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CHEMICAL SCIENCE IN JAPAN

INTRODUCTION

A month's tour of Japan was undertaken in the early autumn of 1972 for the purpose of surveying the current status of chemical science and technology. Universities, industrial laboratories, government installations and one private research foundation were visited to exchange information and to scrutinize chemistry research in these institutions. Emphasis was placed on organic chemistry, physical organic chemistry, and polymer science, but other chemical and related fields were also appraised.

Fourteen different institutions on Honshu and Kyushu Islands were visited. One meeting sponsored by the Chemical Society of Japan was attended: the Radical Reaction Conference, held in Kyoto on 5 and 6 October. The facilities surveyed are given in chronological order in the table below with dates and the name of the individual who served as prime contact and coordinator:

<u>Date</u>	<u>Institution</u>	<u>Prime Contact</u>
September 22	Tokyo Metropolitan University	Prof. M. Kobayashi
September 25	Kyushu University	Dr. T. Kunitake
September 27,28	Hiroshima University	Prof. T. Hanafusa
September 29	Mitsubishi Rayon Company	Mr. N. Kusakawa
September 30	Osaka City University	Dr. N. Furukawa
October 2	Honny Chemicals, Kobe	Mr. H. Endo
October 3	Radiation Center of Osaka Prefecture	Dr. M. Hamada
October 5	Osaka University (at Radical Reaction Conference, Kyoto)	Prof. Y. Yukawa
October 5,6	Radical Reaction Conference, Kyoto	Dr. A. Ohno
October 6	Kyoto University	Dr. I. Tabushi
October 7	Sagami Chemical Research Center, Sagamihara	Dr. A. Ohno
October 8,9	Gumma University, Kiryu	Prof. W. Tagaki
October 11	Tokyo University	Prof. K. Tokumaru
October 13,14	Tohoku University, Sendai	Dr. T. Tezuka
October 16	Japan Atomic Energy Research Institute, Tokai	Dr. E. Tachikawa

Seminar Talks were given by the writer at two universities and one industrial research center. Lectures on "The Use of Isotopes in Studying the Mechanisms of Organic Reactions" were presented at Hiroshima and Tohoku Universities. A talk on "The Polymer Research Program of the Office of Naval Research" was offered at the Mitsubishi Rayon Company.

GENERAL REMARKS

The Western visitor cannot help but notice the tremendous growth and remarkable prosperity achieved by Japan in recent years. It is evident that the Japanese have profited by the American occupation and have emulated American business methods. The industrial scene is one of substantial growth along with astute exploitation of world markets for Japanese products. Substantial success is particularly evident in electronics and optics in which the high quality of many items have become widely recognized. The chemical industry, on the other hand, while growing at a remarkable rate, still can stand some improvement in such areas as product development and marketing research. Nevertheless progress is excellent in chemical and related fields as evidenced by the many fine products on the market. Japanese companies are often paternal although salaries and wages are not high in comparison with Western pay scales. Jobs tend to be permanent and fringe benefits such as housing allowances, life insurance, health plans, and the like are quite generous. Some companies even provide pay increases as families grow in size.

The university scene is impoverished by U. S. standards. Teaching salaries are low and research support quite meager. Nevertheless high academic standards are maintained, particularly in the former Imperial universities, and a great deal of first class research is accomplished. The resulting papers are published in Japanese journals as well as in U. S. and European periodicals. Despite thin budgets, Japanese chemists travel to meetings in their own country and the more prominent ones at least are able to participate in scientific conferences abroad. The high standards for admission to the universities result in careful selection of scholars. The quality of graduate education is high and students are truly dedicated and work very hard.

There are about thirty-five publicly-supported institutions of higher learning in Japan, including the former Imperial universities, where the better research opportunities are concentrated. Private universities are also available at which high fees must be paid by students and where attempts are made to balance the books by encouraging outside research contracts, grants and other benefactions familiar to officials of private colleges in the United States. Relatively few private universities participate in graduate education in science and engineering and most of those who do emphasize the latter discipline.

All Japanese universities that offer the doctoral degree are organized around the koza which serves as the basic unit for teaching and research. The group is headed by a full professor who has under him an assistant professor and two assistants. A limited amount of research support (usually about \$13,000 a year) is accorded each koza. Most schools that offer degrees only up to the master's level are structured like their American counterparts. Gumma University in Kiryu is perhaps an exception to this rule, for there are fourteen koza in chemistry at that institution. The professor is a very highly regarded individual, enjoying prestige similar to that of his European counterpart. Unfortunately, however, the openings for professorships are rare and the younger scientists find only very limited opportunities for promotion. The ministry of Education

doles out the funds to each professor which are too small to begin with and which frequently do not vary with the needs of the individuals or with the quality of their research.

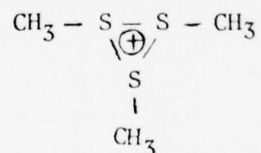
The results of visits to the various activities are presented in chronological order in the sections which follow.

TOKYO METROPOLITAN UNIVERSITY

Tokyo Metropolitan University is a new public university created after World War II from a former high school. It is a large institution with a student population of 25,000 to 30,000 and is presently outgrowing its campus within the city. Plans are under consideration to build a new plant in one of the suburbs of Tokyo. The chemistry laboratories on the present campus are old but adequate. They are well equipped with the latest Japanese-made spectrometers, gas chromatographs, centrifuges, electron microscopes, etc.

On 23 September, accompanied by Dr. Atsuyoshi Ohno of the Sagami Chemical Research Center, the Chemistry Department of Tokyo Metropolitan University was visited. Professor Michio Kobayashi and Assistant Professor Hiroshi Minato discussed their research efforts in the field of organic sulfur chemistry. The group presently includes one Ph.D. candidate and five students who are working for the M.S. degree. In addition, about eleven undergraduates are conducting senior honors programs under the guidance of these professors. A great deal of the research is concerned with cationic arylation and reactions involving aryl and aroyl sulfur compounds.

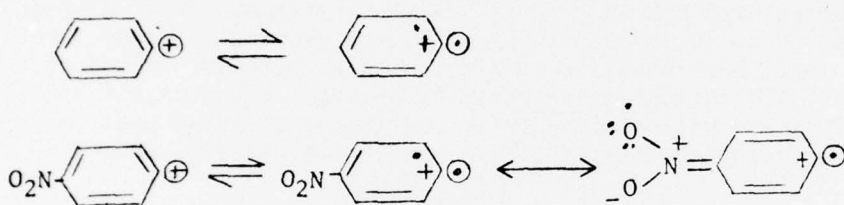
In the methylation of methyl trisulfide, $\text{CH}_3\text{-S-S-S-CH}_3$, a cationic intermediate of the form



is postulated by Minato.

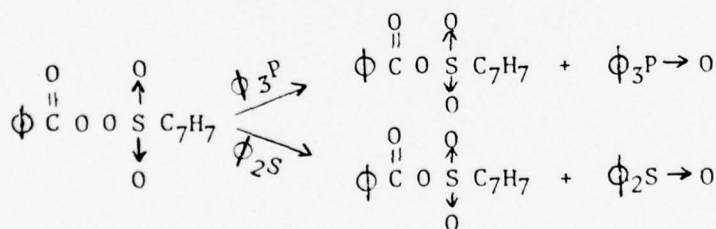
N. Kamigata, M. Kobayashi and H. Minato have investigated the catalytic arylation of substituted benzenes with p-nitrophenyl cation generated from p-nitrobenzenediazonium tetrafluoroborate in acetonitrile and from p-nitrophenylazo p¹-tolyl sulfone in the presence of trifluoroacetic acid. Benzenediazonium tetrafluoroborate produces substituted diphenyls in aprotic polar solvents when some substituted benzene is present. The partial rate factors in this phenylation are electrophilic and the reactive intermediate is believed to be the phenyl cation.

In this work, p-nitrophenyl cation was produced from p-nitrobenzenediazonium tetrafluoroborate in acetonitrile or from p-nitrophenylazo p'-tolyl sulfone and trifluoroacetic acid. A substituted benzene was mixed with the compound generating the p-nitrophenyl cation, and the isomer distributions and partial rate factors in the p-nitrophenylation were determined. The selectivity of the p-nitrophenyl cation was found to be low compared with those of nitronium or sulfonyl cation, but similar to that of phenyl cation. The explanation for this behavior is that, because of the diradical cation nature of the aryl cations, p-nitrophenyl cation is more stable and less reactive than phenyl cation



The p-nitrophenyl cation functions as a cation diradical with concerted uncoupling of a pair of π electrons, one of which goes into the vacant Sp^2 σ -orbital.

Kobayashi, Minato and Hisada studied the reactions of benzoyl p-toluenesulfonyl peroxide (BTP) with several nucleophiles. The investigations revealed that in the decomposition of this compound under various conditions, the O-O bond undergoes heterolytic cleavage, and that this is the main reaction unless some base is present to suppress autocatalysis. Reactions of BTP with triphenylphosphine and with diphenyl sulfide produced benzoyl p-toluenesulfonate

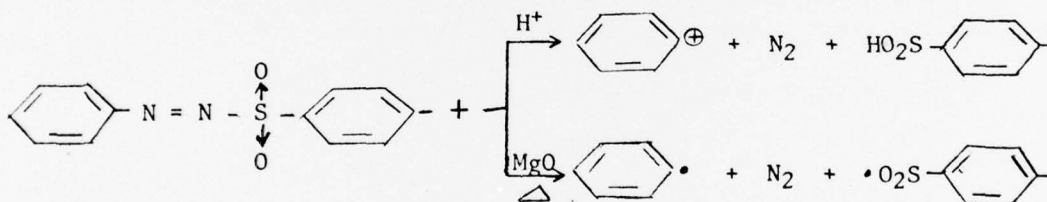


In order to study the mechanisms of these reactions, BTP was labeled at the carbonyl group with ^{18}O and the products of the reactions with Φ_3P and Φ_2S analyzed. In the reaction of benzoyl p-toluenesulfonyl peroxide with triphenylphosphine, 88% of carbonyl oxygen-18 was retained in the carbonyl oxygen of the benzoyl p-toluenesulfonate formed, while in the reaction of BTP with Φ_2S , only 58% of the ^{18}O in the starting peroxide was found in the carbonyl oxygen of the

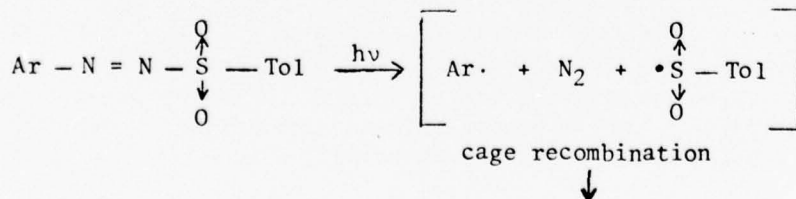
benzoyl p-toluenesulfonate formed. Reaction schemes were developed to explain these results. It should be pointed out that in the reactions of BTP with Φ_3P and Φ_2S the peroxidic oxygen attacked is the one adjacent to the benzoyl group, and not the one adjacent to the more electron-withdrawing tosyl group. The fact that both $\Phi_3P \rightarrow O$ and $\Phi_2S \rightarrow O$ contain some excess ^{18}O can be explained by assuming that either the nucleophiles attack both the carbonyl and peroxidic oxygen atoms or that the attack is entirely at the peroxidic oxygen atom, followed by some scrambling before the anhydride is formed. The first possibility is less likely because both benzoyl peroxide and m-nitrobenzenesulfonyl peroxide react with triphenylphosphine at their peroxidic oxygens.

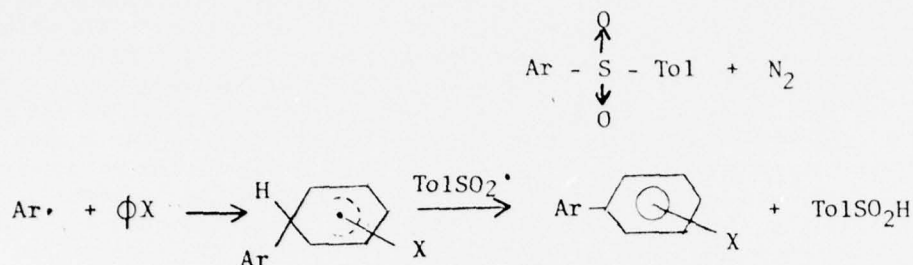
The reaction of BTP with p-tolylmagnesium bromide was also investigated and the products found were p-tolyl p-toluenesulfonate and benzoic acid. Using BTP with the sulfonyl group tagged with O-18 in this reaction, it was found that the two sulfonyl oxygens of BTP were completely retained in the two sulfonyl oxygens of the product p-tolyl p-toluenesulfonate.

M. Kobayashi, S. Fujii and H. Minato investigated the photolysis of phenylazo p-tolyl sulfones. When phenylazo p-tolyl sulfone is put in an acid medium, phenyl cation is formed (heterolysis), but when this compound is heated in a medium containing magnesium oxide, pyridine or quinoline, which captures p-toluenesulfonic acid, phenyl radical is produced



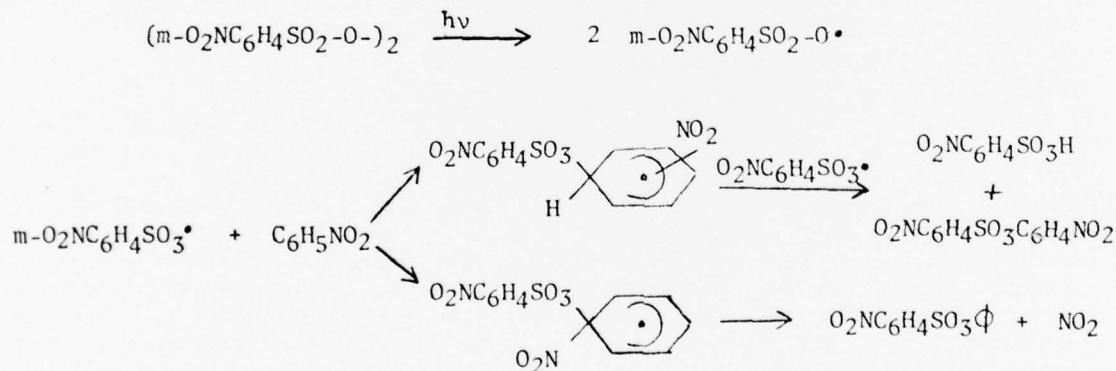
Photolysis of phenylazo p-tolyl sulfone and p-chlorophenylazo p-tolyl sulfone were carried out in aromatic solvents at room temperature. Isomer distributions and partial rate factors in phenylation were determined in anisole, ethylbenzene, chlorobenzene, benzonitrile and nitrobenzene. V-shaped Hammett plots were obtained for these phenylation reactions which indicated that the biphenyls produced originated from attack of phenyl radical on aromatic solvents. The mechanism of photolysis of phenylazo p-tolyl sulfone involves the formation of p-tolylsulfonyl radicals





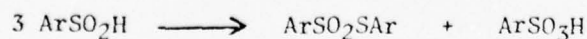
M. Kobayashi, M. Sekiguchi and H. Minato studied aromatic substitution with the arenesulfonyloxy free radical. In this research, *m*-nitrobenzenesulfonyl peroxide was photolyzed in nitrobenzene and benzonitrile, and it was found that aromatic substitution with the sulfonyloxy free radical takes place producing aryl *m*-nitrobenzenesulfonates. In nitrobenzene, thermolysis of *m*-nitrobenzenesulfonyl peroxide gave only meta-nitrophenyl sulfonate, while the photolysis produced a mixture of *o*-, *m*- and *p*- isomers. These results show that the photolytic sulfonyloxylation involves *m*-nitrobenzenesulfonyloxy free radical.

