



Title	Molecular Chemistry. Summary International Report, July 1995-June 1996
Citation	Memoirs of the Faculty of Engineering, Hokkaido University, 19(3), 441-457
Issue Date	1996
Doc URL	<a href="http://hdl.handle.net/2115/38077">http://hdl.handle.net/2115/38077</a>
Type	bulletin (other)
File Information	19(3)_441-457.pdf



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International Society of Electrochemistry 46th Annual Meeting, Xiamen, China, August 27-September 1, 1995

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### FLUORINATIVE $\alpha$ -CLEAVAGE OF KETONES BY ELECTROCHEMICAL OXIDATION IN HF-BASE SOLUTIONS

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Electrochemical fluorination of ketones was carried out in HF-base solutions such as 5HF-Et<sub>3</sub>N complex. When 2,2-dimethylcyclopentanone was employed, the selective cleavage of carbon-carbon bond followed by the fluorination at its  $\alpha$ -carbon took place to give 5-fluoro-5-methylhexanoyl fluoride, which in turn converted to the corresponding methyl ester without isolation. Having two substituents at  $\alpha$ -carbon of ketones is critical to obtain the  $\omega$ -fluorocarboxylic acid esters selectively, and 2-methylcyclohexanone or cyclopentanone gave the desired  $\omega$ -fluorocarboxylic acid esters only in moderate or low yields with some by-products. Thus, di-substituted cyclohexanone derivatives at their  $\alpha$ -carbon such as 2,2-dimethylcyclohexanone and 2-chloro-2-methylcyclohexanone gave the corresponding 6-fluoroheptanoic acid ester derivatives in good yields. Interestingly, the ester group in substrate survived to afford  $\omega$ -fluorodicarboxylic acid ester selectively under the reaction conditions.

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Pre-Meeting on 11th European Symposium on Fluorine Chemistry (Slovenia), September 15, 1995 Bremen, Germany

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### Triethylamine-Pentakis(Hydrofluoride) : Et<sub>3</sub>N-5HF

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The amount of HF which can combine with the base forming stable HF-Base solutions is dependent on temperature and bases employed. The refluxing solution of HF combined with Et<sub>3</sub>N at around 170°C is commercially available and has a composition of 3 moles of HF to one mole of Et<sub>3</sub>N. Five equiv amount of HF can combine with Et<sub>3</sub>N at 120°C. <sup>1</sup>H-NMR spectrum of Et<sub>3</sub>N-nHF with n=3 and 4 gave a broad singlet at  $\delta$ =8 to 9 indicating the rapid proton exchange between ammonio group (Et<sub>3</sub>NH<sup>+</sup>) and free Et<sub>3</sub>N. In a solution with a composition of Et<sub>3</sub>N-5HF, NMR spectra showed a clear triplet pattern with an N-H coupling constant of

50Hz, indicating the occurrence of exclusive protonation of the nitrogen atom in  $\text{Et}_3\text{N}$ . Cyclic voltammograms in  $\text{Et}_3\text{N}-n\text{HF}$  are examined. The stability of  $\text{Et}_3\text{N}-5\text{HF}$  against the anodic oxidation was higher than those of  $\text{Et}_3\text{N}-n\text{HF}$  with  $n=3$  or 4. Cathodic currents of  $\text{Et}_3\text{N}-n\text{HF}$  due to the hydrogen evolution appeared at  $-0.1$  V or below on the voltammograms. Decreasing value of  $n$  in  $\text{Et}_3\text{N}-n\text{HF}$  brought about the cathodic current at more cathodic potentials.

This novel HF-Base solution has been found to be a useful hydrofluorination reagent for reactive alkenes.

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11th European Symposium on  
Fluorine Chemistry, September  
17-22, 1995 Bled,  
Slovenia

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### SELECTIVE HYDROFLUORINATION REACTION OF FUNCTIONALIZED ALKENES WITH $n\text{HF}-\text{Et}_3\text{N}$ COMPLEXES

Shoji HARA, Hiroyasu SHIRATO, Eiji HAYASHI, Mikio KAMEOKA,  
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Pyridine-HF complex has been used for the hydrofluorination reaction of the simple alkenes successfully. However its application for the functionalized alkenes is generally unsuccessful because the undesired side reactions were caused by their high acidity.

