lack of agreement with the observed structure. (See figure 1 of the comment by Olah et al. for the numbering of atoms.) (i) The calculations indicate more pronounced alternation of bond lengths within toluene, 1.424/1.370/1.403 Å according to Olah et al. and 1.425/1.367/1.405 Å according to Schleyer et al., as opposed to 1.40/1.37/1.38 Å observed by us (I). (ii) The geometry around C4 is calculated to be rather different from that of sp², as illustrated by Olah et al. The H attached to C4 is depicted as deviating significantly from the aromatic plane. Schleyer et al. (10) calculated the C3-C4-H angle to be 117°, whereas we observed it to be 120.5°. Neither group reports the extent of deviations of C4 from the plane of the remaining five atoms, but we expect that calculated deviations are significant, as in figure 1 of the comment by Olah et al. The observed toluene molecule, however, is essentially planar, the largest C-C-C dihedral angle being 1.7°. (iii) The calculations misplace the Si atom considerably with respect to the arene ring, as best illustrated by the Si-C4–C1 angle, calculated by Olah et al. to be 110.3°, calculated by Schleyer et al. to be 114°, and measured by us in the crystal to be 104°. In general, the calculations give a much tighter binding between Si and toluene, as might be expected for an ion-molecule complex in the gas phase. Thus the theoretical calculations lead to misinterpretation of the observed structure in the crystal.

The theoretical calculations of Olah et al. and Schleyer et al. indicate that the 29Si chemical shift reflects geometry more than positive charge density. The observed chemical shift of about 8 to 90 reflects the geometry of the trialkylsilyl portion of the structure, which is well reproduced by calculation, but does not address the critical issues of the positive charge density on Si and the bond order between Si and the arene. The experimental values of chemical shift are perfectly reasonable for Si with low bond order to toluene and high positive charge density.

The operational definition of a silylium ion is that positive charge is predominantly on Si, whereas that of an arenium ion (σ complex) is that positive charge is found predominantly on the arene ring and its substituents. The distinction may be made by quantifying the bond order between Si and the para C of toluene and by quantifying the amount of positive charge on Si and toluene. As noted above, Pauling's equation estimates the Si-C bond order to be 0.28 to 0.35. Schleyer et al. (10) calculate the gas-phase Wiiberg bond index to be 0.44 for the complex of benzene with H3Si+. The value should be lower for Me3Si+ and even lower in the condensed phase, so that modern theory is in fundamental agreement with Pauling's method which shows that there is only about a third of a bond between Si and toluene. Schleyer et al. calculate an association energy of about 30 kcal mol⁻¹ between Me3Si+ and toluene in the gas phase, and a lower value should be observed in condensed phase, as indicated by fast exchange on the NMR time scale. Compared with a full C-Si bond dissociation energy of 90 kcal mol⁻¹ (11), the calculated energies also suggest about a third of a covalent bond.

The amount of charge on atoms is a more difficult quantity to assess. Schleyer et al. (10) calculate the charge on Si in the gas-phase complex between Me3Si+ and toluene to be +0.71, leaving only a small amount of charge to be distributed over the atoms of toluene. For comparison, they calculate +0.43, in the neutral methylsilane. We have been able to assess the amount of charge in toluene experimentally by examining the 13C shifts in the solid (7). Introduction of positive charge into toluene in a σ complex of the type illustrated by Olah et al. should result in appreciable downfield movement of the chemical shift for C1/C3/C5, upfield movement for C4, and downfield movement for CH3. In the solid state, however, all these resonances are essentially unchanged from those of free toluene. Thus experiment does not support the σ complex model. None of our observations, however, are in disagreement with the η1, π complex model of Reed et al. (6), which is expected to have an undistorted, planar toluene ring and charge predominantly on Si.

In summary, theoretical calculations of bond order, theoretical calculations of charge density on Si, theoretical and experimental assessments of association energies (when differences between gas and condensed phase are taken into consideration), experimental determination of 13C chemical shifts of bound toluene, and observation of fast exchange on the NMR time scale all indicate that there is about a third of a covalent bond or less between Me3Si+ and toluene and that the preponderance of positive charge is on Si. Consequently, as we concluded in our report, triethyldisilyle tetraakis(pentafluorophenyl)borate is best termed a silyl cation with weak coordination to toluene.

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Response: The description of Et3Si(toluene)+ as a σ silylated arenium ion by Olah et al. (and by Schleyer et al. (1)) appears to arise from an emphasis on calculated structure in preference to observed structure and from the expectation that Si chemistry will closely follow C chemistry. It is becoming apparent however, that unlike carbenium ion (R3C⁺) chemistry, that for the silylium ion can be approached incrementally. Thus, Et3Si(toluene)+ is a hybrid of a π-complexed silyl cation and a σ-complexed arenium ion (Scheme 1). The legitimate polemic then becomes one of degree. We concur with Lambert et al. that the observed structure is consistent with a predominantly contribution from a positively charged Si rather than C species. Theoretical calculations at the HF/6-31G* level produce a value for the critical Si-C-C angle that is too large by about 6° to 10°, thereby conferring atart factual predominance of the arenium ion structure. Olah et al. and Schleyer et al. (1) state that Si hyperconjugation could explain the long Si-C distance (2.18 Å). Hyperconjugation contributes a further resonance form of the very type they discount, that is, one with ionic R-Si⁺ and no covalent bond.

