JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2002; **15:** 667–671

A stable β-silyl carbocation with allyl conjugation

Joseph B. Lambert,* Chunqing Liu and Timur Kouliev

Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, USA

Received 18 February 2002; revised 16 April 2002; accepted 18 April 2002

ABSTRACT: The carbocation $Et_3SiCH_2C^+Ph(CH{=}CHPh)$ has been found to be stable at room temperature with tetrakis(pentafluorophenyl)borate as the anion and benzene as the solvent. The cation constitutes the first stable β-silyl carbocation in which positive charge is delocalized both allylically and benzylically. Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: allylic conjugation; benzylic conjugation; carbocations; hyperconjugation; silicon

INTRODUCTION

Early studies of the ability of silicon to stabilize positive charge on a carbon at the β-position ($R_3Si—C—C^+$) focused on understanding the mechanism of the interaction (for a review, see Ref. 1). The two major mechanisms of positive charge delocalization in carbocations involve donation of π or of n electrons to the empty p orbital, for example, respectively in allylic ($CH_2{=}CH—CH_2^+ \leftrightarrow {}^+CH_2—CH{=}CH_2$) and oxonium ($CH_3O—CH_2^+ \leftrightarrow CH_3O^+{=}CH_2$) ions. A much weaker mechanism involves resonance donation of σ electrons in CH or CC hyperconjugation (as in $H—CH_2—CH_2^+ \leftrightarrow H^+\ CH_2{=}CH_2$). Induction also plays a role, destabilizing in the case of electron-withdrawing substituents such as the double bond and the oxygen atom in the above allylic and oxonium examples and stabilizing in the case of electron-donating substituents such as trimethylsilyl. Silicon at the β-position thus offers the twofold advantage of stabilization both through induction as a result of its electropositivity and through enhanced hyperconjugation as a result of its high polarizability and the appropriate energy of the C—Si bond. Stereochemical and kinetic studies demonstrated that hyperconjugation is the major mechanism of the β effect of silicon and that induction plays a minor role.[2]

Chemists also tried to observe a β-silyl carbocation directly under stable ion conditions.[3] Olah's studies in magic acid failed because the highly electrophilic silicon atom suffered nucleophilic attack and elimination. Hyperconjugation moves positive charge from carbon to silicon in Olah's system ($Me_3Si—CH_2—CPh_2^+ \leftrightarrow Me_3Si^+\ CH_2{=}CPh_2$), heightening the electrophilicity of silicon. Even magic acid contains nucleophiles ('X') strong enough to attack silicon and lead to loss of $Me_3Si—X$ and formation of $CH_2{=}CPh_2$, which was protonated under the reaction conditions to form $CH_3Ph_2C^+$ as the only observable carbocation.[3]

In 1996, we utilized conditions developed for the preparation of stable silylium ions to generate the first simple, stable β-silyl carbocation.[4] Addition of the solvated silyl cation Et_3Si^+ to $CH_2{=}CPh_2$ produced $Et_3SiCH_2CPh_2^+$, which was stable at room temperature for weeks. The stability of this ion arose because of internal stabilization by the various substituents and because of the use of conditions with minimal nucleophilicity. The anion was tetrakis(pentafluorophenyl) borate [$(C_6F_5)_4B^-$, abbreviated here as TPFPB], and the solvent was an arene such as toluene or benzene. Siehl *et al.* later observed similar ions under magic acid conditions by rigid exclusion of water and other nucleophiles.[5]

We also were able to isolate germanium analogues.[6] In unpublished work (with Y. Zhao) we found that the phenyl groups were critical in observing stable β-silyl carbocations. Omission of even one phenyl ring failed to yield isolable ions. Thus, when styrene, α-methylstyrene or isobutene was used in place of 1,1-diphenylethene, no stable ions were formed. Apparently the ions were present briefly, as we were able to carry out successful trapping experiments. The observed β-silyl carbocation from the addition of triethylsilylium to 1,1-diphenylethene, $Et_3SiCH_2CPh_2^+$, is stabilized once by Si hyperconjugation and twice by benzylic conjugation. Replacement of one or both phenyl groups with methyl or hydrogen considerably reduced the stability of the cation and rendered it unisolable.