A variety of  $n\text{HF}-\text{Et}_3\text{N}$  complexes ( $n=3-6$ ) were prepared from anhydrous HF and  $\text{Et}_3\text{N}$ , and used for the hydrofluorination reaction of the functionalized alkenes. Most stable and commercially available  $3\text{HF}-\text{Et}_3\text{N}$  complex showed no reactivity towards alkenes but  $4-6\text{HF}-\text{Et}_3\text{N}$  complexes reacted with functionalized alkenes to give the corresponding hydrofluorination products. When two carbon-carbon double bonds existed in a molecular and one of them was deactivated by the carbonyl group, the hydrofluorination reaction took place at another double bond selectively. On the other hand, 5-alkenals cyclized to the cyclic fluoroalcohols stereoselectively.

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11th European Symposium on  
Fluorine Chemistry, September  
17-22, 1995 Bled,  
Slovenia

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**PREPARATION OF FLUOROARENES BY THE DECOMPOSITION  
OF DIARYLIODONIUM COMPLEXES SALTS  
USING HF-BASE, Et<sub>4</sub>NF-HF OR KF-HF**

Tsuyoshi FUKUHARA, Manabu SEKIGUCHI, Jun NAKAHIGASHI,  
Shoji HARA, and Norihiko YONEDA  
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Hokkaido University, Sapporo 060, Japan

The thermal decomposition of diaryliodonium salts in HF-base (base: Et<sub>3</sub>N, pyridine etc.), Et<sub>4</sub>NF-HF or KF-HF complexes has been successfully carried out to prepare fluoroarenes (ArF). In Et<sub>4</sub>NF-nHF (n: 4-8) solutions, for example, diaryliodonium salts decomposed rapidly and the corresponding ArF were obtained in good yields.

On the other hand, unsymmetry diaryliodonium salts such as phenyl-2,4,6-trimethylphenyliodonium tetrafluoroborate decomposed in two ways.

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11th European Symposium  
on Fluorine Chemistry,  
September 17-22, 1995  
Bled, Slovenia

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**DEAMINATIVE FLUORINE-CONTAINING FUNCTIONALIZATION  
OF AMINO ARENES USING FLUORINE-CONTAINING ACIDS  
WITH OR WITHOUT BASES**

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Aromatic (including heterocyclic) compounds having fluorine-containing functional groups (ArX: X=F, OSO<sub>2</sub>CF<sub>3</sub>, OSO<sub>2</sub>F, OCOF<sub>3</sub> and so on) have been readily prepared in good yields by the diazotization of the corresponding amino arenes (ArNH<sub>2</sub>) followed by the thermal or photochemical in situ decomposition of intermediate diazonium ions (one-stage deaminative fluorine-containing functionalization of ArNH<sub>2</sub>), or by the fluorine-containing functionalized dediazonation of aromatic diazonium salts (ArN<sub>2</sub>Y: Y=Hal, BF<sub>4</sub>, OSO<sub>2</sub>CF<sub>3</sub>) in fluorine-containing acids (HX) with or without bases.

The functions of bases in HX-Base solutions will be discussed on the diazotization of ArNH<sub>2</sub> and the fluorine-containing functionalized dediazonation of the corresponding di-

azonium intermediates.

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1995 International Chemical  
Congress of Pacific Basin  
Societies. December 17-22,  
1995 Honolulu, USA

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## PROGRESS IN DEAMINATIVE FLUORINATION OF AMINOARENES

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Deaminative fluorination of aminoarenes to obtain fluoroarenes, namely the diazotization of aminoarenes followed by *in situ* dediazonation of intermediate diazonium salts (the Balz-Schiemann Reaction), has many difficulties for the effective preparation of fluoroarenes having polar substituents like a hydroxyl group. Based on recent progress in the studies of the diazotization of aminoarenes and fluoro-dediazonation of arene diazonium salts, primary factors for the efficient fluorination of arene fluorides in the one-stage deaminative fluorination of aminoarenes using HF or HF-Base solutions have been elucidated. Also, the facile preparation of arene fluorides having polar substituents, such as hydroxyl, alkoxy halogens, nitro, mercapto, carboxyl, trifluoromethyl and so on, has been successfully carried out by the photo-induced fluorinative decomposition of arene diazonium intermediates.

Development of a semi-commercial scale process for the one-stage transformation of aminoarenes to fluoroarenes using HF was also described.

