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CONFERENCIES

International Symposium “Reactive Intermediates and Unusual Molecules” ISRIUM-2001

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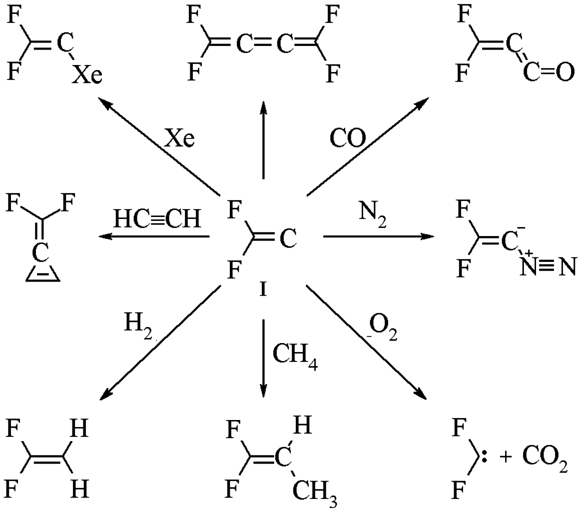
The regular annual symposium dedicated to advances in chemistry of reactive intermediates and unusual molecules took place from September 8 to 13, 2001 in Nara (Japan) This Symposium was organized by Professor H. Tomioka from Mi University. Similar Symposia previously had taken place both in Japan (1980, 1989, 1996) an in other countries: Australia (1991, 1994), Austria (2000), Poland (1995, 1999), USA (1983, 1986, 1995, 1997, 2000), Switzerland (1998).

14 Oral reports and 50 posters from scientists of 14 countries were presented at the Symposium. The modern studies in this field are focused on preparation and observation of intermediates or unusual molecules with elevated stability and long life time. On the other hand a number of investigation grows treating very reactive and short-lived species and molecules. The topics of reports and posters may be divided in three main groups: – chemistry of carbenes, nitrenes and the other carbene analogs; – radicals, biradicals, ion-radicals; – unusual molecules.



W. Sander (Germany) described various reactions of a new kind of carbene, 2,2-difluorovinylidene (**I**), which formed at photolysis of difluoroacetylene. This carbene is a very strong electrophile and readily reacts with acetylene to afford difluoromethylenecyclopropene, it inserts into H7_h and C–H bonds, dimerizes, and adds to carbon monoxide, nitrogen, and xenon, and in reaction with oxygen furnishes difluorocarbene and carbon dioxide.

R. Moss (USA) reported on fragmentation of alkoxyhalocarbenes arising at treating 3-halo-3-alkoxydiazirines with Lewis acids ($AlCl_3$, SbF_4). The fragmentation results in carbenium ions. For instance, thus generated 2-norbornyl cation possesses memory effect and probably has a classical structure.

Dialkoxycarbenes having nucleophilic character react with dimethylacetylenedicarboxylate to yield cyclopropenes. The latter are in equilibrium with vinylcarbenes (ylides) that readily react with nucleophilic agents (J.Warkentin, USA).

The application of modern procedures and calculations allowed an establishment of stereochemical features in the thermal and photochemical rearrangements of a series of substituted naphthylcarbenes (R. McMahon, USA).

The lazer flash-photolysis (LFP) on azido derivatives of diphenylmethane and biphenyl demonstrated that nitrenes arising at denitration are in the singlet spin state (M.Platz, USA). The introduction of bulky substituents (especially chlorine atoms) into the *ortho*-position to the nitrene center considerably increases the half-life of the species.

The technique of vacuum flash-thermolysis (FVT) was used for establishing the rearrangement mechanism 2-quinoxalylcarbene – 4-quinolylnitrene (C. Wentrup, Australia) or 2-pyridylchlorocarbene – 2-chlorophenylnitrene (R. Sheridan, USA).