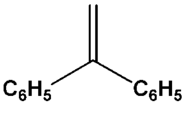
In the present investigation, we considered whether the phenyl group can be replaced by a double bond and still yield a stable β-silyl carbocation. The question thus is whether allylic stabilization can serve as successfully as

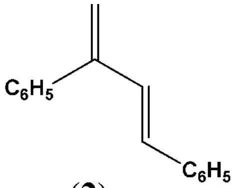
---

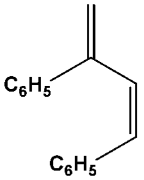
*Correspondence to: J. B. Lambert, Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, USA.
E-mail: jlambert@northwestern.edu

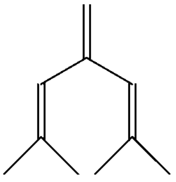
Contract/grant sponsor: National Science Foundation; *Contract/grant number:* CHE-0091162.

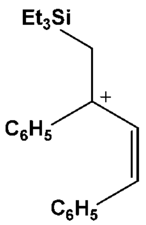
did benzylic stabilization. On the basis of our previous unpublished work (with Y. Zhao), we concluded that two such π donors are needed. We examined systems in which positive charge could be stabilized by one phenyl and one double bond or by two double bonds. Thus, by analogy with the diphenyl system **1** (to which the solvated silyl cation was added to produce the cation), we synthesized 1,3-diphenyl-1,3-butadiene in both its *E* (**2**) and *Z* (**3**) forms and 2,6-dimethyl-4-methylene-2,5-heptadiene (**4**). Addition of the solvated silyl cation to these species respectively gives **5** (illustrated as the *Z* form) and **6**. In **5**, positive charge is stabilized by silicon, phenyl and the double bond. In **6**, positive charge is stabilized by silicon and two double bonds. These systems enable us to examine the ability of double bonds, through allylic resonance, to supplement hyperconjugation from the C—Si bond and permit the isolation of stable β-silyl carbocations.

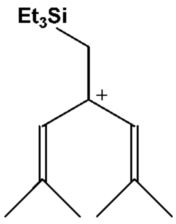

(1)


(2)


(3)


(4)

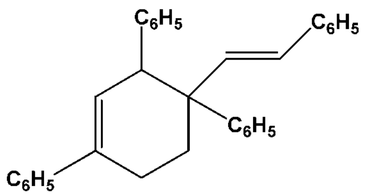

(5)

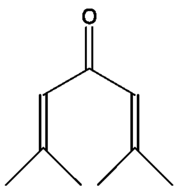

(6)

RESULTS AND DISCUSSION

Synthesis

Substrates **2**–**4** were selected because of their ready accessibility. Alkene **2/3** is available from α-methylstyrene in four steps.[7] Previous studies of 1,3-diphenyl-1,3-butadiene[7,8] indicated that the *E* isomer **2** is unstable to Diels–Alder dimerization and forms **7**. Greater steric hindrance in the *Z* isomer **3** rendered it stable and isolable. Consequently, all our experiments focused on the *Z* isomer **3**. Substrate **4** with potential stabilization from two double bonds was readily prepared by the Wittig reaction on phorone (2,6-dimethyl-2,5-heptadien-4-one) (**8**).


(7)


(8)

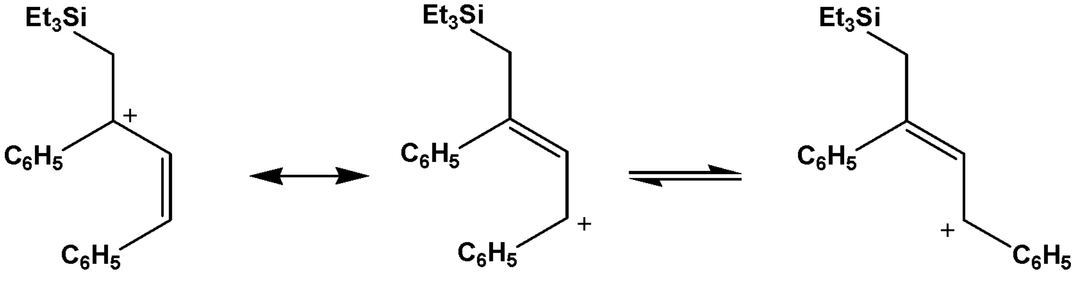
Preparation and characterization of the cations

To produce the β-silyl carbocations, triethylsilylium TPFPB was added to the alkenes **3** and **4**. The solvated silyl cation in turn was produced by the reaction of triethylsilane with trityl TPFPB. These reactions were carried out at room temperature in NMR tubes using syringe techniques within a glove-box. The solvent was deuterated benzene.