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1995 International Chemical  
Congress of Pacific Basin  
Societies. December 17-22,  
1995 Honolulu, USA

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## ELECTROCHEMICAL FLUORINATION OF CARBONYL COMPOUNDS USING HF-BASE

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Shoji HARA, and Norihiko YONEDA

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HF-Base solution is well known as a good source of fluoro substituents for the oxidative fluorination of organic compounds. We have carried out the electrochemical fluorination of carbonyl compounds such as aliphatic aldehydes and ketones using nHF-Base (Base=Pyridine

or  $\text{Et}_3\text{N}$ ). The selective displacement of formyl hydrogen ( $-(\text{C}=\text{O})-\text{H}$ ) to fluorine in aliphatic aldehydes took place successfully to give acyl fluorides. On the other hand, fluorinative  $\alpha$ -cleavage of ketones took place to give acyl fluorides and alkyl fluorides. From cyclic ketones,  $\omega$ -fluorocarboxylic acid esters could be obtained by the esterification of the resulting acyl fluorides.

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1996 International Symposium on Organic Reactions  
April 6-9, 1996 Sendai,  
Japan

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### **Triethylamine-Pentakis(Hydrofluoride) $\text{Et}_3\text{N}\cdot 5\text{HF}$ as a Useful Electrolyte in the Electrochemical Fluorination**

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Tsuyoshi FUKUHARA, and Norihiko YONEDA  
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The displacement of formyl hydrogen to fluorine took place most effectively by the electrolysis of aldehydes using  $\text{Et}_3\text{N}\cdot 5\text{HF}$  electrolyte. Under the conditions of electrochemical oxidation in  $\text{Et}_3\text{N}\cdot 5\text{HF}$ , fluorinative  $\alpha$ -cleavage of cycloketones took place efficiently affording  $\omega$ -fluoroacyl fluorides to give the corresponding esters by the subsequent alcoholysis of initially formed fluorinated acyl fluorides. The electrochemical oxidation of alkoxycarbonylmethylidencycloalkanes caused ring expansion with the incorporation of two fluorines in a ring to afford the fluorinative cyclic esters in the presence of  $\text{Et}_3\text{N}\cdot 5\text{HF}$ . The electrochemical fluorination of  $\beta$ -ketoesters could be achieved in  $\text{Et}_3\text{N}\cdot 5\text{HF}$  using an aryl iodide as a mediator to produce monofluorinated ketoesters in good yields. Iodoarene difluoride seems to be the key intermediate of the reaction which is formed electrochemically in situ and used for the fluorination of ketoesters.

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4th Bilateral Meeting for the  
Japanese-Chinese Fluorine  
Chemists. April 29-May 1,  
1996 Shanghai, China

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**Triethylamine-Pentakis(hydrofluoride)  $\text{Et}_3\text{N}\cdot 5\text{HF}$   
as a Useful Fluorinating Agent for the Organic Compounds**

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The utilization of anhydrous hydrogen fluoride (AHF), which is not expensive and is readily available, is obviously among the most attractive fluorinating agents. AHF has a strong ability for the fluorination of various compounds. However, AHF is an extremely hazardous chemical due to its low boiling point (19.5°C) and high toxicity. Thus, reactions using AHF are invariably accompanied by severe handling difficulties and undesirable side reactions. In order to overcome these difficulties, an AHF solution of Lewis base organic compounds which contain an atom having a pair of electrons such as ketones, amines, alcohols, ethers and so on, has been employed widely as a convenient reagent for fluorination reactions.

Over the years, the fluorination of organic compounds using HF-Base has been investigated also in our laboratory and some new results in this area, namely, Triethylamine-Pentakis(hydrofluoride)  $\text{Et}_3\text{N}\cdot 5\text{HF}$  will be presented as a useful fluorinating agent for selective hydrofluorination of carbon-carbon double bond in functionalized unsaturated hydrocarbons, fluorinative cyclization of alkenals, electrochemical formyl hydrogen-exchange fluorination of aldehydes, electrochemical fluorinative  $\alpha$ -cleavage of cyclic ketones and electrochemical fluorination of  $\beta$ -dicarbonyl compounds using ArI as mediator.

