

# A Report of the 21st Symposium on Heteroatom Chemistry of the Chemical Society of Japan

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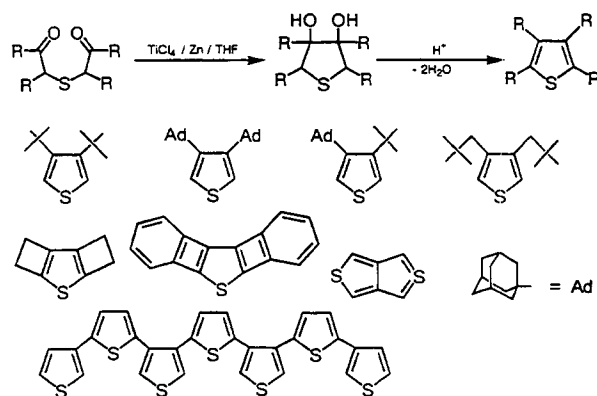
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*Received 20 January 1994*

The 21st Symposium on Heteroatom Chemistry of the Chemical Society of Japan was held at Kuroda Hall in Toyama University, located on the Japan Sea side, i.e., Ettyu in the Hokuriku area of Japan, during the period of December 9–11, 1993, and it was an excellently organized meeting. It was the first one to be held in the area on the Japan Sea side. This time, Prof. Toru Koizumi of Toyama Medical and Pharmaceutical University organized the symposium, and it was based on four plenary lectures, each of 50 minutes, one invited lecture, and 56 oral presentations, each of 20 minutes duration. On the first day, a beautiful Tateyama mountain range topped with snow could be seen, which is a part of the Japan Alps. The number of participants was over 250, the people coming mainly from universities and industries located in all parts of Japan. Here we had one plenary lecture by Prof. Y. H. Kim of the Korea Advanced Institute of Science & Technology in Korea and one foreign invited lecture by Prof. M. G. Voronkov at the Irkutsk Institute of Organic Chemistry of the Russian Academy of Sciences. There were also three plenary lectures by Japanese chemists, Prof. Juzo Nakayama of Saitama University, Prof. Hitomi Suzuki of Kyoto University, and Associate Prof. Takayuki Kawashima of Tokyo University.

Professor Juzo Nakayama gave the first plenary lecture entitled "A New Thiophene Synthesis

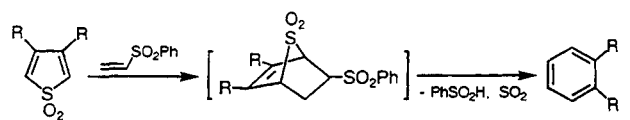
and Its Applications." It was a well-conceived study designed to provide bulky-alkyl substituted thiophenes via intramolecular reductive coupling reactions of diketo sulfides, followed by acid-catalyzed dehydration of the resulting thiolanediols. This method is a very powerful one that is applicable to the preparation of various interesting thiophene derivatives, as shown subsequently. Especially, a nonclassical thienothiophene was prepared by this method.



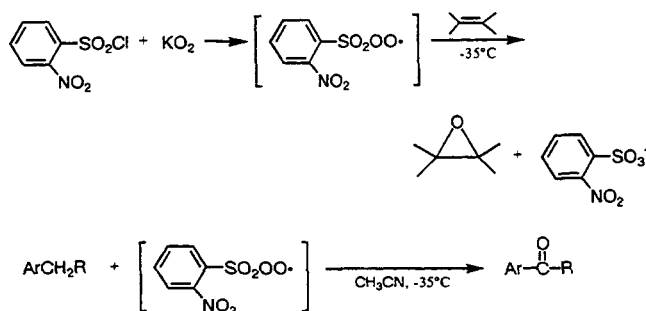
Selenophenes could also be synthesized by a similar method. As one of several utilizations of these thiophenes, 1,2-di-bulky alkyl substituted benzenes could be synthesized via the Diels–Alder reaction of thiophene dioxides with phenyl vinyl

