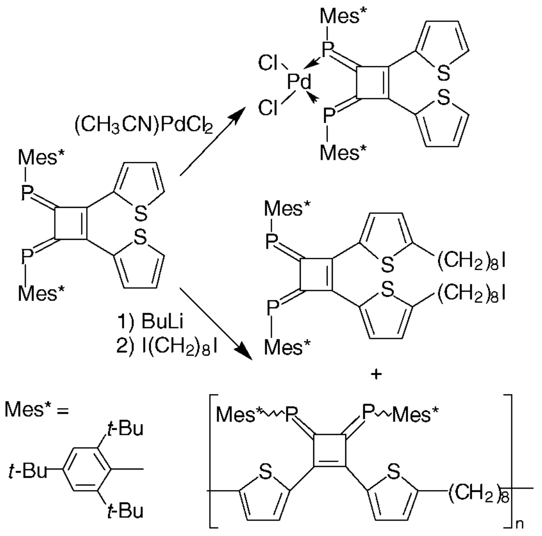
O27. “Syntheses and Properties of Three-membered Ring Compounds Involving Pentacoordinate Phosphorous-Carbon Bonds in the Ring” by S. Sase, N. Kano, and T. Kawashima (The University of Tokyo).



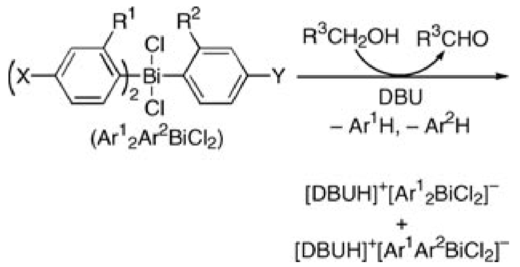
O28. “Synthesis and Isomerization of Diastereomeric Hypervalent Phosphoranes Bearing a Modified Martin Ligand” by Y. Yamamoto, K. Kakuda, K. Sena, M. Tada, and K.-y. Akiba (Hiroshima University; Waseda University).



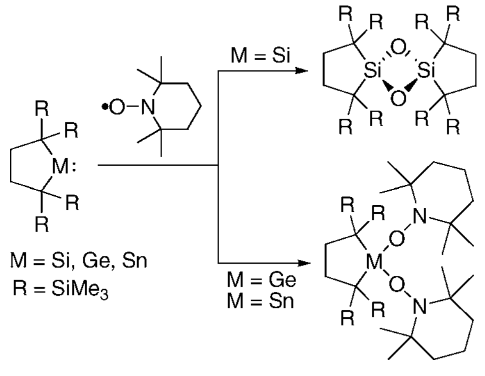
O29. “Preparations and Properties of Some New Sterically Protected 3,4-Diphosphinidenecyclobutenes Bearing Thienyl Groups at the 1,2-Positions” by K. Toyota, A. Nakamura, K. Horikawa, K. Abe, and M. Yoshifuji (Tohoku University).



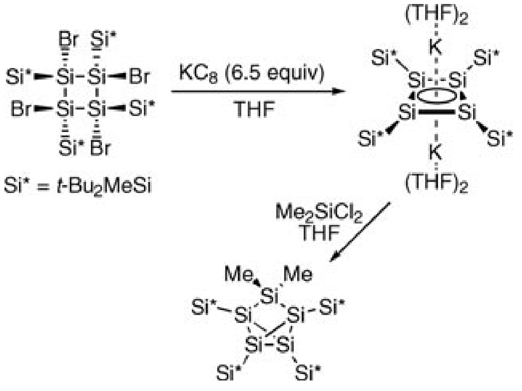
O30. “Substituent Effects on the Alcohol Oxidation with Triarylbismuth Dichlorides and DBU” by Y. Matano, S. Kusakabe, H. Yamada, and H. Imahori (Kyoto University).



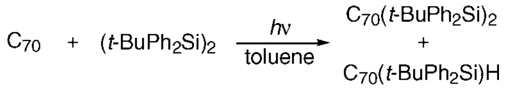
O31. “Reactions of Stable Heavier Group-14 Divalent Species with Persistent Radicals” by H. Masuda, S. Ishida, T. Iwamoto, C. Kabuto, and M. Kira (Tohoku University).



O32. “Silicon Analogue of Cyclobutadiene Dianion: Synthesis, Structure, and Reactivity” by T. Matsuno, M. Ichinohe, and A. Sekiguchi (University of Tsukuba).