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189th Electrochemical Society Meeting May 5-10, 1996  
Los Angeles, USA

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**Electrochemical Fluorination of Carbonyl Compounds in HF-Base**

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The electrochemical fluorination of carbonyl compounds, such as aldehydes, ketones,  $\beta$ -keto esters, and  $\alpha,\beta$ -unsaturated esters has been successfully achieved in HF amine complexes. In all cases, the oxidative fluorination reactions took place to give fluorinated products in good yields.

The electrochemical fluorination of  $\beta$ -keto esters could be achieved in  $\text{Et}_3\text{N}$ -5HF using aryl iodides as a mediator. Monofluorinated keto esters were obtained in good yields. Iodoarene difluorides seem to be the key intermediate of the reaction which is formed electrochemically in situ and used for the fluorination of keto esters. As iodoarene difluorides change to iodoarenes again after the fluorination, a stoichiometric amount of iodoarene is not necessary. Some iodoarenes, such as iodobenzene, iodotoluene, iodobenzoic acid ester, iodonitrobenzene, iodomesitylene, were applied to the reaction and iodotoluene gave the best results.

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1996 International Symposium on Organic Reactions—Sendai, April 6-9, 1996, Sendai, Japan

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### Regioselectivity in the Electrochemical Carboxylation of Substituted Allylic Halides Using a Reactive-metal Anode

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Takashi KABUKI and Hisanori SENBOKU  
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Hokkaido University, Sapporo 060, Japan

Detailed studies on a regioselectivity in the electrochemical carboxylation of substituted allylic halides were carried out. Electrochemical carboxylation of  $\gamma$ -alkyl-substituted allylic halides in the presence of atmospheric carbon dioxide using a platinum cathode and a magnesium anode gave a mixture of 4-substituted (**A**) and 2-substituted 3-alkenoic acids (**B**) in a ratio of 9:1. Similar electrochemical carboxylation of cinnamyl halides gave a 4:6 mixture of the acids **A** and **B**, whereas that of  $\gamma,\gamma$ -diphenylallyl bromide and 9-bromoethylideneffluorene gave the acids **A** and **B** in a ratio of 9:1. These complex regioselectivities in the present electrochemical carboxylation can be rationalized by both a bulkiness of the  $\gamma$ -substituents of allylic halides and a relative stability of two canonical forms in the allylic carbanions which are generated by a two-electron reduction of allylic halides. Stability of allylic carbanions was also examined by using *MM2* and *ab initio* calculations.



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1995 International Chemical  
Congress of Pacific Basin  
Societies, December 17-22,  
1995, Honolulu, U. S. A.

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### **Reactivity of Electrogenerated Reactive Zinc and Various Zinc Powders**

Masao TOKUDA, Nobuhito KURONO and Nobuo MIMURA

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Reactive zinc metal (EGZn) was readily prepared by electrolysis of a DMF solution containing 0.1M  $\text{Et}_4\text{NClO}_4$  in a one-compartment cell fitted with a platinum cathode and a zinc plate anode. The EGZn showed a higher reactivity in the allylation or isoprenylation of aldehydes and ketones than that of commercially available zinc powders. Characterization of EGZn and six kinds of commercial zinc powders was carried out by a scanning electron microscope (SEM), an X-ray diffraction, and a measurement of surface area. The EGZn was found to be an aggregation of very fine particles (less than 0.1  $\mu\text{m}$  in diameter) and had an extremely large surface area (23.8  $\text{m}^2/\text{g}$ ), which might be one of the major reasons for its high reactivity. X-Ray diffraction of EGZn showed that the EGZn had a hexagonal crystal structure, which is a typical crystal form of zinc metal.

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189th Meeting of The  
Electrochemical Society,  
May 5-10, 1996, Los Angeles,  
U. S. A.

