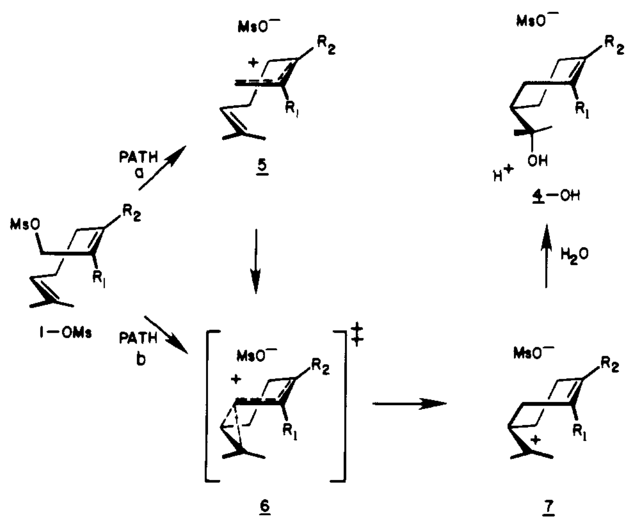
Scheme I. Mechanisms for Cyclization of 1a-d-OMs



neryl/geranyl rate ratios (k_1/k_2), which increased abruptly from 1.2–2.2 for the parent compounds and the 2-fluoro derivatives to 14.2–15.0 for the difluoromethyl and trifluoromethyl compounds.

A similar discontinuity is seen in the product distributions for methanesulfonates **1a**–**d**-OMs listed in Table II.[19] The parent methanesulfonates and the 2-fluoro derivatives gave very similar distributions of allylic and cyclic isomers. Product distributions for the difluoromethyl and trifluoromethyl compounds were, however, markedly different. The most striking trend is the abrupt increase in the ratio of cyclic (**4**) to noncyclic (**1** + **2** + **3**) alcohols from 0.8 to 19 for the neryl derivatives.

The discontinuities in neryl–geranyl rate ratios and in cyclic–acyclic product ratios for the neryl series between the 2-fluoro and the 3-difluoromethyl derivatives signal a change in mechanism which we interpret as the onset of π participation by the remote double bond. Our observations are similar to those reported in the 7-norbornenyl system where π participation also begins abruptly as a function of increasing electron demand.[20] Since the parent neryl system is rather far removed from the break point $(1.6 \times 10^2 < k_{1a}/k_{\text{break}} < 2.6 \times 10^4)$, a neryl–geranyl rate ratio (k_{1a}/k_{2a}) of greater than unity in the parent system is not the result of delicately balanced competing assisted and nonassisted pathways but rather is caused by more subtle conformational effects. The assisted pathway does, however, become dominate for the less reactive difluoromethyl and trifluoromethyl derivatives. Stepwise (path a) and concerted (path b) mechanisms are presented in Scheme I. The driving force for both cyclizations is formation of a relatively strain-free cyclohexenyl ring with concomitant loss of the C(6)–C(7) double bond.

Although the conformation of the side chain exerts little influence on the reactivity of the allylic moiety, it is important with regard to which products are obtained. Since the cyclization is stereospecific and neryl cation **5** is an intermediate, that portion of **1**-OMs which cyclizes must adopt a folded conformation (the anti-endo orientation[21] is shown in Scheme I) before ionization. In view of the high proportion of α-terpineol formed during solvolysis, neryl systems must favor a folded conformation in polar solvents. Reaction from an extended conformation is also possible and may, in fact, account for most of the acyclic products.[22] While we cannot determine precisely how **5** partitions among various reaction pathways when in a folded orientation, cyclization is at least 5 times faster than reaction with water during solvolysis of *N*-methyl-4-(neryloxy)pyridinium methyl sulfate[23] in aqueous sodium bicarbonate. Thus, the intramolecular alkylation reaction is considerably faster than conformational reorientation of the side chain and reaction of the allylic cation with water.

Since ionization and cyclization are distinct steps during solvolysis of nerol and its derivatives, it follows that they are also distinct steps during solvolysis of the slightly more reactive linalyl system. Thus, the direct cyclization of nerol and the allylic cyclization of linalool merge into a set of mechanistically related reactions sharing a common allylic cationic intermediate following the initial ionization step.

Alkylations that are stepwise *and* stereospecific require a delicate balance of conformational control in the reactant(s) and reactivity in the initial cationic intermediate. These points are illustrated by three examples. If the 3,3-dialkylallylic cation typical of terpenes is sufficiently destabilized, for example, by fluorinated substituents, the reaction becomes concerted. If, however, the cation is made too stable by additional alkyl substituents at C(1) and C(3), the reaction is stepwise, but stereorandom.[24] Finally, the intermolecular alkylation of dimethylallyl acetate by dimethylallyl cation, a system with no restraints on the orientation of the reactants, is stereorandom.[25] One should, therefore, anticipate a spectrum of mechanisms for biomimetic and enzymatic olefin alkylation reactions which depend on the nature of the electrophile and the double bond.