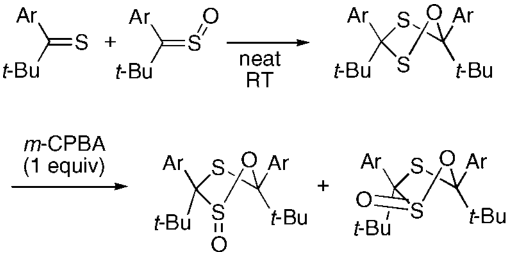


O33. “Photochemical Bissilylation of C_{70} with Disilane” by T. Wakahara, G. M. A. Rahman, Y. Maeda, M. Kako, S. Sato, T. Akasaka, K. Kobayashi, and S. Nagase (University of Tsukuba; The University of Electro-Communications; Institute for Molecular Science).

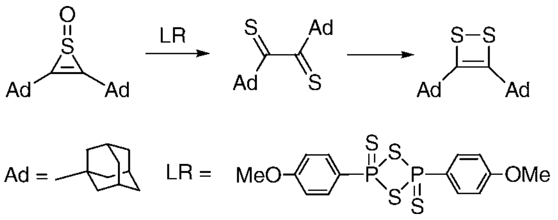


$$C_{70} + (t\text{-BuPh}_2\text{Si})_2 \xrightarrow[\text{toluene}]{h\nu} \begin{array}{c} C_{70}(t\text{-BuPh}_2\text{Si})_2 \\ + \\ C_{70}(t\text{-BuPh}_2\text{Si})\text{H} \end{array}$$

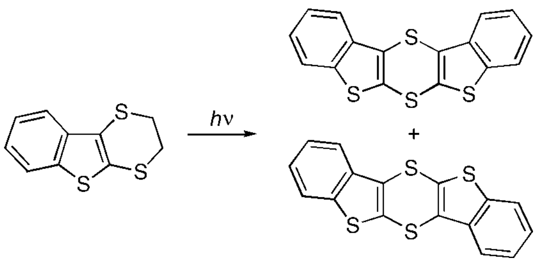
O34. "Preparation and Reactivities of 3,5-Diaryl-3,5-di-*t*-butyl-1,2,4-oxadithiolanes and Their Oxides" by H. Oshida, A. Ishii, and J. Nakayama (Saitama University).



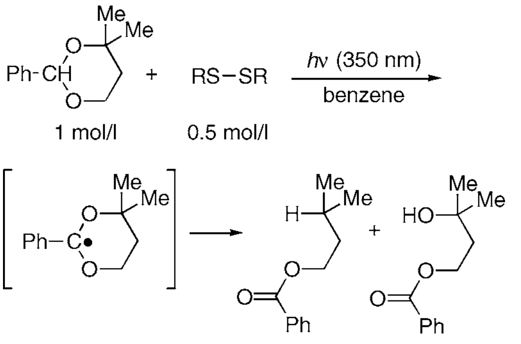
O35. "Synthesis, Isolation, and Characterization of α-Dithiones" by Y. Ono, Y. Sugihara, A. Ishii, and J. Nakayama (Saitama University).



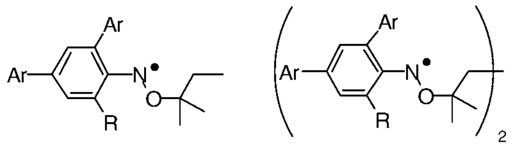
O36. "Synthesis, Structure, and Chemical Properties of 1,4-Dithiin Bearing Benzothiophene" by T. Yamamoto, R. Sato, Y. Kawai, S. Nakajo, and S. Ogawa (Iwate University; Kyoto University).



O37. "Factors Affecting the Reactivity of Thiyl Radical" by M. Tada, N. Sakurai, E. Katayama, K. Murofushi (Waseda University).

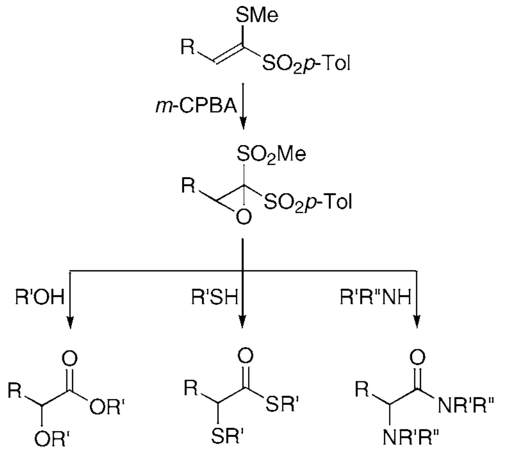


O38. "Isolation and Characterization of Stable Oxyaminyl Radicals" by T. Nishi, Y. Miura, and Y. Tegi (Osaka City University).