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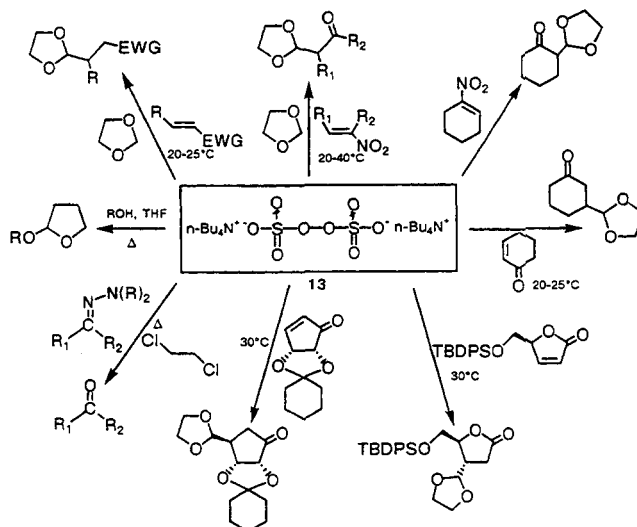
sulfone, followed by the elimination of benzenesulfinic acid and sulfur dioxide. This sequence of reactions occurred in spite of the lack of apparent diene properties of the original thiophene.



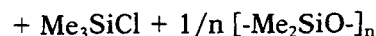
The second plenary lecture was presented by Prof. Y. H. Kim of the Korea Advanced Institute of Science & Technology (KAIST), who spoke on the "Formation and Characterization of a Sulfonyl Peroxy Radical and a Sulfate Radical: Application to Organic Synthesis." This is a very good extension of the work that he carried out when he spent a few years in Shigeru Oae's Laboratory at Tsukuba University (*Tetrahedron*, 37, 1980, 37). The first part of his lecture was the generation of arenesulfonyl peroxy radicals by the reaction of arenesulfonyl chlorides with potassium superoxide ( $\text{KO}_2$ ) and their utilization to prepare epoxides with high regioselectivity from olefins and also their oxidation of active methylene groups such as benzylic groups to carbonyl groups. The 2-nitrobenzenesulfonyl peroxy radical prepared from 2-nitrobenzenesulfonyl chloride in situ was the most reactive one. The above oxidations proceed even at  $-35^\circ\text{C}$ . Professor Kim also carried out a trapping experiment of the peroxy radical with 5,5-dimethyl-1-pyrrolin-1-oxide (DMPO) to obtain the ESR spectrum of the nitroxyl radical produced. The last part of his lecture was the successful generation of the tetrabutylammonium sulfate radical from tetrabutylammonium peroxy disulfate, which was prepared from potassium peroxydisulfate and tetrabutylammonium hydrogen sulfate in a mixture of water and dichloromethane. Successive extraction with dichloromethane gave the compound as a stable white solid. This remained a stable for about 1 month at room temperature, and its synthetic utilization toward tetrahydrofuran and 1,3-dioxolane, etc., is shown below.



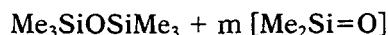
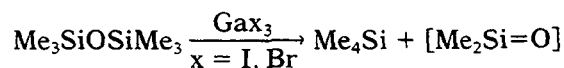
EWG = an electron-withdrawing group.



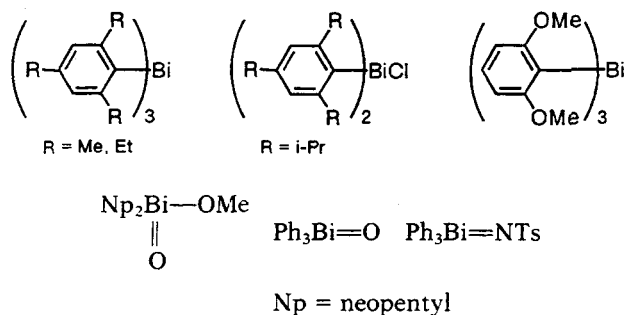
The invited lecture of Prof. M. G. Voronkov of Irkutsk's Institute of Organic Chemistry was assisted by Dr. Yana Droztova, who has been spending her postdoctoral period with Prof. A. Ohno of Kyoto University, since Prof. Voronkov could not see the slides. Although it was a short lecture, it provided an interesting comparison with the work of H. Schmidbaur who discovered the following reaction involving  $\text{GaCl}_3$ .