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### **Electrochemical Carboxylation of Vinyl Halides-Synthesis of $\alpha,\beta$ -Unsaturated Carboxylic Acids**

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We found that electrochemical carboxylation of various vinylic bromides in the presence of atmospheric carbon dioxide using a platinum cathode and a magnesium anode readily took place to give the corresponding  $\alpha,\beta$ -unsaturated carboxylic acids. Electrolysis of phenyl-substituted vinylic bromides in a DMF solution containing 0.1M  $\text{Bu}_4\text{NBF}_4$  in the presence of atmospheric carbon dioxide under optimized conditions gave the corresponding phenyl-substituted 2-alkenoic acids in 63-92% isolated yields. For example, electrochemical carboxylation of *E*-1-bromo-1,2-diphenylethene gave 2,3-diphenylpropenoic acid in a 92% yield. On the other hand, 2-alkenoic acids or 1-cycloalkene-1-carboxylic acids were obtained in lower yields by the

electrochemical carboxylation of aliphatic vinylic bromides. Acryl acid carrying a trimethylsilyl group at  $\alpha$ -position, which would be a useful synthetic intermediate, was obtained in a 57% yield by the electrochemical carboxylation of (1-bromovinyl)trimethylsilane. Stereochemical studies showed that thermodynamically less stable *Z*-isomers were preferentially produced from either *E*- or *Z*-vinylic bromides in these electrochemical carboxylations.

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15th International Congress  
of Heterocyclic Chemistry  
August 6-11, 1995, Taipei,  
TAIWAN.

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**SYNTHESIS OF BENZOLACTONES AND BENZOLACTAMS VIA  
AROMATIC METALLATIONS : A NEW ENTRY TO THE SYNTHESIS OF  
ISOQUINOLINE ALKALOIDS**

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Benzolactone and benzolactam units are found in some groups of biologically active, naturally occurring heterocyclic compounds. We have developed a new method for the synthesis of such heterocycles, based on the carboxylation or carbonylation via aromatic metallations induced by halogen-metal exchanges, leading to isoquinoline alkaloids. Stereoselective hydride reduction of 1-(2-bromobenzoyl)-3,4-dihydroisoquinolines, followed by carboxylation of the resultant amino-alcohols with CO<sub>2</sub> gas via a halogen-lithium exchange with BuLi, gave the corresponding benzolactones. Palladium-catalyzed carbonylation [Pd(OAc)<sub>2</sub>-PPh<sub>3</sub>/K<sub>2</sub>CO<sub>3</sub>/CO/boiling toluene] of the above 1-(2-bromo- $\alpha$ -hydroxybenzyl)-1,2,3,4-tetrahydroisoquinolines was found to be accelerated by an addition of Me<sub>3</sub>SiCl, and resulted in the almost quantitative formation of phthalideisoquinoline alkaloids after 20 h.

1-(2-Bromobenzyl)-1,2,3,4-tetrahydroisoquinolines were also subjected to the similar palladium-catalyzed carbonylation. The products, 8-bervinones, were subsequently treated with LiAlH<sub>4</sub> to give the corresponding protoberberine alkaloids in good yields.

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1996 International Symposium  
on Organic Reactions-Sendai  
April 6-9, 1996, Sendai,  
JAPAN

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### **IODINATION OF ANILINES AND BENZYLAMINES WITH MERCURY(II) OXIDE-IODINE REAGENT**

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Our recent studies on the iodination and oxidation of amino compounds with mercury(II) oxide-iodine reagent were described. Treatment of aniline and N-alkylanilines with mercury(II) oxide (0.5 mol equiv) and iodine (1 mol equiv) in CH<sub>2</sub>Cl<sub>2</sub> at room temperature gave the corresponding 4-iodo derivatives in good yields. Acetanilide was also converted to the 4-iodo derivative, but at the much slower rate. Benzocyclic amines, such as indoline, oxindole, 1,2,3,4-tetrahydroquinoline, and 2,3,4,5-tetrahydro-1H-benzazepine, gave the 5-, 6- or 7-iodo compound, respectively. Indole and N-methylindole accepted displacement with the halogen atom at their 3 position under the careful treatment with the reagent.

A similar treatment of anilines bearing a substituent such as NO<sub>2</sub>, halogen or carbonyl group, including 4-iodoaniline described above, resulted in the ready formation of the corresponding azobenzenes. Benzylamine refused the nuclear iodination under these conditions, and, instead, gave exclusively N-benzylidenebenzylamines, which was also obtained by an identical treatment of dibenzylamine. Benzhydrylamine gave a similar dimeric imino compound.

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1995 International Chemical  
Congress of Pacific Basin  
Societies, December 17-22,  
1995, Honolulu, U. S. A.