The fact that phenyl *m*-nitrobenzenesulfonate was found in the photolysis of *m*-nitrobenzenesulfonyl peroxide in nitrobenzene is explained by attack of *m*-nitrobenzenesulfonyloxy radical on nitrobenzene at the carbon atom connected with the nitro group. The reactions are as follows:



Free radical displacement of a nitro group on arenes by sulfonyloxy radicals is unique.

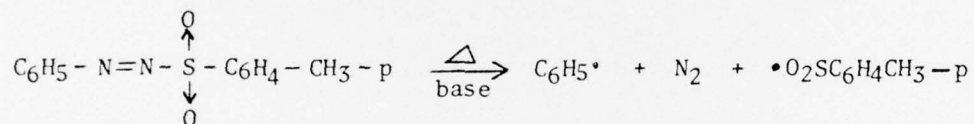
Another study done by Kobayashi's group, in collaboration with H. Minato and Y. Ogi, involves oxygen exchange of benzenesulfinic acids in water. It had been known for many years that a benzenesulfinic acid yields a thioisulfonate and a benzenesulfonic acid by disproportionation



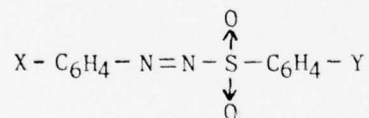
Kobayashi and co-workers found that when arenesulfinic acids were heated for several hours in water labeled with oxygen-18, the ^{18}O contents of the products (thiosulfonate and sulfonic acid) and the sulfinic acid recovered were almost the same. This result indicated that the rate of oxygen exchange is much faster than that of disproportionation. The rates of oxygen exchange of benzoic acid and benzaldehyde and those of p-toluenesulfinic acid and methyl phenyl sulfoxide were measured, and the results compared. In the carbonyl compounds, the rate of oxygen exchange was much faster than that of the acid, while in the sulfinyl compounds the rate of oxygen exchange was a great deal faster than that of the sulfoxide, which actually exchanged hardly at all even when heated at 60°C . for 23.3 hours.

Kobayashi's group determined the rates of oxygen exchange for solutions of different sulfinic acid concentrations and found that these rates were faster at the higher concentrations. Thus, any direct reaction between the sulfinic acid and water is unlikely under their experimental conditions. The mechanism they propose for the oxygen-exchange reaction involves the formation of the sulfinic anhydride (sulfinylsulfone) as an intermediate.

M. Kojima, H. Minato and M. Kobayashi conducted a kinetic study on the homolysis of aryl arylazo sulfones. Phenylazo p-tolyl sulfone undergoes homolysis in the presence of bases such as pyridine, quinoline and magnesium oxide which suppress heterolysis catalyzed by acidic products.



In the present research, substituted aryl azo sulfones of the type



were synthesized and rates of homolyses in chlorobenzene were determined in the presence of a base for suppression of acid catalysis at 80 - 118°C . The X substituents were p- $(\text{CH}_3)_2\text{N}$, p- CH_3O , p- CH_3 , p- Cl , p- NO_2 , m- CH_3O , m- CH_3 , m- NO_2 and H. The Y substituents were p- CH_3 , H, p- Cl and m- NO_2 . The rates of decomposition of these azo compounds containing electron-supplying and electron-withdrawing substituents (except p-methyl) were smaller than those of the non-substituted azo compounds.

The rates of decomposition of these azosulfones followed first-order plots in the presence of a base. Rate constants and activation parameters were obtained.

An isokinetic relationship was found to hold between ΔH^\ddagger and ΔS^\ddagger values, and β is equal to 101.0°C. This fact indicates that all the azosulfones decompose by the same mechanism. The substituents on the benzenesulfonyl group have little influence on the rates, while the substituents on the phenylazo group decrease the rates (especially the electron-supplying substituents). A linear relationship appears to hold for azosulfones containing electron-supplying substituents but not for those with electron-withdrawing substituents. These results contrast with those obtained with substituted phenylazotriphenylmethanes and aryl azo sulfides. In the latter cases, the rates of the azo compounds with electron-withdrawing substituents were especially small.

N. Kamigata, H. Minato and M. Kobayashi investigated the kinetic hydrogen isotope effect in aromatic phenylation with phenyl radical. A large isotope effect ($k_H/k_D = 6.6$) was observed in the phenylation of arenes when the phenyl radical was generated from benzoyl peroxide in very dilute solutions but no isotope effect was found in phenylations with N-nitrosoacetanilide (NNA) or phenylazotriphenylmethane. In order to try to understand the reasons for these differences, a number of deuterated arenes were phenylated with phenyl radicals produced from $\Phi N_2BF_4 - NaNO_2$, benzoyl peroxide, N-nitrosoacetanilide and azotriphenylmethane. The isotope effect was found to be quite small in the case of chlorobenzene ($k_H/k_D = 1.10 - 1.23$) but was considerably larger in the case of nitrobenzene ($k_H/k_D = 1.29 - 1.61$). It is of interest that the isotope effects are different at different positions in these arenes. Values of k_H/k_D in the phenylation of chlorobenzene and of 1,3,5-tri-t-butylbenzene are only slightly larger than unity while in the phenylation at the 2-position of m-dinitrobenzene with phenylazotriphenylmethane the hydrogen isotope effect is very large, ~ 11 . The differences in magnitude of these isotope effects is explained on the basis of resonance stabilization of the intermediate cyclohexadienyl radical in the case of m-dinitrobenzene whereas the t-butyl group has no capacity for resonance stabilization, accounting for the absence of an isotope effect in 1,3,5-tri-t-butylbenzene. The very high value of k_H/k_D for phenylation at the 2-position of m-dinitrobenzene (~ 11) is rationalized by invoking quantum mechanical tunneling or assuming that in the free-radical substitution at such an over-crowded position the activation entropy factor varies with the isotopes.

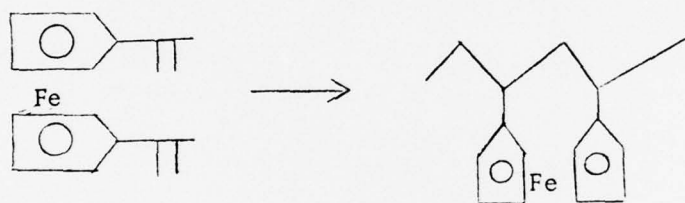
KYUSHU UNIVERSITY

Kyushu University, one of the former Imperial universities, was visited on 25 September. This well-known institution of higher learning has three campuses in the City of Fukuoka on Kyushu Island and possesses a student enrollment of about 15,000. Only one of the campuses was visited on this trip and this was the one where the Faculty of Science and the Faculty of Engineering are located. In particular, discussions were carried on in the Department of Organic Chemistry and the Applied Chemistry Department of the Faculty of Engineering. The laboratories visited were all in relatively old buildings but were well equipped with modern Japanese instrumentation.

Professor T. Matsuo and Dr. T. Kunitake described briefly the academic structure under which chemistry is taught at Kyushu University. Most of the chemistry courses are given in the Faculty of Engineering, either by the Department of Organic Synthesis or by the Department of Applied Chemistry. Chemistry is also taught by the Faculty of Science and Biochemistry is located in the Faculty of Medicine and Agriculture.

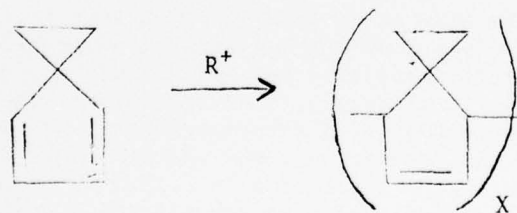
The Department of Organic Synthesis of the Faculty of Engineering is composed of six chairs: Physical Organic (Theoretical), Catalysis and Enzymes, Organic Synthesis-Olefins and Petrochemicals, Polymer Synthesis, Organic Analysis and Reaction Engineering (Chemical Engineering). Professor Matsuo is in charge of the Department of Organic Synthesis and Dr. Kunitake heads the Polymer Synthesis group within it. The Applied Chemistry Department of the same faculty is composed of the following chairs: Inorganic Chemistry and High Temperature Chemistry, Polymer Chemistry: Material Science of Polymers, Applied Physical Chemistry, Industrial Organic Chemistry, Polymer Chemistry II and Chemical Reaction Engineering.

Dr. Kunitake described in brief some of his research interests which include vinyl polymerization involving C-C and C-O bonds, cyclopolymerization to form chains, cationic polymerization and copolymerization, bioorganic polymer systems, the mechanism of catalysis, and model enzymes. In one project he investigated the cyclopolymerization of 1,1'-divinyl ferrocene to form long-chain compounds



The resulting polymers are being tested for electronic and electrical properties. Kunitake is engaged in a cooperative effort with Professor Cohen at Johns Hopkins University in the field of ferrocene polymers to try to develop materials with useful electrical properties. A simple ferrocene polymer has been made which is a semiconductor with a resistivity of $10^6 - 10^8$ ohms/cm.

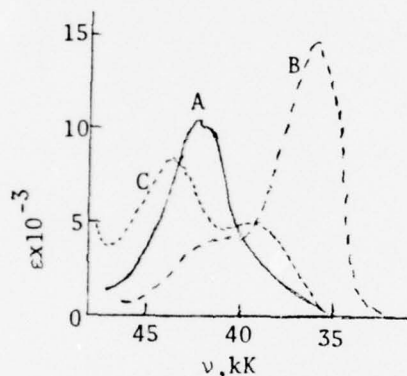
In the areas of cationic polymerization and the mechanism of catalysis, an interesting result was obtained with a spiro monomer



This polymer is very stiff and has a Tg that is probably $> 200^\circ\text{C}$.

In the area of bioorganic polymer systems, Kunitake is developing a model for hydrolytic enzymes, such as chymotrypsin. In this research attempts are being made to put functionality into a synthetic organic system. In the first stage, efforts are directed toward inserting a binding capability and later on it is hoped to be able to put in catalytic activity.

Professor Taku Matsuo described two of his research efforts. The first of these involved a study of the nature of the electronic absorption bands of formylpyrroles and acetylpyrroles. The work was undertaken because no data existed on the electronic spectra of pyrroles except for pyrrole itself. The characteristic ultraviolet absorption bands of formyl- and acetylpyrroles were studied to try to interpret the nature of these spectra relative to the electron transfer from the pyrrol to the carbonyl group. The u.v. absorption spectra of acetylpyrroles in n-hexane are shown in Figure 1. The electronic spectra of formylpyrroles closely resemble those of the corresponding acetylpyrroles



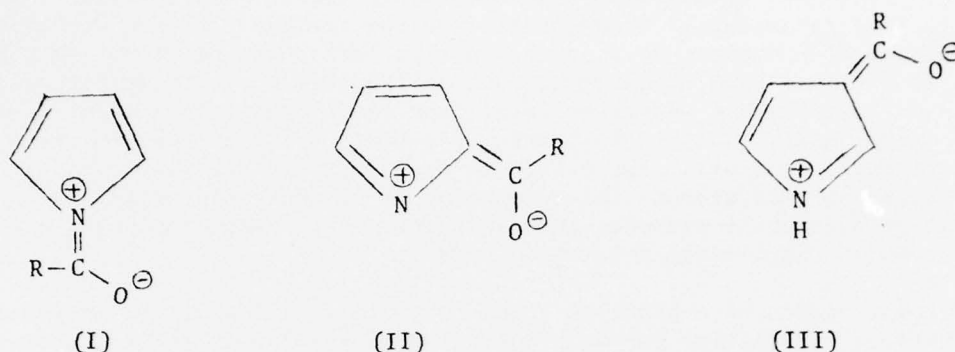
(from Bull. Chem. Soc. Japan, 45, 1349 (1972)).

Fig. 1. The ultraviolet absorption spectra of acetylpyrroles in n-hexane.

A, 1-acetylpyrrole; B, 2-acetylpyrrole;
C, 3-acetylpyrrole.

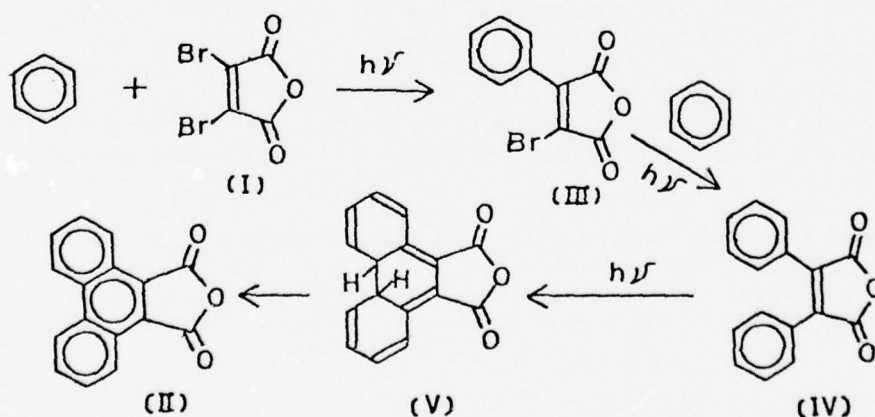
Electron transfer from the pyrrol to the carbonyl group appears to account for the lowest energy transitions of 2- and 3-acetylpyrroles and the corresponding formylpyrroles, and also the second lowest transitions of 3-acetylpyrroles. The longest wavelength absorption bands disappeared in 1-acetyl- and 1-formylpyrrole when the conjugation between the pyrrol and carbonyl groups was inhibited by steric hindrance. Solvent effects on the absorption band were so small that the extent of electron transfer was considered to change very little during the transition. NMR spectroscopic rate studies showed that the barrier to internal rotation in 1-formyl- or 1-acetylpyrrole was higher than that of the correspondingly substituted 2- and 3- isomers.

This result indicated that the ionic form (I) makes a more significant contribution to the ground state of the 1-substituted pyrroles than the ionic forms (II) and (III) to the ground states of 2- and 3- acylpyrroles, respectively



Brown and Hefferman's FESCF MO calculations were applied and supported the above results.

In the second research program, T. Matsuo, Y. Tanoue, T. Matsunaga and K. Nagatoshi investigated some photochemical reactions between dibromomaleic anhydride and benzene or its homologues. When dibromomaleic anhydride in benzene or its substituted derivatives were irradiated, α -aryl- α' -bromomaleic anhydrides were produced. Further irradiation resulted in the formation of phenanthrene-9,10-dicarboxylic anhydrides. This is the first example of a direct, photochemical transformation of maleic anhydride homologues into polycyclic aromatic hydrocarbons. The formation of the final product (II) may be described in the scheme shown below (In the first step, charge-transfer complexes were also found to participate in the reaction.)