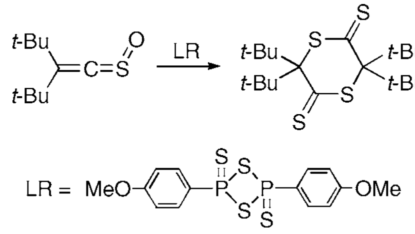


Ar = C_6H_5, 4-ClC_6H_4 R = C_6H_5, 4-ClC_6H_4, *t*-Bu

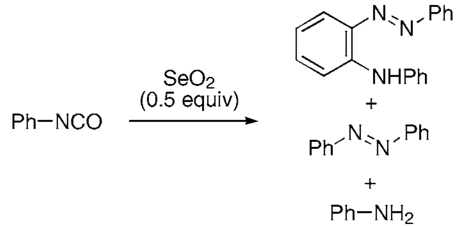
O39. "Novel Synthesis of α-Substituted Carboxylic Derivatives Using 1,1-Disulfonyloxirane and 1-Sulfonyl-1-thiooxirane" by S. Matsumoto, M. Ishii, K. Kimura, A. Tanaka, and K. Ogura (Chiba University).



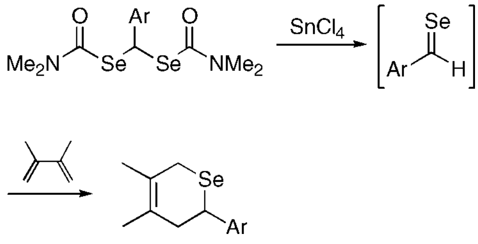
O40. "Synthesis and Reaction of 1,4-Dithiane-2,5-dithione from Thioketene *S*-Oxide" by T. Shigetomi, K. Shioji, and K. Okuma (Fukuoka University).



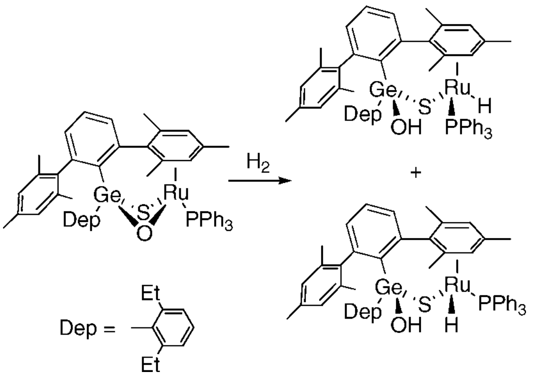
O41. "New Method for the Generation of Nitrenoid Species from Isocyanate" by K. Maeda, Y. Nishiyama, and N. Sonoda (Kansai University).



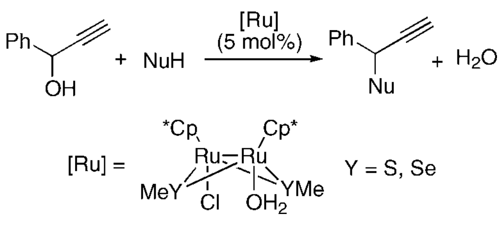
O42. “Novel Generation of Selenoaldehydes through Stannic Chloride-Induced Cleavage of Bis(*N*,*N*-dimethylcarbamoylseleno)methanes” by K. Shimada, Y. Gong, H. Nakamura, R. Matsumoto, S. Aoyagi, and Y. Takikawa (Iwate University).



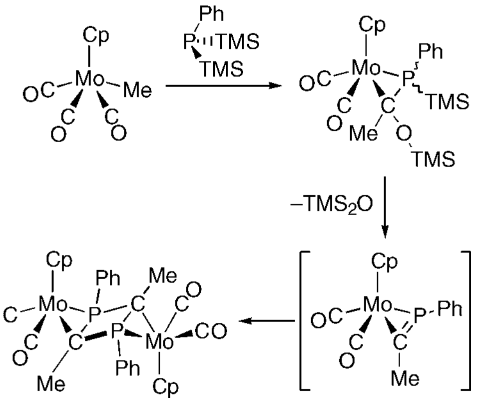
O43. “Dihydrogen-Proton Interconversion by Germanium-Ruthenium Dinuclear Complexes Bridged by Chalcogen Atoms” by T. Matsumoto, Y. Nakaya, and K. Tatsumi (Nagoya University).