Reaction of the solvated silyl cation with (*Z*)-1,3-diphenyl-1,3-butadiene (**3**) was expected to produce the β-silyl carbocation **5**, in which the positive charge is stabilized by the silicon at the β-position, by the single phenyl ring, and by the double bond. The ^{1}H spectrum of the dark red product was very simple, containing a set of resonances in the region δ 6.4–7.4 from aromatic and alkenic resonances, two methyl and two methylene singlets in the region δ 0–1 from the ethyl group in the product and the ethyl group in excess triethylsilylium TPFPB, and a sharp singlet at δ 3.18. This singlet is appropriate for the methylene group between silicon and the carbon bearing positive charge. It is shifted to high frequency because of sp^2 character conveyed by hyperconjugation ($Et_3Si—CH_2—CPhR^+ \leftrightarrow Et_3Si^+$ CH_2 $=CPhR$, in which R is the phenylvinyl group). The general appearance of the spectrum and the resonance position of the methylene carbon are very similar to those of the product from diphenylethene ($Et_3SiCH_2CPh_2^+$), in which the methylene carbon resonates at δ 3.64.[6]

The ^{29}Si spectrum contained a resonance from excess solvated triethylsilylium TPFPB at δ 91.6, and two other peaks at δ 34.2 and 28.5. The β-silyl carbocation from diphenylethene had a single ^{29}Si peak at δ 46.4.[4] The lower frequency positions of the peaks for **5** suggest less transfer of positive charge to silicon.

In the ^{13}C spectrum, in addition to saturated resonances from the ethyl carbons, resonances from the product triphenylmethane and other aromatic resonances in the region δ 120–160 from the anion and the phenyl groups on the cation **5**, there were resonances at δ 57.2, 193.7 and 235.7. The resonance at δ 57.2 is from the CH_2 group between silicon and the tertiary carbocation carbon. Charge delocalization by allylic resonance places positive charge at two positions (**5** ↔ **9**). The chemical shift δ 235.7 compares with δ 225.7 for the cation from

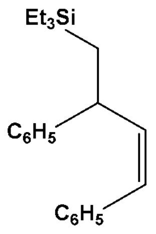


(5) **(9)** **(10)**

diphenylethene ($Et_3SiCH_2CPh_2^+$). This resonance is from the tertiary carbocation carbon in **5**, and the higher frequency position suggests more positive charge on this carbon than in $Et_3SiCH_2CPh_2^+$. The chemical shift δ 193.7 is appropriate for the secondary carbocation in **9** (from allylic delocalization as compared, for example, with δ 200.2 for Ph_2CH^+) (for a general discussion of the ^{13}C resonances of unsaturated carbocations, see Ref. 9). The aryl carbons on to which positive charge is delocalized typically are in the range[9] δ 140–145 and so appear with other aromatic resonances. Note that **5** and **9** are resonance hybrids of a single carbocation.

These observations indicate that there is less delocalization of charge to the double bond than to the second phenyl ring in $Et_3SiCH_2CPh_2^+$. The observation of two ^{29}Si peaks may reflect the presence of *E/Z* isomers (**10**), but we have no clear evidence on this issue. These experiments were repeated in dichloromethane at −50 °C. No NMR peaks characteristic of a carbocation were obtained. Evidently this solvent is too nucleophilic to permit formation of the cation as a long-lived species.

The cation was trapped by reaction with triethylsilane in the presence of a catalytic amount of trityl TPFPB.[6] The peaks characteristic of carbocationic character disappeared: ^1H at δ 3.18, ^{13}C at δ 235.7 and 193.7 and ^{29}Si at δ 34.2 and 28.5. The spectra were consistent with the expected product, **11** (stereochemistry indeterminate), including in particular the benzylic proton at δ 2.67. The mass spectrum confirmed the structure.