A visit was paid to the world-renowned polymer chemist Professor M. Takayanagi at Kyushu University. Takayanagi is interested in the internal mechanical properties of polymers in terms of molecular concepts and in mechanical relaxation phenomena. He is noted for inventing the Rheovibron instrument which is used to determine transitions that occur in polymers as a function of temperature. This apparatus is complementary to the torsion pendulum device developed by Gillham of Princeton University, but the latter equipment may be used to determine transitions which occur down to liquid nitrogen temperatures, while the Rheovibron method cannot go below room conditions. Takayanagi discussed the general utility of his instrument for elucidating the mechanical properties of crystalline polymers. He cited its usefulness in studying drawing of materials, heat treatment, interpretation of viscoelastic properties, investigation of very small elements such as in a mosaic, x-ray analyses, and interpretation of complicated relaxation curves.

Takayanagi presented a paper on "Some Morphological Factors on Thermomechanical Analysis of Crystalline Polymers" before the Division of Polymer Chemistry at the New York City Meeting of the American Chemical Society in August 1972. This lecture reported some recent results with the Rheovibron which underline the importance of the structural implications of morphology and super structure of crystalline polymers on the explanation of thermomechanical analysis (TMA) data. The major areas covered comprised the relationship of mosaic structure to the relaxation mechanism of bulk crystallized linear polyethylene, the effect of tie-links connecting the neighboring lamellae of uniaxially oriented polymers on the TMA data and the properties of samples with shish-kebab structure produced by stress-induced crystallization.

Takayanagi traveled to Europe after his presentation at the New York Meeting of the American Chemical Society to give papers at two international meetings. On September 7, at the International Congress on Rheology, in Lyon, France, he lectured on "General Equation of Stress-Strain Behavior in Crystalline Polymers." In this talk, he developed his original treatment for the plastic deformation of crystalline polymers. In contrast to metals, crystalline polymers exhibit remarkable strain hardening. Unfolding of molecular chains progresses from folded structure in lamellar crystals, producing a rapid increase in deformation stress. Takayanagi found that to describe this sort of deformation process in crystalline polymers, it is necessary to employ true stress and true strain instead of nominal stress and nominal strain. The equation derived for the true stress-strain relationship was applied successfully to isotactic polypropylene, polyoxymethylene and polytetrafluoroethylene.

The second European meeting was the Battelle Colloquium on Deformation and Fracture of High Polymers at Kronberg, Germany, held on September 11-16, 1972. At this conference, Takayanagi spoke on "Plastic Deformation of Crystalline Polymers in Solid State Extrusion Through Tapered Die." Solid crystalline

polymers change their super structure during the extrusion process through a tapered die from the spherulitic structure to the fibrous form. A theoretical treatment based on the free body and upper bound approaches for the solid state extrusion of crystalline polymers was developed, taking into account their remarkable strain hardening properties. The strain hardening process in uniaxial extension was formulated in a general way. Comparisons of calculations using this theory were found to compare well with observed extrusion pressures as a function of die for several polymers.

Takayanagi has been working for a number of years on plastic deformation of crystalline polymers. The materials studied were first melted on a hot plate and then quenched in cold water. Tensile testing was carried out on the solid materials after quenching. Efforts were made to analyze this process in order to understand the differences in molecular deformation between metals and crystalline polymers. Uniaxial extension was employed to interpret solid-state extrusion. The crystalline polymers exhibit anisotropy and show remarkable strength hardening. Takayanagi found that he could not use nominal stress (σ) and nominal strain (s) in this work for the plasticity or large deformation of polymers required the use of true tensile stress (σ) and true tensile strain (ϵ) to interpret the deformation mechanisms. Composite stress-strain curves are expressed by the following equation:

$$\log \left(\frac{\sigma}{\sigma^*} \right) \cdot \log \left(\frac{\epsilon}{\epsilon^*} \right) = -c$$

true stress true strain

c is a constant that is characteristic of polymer species only; it is chemical in nature.

In addition to the above contacts, the writer also met with Professors Keihei Ueno and Yukito Murakami of the Department of Organic Synthesis of the Faculty of Engineering. Both of these scientists work in the area of organometallic compounds and metal ion chelation. Along with T. Matsuo, these professors obtained their doctorates at Clark University when Dr. Arthur E. Martell, now at Texas A&M University, was there.

Murakami outlined some of his recent research efforts on organic phosphates and transition metal complexes of pyrrole pigments. The work was undertaken in order to learn more about the structural properties of metalloporphyrins and related compounds of biological significance with regard to the nature of the coordinate bonds involved. In order to accomplish these objectives, transition-metal complexes of a variety of pyrrole pigments were investigated by means of spectral and magnetic measurements. In particular, cobalt (II) and nickel (II) complexes of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac and cobalt (II), nickel (II) and copper (II) complexes of certain dipyrromethenes were synthesized and examined by near ultraviolet, visible, near infrared, nmr, electron spin resonance, vapor pressure osmometry and mass spectroscopy.

The ligand field bands for these metal complexes provided information on their geometry around the central metal atoms. The copper complexes of the dipyrromethenes assume the tetragonally distorted tetrahedral configuration. The nickel and copper complexes of the dipyrromethenes are nearly regular tetrahedral. The cobalt complex of 1,19-dideoxy-8,12-dicarbethoxy-1,3,7,13,17,19-hexamethylbiladiene-ac is approximately tetrahedral but the nickel atom is subjected to the square-planar ligand field in the analogous complex. Additionally, the cobalt complex is dimeric while the nickel complex is monomeric with a ligand to metal ratio of 1:1. The six copper (II)-dipyrromethene complexes were studied by esr spectroscopy to obtain information on the behavior of d electrons under the ligand field of D_2 symmetry. A correlation was found that provides evidence for the increase of orbital excitation energies with the distortion from tetrahedron toward square planarity in coordination geometry. Some additional investigations employing electronic and vibrational spectroscopy were conducted on the cobalt (II), nickel (II) and copper (II) complexes of substituted dipyrromethenes in order to obtain more information on their molecular structures. The energy level diagrams for metal d electrons were evaluated in terms of a point-charge ligand field model but a satisfactory analysis of the ligand-field bands was not obtained. Some information on the nature of the coordinate bond in these complexes was inferred from the skeletal stretching mode of the pyrrole rings in the 1600 cm^{-1} range.

Murakami also conducts research on organic phosphates. In a typical investigation, Y. Murakami, J. Sunamoto and H. Ishizu studied participation of neighboring groups and effects of metal ions on the hydrolysis of 3-hydroxy-2-pyridylmethyl phosphate. The results were compared with earlier work on pyridylmethyl and 8-quinolyl phosphates in order to determine which neighboring group, the 1-pyridinium or the 3-hydroxy group, provided the major contribution to intramolecular catalysis in the hydrolysis. The reactive species in hydrolysis were found to be neutral zwitterion, monoanion and dianion species in order of increasing reactivity. This trend in reactivity was not observed in earlier work with compounds not containing the hydroxyl group. Activation parameters indicated a unimolecular transition state for spontaneous hydrolysis and pointed to the A1 mechanism for the acid catalyzed reaction. It is believed that the anomalously high reactivity of the dianion species is due to participation of the 3-hydroxy group in the reaction process. The process probably involves intramolecular transfer of the hydroxyl proton to the ester oxygen in a pre-equilibrium stage, followed by P-O bond cleavage in the subsequent transition state to give the products. Introduction of the 3-hydroxyl group into 2-pyridylmethyl phosphate altered the catalytic activity of various metal ions. Only iron III and thorium IV ions increased the rate significantly.

HIROSHIMA UNIVERSITY

Hiroshima University was visited on 27 and 28 September. The major discussions here were with Professor T. Hanafusa and Dr. T. Suzuki of the Chemistry Department. Both of these scientists are organic chemists with interests in synthesis, structure and properties of organic compounds as well as the mechanisms of organic chemical reactions. Hanafusa has done work with active nitrogen and spent a year in Professor Norman Lichtin's laboratory at Boston University. Suzuki received his doctoral degree at Kyoto University and only recently moved to Hiroshima.

Hanafusa and Lichtin have collaborated on research in the area of reactions of active nitrogen with organic substrates. Some work done with isoprene a few years ago demonstrated the complexity of this type of reaction. The paper was published in the Canadian Journal of Chemistry, 44, 1966 p. 1230.

The writer gave a seminar talk before the Chemistry Department on September 28 on "The Use of Isotopes in Studying the Mechanisms of Organic Reactions." A representative of the Mitsubishi Rayon Company was in attendance.

MITSUBISHI RAYON COMPANY

On 29 September a visit was paid to the Mitsubishi Rayon Company in Otake, Japan, in company with Dr. T. Suzuki of Hiroshima University. Otake is in Hiroshima Prefecture and is a 40-minute train ride from the city. The Otake Plant manufactures Vonnell acrylic fiber, methyl methacrylate resin, Shinko rayon staple, Hipolan high performance rayon and acrylonitrile. The Central Research Laboratories are also located in Otake where research and development projects related to the Company's product lines are conducted.

Dr. Fumio Fujikura, the General Manager of the Central Research Laboratories, described briefly the programs of his facility. In addition to product-related R&D, there is a sizable basic research group in polymer science that is looking for new polymers with fiber forming properties. The three major fields of effort in the Laboratories are:

- (1) Carbon fibers
- (2) Woven fabrics from viscose fiber
- (3) Synthetic paper (they have a working arrangement with Hercules)

Other research is done on organic polymers, organic polyamides and polyesters, high-temperature polymers; and hollow fibers, especially for use in artificial kidneys. The staff of the Central Research Laboratories consists of about 520 people, of whom 120 are university graduates with 30 of the latter possessing doctor's degrees. The laboratories and pilot plants are most impressive.

The work areas are kept very clean and orderly. There is no ^{lack} ~~wanting~~ of necessary instrumentation and the facility abounds with a great variety of the latest Japanese spectrometers, chromatographs, electron microscopes, and other types of measuring equipment.

Mitsubishi Rayon is one of the largest manufacturers of acrylic fiber in the world. The uses of this fiber, which is marketed under the trade name VONNEL, include jerseys, underwear, casual wear, sweaters, home furnishings, blankets, comforters, hand knit yarns and socks. The company also produces SILPALON acrylic filament which is used in high grade knitted outerwear.

Shinko Ester Co., Ltd., a wholly owned subsidiary of Mitsubishi Rayon manufactures SOLUNA polyester filament which is used in knitted products and woven fabrics. Polypropylene staple and filament both are produced for a variety of domestic and industrial applications. Rayon, acetate and nylon 6.6 are manufactured by Mitsubishi Rayon. The nylon 6.6 is produced by a joint venture of the Monsanto Company of the U.S.A., Mitsubishi Rayon and Wako Spinning.

Mitsubishi Rayon is a major manufacturer of plastics. The company is one of the largest producers in the world of methyl methacrylate resin which is distributed under the trade names of ACRYESTER for monomer, ACRYPET for injection molding pellet, ACRYCON for compression molding powder, and SHINKOLITE for cast sheet. In addition, SHINKOLAC ABS resin is used in parts of electric appliances, automobile bodies, boats, containers and furniture. Mitsubishi Rayon manufactures DURACRON thermosetting paint resins and METHALICA thermoplastic paint resins for a licensing agreement with PPG Industries, Inc. of the U.S.A. Acrylic ester and acrylic blend resins are also made by Mitsubishi Rayon.

Other products of Mitsubishi Rayon include synthetic paper, polypropylene film, acrylonitrile chemicals, chemical fertilizers, low density polyethylene and a silicone surfactant. The May 1972 annual report of Mitsubishi Rayon indicated that the total sales, world wide, of the company's textile products amounted to more than two hundred million dollars. Other products swelled the overall total sales to about \$240,000,000. Small but substantial decreases in both sales and profits were noted from the previous year, a development which management attributed mostly to the adverse effect of the new economic policy of the United States Government.

OSAKA CITY UNIVERSITY

On Saturday, 30 September, a meeting was held with Professor Naomichi Furukawa of Osaka City University, who is a physical organic chemist, at the Plaza Hotel in Osaka. The main subject of the discussion was the current situation at this municipal institution which has been torn for some time by both student

and faculty dissension. There have been many protests and serious riots and the faculty is reported to be split into two opposing factions. Not all of the problems involved are related to world peace and the war in Southeast Asia, for there is evidently strong feeling on the part of some students that curriculum reform to provide courses of a more pragmatic nature must be implemented. Indeed, Furukawa had to leave shortly after lunch in order to return to the university for a faculty meeting which had been called to discuss proposed curriculum changes.

A plan to visit Professor Shigeru Oae, a world-renowned organic chemist who has made many significant contributions to the field of sulfur compounds, was not consummated. It was learned that Oae had been suspended from teaching and research by the Osaka City University administration as a result of a controversy with a radical student faction, and could not be seen there. An opportunity to meet with Oae would be provided at the Radical Reaction Conference in Kyoto on 5 and 6 October where he was scheduled to give a plenary lecture. Unfortunately Oae cancelled his plans to attend this meeting at the last minute, and it turned out that it was not possible to meet with him at all on this trip.

HONNY CHEMICALS, LIMITED

On October 2 a visit was paid to the Head Office of Honny Chemicals in Kobe and to the Akashi plant and laboratory. Mr. Hiroshi Endo, Manager of the Research and Development Division, acted as guide and interpreter. At the Head Office in Kobe, Mr. Shoji Yoshida, the President of Honny Chemicals, and Mr. Kunita Kondo, his assistant, were met for a brief general discussion. Mr. Yoshida has built up a very competent operation in a rather short time and is regarded as a brilliant industrial manager. He does not speak English but his assistant, Mr. Kunita, makes up for this deficiency, being very fluent in the language. Indeed he supplied the basic information on the company's operations during this interview.

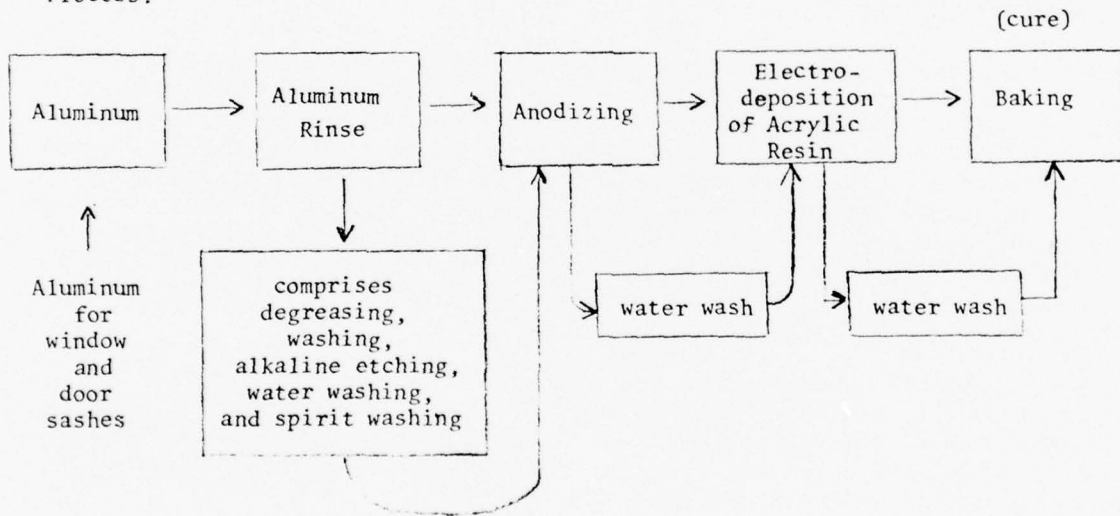
Honny Chemicals produces plastics and coatings and is especially noted for the Honnylite Process which deposits acrylic resin coatings (both clear and colored) on metals, textiles and other materials. The company is also interested in smoke generation and flame retardants and is engaged in research on inorganic-organic polymers and block copolymers.