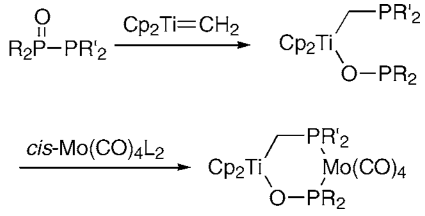
O44. “Preparation of a Series of Chalcogenolate-Bridged Diruthenium Complexes and Their Catalytic Activities Toward Propargylic Substitution Reactions” by H. Imajima, Y. Nishibayashi, M. Hidai, and S. Uemura (Kyoto University).



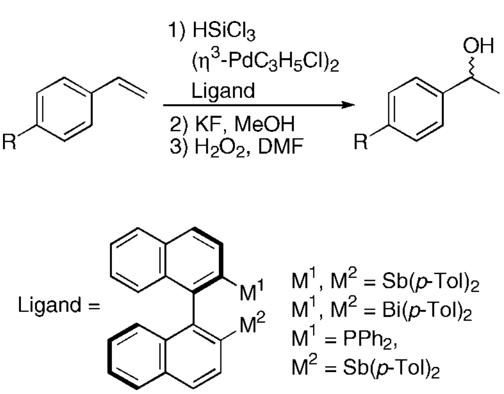
O45. “Synthesis and Reactivity of Complexes with Three-Membered Ring Consisting of Mo, P, and C” by H. Nakazawa, M. Iimori, and K. Miyoshi (Osaka City University; Hiroshima University).



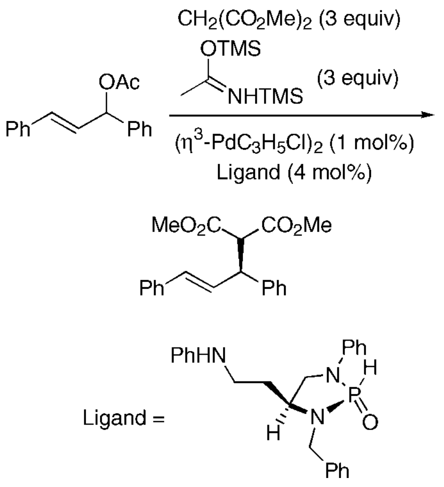
O46. “Syntheses, Structures, and Reactivities of Titanadiphosphine Chelates and Their Transition Metal Complexes” by T. Mizuta, J. Ushio, T. Katayama, and K. Miyoshi (Hiroshima University).



O47. “Synthesis of New Optically Active Organoantimony and Bismuth Compounds Comprising 1,1′-Binaphthyl Core and Its Evaluation for Palladium-Catalyzed Asymmetric Reactions” by S. Yasuike, S. Kawara, S. Okajima, H. Seki, K. Yamaguchi, and J. Kurita (Hokuriku University; Chiba University).



O48. “A Novel P-Chiral Diaminophosphine Oxide: Application to Catalytic Asymmetric Synthesis” by T. Nemoto, T. Masuda, T. Matsumoto, T. Hitomi, and Y. Hamada (Chiba University).



POSTER PRESENTATIONS

P01. “Transition-Metal-Catalyzed Reactions of Acetylenes with Phenyl Chalcogenides” by S. Nagata, I. Kamiya, and A. Ogawa (Nara Women’s University).

P02. “Transition-Metal-Catalyzed Thiocarbonylation of Carbon-Carbon Double Bond Compounds with Thiols and Carbon Monoxide” by M. Kajitani, I. Kamiya, M. Tanaka, and A. Ogawa (Nara Women’s University).

P03. “Synthesis of $Pt(Cl)(SAr)(PPh_3)_2$ and Their Reactions with Alkynes” by F. Yamashita, H. Kuniyasu, and N. Kambe (Osaka University).

P04. “Studies on the Reactivities of *trans*-$Pt(H)(SAr)(PPh_3)_2$ toward Alkynes” by S. Asano, H. Kuniyasu, A. Ohtaka, H. Kurosawa, and N. Kambe (Osaka University).