(11)

Substrate **4** (2,6-dimethyl-4-methylene-2,5-heptadiene) was prepared in order that double allylic stabilization can replace double benzylic stabilization in $Et_3SiCH_2CPh_2^+$. Procedures identical with those used for 1,1-diphenylethene and (*Z*)-1,3-diphenyl-1,3-butadiene were used. Upon stoichiometric treatment with the solvated silyl cation Et_3Si^+ $TPFPB^-$ either at room temperature in C_6D_6 or at −50 °C in CD_2Cl_2, **4** produced a dark brown solution that exhibited no ^{13}C resonances at higher frequency than δ 145 and no ^{29}Si resonances above δ 10. Moreover, treatment of the benzene solution with triethylsilane as a hydride source and a catalytic amount of trityl TPFPB resulted in the loss of none of the principal resonances, confirming that they did not derive from a carbocation. We conclude that no β-silyl carbocation was observed under the reaction conditions from **4**.

It is important to recognize that cation **6** has numerous methyl protons that can initiate decomposition through elimination, whereas cation **5** has no such protons. The failure to observe the doubly allylic β-silyl cation may be the result of this difference rather than inherent instability. This hypothesis would have to be tested by use of a substrate such as $CH_2{=}C(CH{=}CHPh)_2$.

CONCLUSIONS

A tricoordinate, tertiary carbocation has three opportunities for stabilization by its substituents. Thus three π donors, as in the triphenylmethyl carbocation, Ph_3C^+ (trityl or tritylium), provide the strongest stabilization. In the known[4–6] β-silyl carbocation $Et_3SiCH_2CPh_2^+$, C—Si hyperconjugation ($\sigma\pi$ conjugation) has replaced benzylic conjugation of one of the phenyl groups of trityl. Nonetheless, the cation is sufficiently stable to exist for long periods of time at room temperature under our conditions[4,6] or at −100 °C under magic acid conditions.[5] We found in this study that replacement of a second phenyl group on trityl with phenylvinyl still permits observation of a cation that is stable at room temperature. This cation, **5**, is stabilized by C—Si hyperconjugation, benzylic conjugation and allylic conjugation. Replacement of both the second and the third phenyl rings of trityl by dimethylallyl groups, however, does not permit the isolation of a stable carbocation (**6**) at room temperature or at −50 °C under the current conditions. This cation would have been stabilized by C—Si hyperconjugation and twice by allylic conjugation.

It is evident from these observations that allylic conjugation is not so effective as benzylic conjugation in stabilizing a carbocation. When benzylic stabilization is replaced entirely by allylic stabilization, no cation is observed. We even used the most favorable substitution mode of the allylic group (dimethylallyl) in **6**, in which allylic delocalization moves charge to a tertiary position ($R'R''C^+$—$CH{=}CMe_2 \leftrightarrow R'R''C{=}CH$—$CMe_2^+$ in which R′ is $Me_2C{=}CH$ and R″ is Et_3SiCH_2). This structure, however, may be susceptible to elimination. It may be noteworthy that in the case of cation **5**, allylic delocalization moves charge to a benzylic position, from which charge may be further delocalized ($R'R''C^+$—$CH{=}CHPh \leftrightarrow R'R''C{=}CH$—$^+CHPh \leftrightarrow R'R''C{=}C$—$CH{=}Ph^+$, in which R′ is Ph and R″ is Et_3SiCH_2). This additional delocalization may provide an increment of stabilization that is critical.

The range of β-silyl carbocations that may be observed under stable ion conditions (low nucleophilic anion, hydrocarbon or halocarbon solvent, temperature −50 °C or higher) is therefore relatively circumscribed. Stabilization in addition to that from the β-silyl group always is necessary, and further stabilization by allylic conjugation alone does not suffice.