After a brief general discussion at the Head Office, Mr. Endo accompanied the writer on a visit to the Akashi plant and laboratory. There the Honnylite plant which is fully automated and controlled by a computer was seen. The particular product in process was the treatment of aluminum door and window sash in which the aluminum frames are cleaned, etched, rinsed, anodized, electroplated with the acrylic resin, baked and finally cured to produce a strong, adherent protective coating. The laboratory actually consists of two sections,

Laboratory No. 1 and Laboratory No. 2 which divide the research and development responsibilities. Mr. Endo is General Manager of Laboratory No. 1 and Dr. John M. Witzel, formerly of the General Electric Company Chemicals Division in the U.S.A. and who took early retirement in order to go to Japan, is presently General Manager of Laboratory No. 2. Another American, Dr. Gordon M. Parker, is a section manager under Dr. Witzel. Both men are under one, two or three year renewable agreements at their discretion or that of the company. As an interesting sidelight, Dr. Parker came to Japan originally on an NSF fellowship at Kyoto University, has a Japanese wife and speaks the language quite fluently. The two Americans speak very highly of President Yoshida's management acumen. They concur that science in the Japanese chemical industry is very good, but that technology and product development can still stand some improvement.

The Honnylite Process provides an excellent example of an automated chemical plant. The process was developed at Honny Chemicals and is patented in Japan and several foreign countries including the U.S.A., Australia and West Germany. The procedure is clean, fast, efficient and economical. The entire process is operated by automatic control from a console installed in the laboratory. Messrs. Agu and Ono are in charge of the plant.

The diagram below summarizes the various steps involved in the Honnylite Process.



The spirit wash removes an impurity which is produced by etching.

The product after baking is a smooth, tightly adhering acrylic coating that can be either clear or in color, such as gold. The resulting window and door sash have stood up very well under Japanese climatic conditions for months and years.

Dr. John M. Witzel, General Manager of Laboratory No. 2, described the research and development efforts of his group. The overall program is concerned with three major areas:

- (1) Coatings - metals, textiles, other materials.
- (2) Smoke generation and flame retardants.
- (3) Polymers - includes particularly block copolymers and inorganic-organic polymers.

The polymer research is aimed at novel types of polymers such as new linear thermoplastics containing crystalline and non-crystalline units. There is interest in flame retarding polymers and pollution problems related to polymers. Basically, all polymer efforts are pointed to the objective of producing new and improved coatings. Some work is being done in connection with composites, too. One major project in the polymer field is underway under the direction of Dr. Gordon Parker, who studied with Professor Furukawa at Kyoto University and obtained his Ph.D. from that institution. This project requires a great deal of exploratory work with no market information currently available. It is illustrative of the challenge that Honny Chemicals must meet in order to become competitive with other chemical industries in Japan and abroad.

RADIATION CENTER OF OSAKA PREFECTURE

A visit was paid to the Radiation Center of Osaka Prefecture at Sakai on 3 October. The political divisions of Japan (46), somewhat similar to U. S. States, are called prefectures and one of these is named Osaka, not to be confused with Osaka City which is situated within its geographic limits.

The Radiation Center was constructed during the period 1958-1961 under support of the Osaka Prefectural Government. The buildings are functional in design and are well equipped for work in nuclear chemistry, physics, biology, and medicine. At the present time this center is the largest facility in Western Japan for utilization of isotopes and radiation in chemistry, physics, agriculture, the food industries, medical science, and hygiene. The center employs about 125 people under the directorship of Dr. Osamu Toyama. There are six departments in the organization: the Office of Administration; Health, Physics and Instrumentation; Physics; Chemistry; Applied Biology; and Medicine and Hygiene. The laboratories are spacious and well equipped with the necessary instrumentation. There are a library, meeting rooms, study rooms, and a good sized auditorium. The facility is equipped with hot caves for a linear

accelerator (17 Mev) and cobalt-60 sources where irradiations are performed for sterilization, improvement of plant species, radiography, and chemical reactions.

The Department of Chemistry is comprised of twenty-four persons. Dr. Jitsuo Tsurugi is the Chairman and he led the discussions. Also met were Drs. M. Hamada, R. Kiritani, and T. Fukumoto. The program of this department involves research on chemical effects in nuclear transformations, pulse radiolysis, isotope analysis, ion-molecule reactions in radiation chemistry, radioassay of organic compounds, reaction mechanisms by isotopic tracers, radiation effects and improvement of high polymers, radiation-induced telemerization and isotope labeling of organic compounds. The Polymer Laboratory is engaged in synthesis and testing of ion exchange membranes, especially those required for desalination and for elimination of ions causing water pollution. Some work is being done on a vinyl phosphate-styrene copolymer and the results are promising to date.

M. Hamada and E. Kawano studied tritium labeling of hexachlorocyclohexane isomers by the gas exposure method. The work was concerned with an extension of the well-known technique of isotopically labeling organic compounds by exposure to tritium gas. α -, β -, γ -, and δ -isomers of 1,2,3,4,5,6-hexachlorocyclohexane were selected for this investigation because both some stereochemical preference in the substitution by tritium and considerable stereochemical inversion at each carbon atom could be anticipated during tritiation. The results indicated that the α -isomer is stereochemically stable and there are few opportunities to lead to the inversion of configuration during tritiation. A close correlation exists between the intramolecular distribution of the activity in the parent compound and the yield of tritiated isomers obtained by inversion.

A second study was undertaken to investigate the specific labeling of a certain hexachlorocyclohexane by the tritiation of its steric isomer and to isolate the tritiated pentachlorohexane from the tritiated product of a hexachlorocyclohexane. The results obtained after tritiating appropriate hexachlorocyclohexane isomers showed that in general a specifically labeled isomer could be separated from the tritiated product of the isomer in which steric conformation around one carbon atom is different from that of the other, and that such a labeled isomer is rather easily produced by the tritiation of a sterically less stable one.

Hamada and M. Chubachi investigated the preparation of tritium-labeled compounds by hydroboration procedures. The technique employed involved an application of the hydroboration reaction developed by H. C. Brown of the U.S.A. The use of hydroboration rendered it possible to conveniently label olefinic compounds with tritium, a process that was very difficult to carry out by conventional labeling procedures. In this research, several olefinic compounds were tagged with diborane-t generated from tritiated sodium borohydride, followed by displacement to the corresponding tritiated olefin by

treatment with 1-decene. Oxidative degradation of the purified compounds was employed to obtain the intramolecular distributions of tritium in each case. Cyclohexene, styrene, anethole, safrole and isosafrole were chosen for this study.

The results showed in general that over 80% of the tritium was incorporated in double-bond positions of the carbon chain. Nearly 90% of tritium introduced into anethole, safrole and isosafrole was found in these positions. The data obtained from several compounds showed that the minor hydrogenated position between double-bonded carbons is more labeled with tritium than any other position and is thus consistent with the anti-Markownikoff's rule established by H. C. Brown and co-workers for the hydroboration reaction.

Hamada and Chubachi also conducted some research on the origin of the carbons of the dihydrofuran ring and C-6 in the biosynthesis of rotenone. Experimentally, acetate-2-¹⁴C, mevalonic acid-2-¹⁴C lactone and methionine-methyl-¹⁴C were injected by use of a cotton wick inserted, respectively, into the stem of *Derris elliptica* plants growing in soil. The distribution of carbon-14 in the labeled rotenone was determined after 8-15 days by degradation procedures. When mevalonic acid-2-¹⁴C lactone was incorporated into rotenone, equal activity was observed at C-7' and C-8', indicating that these carbons are derived from the 2C of mevalonic lactone. When methionine-methyl-¹⁴C was administered, about 80% of the total radioactivity entered the two methoxyl groups, demonstrating that methionine is an efficient precursor of the methoxyl group. It is also suggested that methionine may be a precursor of the carbon at C-6.

In a related study, Hamada and Chubachi investigated photo-oxidative ring contraction of dehydrorotenone to coumarono-chromone. The results proved that dehydrorotenone is photochemically oxidized to chromemo-chromone which is subsequently converted to coumaro-chromone by a ring contraction.

A practical use for tritium labeling resulted from a project at the Radiation Center of Osaka Prefecture to find a way of evaluating different lubrication procedures for a two-cycle gasoline engine. The study was carried out by introducing tritium-labeled oil continuously (or instantaneously) during steady running of the engine by three different lubricant supply methods (mixed, crankcase and manifold). After stopping the engine, it was disassembled to seven groups of engine parts. Every part was washed thoroughly with commercial first grade toluene to collect the remaining labeled oil. Aliquots of the solution in each group were diluted with scintillation solution and radioassayed, from which the amount of lubricating oil remaining in each part of the engine was determined. The performances of the three methods of lubrication were then compared.

The results indicated that even with steady state running of the engine, the crankcase method tends to provide non-uniform oil distribution between two

cylinders. The three methods investigated seem to have similar lubricating performances with regard to oil distribution in bearing parts with one or two exceptions. The total amount of oil remaining in the running engine is approximately the same for all three cases. The total amount of oil in the crankpin part is larger in the crankshaft method than in the other two. The reverse is experienced for the pistonpin part.

M. Hamada and R. Kiritani conducted a study of tritium labeling of aromatic compounds in acidic media and the intramolecular distributions of radio-activities in the tritiated compounds. In this research the acid-catalyzed hydrogen exchange reactions of a number of organic compounds were investigated in detail. The tritiated phosphoric acid-boron trifluoride complex ($\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$) and several other tritiated acids were employed as the tritiating agents. A practical degradation scheme was utilized to determine the intramolecular distributions of tritium in some of the labeled compounds.

In order to study the effect of the acidity of tritiating agents on tritium incorporation, several such reagents were mixed with cyclohexane, benzene or naphthalene dissolved in cyclohexane and each mixture was stirred at room temperature for periods up to 20 hours. The specific activities of the separated and purified compounds were obtained by liquid scintillation counting. It was found that cyclohexane was not labeled with tritium in an acidic medium in contrast to benzene and naphthalene in which some tritium incorporation occurred. Therefore, cyclohexane proved to be a useful solvent for the tritium labeling experiments. The best tritiating agent was found to be $\text{TH}_2\text{PO}_4 \cdot \text{BF}_3$ complex. Except for aliphatic or alicyclic compounds, high acidity of tritiating reagent and prolonged reaction time provide the best exchange. The detailed results showed that the order of tritiation of the compounds is the same as that of electrophilic substitution reactions of aromatic compounds.

J. Tsurugi, S. Murakami and K. Goda performed some research on the charge transfer complexing mechanisms of antioxidants. In this work they studied the fate of aromatic amines during thermal oxidation of natural rubber vulcanizates. The results obtained could be interpreted quite well by assuming the intermediate formation of a complex of rubber peroxy radical with the amine followed by slower decomposition of the intermediate. The fate of the amine was discovered by extracting oxidized vulcanizates containing the amine with acetone and then with dilute HCl-ethanol mixture, followed by analysis for the free amine or Kjeldahl nitrogen contents of each of the extracted vulcanizates. The intermediate complex is quite stable to acetone extraction but releases a Würster cation by hydrochloric acid-ethyl alcohol extraction.

Other research projects in the field of organic chemistry at the Radiation Center of Osaka Prefecture included: "Effect of Oxygen on Intensity Exponents of Radiation-Induced Polymerization Rates," "Radiation-Induced cis-trans Isomerization of Polyisoprenes and Temperature Dependence of the Equilibria,"

" γ -Induced Addition of Trichlorosilane to Vinyl Acetate," "A Novel γ -Induced Reduction with Trichlorosilane," "Dialkyl Ether from Alkyl Aliphatic Carboxylate," "A Novel Method for the Preparation of Thiosulfonates," "Synthesis and Decomposition of Alkane- and Arenesulfonyl Aryl Disulfides," "A Tracer Study on the Leaf Alcohol Reaction," " γ -Induced Addition of Trialkyltin Hydrides to Unsaturated Esters," several studies on reductions with trichlorosilane and a long series of investigations on the reactions of aralkyl hydrosulfides with various compounds.

RADICAL REACTION CONFERENCE, KYOTO

The Radical Reaction Conference, sponsored by the Chemical Society of Japan, was convened on October 5 and 6 at the Kyoto University Educational Center. The papers presented at this meeting were in the area of free radical reactions, primarily in the biochemical field. The researches described dealt with proteins and enzymes and the use of model enzyme systems to try to understand better various processes in physiological chemistry. All papers at the conference were given in Japanese and, therefore, the opportunity was taken for informal discussions with Japanese chemists. Most of the second day (6 October) was spent at the Kyoto University Chemistry Department in another part of the city. As mentioned in an earlier section of this report, Professor Shigeru Oae of Osaka City University cancelled his plenary lecture at the Radical Reaction Conference, and it was not possible to see him regarding his research programs.

On the evening of 5 October, immediately after the last paper, a social hour and dinner was arranged at the Educational Center to which the writer was invited. This was a very pleasant affair and provided further opportunities for discussions with Japanese colleagues. In particular, a lengthy conversation was carried on with Professor Y. Yukawa of Osaka University, who is a world-famous physical organic chemist. Yukawa does research on the mechanism of organic reactions and he has made considerable use of various isotopes as tracers. He is also interested in the synthesis of natural products and in a variety of other areas of organic chemistry.

KYOTO UNIVERSITY

A visit was paid to the Chemistry Department of Kyoto University on 6 October. Kyoto University is a former Imperial University and is noted for its high scholastic standards. As a Japanese institution of higher learning, it rates very high on the academic list, just behind Tokyo University which is generally regarded as number one. Kyoto University is comprised of nine faculties, the College of Liberal Arts and the Postgraduate School. Each Faculty is divided into departments and a variety of majors for each research division in the Postgraduate School. The University maintains thirteen research institutes for specific disciplines. The school is spread over nine campuses

and other sites in Kyoto, and in addition, there are School Farms, Forests, and other special facilities outside of the main University area. The student population is in excess of 15,000 and the Graduate School is excellent, being able to attract many foreign scholars.

The Chemistry Department was visited on 6 October under the guidance of Dr. Iwao Tabushi. The Chemistry Department is actually more than one institution and is spread over a number of faculties, depending on the nature of the subfields emphasized. In the Faculty of Engineering, Chemistry is subdivided into the following departments:

- (1) Synthetic Chemistry
- (2) Industrial Chemistry
- (3) Polymer Chemistry
- (4) Hydrocarbon Chemistry
- (5) Chemical Engineering

The Department of Chemistry which represents the basic discipline itself is in the Faculty of Science. Additional chemistry departments include Pharmaceutical Chemistry which is located in the Faculty of Pharmacy, Agricultural Chemistry which is a division of the Faculty of Agriculture, and Medical Chemistry which is part of the Medical School. There is also a Chemical Research Institute situated in Uji City.