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### **CARBONYLATION OF BENZYLAMINES AND $\beta$ -PHENETHYLAMINES VIA ORTHO-PALLADATION : SYNTHESIS OF BENZOLACTAMS.**

Kazuhiko ORITO, Mamoru MIYAZAWA, Motoki YUGUCHI,  
Takashi TOKUHASHI and Masao TOKUDA  
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The benzolactam unit is a skeletal feature of some groups of biologically active alkaloids. Aromatic metallations for carbonylation using benzylamines and  $\beta$ -phenethylamines as substrates were studied to give such heterocyclic compounds. A new method for the regioselective insertion of a carbonyl group *via* a direct palladation in a catalytic manner [Pd(OAc)<sub>2</sub>-PPh<sub>3</sub>]

provided readily 1-isoquinolinones. Regioselectivity of the present carbonylation was found to be different from that of the carbonylation using a stoichiometric amount of  $\text{Pd}(\text{OAc})_2$ . The  $\text{Pd}(0)$ -catalyzed carbonylation by the former method resulted in the efficient formation of an oxazolidinone ring, when the substrate had a structural unit of 1,2-aminoalcohol. These methods were successfully applied to the synthesis of isoquinoline alkaloids.

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1995 International Chemical  
Congress of Pacific Basin  
Societies, December 17-22,  
1995, Honolulu, U. S. A.

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### **$\beta$ -SCISSION OF CYCLOALKOXYL RADICALS GENERATED FROM VARIOUS BENZYLIC ALCOHOLS**

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Photolysis of the hypiodites generated by treatment of a variety of cyclic alcohols derived from 1-indanone, 1-tetralone and 1-suberone with  $\text{PhI}(\text{OAc})_2\text{-I}_2$  were studied. When a solution of 1-indanol, in benzene containing  $\text{PhI}(\text{OAc})_2$  and  $\text{I}_2$  was irradiated with a Pyrex-filtered light, *o*-(2-iodoethyl)benzaldehyde (46%), 1-isochromanone (16%) and 1-indanone (12%) were obtained. Similar reaction of 1-tetralol gave 1-tetralone (85%) and that of 1-suberol gave 1-suberone (17%) and *o*-(2-iodobutyl)benzaldehyde (29%). On the other hand, photolysis of the hypiodite of 1-phenyl-1-cycloalkanols gave the corresponding  $\omega$ -iodo-1-phenyl-1-alkanones, which are inaccessible by the usual synthetic methods, in 64-94% yields. These products are formed via  $\beta$ -scission of the alkoxy radicals generated from the corresponding cycloalkanol hypiodites. The effects of a substituent at the  $\alpha$ -position of hydroxyl group as well as ring size of cyclic alcohols and also the reaction pathways leading to the products are discussed.

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188th Meeting of the Electrochemical Society, October 8-13, 1995, U. S. A.

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### **ELECTROCHEMICAL SYNTHESIS OF AL-TI COMPOSITE OXIDE FILMS ON ALUMINUM**

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The formation of Al-Ti composite oxide films on aluminum has been attempted by an electrochemical technique, and the structure and dielectric properties of the oxide film have been examined by EIS and RBS. Al specimen covered with porous anodic oxide films was immersed in  $Ti^{4+}$  solution and heated in air to deposit  $TiO_2$  in the pores. The specimen was then anodized galvanostatically in a neutral borate solution to fill the pores with  $Al_2O_3$ . The incorporation of  $TiO_2$  in the oxide film and capacitance of the oxide were observed to increase with increasing the number of repetition in  $TiO_2$  deposition.

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188th Meeting of the Electrochemical Society, October 8-13, 1995, U. S. A.

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### **LOCALIZED CU DEPOSITION ON ALUMINUM WITH PULSE YAG LASER**

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Patterning of aluminum has been attempted by copper plating with pulse YAG laser irradiation. Aluminum specimens covered with porous or barrier anodic oxide films were irradiated with pulse YAG laser in  $Cu^{2+}$  containing solutions and cathodically polarized to obtain Cu plating at the laser irradiated area. The specimen covered with porous anodic oxide films showed to be more adequate for surface patterning than that with barrier oxide films.