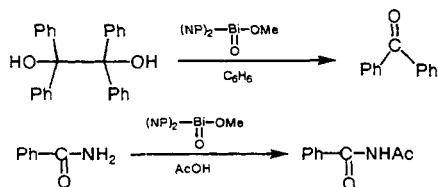
Voronkov et al. replaced Cl by Br or I and found a somewhat different reaction that generated tetramethylsilane in more than 90% yield. This represents a convenient procedure to make viscous permethylpolysiloxane, as shown below. He also mentioned that, unlike boron or aluminum halides, gallium halides, particularly  $\text{GaI}_3$ , are not good Lewis acids but rather function as nucleophilic species.



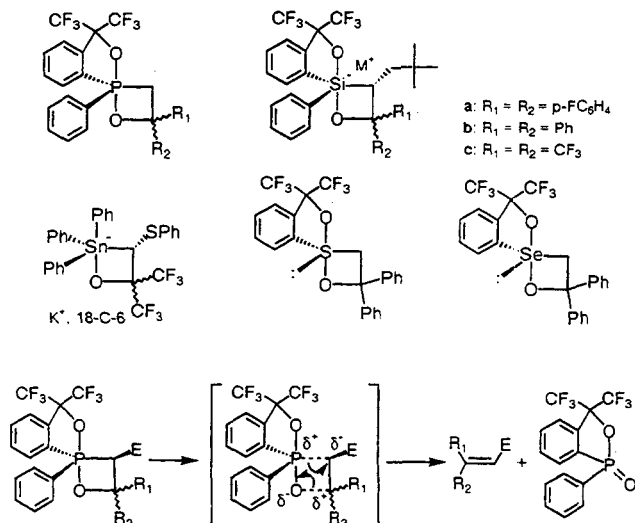
The third plenary lecture was presented by Prof. Hitomi Suzuki of Kyoto University on the subject of "Organobismuth Compounds: Unique Chemistry and Applications." Apart from the interesting works of G. Wittig and D. H. R. Barton, there are few reactions known with Bi compounds that have Bi as the central atom as compared to those of similar, but lighter elements, such as P, As, and Sb. Suzuki isolated the following organobismuth compounds as stable entities.



Tris(2,6-dimethoxyphenyl)bismuthine can be used as a dehydrating reagent for the preparation of esters or amides from primary carboxylic acids and alcohols or amines. Bismuthine oxides, bismuthimines, and methyl bismuthinates were also prepared. The unique character of organobismuth compounds was shown in the reactions of methyl bismuthinates that exhibit weak oxidizing and acylating actions.



The last plenary lecture was presented by Associate Prof. Takayuki Kawashima of Tokyo University who spoke on "Syntheses and Reactions of Oxetanes Containing a Highly Coordinate Group 14, 15, or 16 Element." Hypervalent structures of phosphorus and silicon atoms have been proposed to be intermediates in the Wittig and the Peterson reactions. Prof. Kawashima prepared these hypervalent compounds (pentacoordinate-1,2-oxaphosphetanes, 1,2-oxasiletanides) for the first time as stable entities at room temperature by use of the Martin ligand, as shown below. The structures were determined by X-ray analysis which supported the concept that the two oxygen atoms and three carbon atoms occupy apical and equatorial positions, respectively, as expected. The hypervalent four-membered cyclic Wittig-type intermediates gave the corresponding olefins via slightly polar transition states when heated, as shown below. A 1,2-oxastannetanide, a 1,2-oxathietane, and 1,2-oxaselenetanide were also prepared. The structure of the 1,2-oxaselenetanide was established by X-ray analysis and supported the concept that the two oxygens and two carbons occupy apical and equatorial positions, respectively. The 1,2-oxaselenetanide gave the corresponding ketone at 150°C. Thus, all 1,2-oxetanes, except for the sulfur and selenium derivatives, gave the corresponding olefins quantitatively as in the Wittig and the Peterson reactions. Apparently, the reactions with the 1,2-oxathietane and 1,2-oxaselenetanide gave ketones but not olefins.