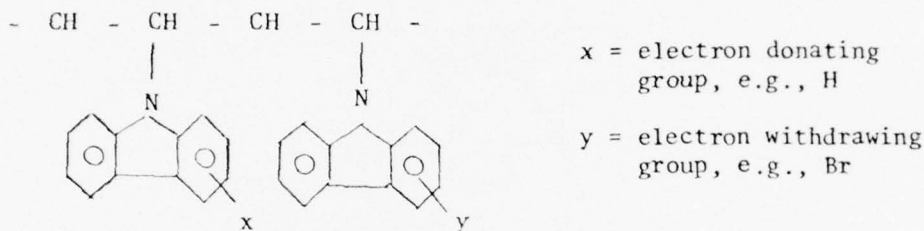
The bulk of the day at Kyoto University was spent in the Department of Synthetic Chemistry of the Faculty of Engineering in discussions with Professor Zen-ichi Yoshida, Assistant Professor Iwao Tabushi, and their assistants. Professor Yoshida is the Head of the Koza (research group supported as a unit) and is the author of over 130 papers on synthetic organic chemistry. The fields he has studied are diverse and include new aromatic systems, intra- and intermolecular interactions, organic photochemistry, organic fluorescent systems, and structure-reactivity relationships. The group is currently working on semiconducting polymers with hydrocarbon backbones to which substituents with potentially mobile electrons are appended such as polyvinyl carbazones and carbonium ions. These may have applications in coatings for photographic film and in photocopying.

Dr. Tabushi is working in the field of synthetic enzymes and is trying to construct a model enzyme system with activity comparable to the natural species. One system involving the incorporation of imidazole rings onto a large organic molecule has resulted in an activity within one to two orders of magnitude of chymotrypsin, a very good preliminary result. Tabushi is also trying to make peptides selectively by synthetic means in a kind of competition with biochemistry.

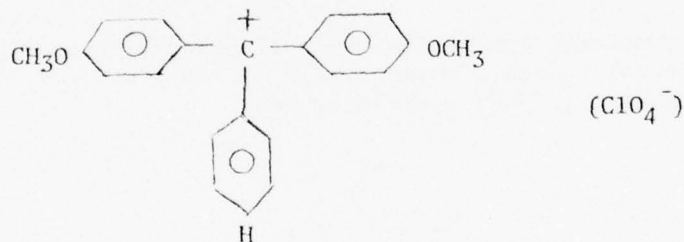
Professor Yoshida was much too busy on the day of the visit for even a cursory discussion of his research interests. However, his more than 130 papers in

the field of synthetic organic chemistry include contributions on a new aromatic system, intra- and intermolecular interactions, organic photochemistry, organic fluorescent systems and structure-reactivity relationships. Individual research subjects range over a wide area of chemical topics, including intermolecular hydrogen bonding involving a π base as the proton acceptor, reactions of metal (III) chelates with sulfur and mercury compounds, reactions of organic boron compounds, charge transfer complexes of 5-membered heteroaromatics, SCF MO calculations of heterocyclic systems, the ortho effect, metalloporphyrins and porphyrin complexes and electronic spectra and structures of organic π systems.

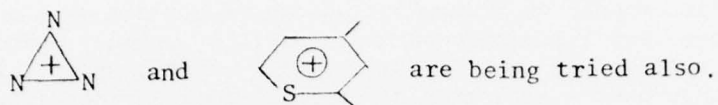
Yoshida's group is currently working on semiconducting polymers with hydrocarbon backbones to which substituents such as polyvinyl carbazones are appended



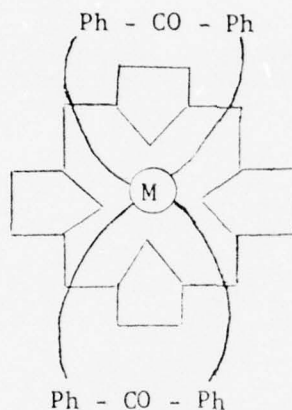
At the present time carbonium ions are being inserted



This is mixed in and the resulting polymer provides a photosensitive coating which can be spread on paper like xerox (similar principle) and used in photographic film in place of AgBr. Matsushita Electric is producing this material and it is now on the market; Yoshida is serving as a consultant. Ricoh, Ltd. is a licensee for the process. In the research, carbonium ions such as

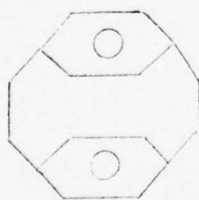


The group is also working on metal complexes of phthalocyanines and porphyrins, e.g.

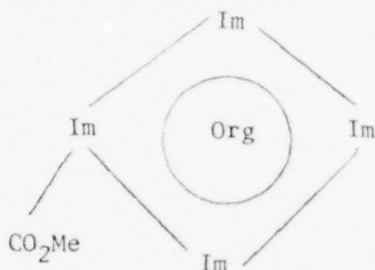


The effort is being coordinated with a research project conducted by Professor Minoru Tsutsui at Texas A&M University and is contributing to a program on synthetic blood.

Tabushi's work on synthetic enzymes is aimed at building a model with the same activity as the natural product; chymotrypsin is being used as the standard. One approach starts with [2 · 2]-paracyclophane



The objective here is to make higher aromatic compounds. In another task, imidazole rings are attached to a large organic nucleus



After synthesis, the hydrolysis of the ester was compared with chymotrypsin as a measure of activity. Tabushi's activity was in the order of $10^4 - 10^5$ as compared with chymotrypsin at 10^6 ; a very good result. Both high selectivity and activity are being sought in the enzyme model syntheses. One suggested application for the synthetic enzymes is in reducing air pollution in which CO_2 would be converted to sugars + oxygen.

SAGAMI CHEMICAL RESEARCH CENTER

The Sagami Chemical Research Center in Sagami-hara was visited on 6 and 7 October. This institute is a unique private research foundation that is devoted primarily to basic research in chemistry. It is supported largely by the Industrial Bank of Japan, with additional contributions by twenty-six Japanese chemical companies. The Center strives to provide basic research related to the needs of various enterprises which may advance existing industrial processes or lead eventually to the development of an entirely new type of industry. Active contact between the Center's research staff and that of the contributing companies is encouraged. Scientific reports of research accomplishments are made public through the respective academic societies. The Center's brochure, in its opening statement, summarizes the far-sighted objectives of the founders: "Sagami Chemical Research Center represents the realization of an ambitious dream of far-sighted businessmen of Japan, men who are not only seeking immediate, practical results, but who are willing to contribute part of their profits toward the future progress and prosperity not only of their own industry but also of other industries in this country."

This research institute is located in a beautiful wooded area in Sagami-hara near one of the best golf courses in Japan. A main three-story building houses the offices, library, lecture hall, cafeteria, and other general facilities. The laboratories are situated in two adjacent two-story buildings.

All three buildings are spacious and well lighted; the total floor space is 91,500 square feet. A dormitory for bachelor researchers with an annex for guests is provided on the 26.5 acre grounds, as is an apartment house for research chemists with families. A baseball field and tennis and volleyball courts are provided for recreation.

The staff of the Sagami Chemical Research Center is comprised of 86 research workers of whom 27 have Ph.D's, 16 Master's, and 6 Bachelor's degrees. The remaining 37 people are research assistants. Research topics are submitted annually to the Research Council of the Center. After review by the Council, the themes are forwarded by the Director of Research for approval by the Board of Trustees and the Board of Counsellors. Autonomy of research is respected provided that the research projects and the manner of their execution do not deviate from the stated objectives of the Institute. The operating expenses of the Center amounted to about 400 million yen (\$1.3 million) in 1971.

The results of the researches conducted at the Institute are reported to all contributing companies as well as to the bank. When the companies are interested in any of the findings, the following procedures are undertaken:

(1) If a concern wishes to conduct a test of biological activity or determine other properties of a compound reported, the required sample will be supplied.

(2) If further development is desired, a joint program will be arranged between the company and the Center.

(3) If the company wishes to commercialize the results, patents and other necessary technical information will be licensed at a reasonable price. Consulting services will be furnished to the industries on request on any subject on which expertise is available. Training of research scientists and assistants is conducted by the Center.

Since its inception, the Sagami Chemical Research Center has pursued a program of basic research with major emphasis on sulfur and nitrogen chemistry. Recently a new objective, namely, simulation of reactions *in vivo*, has been put into effect. The laboratory staff is divided into research groups who work on specific subjects. The titles and membership of these groups are given below:

- Group 1. Preparation of standard solutions for the chemical analysis of essential chemical components in sea and fresh waters and basic studies for the preparation.
Dr. K. Ambe and 5 other members
- Group 2. New techniques for the measurement of soft β -emitters.
Dr. T. Saito and 2 other members

- Group 3. Asymmetric syntheses.
Dr. G. Tsuchihashi and 7 other members
- Group 4. New synthetic approach to biologically active substances.
Dr. K. Kondo and 8 other members
- Group 5. Role of sulfur in unstable species.
Dr. A. Ohno and 4 other members
- Group 6. Novel synthetic reactions toward useful compounds.
Dr. T. Fujisawa and 9 other members
- Group 7. Organometallic reactions.
Dr. M. Fukuyama and 4 other members
- Group 11. Syntheses of amino acids and proteins.
Dr. Y. Isowa and 5 other members
- Group 12. Microwave spectroscopy and its application to the studies of chemical reactions.
Dr. S. Saito and 2 other members
- Group 13. Gas-phase EPR of free radicals and its application to the studies of air pollution.
Dr. H. Uehara and 3 other members
- Group 14. Fundamental and application researches on the catalysis of electron-donor-acceptor complexes.
Dr. M. Ichikawa and 9 other members
- Group 16. Application of electron donor-acceptor complexes to ammonia synthesis.
Dr. Y. Ohtsuka and 2 other members
- Group 17. Syntheses and reactions of organometallic compounds.
Dr. Y. Nagia and 3 other members

Three major research efforts were emphasized at the Sagami Chemical Research Center in 1972. The first of these involved basic and applied research on reaction design. In this work an original idea is explored as the essential first step toward discovering a new reaction. Efforts are then made to improve the reactions found in this way by combining with other reactions or by modification such as changing the functional groups in order to get the most efficient yield and selectivity. Groups 14 and 16 for studies of catalytic reactions by electron donor-acceptor complexes and Groups 7 and 17 for investigations of synthetic reactions with organometallic compounds are typical for

Chemistry and Physics, as well as a fine lecture hall. A new administration building is presently under construction. There is some agitation by radical students and one sign was seen protesting the presence of the American military in Japan and the Viet Nam War.

Professor Waichiro Tagaki is active in organic chemistry research and is beginning to conduct some biochemical investigations in the field of enzymes at Gumma. Not long ago he spent two years at Harvard University with Professor Frank Westheimer. During that period he worked on the enzyme acetoacetate decarboxylase and published with Westheimer a series of four papers on its structure, catalytic activity and reactions with other compounds.

TOKYO UNIVERSITY

The Chemistry Department of Tokyo University was visited on 11 October. This institution of higher learning is regarded as Japan's premier university and can recruit the cream of the student crop. Like Harvard in the United States, many of its graduates have gone on to become leaders in every aspect of Japanese political, business, and professional life. The undergraduate student population is about 13,000 and the graduate school has another 7000. With 61 kozas in chemistry, the University is well equipped to provide a first-class education in nearly every aspect of the field, polymer chemistry being a noteworthy exception.

The Chemistry Department at Tokyo University is composed of three groups:

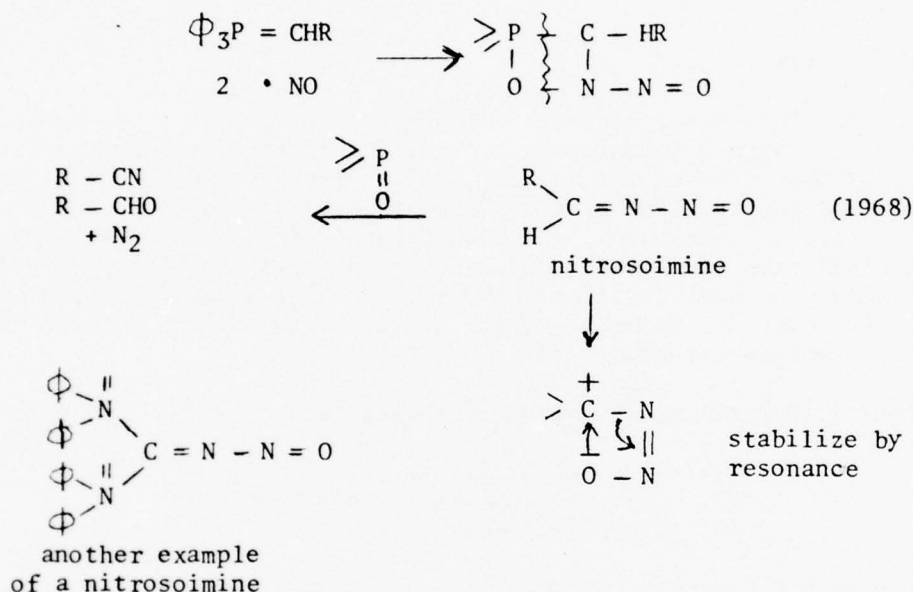
- (1) Physical Chemistry
- (2) Inorganic and Analytical Chemistry
- (3) Organic Chemistry

Physical Organic Chemistry is emphasized in the Organic Chemistry section. The group working in physical organic chemistry research is studying the structural aspects of this field. Another research team is engaged in research on natural products such as terpenes and organic compounds in plants, with emphasis on structural determinations. Rotational isomerism of biphenyl derivatives is under investigation. There is a study in progress on hydrogen bonding between lone pairs of S or O. A group is utilizing Chemical Induced Dynamic Nuclear Polarization (CIDNP) for the detection of free radical reactions. Another research investigation is concerned with the synthetic aspect of organic reactions, mainly with phosphorous-containing compounds. One objective of this work is to generate an intermediate corresponding to nitrene (RN:), e.g. RP: in which there is an apparent similarity.

Professor O. Simamura heads this koza. He is an "elder statesman" in the field of free radical reactions. Assistant Professor K. Tokumaru and Drs. Akiba, Inamoto, and Yoshida are assisting him in the overall research effort. The laboratories are well-equipped, although some of them are quite old and

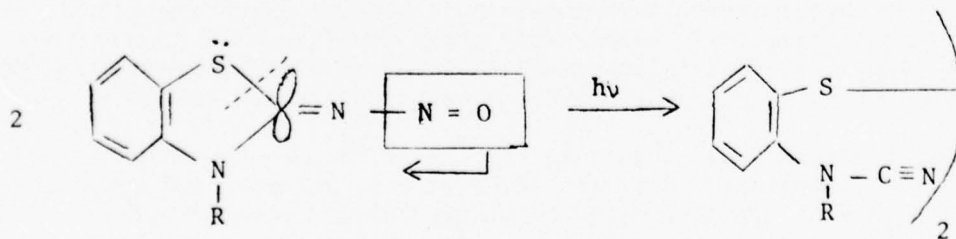
cluttered. Drs. Tokumaru and Yoshida share a common interest in photochemical reactions. Yoshida studies the mechanistic aspects of photochemical reactions in relation to free radical chemistry. He is also interested in the stereochemistry. Dr. Tokumaru investigates excited states in photochemical reactions and derives correlations based on chemical kinetics. Dr. Akiba studies physical organic chemical aspects of reactions involving organic nitrogen, sulfur and phosphorous compounds. Dr. Inamoto is working on reactions involving phosphinothioylidene ($R-P=S$) as an intermediate.