P05. “Pt-Catalyzed Carboselenation of Alkynes Using Selenoesters” by T. Hirai, H. Kuniyasu, T. Kato, Y. Kurata, and N. Kambe (Osaka University).

P06. “Synthesis of Trifluoromethyl-Substituted Alkenes Using Horner Reaction and Their Applications” by S. Yamamoto, H. Sugimoto, O. Tamura, and H. Ishibashi (Kanazawa University).

P07. “Diastereoselective Alkylation of β-Methoxyacylsilanes: Stereoselective Construction of 1,3-Diol Derivatives” by Y. Mikami, M. Honda, and M. Segi (Kanazawa University).

P08. “Ni- or Pd-Catalyzed Dimerizative Silylation of 1,3-Butadienes Using Chlorosilanes” by J. Terao, A. Oda, and N. Kambe (Osaka University).

P09. “Stability of Dicarboxylato-Bridged Hypervalent Molecules” by Y. Sato, Y. Naruse, S. Inagaki, N. Kano, and T. Kawashima (Gifu University; The University of Tokyo).

P10. “Synthesis, Structure, and Reactions of Ethynylsilyllithium” by T. Kadowaki, K. Sakamoto, C. Kabuto, and M. Kira (Tohoku University).

P11. “Structure and Reactions of Stable Trisilaallene” by T. Abe, S. Ishida, T. Iwamoto, C. Kabuto, and M. Kira (Tohoku University).

P12. “Heteroatom Encapsulated Fullerene: Synthesis and Reaction” by Y. Matsunaga, T. Wakahara, Y. Maeda, M. Kako, T. Akasaka, T. Kato, Y.-K. Choe, K. Kobayashi, S. Nagase, H. Huang, and M. Ata (University of Tsukuba; Tokyo Gakugei University; The University of Electro-Communications; Institute for Molecular Science; Sony Corporation).

P13. “Synthesis and Application of Novel λ^3-Iodinane” by T. Nishii and Y. Yamamoto (Hiroshima University).

P14. “Construction of a Novel Tridentate Ligand Derived from 1,8-Dimethoxythioxanthen-9-one and Its Application” by T. Yamaguchi and Y. Yamamoto (Hiroshima University).

P15. “Synthesis of a Novel Tridentate Ligand System Bearing Two Coordinating Sulfur Atoms and Its Application to Synthesis of Hypervalent Main-Group-Element Compounds” by T. Masui and Y. Yamamoto (Hiroshima University).

P16. “Syntheses and Structures of Germanium Compounds Bearing a 1,8-Dimethoxyanthracene Ligand” by T. Unrin-in, H. Murakami, M. Yamashita, A. Kawachi, and Y. Yamamoto (Hiroshima University).

P17. “Synthetic Study of Highly Coordinate Phosphorus Compounds Using a Novel Tetradentate Ligand with Six-Membered Rings” by S. Nakafuji, J. Kobayashi, and T. Kawashima (The University of Tokyo).

P18. “Development of New Sterically Demanding Groups Bearing Substituents at the *para*-Positions and the Applications to Low-Coordinated Phosphorus Compounds” by S. Kawasaki, K. Toyota, and M. Yoshifuji (Tohoku University).

P19. “Introduction of Functional Group at 4-Position of the Crowded Triarylphosphine” by K. Kato, K. Sutoh, F. Murakami, S. Sasaki, and M. Yoshifuji (Tohoku University).

P20. “Synthesis and Properties of 1,2-Diphosphinidenecyclobutene (DPCB) Having Aromatic

Substituents at the 1,2-Positions" by A. Nakamura, K. Toyota, and M. Yoshifuji (Tohoku University).

P21. "Studies on the Synthesis of Novel Heteronuclear Double-Bond Compounds between Heavier Group 15 Elements Utilizing Steric Protections" by T. Yamazaki, T. Sasamori, N. Takeda, N. Tokitoh (Kyoto University).

P22. "Preparation and Structure of Carbonyltungsten(0) Complexes of 2-Pyridylphosphines" by K. Nishide, S. Ito, and M. Yoshifuji (Tohoku University).

P23. "An Unusual Ring Opening Reactions of 4,5-Ethylenedioxy-1,3-diselenole-2-thione and 1,3-Diselenole-2-one-4,5-diester Using Triethylphosphite" by R. Watanabe, Y. Miyake, and M. Iyoda (Tokyo Metropolitan University).