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

1. "Synthesis and Nonlinear Optical Properties of Alkylated Oligothiophene Derivatives" by T. Nakayama, H. Higuchi, J. Ojima, T. Wada, and H. Sasabe (Toyama University).
2. "Preparation of a Polymer Having a Heterocycle and its Application to an Electrochromic Material" by M. Wakabayashi, M. Sakai, A. Ishibashi, and T. Yamamoto (YKK Yoshida Kogyo and Tokyo Institute of Technology).
3. "Preparation and Reactions of S,S,S-Tri-arylthiazynes" by T. Yoshimura, K. Hamada, K. Takeuchi, M. Imada, S. Ono, C. Shimasaki, and E. Tsukurimichi (Toyama University).
4. "A New Method for the Preparation of Alkoxycarbene Complexes of Chromium, Molybdenum, and Tungsten using Sulfonium Salts" by H. Matsuyama, T. Nakamura, and M. Iyoda (Tokyo Metropolitan University).
5. "α-Acetoxylation of Sulfides by Electrolysis, and the Related Reactions and Synthetic Applications" by J. Nokami, T. Ikeda, J. Inada, T. Sako, and K. Kohmoto (Okayama University of Science).
6. "Enzymatic Hydrolysis of the σ-Symmetric Diesters Bearing a Sulfur-Atom Prochiral Center" by Y. Nagao, S. Tamai, S. Miyauchi, C. Morizane, and H. Shimizu (Tokushima University).
7. "Effective Transformations of Optically Active β-Hydroxy Sulfide Derivatives" by H. Kosugi, O. Kanno, K. Hoshino, and H. Uda (Tohoku University).
8. "Asymmetric Syntheses Using β-Silyl Sulf-

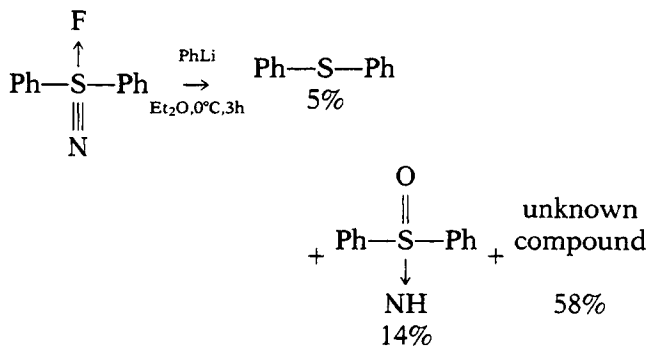
- oxides as Novel Chiral Synthons" by S. Kusuda, K. Kawamura, Y. Ueno, and T. Toru (Nagoya Institute of Technology).
9. "Stereocontrolled Diels-Alder Reactions and Simmons-Smith Reactions Using Optically Active Aminoalcohols" by K. Tanaka, H. Uno, and H. Suzuki (Kyoto University).
10. "Photochemical Behavior of 4-Substituted 1-Aryl-2-(p-tolylsulfonyl)-1,3-Butadienes: Synthesis of a Naphthalene Ring and the Reversible Record of Light Information" by K. Ogura, S. Takahashi, and M. Fujita (Chiba University).
11. "Nucleophilic Substitution Reactions of Sulfenamides" by T. Okuyama, J.P. Lee, and K. Ohnishi (Osaka University).
12. "Synthesis of Cyclopropylaminosulfoxonium Salts from Dimethylaminophenylsulfoxonium Methylide" by K. Okuma, Y. Sato, and H. Ohta (Fukuoka University).
13. "Novel Olefin Cyclizations Using  $\alpha$ -Chlorosulfides as Reactive Species" by H. Ishibashi, A. Nishikawa, C. Kameoka, Y. Nakatani, and M. Ikeda (Kyoto Pharmaceutical University).
14. "Transition-Metal-Catalyzed Carbonylation of Acetylenes with Carbon Monoxide and Thiols" by M. Takeba, A. Ogawa, I. Ryu, N. Kambe, and N. Sonoda (Osaka University).
15. "Preparation and Reactivities of the First Isolable Dithiirane, 3-(1,1,3,3-Tetramethyl-4-oxo-4-phenylbutyl)-3-phenyldithiirane" by A. Ishii, T. Maruta, H. Nagaya, T. Akazawa, J. Nakayama, M. Hoshino, and M. Shiro (Saitama University and Rigaku Corporation).