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International Symposium on  
Plant Aging and Life Predic-  
tion of Corrodible Structures,  
May 15-18, 1995, Japan

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## EVALUATION OF IMPERFECTIONS IN ANODIC OXIDE FILMS ON ALUMINUM BY PIT FORMATION TECHNIQUE WITH CATHODIC POLARIZATION

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Highly pure aluminum specimens covered with barrier-type anodic oxide films were cathodically polarized in neutral solutions by potential scanning to follow the time-variation in the cathodic current, and in the amount of dissolved  $Al^{3+}$  ions. The film structural change during cathodic polarization was examined by scanning electron microscopy, confocal laser scanning microscopy, phase detection interferometric microscopy, and atomic force microscopy.

During cathodic polarization, pit growth was observed by the local breakdown of oxide films and dissolution of the metal substrate. The pit formation behavior was strongly dependent on the film structure and pH-buffering ability of the solution, and the precursor of the pit was suggested to be imperfections in anodic oxide films.

The cathodic polarization is proposed as a technique of the evaluation of the imperfection in the anodic oxide film.

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International Symposium on  
Advanced Materials and  
Technology for the 21st Cen-  
tury (The 117th Meeting of  
JIM), December 13-15, 1995,  
U. S. A.

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## Interfacial Reaction in Joining of $MoSi_2$ to Graphite by SPS Method

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Interfacial reaction between  $MoSi_2$  and graphite in joining process using a spark plasma sintering equipment (SPS) was studied. Joining was carried out at 1673, 1873 and 2073 K for 1.2, 2.4, 3.6 and 7.2 ks. The specimens joined by SPS were evaluated using the four-point

bending strength method. Reaction zone formed at the interface was characterized by SEM, EPMA and XRD. In addition, the suppression of interfacial reaction by interposing a titanium foil between  $\text{MoSi}_2$  and graphite was also done. As a result of the solid-state reaction between  $\text{MoSi}_2$  and graphite,  $\text{SiC}$  and  $\text{Mo}_5\text{Si}_3\text{C}$  are formed at the interface. The morphology of  $\text{SiC}$  changes from island to layer with joining time and temperature. The maximum bending strength is gained in joining at 1873 K with joining time of 1.2 ks, although the bending strength tends to decrease as  $\text{SiC}$  layer grows. When interposing a titanium foil, a titanium carbide layer is formed to suppress the formation of  $\text{SiC}$ .

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International Symposium on  
Advanced Materials and  
Technology for the 21st Cen-  
tury (The 117th Meeting of  
JIM), December 13-15, 1995,  
U. S. A.

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### **High Temperature Oxidation Behavior of $\text{MoSi}_2$ - $\text{SiC}$ Composites**

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Isothermal oxidation tests of  $\text{MoSi}_2$  and  $\text{MoSi}_2$ - $\text{SiC}$  composites at 773 and 1773 K were carried out, and the oxidation behavior was discussed in connection with porosity of the composites. In oxidation at 1773 K, a protective  $\text{SiO}_2$  layer is formed in all specimens regardless of the porosity and the concentration of  $\text{SiC}$ . Even in oxidation at 773 K, the accelerated oxidation behavior is not observed in all specimens, although Mo oxide is slightly formed. It is suggested from these results that pores may have no direct influence on oxidation behavior in the accelerated oxidation region. In addition, oxidation behavior of the composites was also clarified.

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4th International Symposium  
on High Temperature Corrosion and Protection of Materials, May 20-24, 1996, France

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### High Temperature Oxidation of MoSi<sub>2</sub>-WSi<sub>2</sub> Solid Solutions

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The effect of the dissolution of WSi<sub>2</sub> upon the oxidation behavior of MoSi<sub>2</sub> was investigated in a wide temperature range of 773 K to 1773 K in air. MoSi<sub>2</sub> and WSi<sub>2</sub> have outstanding oxidation resistance at high temperatures such as 1773 K as a result of the selective oxidation of Si. Such passive oxidation behavior is identical also in all MoSi<sub>2</sub>-WSi<sub>2</sub> solid solutions. On the other hand, at lower temperatures, especially at medium temperatures like 1073 K, accelerated oxidation which is based on the simultaneous oxidation of W and Si takes place in the 50% WSi<sub>2</sub> specimen. In addition, it was experimentally confirmed that the preoxidation treatment at higher temperature is effective for the prevention of accelerated oxidation.

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Japanese-German Seminar  
on Future Development of  
Polysaccharides, Fundamentals and Applications.  
March 4-8, 1996, Sapporo,  
Japan

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### Synthesis of Chitin-like Polysaccharide by *Acetobacter*.