In fact, it was the original description by Lambert et al. (2) of Et3Si(toluene)+ as a silylium ion where "covalent bonding is weak or absent" that first stirred controversy. Weak π bonding of toluene to Si seems currently to be the best single description of the structure. Certainly the search for a free R-Si⁺ ion must continue, but so must the search for better theory.

In a conceptually related manner, the
observed structure of $i$-Pr$_3$Si(Br$_2$-CB$_1$H$_2$) can be viewed as lying on a continuum between a bromonium ion and a silylium ion (Scheme 2). In describing $i$-Pr$_3$Si(Br$_2$-CB$_1$H$_2$) as a "silyl-bromonium zwitterion," Olah et al. underestimate the contribution of silylium ion character. One can argue about degree, but by the criterion of the C-Si-C angle (117° is observed), the major contributor has silylium rather than bromonium ion character. The silylium ion character is also strongly reflected in the chemical reactivity of $i$-Pr$_3$Si(Br$_2$-CB$_1$H$_2$). It rapidly abstracts chloride from dichlorobenzene and strongly bound fluoride from fluoro- benzene.

In summary, while the metaphor "you can’t get half pregnant" may apply to carbenium ion chemistry, in silylium ion chemistry the important thing is "being more than halfway through pregnancy."

The various criteria currently available for measuring closeness to full-term $R_3$Si$^+$ character ($^{29}$Si NMR, theory, C-Si-C bond angles, reactivity, and so on) give different estimates. But the establishment of substantial, and by most criteria predominant, silylium character in both $i$-Pr$_3$Si(Br$_2$-CB$_1$H$_2$) and Et$_3$Si(toluene)$^+$ cannot be denied.

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**Ca$^{2+}$-Induced Ca$^{2+}$ Release in Response to Flash Photolysis**

S. Györke and M. Fill (1) recently used results obtained with DM-nitrophen (caged Ca$^{2+}$) photolysis to support the hypothesis that Ca release channels from cardiac muscle may "adapt" to a Ca$^{2+}$ stimulus. According to this proposal, a relatively rapid rise in the concentration of Ca$^{2+}$ ([Ca$^{2+}$]) (from about 0.1 µM to 0.2 µM) on the cytoplasmic side of the Ca channels results in the probability that Ca channels of the cell will open ($P_o$) to increase to a high value and then gradually decline to a lower, steady value (Fig. 1A). Their conclusion was based on the assumption that [Ca$^{2+}$] rises in a step-like fashion after the photolysis of the DM-nitrophen, and this assumption was apparently supported by measurements with a Ca$^{2+}$-sensitive electrode. However, the photolysis procedure used by Györke and Fill would have generated an extremely large, transient increase in the [Ca$^{2+}$] (2, 3) (Fig. 1B), which itself might account for the behavior of the channels without there having to be any Ca channel "adaptation."

The occurrence of a Ca$^{2+}$ "spike" in response to photolysis of DM-nitrophen can be explained as follows. Györke and Fill added 3 mM total nitrophen and 2 mM CaCl$_2$ (1), so initially there would have been 2 mM of Ca-nitrophen and 1 mM of free nitrophen in the solution, and thus 0.5 mM of the total nitrophen must have been photolysed in order to raise the steady-state [Ca$^{2+}$] by a factor of 2. As the quantum efficiency of Ca-nitrophen is 2.5 times that of free nitrophen (3), the laser flash would have liberated about 0.42 mM of Ca$^{2+}$ from Ca-nitrophen. Because this liberation would have been faster (half-time <180 µs) (4) than the association of Ca$^{2+}$ with the remaining free nitrophen (initial half-time about 1 ms) (3), the free [Ca$^{2+}$] would have increased briefly to about three orders of magnitude greater than the final steady-state concentration (Fig. 1). In order to raise the steady state [Ca$^{2+}$] by a factor of another 2.5, the second laser flash must have photolysed about 0.27 mM Ca-nitrophen and hence generated another large, though slightly smaller, Ca$^{2+}$ spike. (Even if the free nitrophen were only 0.1 mM, owing to a possible error in the calculated total amount of added nitrophen, the Ca$^{2+}$ spikes would still be two orders of magnitude greater than the change in steady [Ca$^{2+}$].) Such Ca$^{2+}$ spikes would not have been detected by the Ca$^{2+}$-sensitive electrode used by Györke and Fill, which only responded with a time constant of 30 to 50 ms (dotted line in Fig. 1B). Nevertheless, the Ca release channels should have responded acutely to such a fast transient [Ca$^{2+}$] change (the half-activation time was stated as 1.2 ms) (1), with the probability of being open rising markedly during the Ca$^{2+}$ spike before settling to a lower value after the [Ca$^{2+}$] reached steady-state.

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