Akiba is studying reactions of phosphorous and nitrogen compounds. In one series

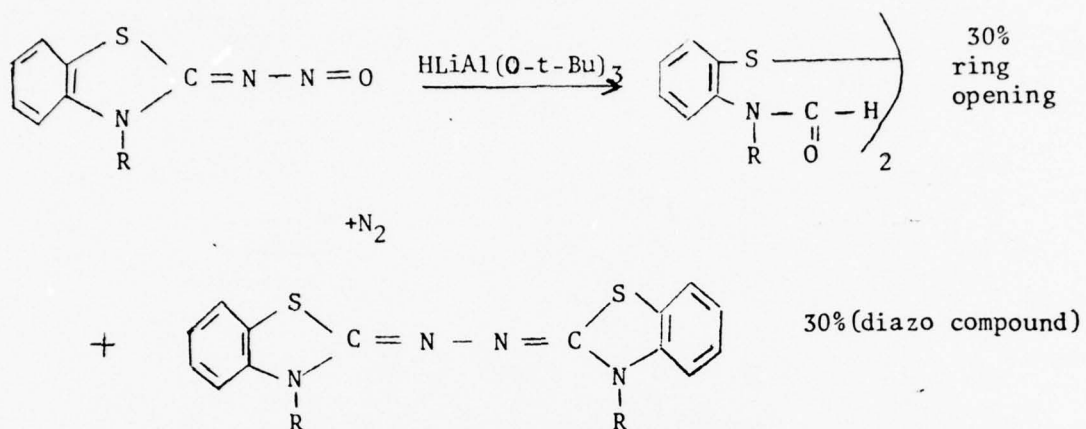


The reactions of nitrosoamines in the presence of light ($h\nu$), lithium aluminum hydride and its derivatives, and Grignard reagents were studied to determine the mechanisms involved.

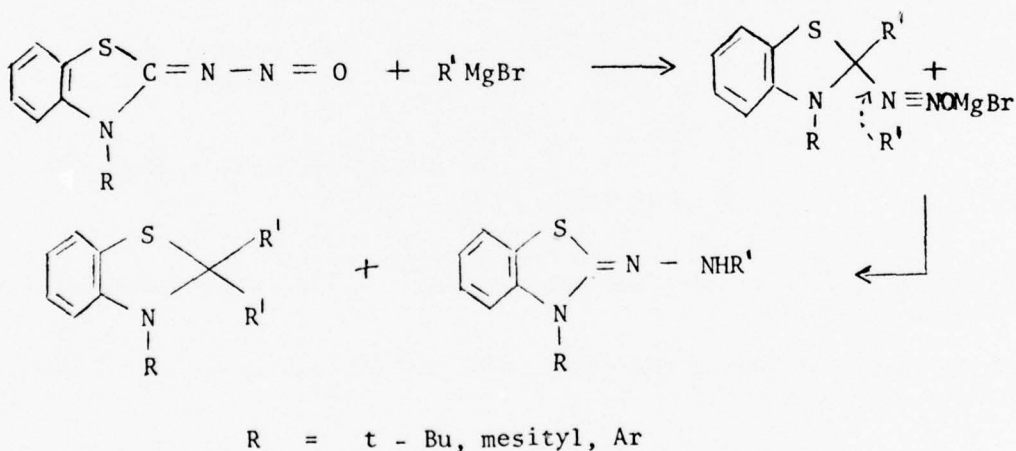
The photochemical reaction was found to produce ring opening exclusively



With LiAlH_4 and its derivatives only partial ring opening occurs and other products are formed.

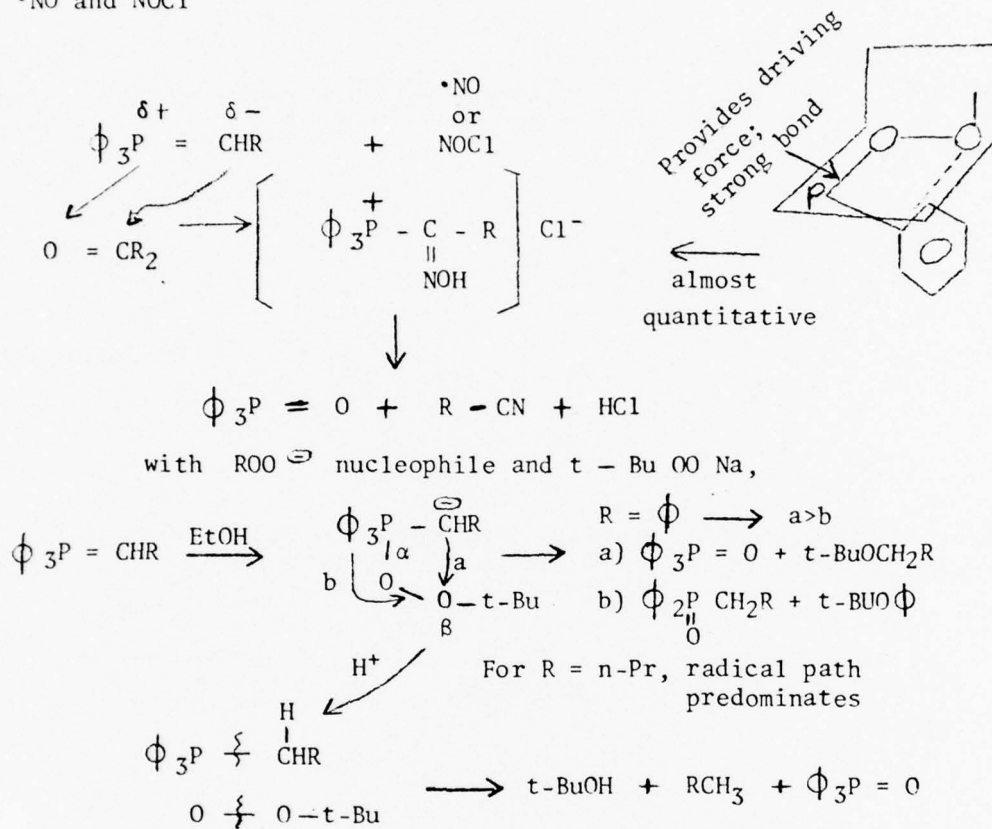


When Grignard reagents are used, ring opening does not take place. With R MgBr , addition to the nitrosoimine occurs as follows:



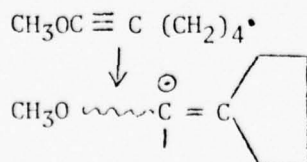
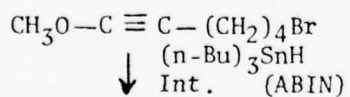
The research is being extended with efforts underway to find another nucleophile, e.g., LiNEt_2 and $\text{BrCH}_2\text{COOEt} + \text{Zn}$

In the area of phosphorous chemistry, Akiba is investigating reactions with $\cdot\text{NO}$ and NOCl



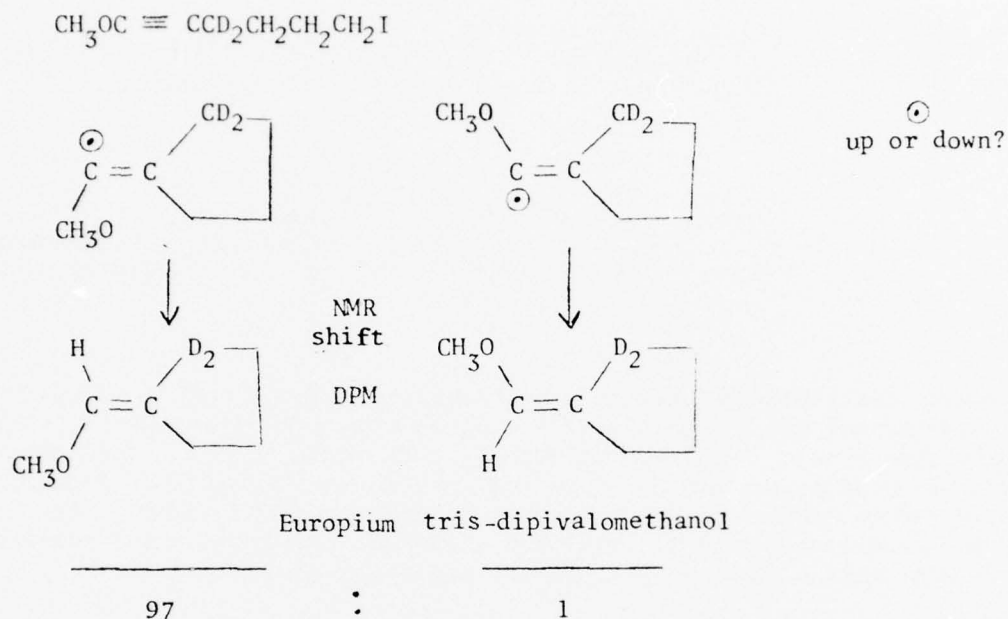
The nature of R determines the major products. The rearrangement to β oxygen is new in P chemistry.

Yoshida is investigating the stereochemistry of some free radical reactions. In one series



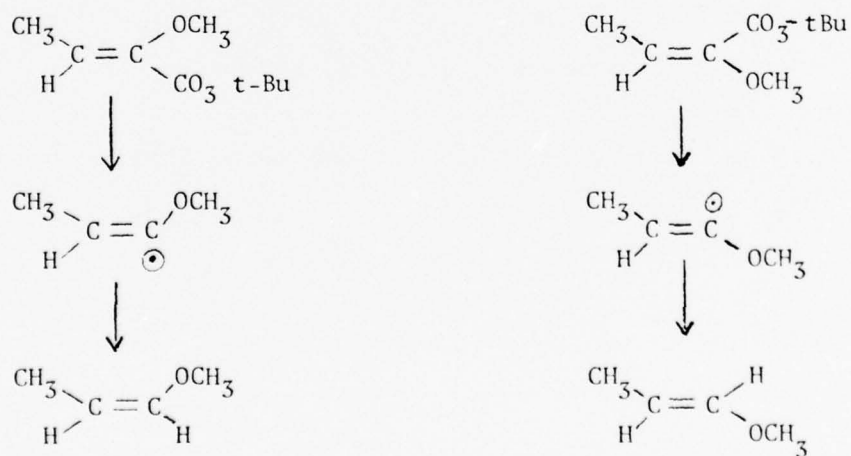
What is the stereochemistry?

In order to determine the stereochemistry, a deuterated iodide was employed



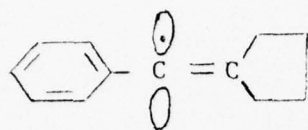
With Φ^- instead of CH_3O^- , equal amounts of cis and trans isomers are formed.

In some work done at the University of Rochester in the U.S.A.

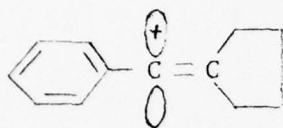


Interconversion is slow compared to H abstraction

Tokumaru used ϕ instead of CH_3O and the interconversion was slow.



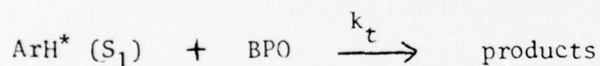
intermediate, instead
of Sp^2 radical



Reference:
Chemical Communications,
No. 15 (1972).

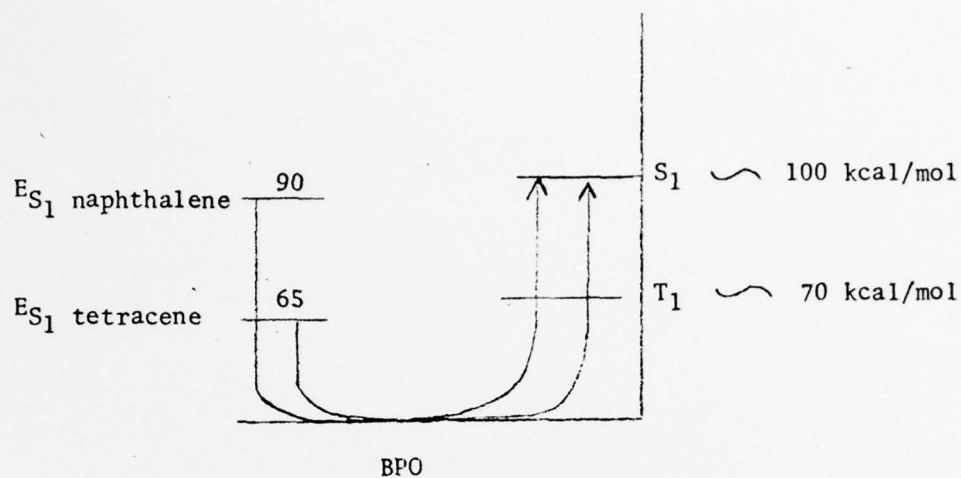
Tokumaru described some recent photochemical studies in which he used both a pulse method and a phase shift technique with a laser to measure singlet state life times. In the first method, a laser pulse of 5 nanoseconds duration was used to produce an S_1 excited state in an aromatic hydrocarbon dissolved in benzene in the presence of benzoyl peroxide (BPO). The kinetics of the resulting processes were then followed. The phase shift measurements were made with a Japanese-made JEOLCO spectrophotometer.

The results may be expressed as follows:



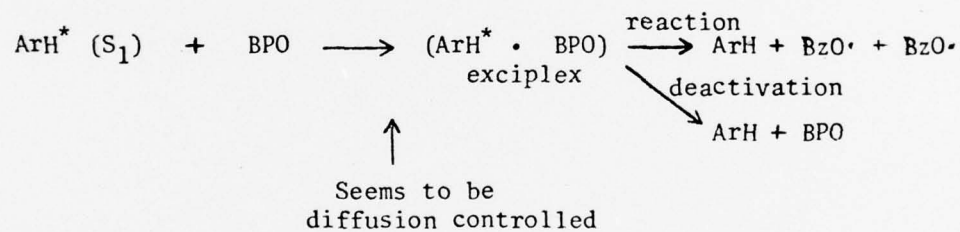
ArH = anthracene, chrysene, naphthalene, or tetracene.

k_t is a diffusion controlled rate constant $\approx 10^{10} \text{ mol}^{-1} \text{ l. sec}^{-1}$

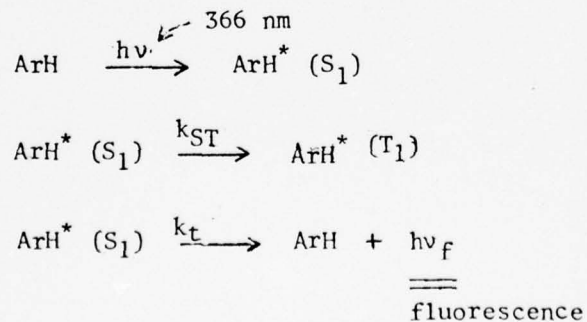


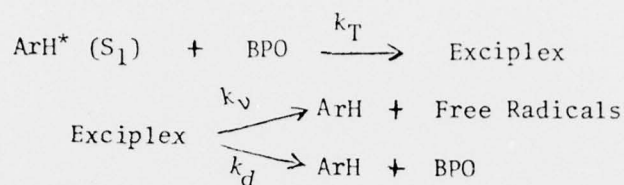
The process is endothermic in vertical excitation transfer.

