

3800 million years ago had already settled down to its present, somewhat humdrum existence. By this point, its exuberant youth seems to have been past, and the relatively stable conditions required for the continuity of life had been established. This observation is surely consistent with the newly reported isotopic data (3), which

strengthen the case for the proposition that life began long before 3500 million years ago. It will require the discovery of less highly metamorphosed rocks of Isua age to prove that the proposition is correct. Ultimately, we may even discover rocks that precede the origin of life on Earth and thus define its advent.

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## ORGANIC CHEMISTRY

# Germanyl and Silyl Cations: Free at Last

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Many efforts extending over a half century have failed to yield free silicon- and germanium-based cations in condensed phases, that is, cations that do not have strong interactions with the solvent and counteranions. Such an achievement would open new possibilities for chemistry involving heavier elements of the same periodic group as carbon. On p. 60 of this issue, Sekiguchi *et al.* (1) report the synthesis of a free germanium cation in the form of an equilateral triangle, analogous to the carbon cyclopropenium cation.

The chemistry of carbon is very different from that of silicon and germanium. Olah won the 1994 Nobel Prize in Chemistry for finding that carbocations were persistent in solution and could be observed spectroscopically (2). The positively charged carbon species are well separated from the anion, so that only general electrostatic cation-anion interactions can occur.

As silicon and germanium, just below carbon in group 14 of the periodic table, are more electropositive, their ions should be even more accessible. Indeed, gas-phase measurements and *ab initio* calculations show silyl and germanyl cations to be more stable thermodynamically than their carbon counterparts, because the positive charge is associated with more metallic elements. Because of their industrial importance—for example, in semiconductor technology—the chemistry of germanium and especially of silicon has been well investigated (3). Positively charged species in the gas phase are implicated in the epitaxial growth of the films used in transistors (4). Nonetheless, efforts to duplicate stable carbocation chemistry for silicon and germanium in solution have failed until recently, and then met with only partial success (5).

There are inherent reasons for these difficulties. Silyl cations, as one commentator put it, have a “voracious appetite for nucleophiles” (6). Silyl cations are so interactive that they will bind practically everything in their environment, especially solvent molecules and the counteranions. Over the years, many claimed to have observed silyl cations, but these reports proved to be premature, based on inadequate evidence. The publications of crystal structures in 1993 (7, 8) were important breakthroughs, but these led to heated debates about the interpretation. Many took part in these debates, including Olah and Pauling, in one of his last scientific contributions, (9). The first x-ray structure reported on  $(C_2H_5)_3Si(toluenes)^+B(C_6F_5)_3^-$  is now agreed to be a complex (see figure, scheme 1) between the trialkyl-substituted silyl cation and the solvent, toluene (the anion is too far away to interact) (7). The second x-ray structure (8) involved the more hindered  $(isopropyl)_3Si^+$  silyl cation, but this molecule interacts with one of the bromines in the  $CB_{11}H_6Br_6^-$  counterion. Subsequent crystallographic studies on various silyl cation systems have given similar results (10); in no case have alkyl-substituted silyl cations that are truly free been found.

Data from an important diagnostic tool, nuclear magnetic resonance (NMR) spectroscopy, underscore this conclusion. The development of accurate quantum mechanical methods for the computation of chemical

shifts, notably the method of Kutzelnigg's group at the University of Bochum, provided reliable prediction of the  $^{29}Si$  chemical shift [around 360 parts per million (ppm)] in truly free  $R_3Si^+$  cations (11). In contrast, the measured  $^{29}Si$  chemical shifts of the compounds whose x-ray structures had been determined were only around 100 ppm (12). The silyl cations in these species certainly are not “free.” Indeed, calculations by my research

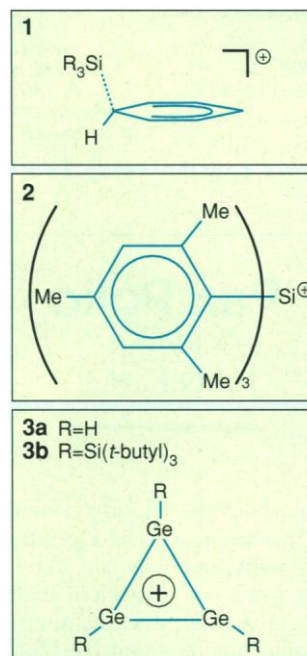
group showed that silyl cations interact significantly even with methane and noble gas atoms, species considered to be essentially inert (13).

Three strategies have been used to try to produce free silyl and germanyl cations in condensed phases. Because a counterion must be present under such conditions to balance the charge, this anion should be as inert as possible. This strategy (7, 8) has not, by itself, led to success. Nevertheless, weakly nucleophilic anions help.