G. Bertrand (France) reported on the properties of carbenes (**II**) containing push-pull and sterically loaded substituents at the carbene center. These carbenes are so stable that they can be isolated in solid state. They exhibit nucleophilic properties: add

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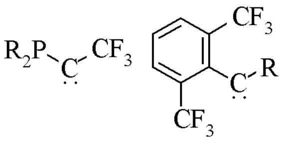
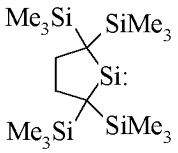
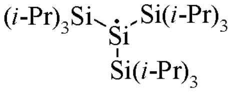


IIa, b



III



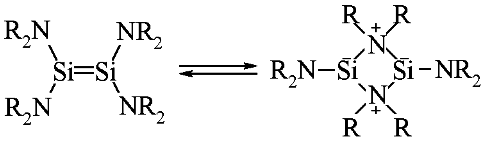
IV

R = NMe*i*-Pr mp 16°C (**a**), PPh_2 mp 69°C (**b**).

to styrene, insert into the Si–H bond, with isonitriles form ketenimines, and dimerize.

A stabilization method for sextet center by introducing bulky groups close to it was applied by M. Kira (Japan) for preparation of stable silylene (**III**). The properties of this silylene were also investigated: it added to the double bond, the addition to butadiene occurred in 1,4-position, insertion into C–Cl bond was observed, etc.

A stabilization was attained in a similar way in preparation of a stable silyl radical, tris(tris-isopropylsilyl)silyl (**IV**). The species has half-life of 5 days at 15°C (H. Matsumoto, Japan). J. Apeloiq (Israel) carried out quantum-chemical calculations of silylenes dimerization and predicted that amino substituted silaethylenes (**V**) and substituted 1,3-diazadisilacyclobutanes (**VI**) should be in equilibrium.

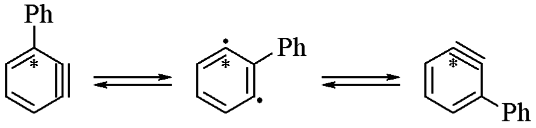


V **VI**

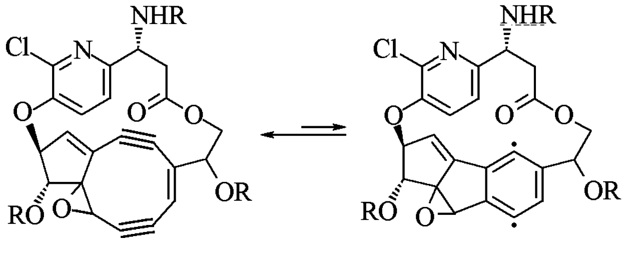
The modern technique of cyclotron-resonance mass spectrometry was used in observing substituted disilabenzene, disilaethylene, and disilaacetylene (P. Gaspar, USA).

N. Tokitoh (Japan) reported on preparation of silacyclopropanebenzene (**VII**) and the first stable germacyclopropanebenzene (**VIII**). Their molecular structure was determined by X-ray diffraction analysis.

M. Jones (USA) by an example of phenyl-substituted dehydrobenzene with ^{14}C label showed that dehydrobenzene underwent a degenerate rearrangement with the triple bond migration in the ring via formation of 1,3-dehydrobenzene.



By ESR spectroscopy at room temperature on the synthetic analog (IX) of the known antitumor antibiotic “C-1027” containing a fragment *cis*-1,4-hexadien-3-yne was observed formation of its isomer 1,4-dehydrobenzene (**X**) (M. Hirama, Japan).



IX **X**

A. de Meijere (Germany) reported on the synthesis of cyclopropyl-substituted nonbenzoid aromatic ions (cyclopropenylium, tropylium, and cyclopentadienylium). In going from ferrocene to pentasubstituted methyl- and further cyclopropylferrocenes the redox potential $E_{1/2}$ alters in this series respectively from +0.475 to –0.070 to –0.13 eV.

The next meeting dedicated to these problems will be held on July 7–12, 2002 in Switzerland (Ascona, http://www-chem.unifr.ch/pc/ascona_02/)