16. "Synthesis, Physical Properties, and Reactions of ( $\eta^5$ -Cyclopentadienyl)(1-aryl-methanamine-N,1-Dithiolato)cobalt(III)" by Y. Mori, M. Takehara, N. Hisamatsu, Y. Kitani, T. Sugiyama, M. Kajitani, T. Akiyama, and A. Sugimori (Sophia University).
17. "Structural Features of Tetraazathiapentalenes Fused with a Pyrimidine Ring: Experimental Evaluation of the Nature of the Hypervalent N-S-N Bond by Restricted Internal Rotation of the Pyrimidine Ring" by K. Ohkata, M. Ohsugi, K. Yamamoto, M. Ohsawa, and K. Akiba (Hiroshima University).
18. "Synthesis and Reactivity of a Highly Coordinate Thiotelluroxide and Related Ammoniotelluranes" by H. Fujihara, T. Uehara, and N. Furukawa (Tsukuba University).
19. "Structures of Metal Complexes Derived from Tetraazathiapentalene Derivatives: Structure Determination of Unstable Compounds by a Rapid X-ray Measurement System" by M. Yasui, N. Manabe, F. Iwasaki, N. Matsumura, and H. Inoue (Electro-Communications University and University of Osaka Prefecture).
20. "Reductive Addition to Electron-Deficient Olefins with (Diacloxyiodo)arenes" by H. Togo, R. Taguchi, M. Aoki, and M. Yokoyama (Chiba University).
21. "Preparation of Highly-Reactive Hypervalent Iodine (III) Reagents and their Reactivity toward Aromatics and Alkynes" by K. Nagata, T. Kitamura, and H. Taniguchi (Kyushu University).
22. "Benzylic Oxidation with Hypervalent (Alkylperoxy)iodinane" by T. Ito, H. Takahashi, and M. Ochiai (Tokushima University).
23. "Reactions of Acylsilanes with Ketone Enolates" by K. Takeda, M. Fujisawa, T. Makino, J. Nakatani, K. Fujimoto, and E. Yoshii (Toyama Medical and Pharmaceutical University).
24. "Reactions of Phenylthioformohydrazide with Carbonyl Compounds in the Presence of Trimethylsilyl Chloride" by Y. Matsubara, K. Kitano, M. Yoshihara, and T. Maeshima (Kinki University).
25. "A New Synthesis of Alkynes, Aldehydes, and Furans from Carbonyl Compounds Utilizing Trimethylsilyldiazomethane" by K. Miwa, T. Aoyama, and T. Shioiri (Nagoya City University).
26. "Synthesis and Reactions of 2-Siladecalin Derivatives" by O. Hoshino, T. Kanesaka, T. Kashiwagi, and K. Shimizu (Science University of Tokyo).
27. "Synthesis and Reactions of Sulfur Containing Disilametallacycles" by S. Sugi, N. Choi, and W. Ando (Tsukuba University).
28. "Organoheteroatom Derivatives of Buckminsterfullerene ( $C_{60}$ )" by T. Akasaka, W. Ando, K. Kobayashi, and S. Nagase (Tsukuba University and Yokohama National University).
29. "Synthesis and Properties of Novel Seven-Membered Heterocyclic Rings Containing Si, Ge, P and As" by J. Kurita, S. Shiratori, S. Yasuike, and T. Tsuchiya (Hokuriku University).
30. "Characterization of an Unusual Hydrogen Bond Involving Group 16 Elements" by M. Iwaoka, T. Senju, K. Sudo, K. Ogawa, and S. Tomoda (Tokyo University).
31. "Synthesis of the First Stable Telluroke-