The second strategy is to hinder the  $Si^+$  environment with bulky groups to such an extent that no interaction with the anion (or solvent) is possible. Although even *tert*-butyl groups attached to  $Si^+$  were not sufficient, Lambert has suc-

ceeded by using 2,4,6-trimethylphenyl- (mesityl) substituents (14). The trimesitylsilyl cation (3) has a  $^{29}Si$  chemical shift at 225.5 ppm, the highest value ever observed for such species. Although this value is still substantially less than the nearly 360 ppm computed for alkyl-substituted  $R_3Si^+$  cations, this difference can be attributed to the influence of the phenyl substituents rather than interactions with the environment.

The third strategy involves the stabilization of silyl or germanyl cations by substituents to such an extent that their interaction with the anion and the environment is suppressed. The new Lambert ion (scheme 2) benefits somewhat from conjugation with



**Cation structures.** Me = methyl group.

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the aryl substituents (14). However, highly electronically stabilized systems can be criticized as no longer being true silyl cations, as the charge is delocalized away from silicon to the substituent atoms. But there is another, quite effective way to delocalize the charge symmetrically among atoms of the same type.

Jemmis *et al.* (15) proposed placement of three germanium atoms in a three-membered  $\text{Ge}_3\text{H}_3^+$  ring (scheme 3a), where the positive charge would be shared. If planar, such ring systems are known to be aromatic, that is, they enjoy extra stabilization due to the two  $\pi$ -electron delocalization. Although a second cyclic  $\text{Ge}_3\text{H}_3^+$  isomer with bridging hydrogens is even more stable than the compound in scheme 3a, groups other than hydrogen would not be expected to bridge. The authors concluded, "our results suggest new opportunities for the experimental observation of free cations of the heavier group 14 elements" (16).

This is exactly what Sekiguchi *et al.* (1) have achieved. The x-ray structure of tris (tri-*tert*-butylsilyl)cyclotragermenium tetraphenylborate  $[(\text{t-Bu}_3\text{SiGe})_3^+\text{BPh}_4^-]$ , where Bu = butyl and Ph = phenyl]

(scheme 3b) shows a virtually symmetrical three-membered cation ring and a remotely situated anion (the nearest distance between a Ge and a phenyl C atom is over 4 Å, which precludes any covalent interaction). The average Ge-Ge bond length, 2.3264 Å, is quite close to the 2.361 Å separation predicted for scheme 3a by the theoretical computations.

Although the bulky (t-butyl)<sub>3</sub>Si substituents in scheme 3b undoubtedly hinder the approach of the anion, our further computations on the parent ion, 3a, indicate that the interaction with nucleophiles is sharply reduced. Hence, as in the new Lambert silyl cation, scheme 2, both steric hindrance and electronic stabilization contribute to the attainment of the long-sought goal: free silyl and germanyl cations in condensed phases.

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#### VACCINES

## Pax Polio

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Our dictionary defines millennium both as a period of a thousand years and as "a hoped for period of joy, peace, serenity, prosperity, and justice" (1). In both senses of the word, one of the early achievements in the approaching millennium will be the global eradication of poliomyelitis. Polio eradication will eliminate disease, reduce disability, and produce direct savings of at least \$1.5 billion per year (2). The eradication initiative has also led combatants to lay down their arms.

In 1988, the nations of the world established a goal of global polio eradication by the year 2000. Progress since then has been exceptional (3). Reported polio cases have declined by 80% since 1988. Wild polioviruses were eradicated from the Western Hemisphere in 1991. Eradication is close in China. In an unprecedented display of international cooperation, 18 contiguous nations of the Middle East, Caucasus, and the Central Asian Republics, including current and

former combatants, united in 1995 to conduct Operation MECACAR, immunizing 56 million children. Almost half the world's children under 5 years of age were immunized during polio campaigns in 51 countries that year. India immunized 93 million children on a single day in January 1996.

Although the strategies are proven effective (4), not all the tools necessary for eradication are in place. An estimated \$600 to \$800 million still need to be mobilized. Political commitment remains weak in several countries where the disease is highly endemic. Probably the greatest threat to polio eradication, though, is war and civil strife. As clinics are destroyed, health workers killed, and the civilian population turned into refugees, war zones become fertile fields for epidemics. The last case of polio in the Americas was a Peruvian boy who was not fully immunized because the local clinic had been destroyed by guerrillas. In Afghanistan, decades of war have resulted in less than 20% of the children being immunized. Wild poliovirus was recently reintroduced into Iran from Afghanistan.

During armed conflict, mass immuniza-



**An excuse for peace.** Measles immunization during days of tranquility in El Salvador. [Photo courtesy of UNICEF]

tion campaigns are not just a requirement for polio eradication, they may offer the only means of reaching vulnerable children. The polio eradication initiative has been the stimulus for a number of remarkable cease-fires for immunization. Starting in 1985, days of tranquility were observed each year in El Salvador so that children could be vaccinated against polio and other diseases (see figure). In 1993, the Philippine Secretary of Health personally negotiated with rebel leaders, giving them vaccine to immunize their own children. Truces between the Tamil Tigers and the Sri Lankan army were observed in 1995 and 1996, with polio vaccine passed across the front lines dur-

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