EXPERIMENTAL

*(Z) 1,3-Diphenyl-1,3-butadiene (**3**).*[7] A solution of 47.2 g (50 ml, 0.4 mol) of α-methylstyrene in 55 ml of CCl_4 was mixed with 78.3 g (0.44 mol) of *N*-bromosuccinimide and stirred at 95–100 °C for 10 h. The solution was cooled, filtered from the precipitated succimide and washed with CCl_4. The solvent was removed by distillation at reduced pressure (house vacuum), and the residue was distilled [90–95 °C/0.45 Torr (1 Torr = 133.3 Pa)] to give 60.7 g (77%) of a mixture of brominated alkenes containing the desired α-(bromomethyl)styrene and also unwanted (*E/Z*)-2-bromo-1-methylstyrene. A solution of 20.8 g (0.11 mol) of the distillate in 100 ml of benzene was mixed with 17.3 g (0.07 mol) of Ph_3P. The resulting phosphonium salt crystallized out in 48 h, and the unreacted and undesired unsaturated bromides remained in solution. The crude, white product was isolated by filtration and washed (3 × 100 ml) with benzene. Recrystallization from dichloromethane–diethyl ether produced 27.6 g (91%) of colorless crystals of the desired phosphonium salt. To 21.4 g (46.6 mmol) of the phosphonium salt in 400 ml of dry tetrahydrofuran cooled to −25 to −50 °C under N_2 was added 18.48 ml (46.2 mmol, 2.5 M in hexane) of butyllithium. The solution of the Wittig reagent was stirred for 30 min and 4.94 g (46.6 mmol) of benzaldehyde were added. The solution was stirred for 1.5 h at room temperature and concentrated by rotary evaporation. Pentane was added to precipitate triphenylphosphine oxide, which was removed by filtration. The filtrate was concentrated by rotary evaporation, and the orange residue was allowed to stand at room temperature for 72 h to complete dimerization of the unwanted *trans* product, **2**. The desired *cis* product, **3**, was purified by chromatography on a silica gel column with pentane as eluent. The dimer of **2** remained on the column to give pure **3**: ^1H NMR ($CDCl_3$), δ 5.27 (d, J = 1.5 Hz, 1H, $CH_2{=}$), 5.54 (d, J = 1.5 Hz, 1H, $CH_2{=}$), 6.37 (d, J = 12 Hz 1H, CH=), 6.63 (d, J = 12 Hz, 1H, CH=), 7.1–7.5 (m, 10H, aromatic); ^{13}C NMR ($CDCl_3$), δ 115.8, 126.5, 127.0, 127.8, 128.0, 128.4, 128.9, 130.4, 131.8, 136.8, 139.3, 144.8. MS 51, 77, 91, 115, 128, 167, 178, 191, 206 (molecular ion); UV (cyclohexane), λ_{max} 250 nm (ε = 16 200).

*2,6-Dimethyl-4-methylene-2,5-heptadiene (**4**).*[7,10] Addition of 39 ml (0.07 mol) of a 1.8 ml solution of phenyllithium in 70:30 cyclohexane–diethyl ether to a stirred solution of 28.6 g (0.08 mol) of methyltriphenylphosphonium bromide in 400 ml of dry diethyl ether under N_2 afforded a solution of the desired Wittig reagent. The solution was stirred for 0.5 h, and 5.5 g (0.04 mol) of phorone in 60 ml of dry diethyl ether was added. The mixture was stirred an additional 0.5 h, H_2O (8 ml) was added, stirring was continued for 0.5 h and $MgSO_4$ was added. The mixture was filtered and the filtrate was washed with saturated aqueous NaCl solution (3 × 100 ml), dried ($MgSO_4$) and filtered. The ether was removed by rotary evaporation and the residue was fractionally distilled at reduced pressure to give 4.2 g of **4**[10] (0.03 mol, 77%, 78–79 °C, 10–20 Torr): ^1H NMR ($CDCl_3$), δ 1.77 (s, 12H), 4.94 (s, 2H), 5.77 (s, 2H); ^{13}C NMR ($CDCl_3$), δ 19.6, 26.9, 116.2, 126.7, 134.6, 143.6; UV (cyclohexane), λ_{max} 218 nm (ε = 15 500). Anal. Calcd for $C_{10}H_{16}$: C, 88.16; H, 11.84. Found: C, 87.98; H, 11.89%.