- tones by Thermal Cycloreversion of 1,3,4-Telluradiazolines" by M. Minoura, T. Kawashima, and R. Okazaki (Tokyo University).
32. "Synthesis of Tellurolestere and Generation of Carbonyllithium via Lithium-Tellurium Exchange Reactions" by T. Takeda, T. Inoue, N. Kambe, A. Ogawa, I. Ryu, and N. Sonoda (Osaka University).
  33. "Chemoselective Reactions of Tellurium Tetrachloride and Tellurium Tetraethoxide Toward Thioamides and Amides" by K. Omote, Y. Aso, T. Otsubo, and F. Ogura (Hiroshima University).
  34. "Preparation and Properties of Novel Donor and Acceptor Molecules Containing a Tellurium Atom" by R. Tamura, Y. Nagata, H. Takasuka, H. Shimizu, A. Matsumoto, and N. Ono (Ehime University).
  35. "Reactivities of Phosphorous Triesters and Their Synthetic Applications" by Y. Watanabe, S. Maehara, E. Inada, C. Nakamoto, T. Yamamoto, and S. Ozaki (Ehime University).
  36. "Electric and Steric Control of Phosphoryl Groups to Avoid Cyclization in Bis-1,2-Phosphorylation of 1,2-Diols and the Application to a New Method for the Synthesis of RNA" by M. Sekine, H. Tsuruoka, K. Shouda, S. Iimura, T. Wada, and K. Furusawa (Tokyo Institute of Technology and Research Institute for Polymers and Textiles).
  37. "A Large Scale Synthesis of  $\alpha,\gamma$ -Dinucleosides Triphosphates (The Cap Structure of Messenger RNA)" by K. Fukuoka, F. Suda, M. Ishikawa, H. Takaku, and T. Hata (Tokyo Institute of Technology and Chiba Institute of Technology).
  38. "Novel Synthesis and Structure of Phosphono Sugar Derivatives from Phosphonenes" by M. Yamashita, A. Iida, H. Mizuno, A. Yabui, T. Oshikawa, T. Hanaya, H. Yamamoto, A. Kakehi, L. Parkanayi, and J. Clardy (Shizuoka University, Okayama University, Shinshu University, and Cornell University).
  39. "Synthesis and Synthetic Applications of  $\alpha$ -Phosphono- $\beta$ -and/or  $\gamma$ -Lactams" by Y. Okada, M. Miyamoto, T. Minami, and J. Ichikawa (Kyushu Institute of Technology).
  40. "Synthesis and Reactions of Boranato-phosphates" by T. Imamoto and E. Nagato (Chiba University).
  41. "Stereochemistry of Optically Active Pentacoordinated Phosphoranes" by K. Kajiyama, S. Kojima, and K. Akiba (Hiroshima University).
  42. "Preparation and Properties of Phosphorane Compounds Containing o-OC<sub>6</sub>H<sub>4</sub>NH or o-OC<sub>6</sub>H<sub>4</sub>O as Chelating Ligands" by H. Nakazawa, K. Kubo, and K. Miyoshi (Hiroshima University).
  43. "Photochemical Reactions of Bis(alkoxyphenyl) Alkylphosphonate Derivatives" by Y. Okamoto, M. Nakamura, T. Tatsuno, M. Shi, and S. Takamuku (Osaka University).
  44. "Preparation of New Sterically Protecting Groups Bearing Electron Donating Substituents and Their Synthetic Applications to Low-Coordinated Phosphorus Compounds" by M. Yoshifuji, K. Toyota, D.-L. An, A. Otoguro, K. Kamijo, S. Sangu, and R. Nakamoto (Tohoku University).
  45. "Oxidation of Trivalent Phosphorus Compounds Initiated by Single-Electron Transfer to Diazonium Salts or Acridinium Salts. Relationship between the Structure and the Reactivity of a Phosphoranyl Radical Intermediate" by S. Yasui, K. Shioji, and A. Ohno (Kyoto University).
  46. "Reaction of Cyclic Phosphorus Ylides with Conjugated Enones" by T. Fujimoto, Y. Kodama, Y. Takeuchi, K. Kai, Y. Uchiyama, K. Ohta, I. Yamamoto, and A. Kakehi (Shinshu University).
  47. "Stereoselectivities of Intermolecular Oxyselenation by Benzeneselenenyl Triflate" by H. Inoue and S. Murata (Nagoya University).
  48. "Syntheses and Stability of Selenothioic Acid S-Organyl Esters" by T. Murai, A. Hayashi, N. Nakagaki, Y. Ogino, T. Kanda, and S. Kato (Gifu University).
  49. "Syntheses and Reactions of 3H-2,1-Benzoxaselenole Selenuranes and Selenonium Salts" by T. Kataoka, Y. Kato, Y. Banno, T. Iwamura, and H. Shimizu (Gifu Pharmaceutical University).
  50. "Theoretical and Experimental Studies of Regioselectivities in Olefin Forming Reactions by Selenoxide Elimination" by N. Kondo, H. Fueno, H. Fujimoto, M. Makino, I. Aoki, and S. Uemura (Kyoto University).
  51. "Selenium-Catalyzed Reductions Suggested from Its Biological Roles" by K. Yanada (Setsunan University).
  52. "Syntheses and Reactions of Five-Membered Cyclic Trichalcogenium Compounds Containing Selenium" by R. Sato, T. Kikuchi, A. Sasaki, and S. Ogawa (Iwate University).
  53. "Synthesis, Structure, and Reactions of