In theory, the energy exchange occurs as follows:



The kinetic analysis is as follows:





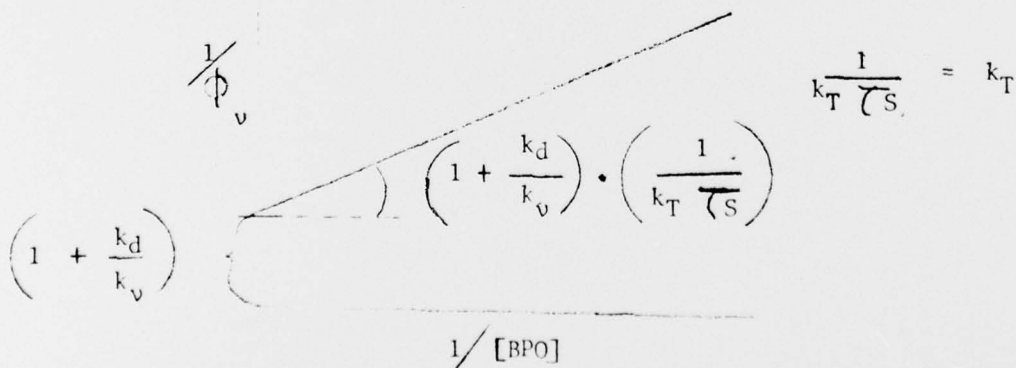
$$\phi_v = \frac{k_T [\text{BPO}]}{k_{ST} + k_T + k_T [\text{BPO}]} \cdot \frac{k_v}{k_v + k_d}$$

$$\frac{1}{\phi_v} = \left(1 + \frac{k_{ST} + k_T}{k_T [\text{BPO}]} \right) \left(1 + \frac{k_d}{k_v} \right)$$

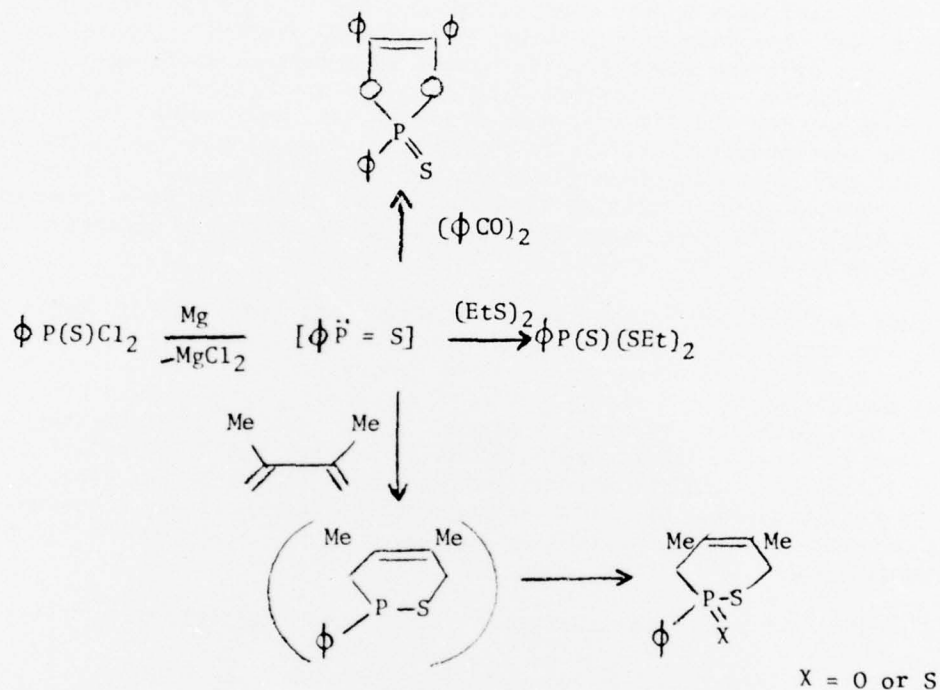
$$\left(\frac{1}{\phi_v} \right) = \left(1 + \frac{1}{k_T \tau_S [\text{BPO}]} \right) \left(1 + \frac{k_d}{k_v} \right)$$

in which $\frac{1}{k_{ST} + k_T} = \tau_S$

Plotting $\frac{1}{\phi_v}$ vs. $\frac{1}{[\text{BPO}]}$:



S. Nakayama, M. Yoshifuji, R. Okazaki and N. Inamoto are investigating reactions of phosphinothioylidene ($R-\ddot{P}=S$) as an intermediate. Dechlorination of phenylphosphonothioic dichloride with magnesium in the presence of 2,3-dimethylbutadiene, benzil, and diethyl disulfide yielded 1,2-thiaphosphorin, 1,3,2-dioxaphospholene and phosphonotrithioate derivatives, respectively. The formation of these products was explained in terms of phenylphosphinothioylidene ($\phi\ddot{P}=S$) as an intermediate



TOHOKU UNIVERSITY

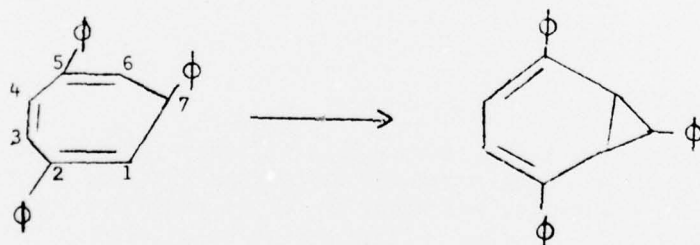
Tohoku University is a large, former Imperial University located in the city of Sendai which is situated about 400 kilometers north of Tokyo on the Pacific Ocean side. The University has about 12,000 students and has several campuses in different parts of the city. There are 39 koza in chemistry and the department is noted for its strength in natural products science. Recently photochemical research has become a major area of activity.

The trip to Sendai was undertaken during the period of 12-15 October. Dr. T. Tezuka of Professor Mukai's group in Organic Chemistry served as host and guide during this period. Visits to the chemistry groups were scheduled for 13 and 14 October and a seminar talk was given by the writer on the afternoon of the fourteenth.

Tohoku University is developing an entirely new campus on a high hill overlooking the city and near the shrine built on the ruins of Sendai Castle. The buildings are very impressive, being made of concrete with a modern, functional design. All structures so far constructed are for science and engineering and it appears that this site will probably be entirely devoted to those fields. Chemistry, Biology, and Geography are housed in their new buildings, as is Engineering Science. A Physics building is under construction. There are some complaints about the quality of construction as well as mistakes in design in some of the new laboratories. It is significant that a number of economies had to be practiced, including moving the old laboratories' benches from their original locations and installing them in the new rooms. Despite these drawbacks, it appears that the new campus will prove to be a very effective educational medium in the near future.

Discussions on chemical research were conducted with Professors T. Mukai and T. Toda, and with Drs. T. Tezuka and H. Tsuruta. Professor Takashi Toda works in the field of photochemistry and valence isomerization. Dr. Tsuruta is studying the structure and energy surfaces of C_9H_{10} hydrocarbons. Professor Mukai and Dr. Tezuka are engaged in organic photochemical investigations. Recent work includes rearrangements in multi-ring systems by irradiation and photosensitization, with structural proof of the final compounds provided by NMR and x-ray analysis. Dr. Tsuruta is investigating reactions of seven- and eight-membered ring compounds leading to carbenes, using photochemical, thermal and chemical means.

Toda is working on structural changes in 7-membered ring compounds. It is known that



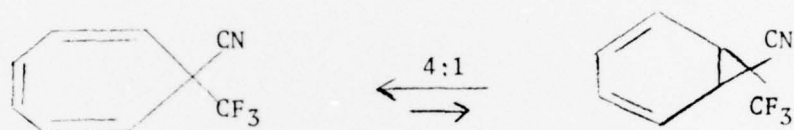
The parent hydrocarbon without the phenyl groups on the 2,5 and 7 positions does not undergo a shift to the analogous bridged structure. With two cyano

groups in the seven position, it is known that a shift to a bridged structure occurs



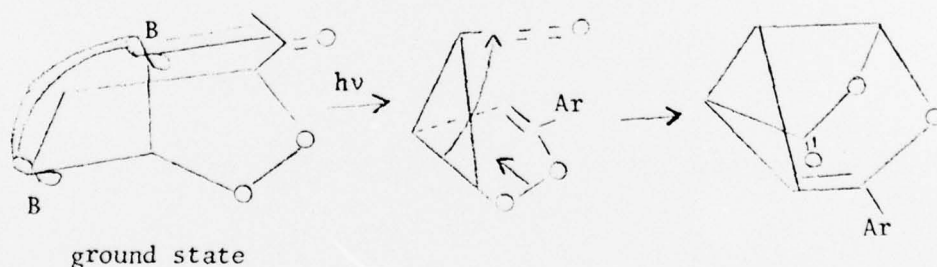
Without the CN groups, the change does not take place. Roald Hoffman pointed out that electron-accepting groups on the 7-position is important to the shift.

Toda's group found in another case



When two CF_3 groups are attached to position seven, only the seven-membered ring is formed. This is true if phenyl groups are situated on the 2- and 5-positions. Phenyl groups in the 2- and 7-positions also will not produce the two-ring diene. Toda believes that dipole-dipole repulsions may be important in these changes.

Tezuka is studying photochemical rearrangements to the triplet state produced by sensitization and irradiation



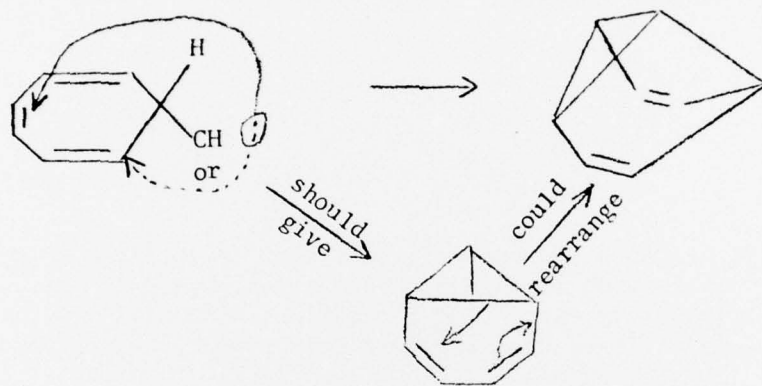
The structure of the product was established by NMR and by x-ray analysis. Miamoto collaborated in this research.

Tsuruta described some very recent research on carbenes:

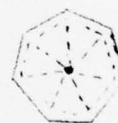


When $n = 1$, \longrightarrow C_9H_{10}

When $n = 0$, \longrightarrow C_8H_8



or 1,5 shift \longrightarrow

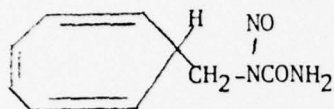


(all
1/2 bonds)

symmetric
structure

This compound has not been prepared; it should have one or two peaks in the NMR spectrum.

A variety of substituted 7-membered ring compounds were synthesized, and



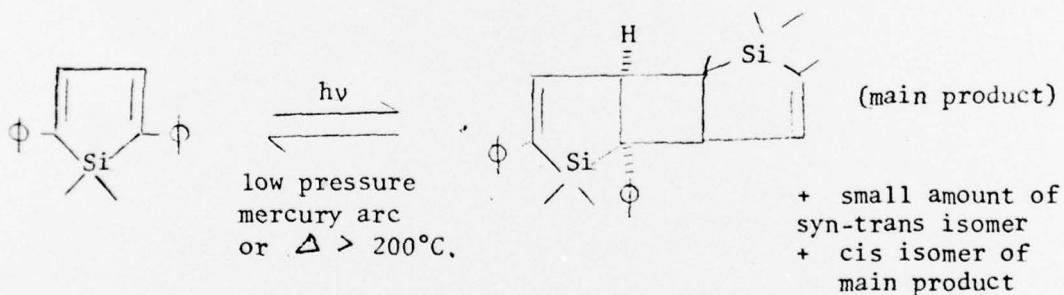
appeared to be an

especially good precursor to a carbene. There seemed to be three good ways to prepare the carbene from this starting material:

- (1) $h\nu$
- (2) Heat
- (3) CuSO_4 or Cu powder

Unfortunately, the reactions yielded disappointing results. An attempt to convert cyclooctatetraene to a tricyclo compound leading to a carbene also failed.

Professor Nakadaira, who worked on the chemistry of natural products up to three years ago, described some photochemical studies on silicon compounds. The first investigation involved a cyclopentadienyl series

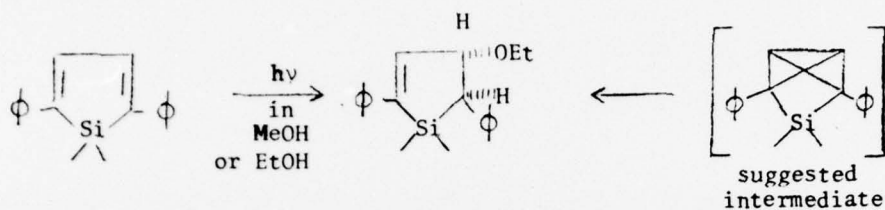


NMR was employed to obtain structure of products. Starting with cyclopentadiene, Hammond reported the formation of the dimer



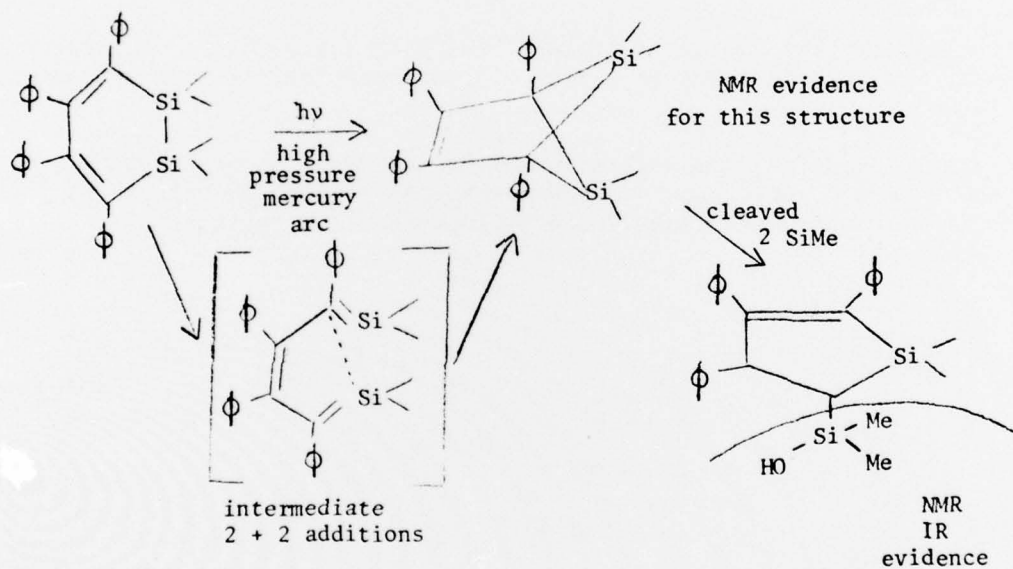
2 + 2
additions

If the cyclopentadienyl silicon compound is irradiated in methanol or ethanol solution, a single ring product is obtained

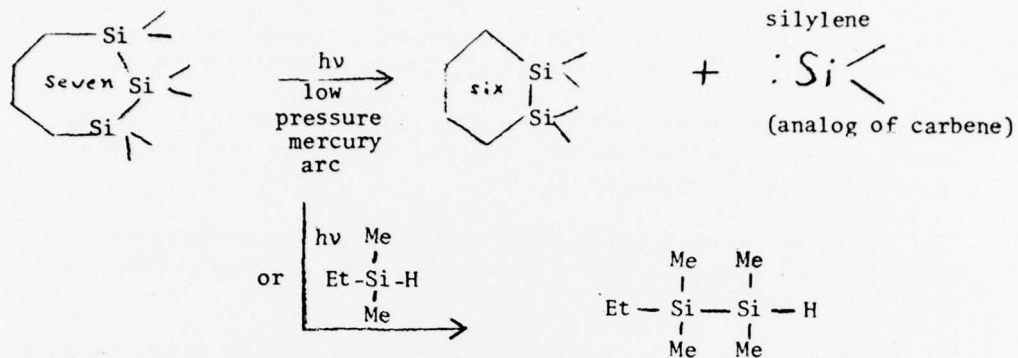


Nakadaira believes that dimerization occurs in a triplet state. He doesn't know if a singlet reaction occurs.