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and Masanobu MUNEKATA  
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Some species of the Gram-negative aerobe *A. xylinum* have the ability to synthesize cellulose as an extracellular polysaccharide. Many researchers have reported that some species of *Acetobacter* are able to produce water-soluble polysaccharides and other species produce both cellulose and water-soluble polysaccharides. The polysaccharide produced by *A. xylinum*, bacterial cellulose (BC), is useful for some commercial applications because of its excellent properties (high mechanical strength, biodegradability, etc.).

Chitin is a widely distributed component in nature as well as cellulose, and it can be regarded as a substitute of cellulose with an N-acetyl group instead of a hydroxyl group at C2.



Tokura et al. have reported that *A. xylinum* subcultured in a medium containing GlcNAc as a sole carbon source synthesized BC containing GlcNAc residue in main chain, GlcNAcBC. GlcNAcBC was degraded by lysozyme and chitinase as well as cellulase and had higher mechanical strength than BC.

We have attempted the synthesis of polysaccharide containing GlcNAc residue by *Acetobacter* which synthesizes water-soluble polysaccharide. In this paper, the synthesis of chitin-like polysaccharide by the bacterium and the results of various characterizations have been reported.

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3rd China-Russia-Japan  
Joint Symposium on  
Advanced Polymers. Octo-  
ber 1-6, 1995, Sapporo,  
Japan

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### **Effect of yeast extract on the yield of bacterial cellulose**

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The contents of culture medium for *Acetobacter xylinum* were carefully examined for improving the yield of bacterial cellulose. High nitrogen percent of C: N molar ratio in medium was preferable for cellulose production. Especially yeast extract showed more effect on increase of cellulose yield than bacto pepton. It seems to be that the cell number increase might be promoted by the certain elements of yeast extract.

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Japanese-German Seminar  
on Future Development of  
Polysaccharides, Fundamen-  
tals and Applications. March  
4-8, 1996, Sapporo, Japan

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### **2-Dimensional Solid State NMR Studies on <sup>13</sup>C Labeled Bacterial Cellulose.**

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<sup>13</sup>C labeled cellulose were synthesized by *Acetobacter xylinum* in the culture which contains <sup>13</sup>C labeled glucose (C2 position), and the solid state high resolution NMR spectra on this

cellulose were recorded by CP/MAS technique. The obtained spectra shows the transition of labelling from C2 to C1, C3 and C5 and its transition rate are revealed as 1.0, 0.7 and 0.19, respectively, which is examined the normal  $^{13}\text{C}$  high resolution NMR spectrum of the hydrolyzed labeled cellulose. From those results, it was possible to partially assign the resonance line of the complex part (C2, C3, C5) of solid state NMR spectra of cellulose and 2-dimensional CH-correlation NMR spectrum of this complex part suggests that the difference between cellulose  $\text{I}\alpha$  and  $\text{I}\beta$  is not only the chain packing style but also the morphological change in glucose molecule itself.

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3rd China-Russia-Japan  
Joint Symposium on  
Advanced Polymers, Octo-  
ber 1-6, 1995, Sapporo Japan

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**Cultivation of *Acetobacter xylinum* in a medium  
with a water-soluble polymer.**

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The culture of *A. xylinum* NCI 1051 or ATCC 10245 was cultured in HS medium with a WSP (methyl cellulose (MC) or carboxymethyl cellulose (CMC), etc.; 0.5 wt%). The yields of BCCs were 1.2-1.8 times that of normal BC (NBC). The contents of WSPs in BCCs estimated from elementary analysis were 11-23 wt% in BCC (MC)s and 34-45 wt% in BCC (CMC) s. The dynamic Young's moduli of BCCs were the same as or larger than that of NBC. It seems that the increases of Young's moduli of BCCs would be resulted from the increases of hydrogen bonding among ribbons. NBC and BCC (CMC) except BCC (MC) were completely degraded by cellulase. In the biodegradation test in soil, BCC (MC) and BCC (CMC) significantly lost their original shapes after four weeks, whereas NBC was completely degraded. BCC (MC) and BCC (CMC) had fine structure compared with that of NBC. Consequently, the decrease in the degradation rate of the BCC (MC) could be due to the decreases in the diffusion rates of cellulosic enzymes secreted by microorganisms in the native soil.