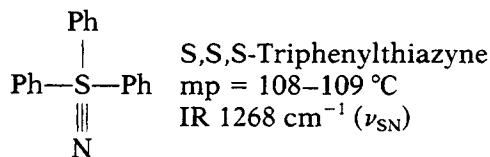
Novel Macrobicyclic Cyclophanes with Chalcogen Atom-Containing Functional Groups in the Cavity" by K. Goto, N. Tokitoh, M. Goto, and R. Okazaki (Tokyo University and National Institute of Materials and Chemical Research).

54. "Synthesis of Selenium-Containing Compounds Using Isoselenocyanates" by K. Sakata, M. Segi, and T. Nakajima (Kanazawa University).
56. "Synthesis and Stereochemistry of Optically Active Selenonium and Telluronium Compounds" by A. Matsuhisa, H. Taka, T. Shimizu, and N. Kamigata (Tokyo Metropolitan University).
57. "Synthesis and Reactions of Optically Active Haloselenuranes and Halotelluranes Bearing an Efficient Ligand, 2-exo-Hydroxy-10-bornyl Group" by N. Kurose, S. Kawanami, T. Takahashi, Y. Arai, and T. Koizumi (Toyama Medical and Pharmaceutical University).

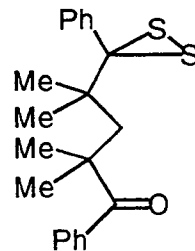
Although there were many interesting oral presentations, only a few noteworthy works can be shown here. Dr. Yoshimura's work presented an interesting result (No. 3). The unknown compound was found to be triphenylthiazine, which has a triple bond of sulfur-nitrogen linkage. This was the first example of an organic thiazine and can explain all the odd phenomena of N-halodiphenylsulfamides which were observed previously (S. Oae and N. Furukawa: ACS Monograph 179, ACS, Washington, DC, 1983).



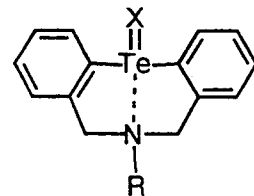
#### Unknown Compound



The first isolation of a dithiirane derivative, 3-(1,1,3,3-tetramethyl-4-oxo-4-phenylbutyl)-3-phenyldithiirane, as a stable, orange-colored crystalline compound, was presented by Prof. Nakayama's group (No. 15). X-Ray analysis supported the assigned structure.

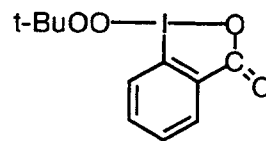


The presentation on the novel preparation and reactivities of thiotelluroxides and selenotelluroxides stabilized by transannular participation of the nitrogen atom of a tertiary amino moiety by Prof. Furukawa's group was very attractive (No. 18).

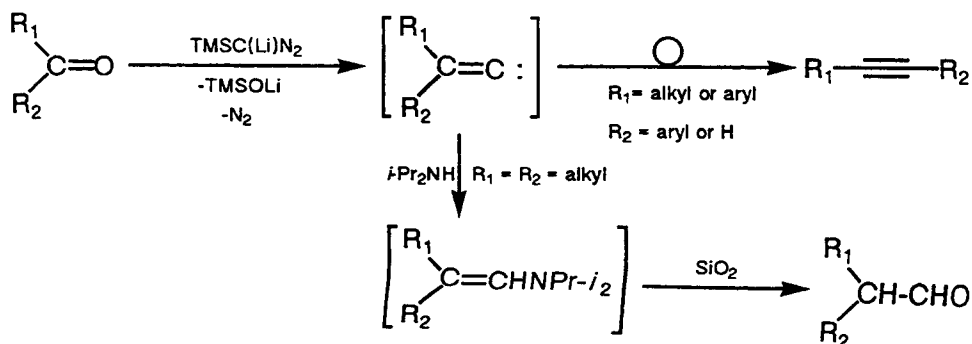


R = Me, CH<sub>2</sub>Ph  
X = S, Se

Professor Ochiai presented the novel preparation of (alkylperoxy)iodinane [1-tert-butylperoxy-1,2-benziodoxol-3(1H)-one] as a stable crystalline compound at room temperature (No. 22). This reagent could oxidize methylene groups of benzylic or allylic ethers to the corresponding esters ( $k_H/k_D = 12-14$ ). The structure was supported by X-ray analysis.