P24. "Formation of Carbon-Phosphorus Bond by Activated Silylphosphines" by M. Hayashi, Y. Matsuura, Y. Watanabe (Ehime University).

P25. "Novel Construction of Tetrahydrofuran Derivatives with Allylic Sulfides" by H. Sato, K. Hirabayashi, T. Shimizu, and N. Kamigata (Tokyo Metropolitan University).

P26. "$[4+2]$ Cycloaddition of Allenyl Thioketene and Imine" by S. Aoyagi, M. Hakoishi, M. Suzuki, K. Shimada, Y. Takikawa (Iwate University).

P27. "Synthesis of Selenite Esters by Reaction of Epoxides with Selenium Dioxide" by M. Aitani, N. Momozaki, Y. Nishiyama, and N. Sonoda (Kansai University).

P28. "A New Method for the Introduction of Phenylseleno Group to Acetylenic Bond" by H. Onishi, Y. Nishiyama, and N. Sonoda (Kansai University).

P29. "Selenium-Catalyzed Reaction of Epoxide with Carbon Monoxide and Sulfur" by C. Katahira, Y. Nishiyama, and N. Sonoda (Kansai University).

P30. "π-Facial Diastereoselectivity for Cyclohexanones or Methylenecyclohexanes Containing a Chalcogen Atom in the Ring" by Y. Aiki, M. Honda, and M. Segi (Kanazawa University).

P31. "Synthesis of Oxiranyl Ketones Using Stabilized Selenonium Ylides and Attempts at Asymmetric Epoxidation" by S. Watanabe, S. Asaga, A. Onai, and T. Kataoka (Gifu Pharmaceutical University).

P32. "Enantioselective Carbon-Carbon Bond Formation Using Episelenonium Ions" by K. Okamoto, Y. Nishibayashi, S. Uemura, and A. Toshimitsu (Kyoto University).

P33. "Palladium-Catalyzed Mizoroki-Heck Type Reaction Using Telluronium Salts" by Y. Nara, K. Hirabayashi, T. Shimizu, and N. Kamigata (Tokyo Metropolitan University).

P34. "Oxidation of Diaryl Telluride by Singlet Oxygen and Chemical Properties of the Products" by M. Endo, M. Oba, K. Nishiyama, W. Ando, and A. Ouchi (Tokai University; National Institute of Advanced Industrial Science and Technology).

P35. "Reaction of S-N Multiple Bond Compounds with Sulfenylating Reagents" by T. Yoshimura, T. Fujie, and T. Fujii (Toyama University).

P36. "Application of Alkoxy-λ^6-sulfanenitriles as Strong Alkylating Reagent" by H. Wei, T. Dong, Y. Wakai, T. Fujii, and T. Yoshimura (Toyama University).

P37. "Synthesis and Properties of Novel Thiirane 1-Imides" by H. Okada, R. Ohtsu, A. Kobiki, Y. Sugihara, and J. Nakayama (Saitama University).

P38. "Synthesis and Properties of Partially Unsaturated Thiacrown Ethers" by T. Kuroiwa, T. Shimizu, K. Hirabayashi, and N. Kamigata (Tokyo Metropolitan University).

P39. "Synthesis of a Stable *O*-Thionitrosoalcohol by Taking Advantage of Steric Protection of a Bulky Bowl-Type Substituents" by K. Takenaka and R. Okazaki (Japan Women's University).

P40. "Synthesis and Reactions of Thioacyl Halides" by K. Mogi, K. Takenaka, and R. Okazaki (Japan Women's University).

P41. "Synthesis of a Thiohydroxylamine" by K. Sakamoto, K. Takenaka, and R. Okazaki (Japan Women's University).

P42. "Syntheses, Structures, and Reactions of Selenate Anions Bearing a Bowl-Type Steric Protection Group" by K. Shimada, K. Goto, and T. Kawashima (The University of Tokyo).

P43. "Synthesis and Reaction of Phosphinoselenoic Chlorides" by T. Kimura and T. Murai (Gifu University).

P44. "Isolation and Stereochemistry of Optically Active Selenoximines" by T. Shimizu, K. Mitsuya, K. Hirabayashi, and N. Kamigata (Tokyo Metropolitan University).