*1-Phenyl-1-(β-phenylvinyl)-2-(triethylsilyl)ethylium tetrakis(pentafluorophenyl)borate (**5**).* In a nitrogen-filled glove-box, 160 mg (0.17 mmol) of triphenylmethyl tetrakis(pentafluorophenyl)borate (TPFPB) (Asahi Glass) and 0.7 ml of dry benzene-d_6 were placed in a valved 5 mm NMR tube. Addition of 25 mg (0.22 mmol) of triethylsilane followed by vertical shaking of the tube with the valve closed produced two layers. The lower, light brown layer contained the solvated silyl cation: triethylsilylium TPFPB. The colorless upper layer, containing the byproduct triphenylmethane and excess triethylsilane, was removed with a syringe. Addition of 45 mg (0.22 mmol) of **3** yielded a dark brown solution of the carbocation: ^1H NMR (C_6D_6), δ 0.18 (s, 2H, $SiCH_2CH_3$), 0.58 (s, 3H, CH_3), 3.18 (2H, $SiCH_2C$), 6.4–7.4 (m, 12H, aromatic and alkenic); ^{13}C NMR (C_6D_6), δ 4.8, 8.1, 57.2, 120–150 (aromatic carbons), 193.7, 235.7; ^{29}Si NMR (C_6D_6), δ 28.5, 34.2 [all spectra also contained peaks from excess triethylsilylium tetrakis(pentafluorophenyl)borate].

Product studies. Triphenylmethyl TPFPB (20 mg, 0.02 mmol) was placed in a valved 5 mm NMR tube, which was pumped for 2 h under high vacuum and placed in a nitrogen-filled glove-box. The tube was opened and charged with 0.27 g (2.3 mmol) of triethylsilane, 0.21 g (1.0 mmol) of **3** and 1 ml of C_6D_6. The tube was shaken vertically for a few minutes and two layers appeared. The colorless top layer was removed and concentrated to give 0.2 ml of a colorless oil, which by GC contained several components. The ^{13}C and ^{29}Si NMR spectra lacked the peaks characteristic of carbocations. The ^{29}Si spectrum contained a single peak at δ 7.4 in addition to the peak from excess Et_3SiH at $\delta - 0.3$. MS of the principal GC peak showed the molecular ion at *m/z* 322, corresponding to the structure 1,3-diphenyl-4-(triethylsilyl)butane (**11**). The next highest peak was at *m/z* 206, from $(M - Et_3Si)^+$.

Acknowledgements

The authors thank the National Science Foundation (Grant No. CHE-0091162) for support of this work and Asahi Glass Company for a gift of triphenylmethyl tetrakis(pentafluorophenyl)borate.

REFERENCES

1. Lambert JB. *Tetrahedron* 1990; **46**: 2677.
2. Lambert JB, Zhao Y, Emblidge RW, Salvador LA, Liu X, So J-H, Chelius EC. *Acc. Chem. Res.* 1999; **32**: 183.
3. Olah GA, Berrier AL, Field LD, Prakash GKS. *J. Am. Chem. Soc.* 1982; **104**: 1349.
4. Lambert JB, Zhao Y. *J. Am. Chem. Soc.* 1996; **118**: 7867.
5. Siehl H-U, Müller B, Malkina O. In *Organosilicon Chemistry III: From Molecules to Materials*, Auner N, Weis J (eds). Wiley-VCH: Weinheim, 1998; 25–40.
6. Lambert JB, Zhao Y, Wu H. *J. Org. Chem.* 1999; **64**: 2729.
7. Mulzer J, Brüntrup G, Kühl U, Hartz G. *Chem. Ber.* 1982; **115**: 3453.
8. Mulzer J, Kühl U, Brüntrup G. *Tetrahedron Lett.* 1978; 2953; Mulzer J, Kühl U, Huttner G, Brüntrup G. *Chem. Ber.* 1988; **121**: 2231.
9. Stothers JB. *Carbon-13 NMR Spectroscopy*. Academic Press: New York, 1972; 217–224.
10. Sorenson, TS. *Can. J. Chem.* 1964; **42**: 2781.