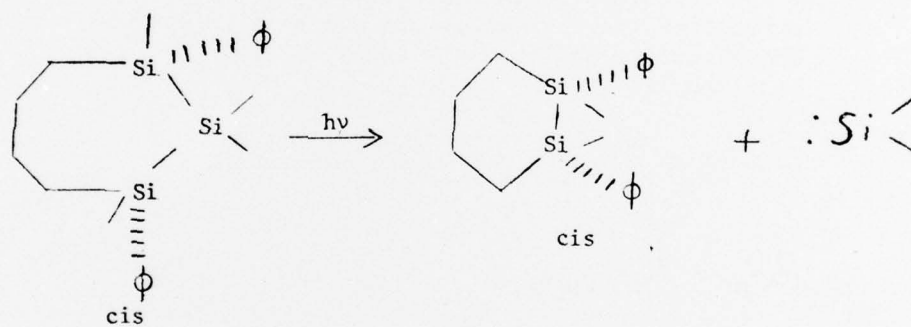
In the second stage of the research, an entirely new system is being investigated



In another series:



Nakadaira is interested in the state of silylene. Silylene is generally a singlet; it gives only the reaction product but no recombination product. If the reaction takes place in a stepwise manner, the course might be



cis 99% : 95%

It is not possible to say if reaction is completely or nearly stereospecific. Efforts are now in progress to determine ESR spectra of silylenes.

Professor Tsunematsu Takemoto and his group are conducting research in natural products chemistry, an area in which Tohoku University is noted for its strength. The programs include investigations on insect hormones, steroids, terpenoids, metabolites and a variety of chemical compounds extracted from plants native to Japan. Some examples of the research efforts are cited below:

(1) Absorption, distribution, metabolism and excretion of the insect metamorphosing hormone, ecdysterone, were studied using its tritium-labeled derivative in mice.

(2) An insect moulting hormone "commisterone" was isolated from the leaves of Cyanotis vaga and was identified through NMR measurements as ecdysterone.

(3) From Zedoary, Curcuma zedoaria (Zingiberaceae), a new sesquiterpenic dione was isolated and designated as dehydrocurdione. The structure of this compound was elucidated by chemical and physico-chemical means.

(4) Khellol, ammiol, caffeic acid dimethyl ether and cimifugin, a new bitter coumarin derivative, were isolated from the aqueous extract of the rhizome of Cimicifuga simplex WORMSK (Ranunculaceae). The structure and absolute configuration of cimifugin were found to be I and II:



(5) From the flowers of Rhododendron japonicum Suringer (Ericaceae), a well-known poisonous tree in Japan, four toxic diterpenoids, rhodojaponin I, II, III and IV were isolated, together with other constituents. The chemical structures involved were identified.

(6) Fusidic acid, a steroidal antibiotic was obtained from Isaria kogane, a Basidiomycetes.

(7) Oleanolic acid was incubated with Colletotrichum phomoides and the fermentation product was chromatographed. Three metabolites were isolated and their structures established.

(8) The isolation, chemistry, structure determinations, synthesis and metabolism of the arthropod moulting hormones (ecdysterols) from Achyranthes and Cyathula plants belonging to the amaranthaceous family were achieved. Physiological properties of the ecdysterols in higher animals and the biological activity in arthropods (and insects in particular) were investigated.

JAPAN ATOMIC ENERGY RESEARCH INSTITUTE

The Japan Atomic Energy Research Institute (JAERI) has its Head Office and Isotope Center in Tokyo and research establishments in Tokai, Takasaki and Oarai, with a total personnel of 2,173. The main research center of JAERI is located on a three square-kilometer compound in Tokai-Mura which is about 130 kilometers northeast of Tokyo. Mura is the Japanese word for village but this one has over 40,000 people. In general, when a community passes 30,000 it can apply for city status. This is not being done with Tokai because of feeling against atomic energy research which it is believed is easier to handle with a village government than a city. The village status is readily observable by the visitor by the obvious deficiency in stores and commercial enterprises as well as the agricultural surroundings. The atomic energy center at Tokai has been in existence about fifteen years, during which period about two dozen concrete buildings have been erected to house a variety of nuclear research and development facilities. Among these facilities are three research reactors, a power demonstration reactor, four critical assemblies for studies of reactor physics, a Van de Graaff machine, a linear accelerator, a hot laboratory for studies of irradiated fuels and materials, equipment for reprocessing of spent fuels, a waste treatment plant, and a nuclear fusion research laboratory. There is an extensive radioisotope center which is producing and distributing processed radioisotopes, labeled organic compounds, radiation sources and radionuclides. An atomic power plant is associated with JAERI which is currently being upgraded from 45 megawatts to 90 megawatts output of electricity.

The Japan Atomic Energy Research Institute at Tokai was visited on 15 and 16 October. Dr. Enzo Tachikawa, Head of the Hot Atom Chemistry group, served as guide and provided a complete tour of the facilities. This included the Division of Chemistry, the Division of Physics, the Plutonium Building, the three research reactors, the Van de Graaff, the linear accelerator, the radioisotopes plant, the Tokomak nuclear fusion machine (with which extreme difficulty is being experienced in making it work), and the waste disposal system.

There are three major programs in the Chemistry Division: (1) Solvent extraction--mainly rare earth and actinides, (2) Purification of uranium and plutonium by the mercury amalgam method, and (3) Hot atom chemistry. In general, the objective is to recover useful elements from spent fuel. The Division of Chemistry is subdivided into five departments: (1) Analytical Chemistry,

(2) Radiochemistry, (3) Radiation Chemistry (^{60}Co source and nuclear reactors), (4) Burn-up Chemistry (to fragments; determine amount of ^{235}U left in fuel), and (5) Fluorine Chemistry (production of fuel) with fluoride to make it more radiation resistant).

The other large research division is Physics. Here the major objective is the production of artificial heavy elements. The group is irradiating $^{241}\text{americium}$ to produce curium, separate this element and purify it. In the near future an attempt will be made to separate and identify berkelium. In the past emphasis was placed on this phase of the effort. In the future work based on spent fuel will be the major activity.

Dr. Hiroshi Amano, Deputy Chief, Division of Production of the Radioisotope Centre, outlined the efforts of this facility to the writer and showed him around the plant. The Radioisotope Centre is presently producing a number of processed radioisotopes, labeled organic compounds and radionuclides. In particular ^{198}Au , ^{35}S and ^{51}Cr are being processed; the gold isotope is being sold to hospitals in Japan for medical tracer purposes. None of the radioisotopes manufactured are being sold outside of Japan as a matter of policy.

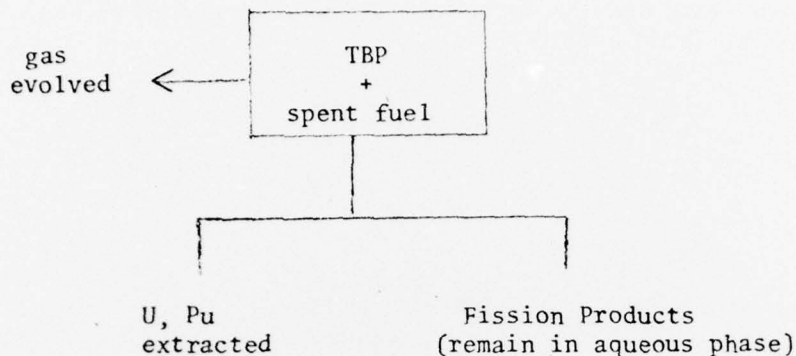
The 10-kilogauss Tokomak nuclear fusion machine is not operative mainly because of difficulty in maintaining a vacuum. It is currently disassembled for repairs. ~~The main purpose in using it will be to generate energy.~~ It cost one-half billion yen.

The 180 MEV linear accelerator operates over a path of 100 meters. It is being used for (1) neutron bombardment, (2) making radioisotopes, and (3) photochemical reactions (just getting underway).

There is a 10,000 Curie ^{60}Co source at Tokai which is being used mainly for nuclear chemistry studies at the present time.

Dr. T. Ishimori is Director of the Division of Chemistry at the Japan Atomic Energy Research Institute (JAERI) at Tokai-Mura. Under him, Dr. Enzo Tachikawa is Head of the Department of Hot Atom Chemistry. Tachikawa and members of his staff reviewed several of the research programs going on in the Division of Chemistry.

Dr. Akatsu discussed research on solvent extraction which has been coordinated at Tokai over the past ten years. The major effort has been directed toward recovery of useful elements from spent fuel. Tri-n-butyl phosphate (TBP) is commonly used in reprocessing this material. After irradiation in the reactor, the fission products are removed, separated from the uranium and purified. Then the spent fuel is treated with TBP and dissolved in nitric acid. The process may be represented schematically as follows:



With TBP as the organic phase and HCl, H₂SO₄ or HNO₃ as the added acid, the distribution coefficients for 50 or more elements were determined. A number of other organic extraction agents were investigated also, including a variety of alkyl amines, esters, and ketones. The group is now studying solvent extraction using a fused salt with a melting point near room temperature and tri-n-butyl phosphate. Two examples of salts tried are Mn(NO₃)₂ · 6H₂O with a melting point of 26°C. and Ca(NO₃)₂ · 4H₂O with a melting point of 42.5°C. The distribution ratios obtained with these salts and TBP were higher than in the aqueous phase.

Tachikawa discussed the work of the Hot Atom Chemistry group. In the research program, use is made of hot atoms produced by photolysis in nuclear reactions with very high kinetic energies being achieved. For example



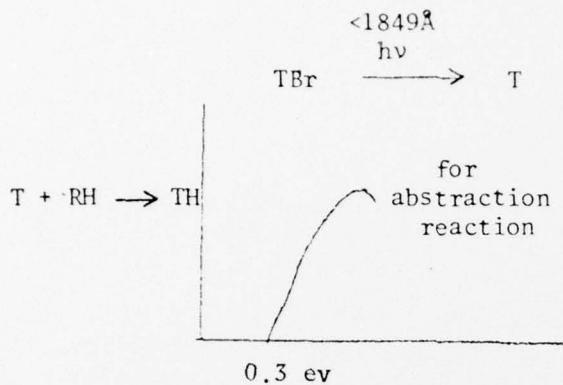
Three main types of nuclear reactions may take place:

- (1) Hydrogen atom -- HT
- (2) Hydrogen substitution -- RH + T \longrightarrow RT + H
- (3) Addition, e.g., to C = C

Ordinarily, (1) and (3) only are observed. The energies available from these reactions are:

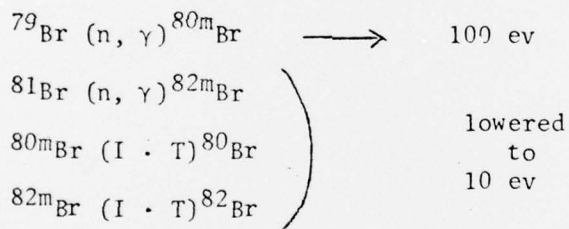
- (1) 1 to 10 kcal/mole
- (2) \geq 40 kcal/mole (calculated)
- (3) 0 to 5 kcal/mole

High energy T can react because Roland at University of California, Irvine produced tritium of about 5 eV.

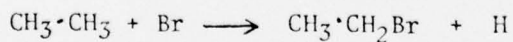


For substitution, T reacts at about 5 eV (est.).

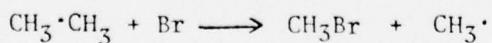
Bromine may be activated by the (n, γ) process



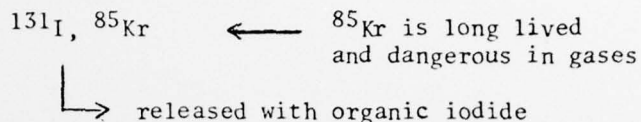
The lower the ΔH , the higher the activity and ΔH is higher for H abstraction.



but at lower K.E.,



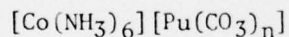
When spent fuel is dissolved in HNO_3 , radioactive gases are produced. The most important process involved is



One problem still to be solved is how the product $\text{CH}_3^{131}\text{I}$ is formed. Also when uranium and HNO_3 react in spent fuel, there is the question as to where the C and H originate. It is known that 4-7% of the total ^{131}I in spent fuel goes to $\text{CH}_3^{131}\text{I}$ and separation of this product is not easy. An attempt was made to use adsorption on activated charcoal without success, both in presence and absence of added KI. Tachikawa and his group are currently trying to understand how the $\text{CH}_3^{131}\text{I}$ is formed as a first step to finding a way to suppress its formation.

The origin of the carbon found in the products is also a mystery. One possibility is that it comes from CO_2 . The results of an investigation using ^{14}C as a tracer eliminated this route. Efforts are still being made to uncover the origin of the carbon.

Another large group is working on plutonium chemistry in the Plutonium Laboratory. Studies are being conducted there on plutonium, americium, curium and berkelium (hopefully). One specific complex synthesized was



An important project of the Plutonium Chemistry group is the preparation of transuranium elements. An oxide of americium, AmO_2 , was prepared in a nuclear reaction. After irradiation of $^{241}\text{AmO}_2$ samples, ^{244}Cm was found and identified. Efforts are now underway to try to make berkelium.