P45. "Chiral Crystallization of an Optically Active Seleninic Acid" by Y. Nakashima, T. Shimizu, K.

Hirabayashi, M. Yasui, M. Nakazato, F. Iwasaki, and N. Kamigata (Tokyo Metropolitan University; The University of Electro-Communications).

P46. “Substituent Effect Toward Racemization of Optically Active Selenoxides” by T. Soma, T. Shimizu, K. Hirabayashi, and N. Kamigata (Tokyo Metropolitan University).

P47. “Evaluation of Contribution from Each Molecular Orbital on ^{77}Se NMR Chemical Shifts with Its Applications to Organic Selenium Chemistry” by T. Nakamoto, D. Shimizu, S. Hayashi, W. Nakanishi, and M. Hada (Wakayama University; Tokyo Metropolitan University).

P48. “Electronic Structures of Hypervalent Bonds Constructed by Group 16 Elements: Evaluation Based on Their Oxidation and Reduction Potentials” by K. Tanimoto, M. Uegaito, S. Hayashi, and W. Nakanishi (Wakayama University).

P49. “Examination of Multi-Center Nonbonded Interactions Containing Group 16 Atoms by AIM” by K. Kawabata, S. Hayashi, and W. Nakanishi (Wakayama University).

P50. “Synthesis and Reactions of Spirotellurane Bearing Chalcogen Ligands” by S. Ogawa, Y. Takase, S. Nakajo, and R. Sato (Iwate University).

P51. “Properties of 2-Silaimidazolium Cation” by S. Ishida, T. Nishinaga, and K. Komatsu (Kyoto University).

P52. “Synthesis of 1,3-Dicyano-5,10-methano-[10]annuleno[3,4-*c*]thiophene and Formation of a DMAD Adduct” by S. Kuroda, T. Fukuda, Y. Wada, H. Takamatsu, M. Kyougoku, R. Miyatake, and M. Oda (Toyama University).

P53. “Synthesis and Properties of Oligo(thienylfuran)” by Y. Miyata, T. Nishinaga, and K. Komatsu (Kyoto University).

P54. “Synthesis and Properties of Novel π-Expanded Benzo[*c*]thiophene Derivatives” by Y. Shimizu, T. Okujima, H. Uno, and N. Ono (Ehime University).

P55. “Synthesis and Reactivities of Thianthrene Derivatives: Attempts to Synthesize Functional Thianthrene Derivatives” by H. Morita, T. Iwasawa, Y. Oida, T. Nakajima, and Y. Kumafuji (Toyama University).

P56. “Synthesis of Novel Metal-Coordinated Donors with TTF Unit” by K. Sako, Y. Katayama, D. Hattori, and H. Tatemitsu (Nagoya Institute of Technology).

P57. “Synthesis and Properties of Tetracyanoazulenequinodimethane-TTF Complexes” by O, Sato, M. Sato, K. Takahashi, and T. Shirahata (Saitama University; Tohoku University; RIKEN).

P58. “Basicity, Complexation with Amines, and X-Ray Structure of Phenol Oligomers” by N. Hayashi, K. Sato, T. Matsumoto, and H. Higuchi (Toyama University).

P59. “Synthesis and Molecular Recognition of Oligo(*m*-ethynylpyridine)s” by H. Abe, M. Waki, H. Machiguchi, and M. Inouye (Toyama Medical and Pharmaceutical University).

P60. “Aggregation of Bismuthanes Bearing Supramolecular Synthons” by T. Murafuji, N. Fujimoto, Y. Miyoshi, Y. Urabe, Y. Sugihara, and H. Uno (Yamaguchi University; Ehime University).

P61. “Self-Assembly of Bis(4-hydroxyphenyl)-dibromotellurane Based on the Combination of Hydrogen Bonds and Interaction between Heteroatoms” by K. Kobayashi, A. Shuto, and K. Yamaguchi (Shizuoka University).

P62. “Dynamic Covalent Chemistry of Heteroatom Systems Directed Toward Assembling and Disassembling of Topological Supramolecules” by T. Takata, T. Oku, and Y. Furusho (Tokyo Institute of Technology; ERATO).

We look forward to the 31th Symposium on Heteroatom Chemistry to be held in December of 2004 in Wakayama and to be organized by Prof. Waro Nakanishi of Wakayama University. We hope that many chemists from various academic institutes and industries will participate in this Symposium.