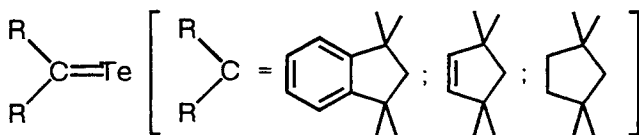
Another interesting reaction is the use of trimethylsilyldiazomethane to produce alkynes from aldehydes or ketones, presented by Prof. Shioiri's groups (No. 25).



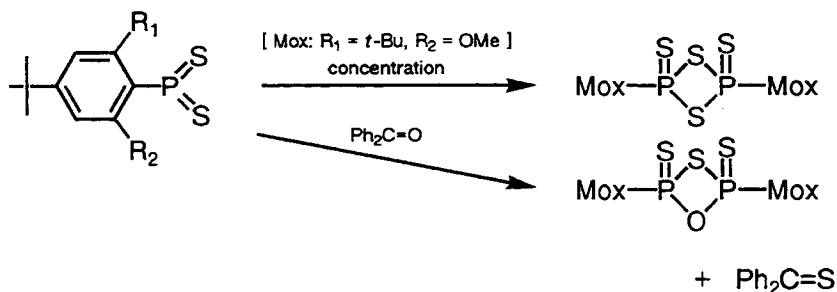
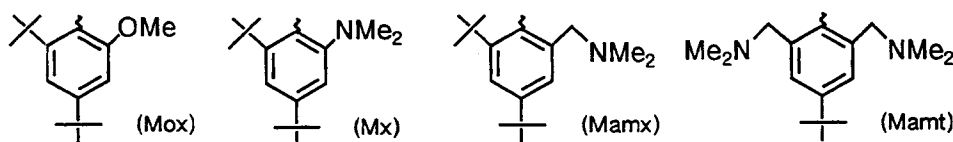
**TABLE 1**  $^{31}\text{P}$  NMR Data of Dithioxophosphoranes

Protecting Group	$R_1$	$R_2$	$\delta_P$
Ar	<i>t</i> -Bu	<i>t</i> -Bu	298.2
Ar'	<i>t</i> -Bu	Me	285.2
Mox	<i>t</i> -Bu	OMe	277.6
Mx	<i>t</i> -Bu	NMe <sub>2</sub>	170.6
Mamx	<i>t</i> -Bu	CH <sub>2</sub> NMe <sub>2</sub>	148.9
Mamt	CH <sub>2</sub> NMe <sub>2</sub>	CH <sub>2</sub> NMe <sub>2</sub>	145.3

The preparation of the first stable telluroketones presented by Prof. Okazaki's group was also significant (No. 31). There is a good correlation between UV absorption (nm) and  $^{125}\text{Te}$  ( $\delta$ ) chemical shift which is expressed by the following equation:  $^{125}\text{Te}$  ( $\delta$ ) =  $-2456 + 6.433 \lambda_{\text{max}}$  (nm).

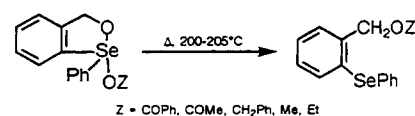
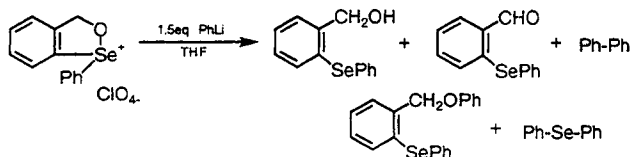


Professor Yoshifuji's group carried out many modifications of aromatic groups, and nicknamed them, as shown below (No. 44). The following conversions are novel. These workers were successful in making not only thiobenzophenone but also a type of the Lawesson reagent.



### Systematic Modification of Ar Groups

The lecture No. 49 deserves recognition, since the indicated group, together with Prof. M. Hori, was one of the earliest to claim an example of the ligand coupling reaction via a hypervalent intermediate. This group showed that the following selenuranes react with organometallic reagents in the following manner. Thus, the reaction of 3H-2,1-benzoxaselenolium salt with phenyllithium gave five products, while thermal reaction gave a selenide as a sole product, as shown below



We look forward to The 22nd Symposium of Heteroatom Chemistry to be held in January of 1995 in Nagoya and to be organized by Prof. Takeshi Toru of Nagoya Institute of Technology. We hope that many chemists from various academic institutes and industries will participate in the 22nd Symposium.