Acknowledgment. This work was supported by the Institute of General Medical Sciences of the National Institutes of Health, GM 21328.

Registry No. **1a**-OH, 106-25-2; **1a**-OMs, 80359-44-0; **1b**-OH, 80359-45-1; **1b**-OMs, 80359-46-2; **1c**-OH, 80359-47-3; **1c**-OMs, 80359-48-4; **1d**-OH, 80375-23-1; **1d**-OMs, 80359-49-5; **2a**-OH, 106-24-1; **2a**-OMs, 78130-96-8; **2b**-OH, 80359-50-8; **2b**-OMs, 80359-51-9; **2c**-OH, 76480-98-3; **2c**-OMs, 80359-52-0; **2d**-OH, 76481-03-3; **2d**-OMs, 80359-53-1; **3a**-OH, 78-70-6; **3b**-OH, 64031-55-6; **4a**-OH, 98-55-5; **4b**-OH, 80359-54-2; **4c**-OH, 80359-55-3; **4d**-OH, 80359-56-4.

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[19] Satisfactory IR, NMR, and mass spectra were obtained for all new compounds.

[20] Gassman, P. G.; Fentiman, A. F. *J. Am. Chem. Soc.* **1970**, *92*, 2549–2551.

[21] Poulter, C. D.; King, C. H. R. *J. Am. Chem. Soc.* **1982**, *104*, 1420–1422.

[22] Bunton and co-workers[15] recently analyzed acyclic/cyclic product ratios in terms of competing pathways for solvolysis from extended and folded conformations.

[23] α-Terpineol is formed stereospecifically in 82% yield under these conditions.[21]

[24] Ladika, M.; Bregovec, I.; Sunko, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 1285–1286.

[25] King, C. H. R.; Poulter, C. D. *J. Am. Chem. Soc.* **1982**, *104*, 1413–1420.

Silylene Rearrangements in the Reactions of Recoiling Silicon Atoms with Trimethylsilane

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Atoms created in nuclear transformations are usually born as high-energy cations that have broken free from the molecules in which their parent atoms were covalently bonded.[1] Before a recoiling atom can incorporate itself by its reactions in a new molecule, it must lose much of its initial kinetic energy in a series of collisions in which electron exchange and electronic transitions can also occur.[2] Thus the interpretation of the results of hot-atom experiments can be complicated by the simultaneous presence of several different charge and electronic states of the reacting species.

The exploration of atom–molecule reactions above their threshold energies is a major task of hot-atom chemists, and where

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[1] A. P. Wolf, *Adv. Phys. Org. Chem.*, **2**, 201 (1964); R. Wolfgang, *Prog. React. Kinet.*, **3**, 97 (1965); D. S. Urch, *Radiochemistry* (*London*), **2**, 1 (1975).

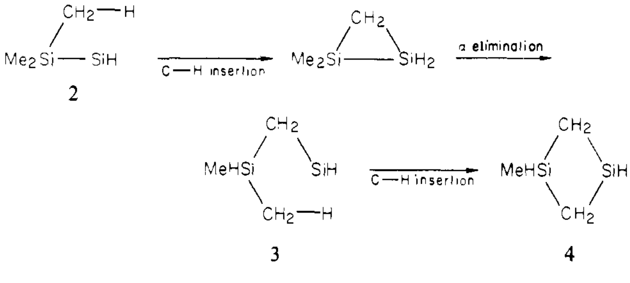
[2] P. J. Estrup and R. Wolfgang, *J. Am. Chem. Soc.*, **82**, 2661 (1960); R. Wolfgang, *J. Chem. Phys.*, **39**, 2983 (1963).

0002-7863/82/1504-1424$01.25/0

Scheme I

$$^{31}Si + HSiMe_3 \rightarrow {}^{31}SiH_2, {}^{31}SiHMe$$
$$^{31}SiH_2 + HSiMe_3 \rightarrow H_3{}^{31}SiSiMe_3$$
$$^{31}SiHMe + HSiMe_3 \rightarrow MeH_2{}^{31}SiSiMe_3$$

Scheme II



comparisons have been made, the recoil reactions differ significantly from their thermal counterparts.[3] This is the case for the reactions of recoiling silicon atoms with trimethylsilane, reported here. Free atoms were produced by the $^{31}P(n,p)^{31}Si$ nuclear transformation induced in gaseous mixtures of phosphine and trimethylsilane by cyclotron-produced fast neutrons.[4,5] The products detected are given below in order of increasing vapor-chromatographic retention times.[6,7]

$$n + PH_3 \rightarrow p + {}^{31}Si + 3H$$

$$^{31}Si + HSiMe_3 \xrightarrow[PH_3]{} {}^{31}SiH_4\ (2\%) + H_3{}^{31}SiMe\ (0.5\%) + \text{unknown}\ (0.1\%) + H_3{}^{31}SiSiMe_3\ (36\%) + MeH_2{}^{31}SiSiMe_3\ (10\%) + \text{unknowns}\ (5\%) + \underset{\mathbf{1}}{Me_3Si^{31}SiH_2SiMe_3}\ (5\%) + A\ (3\%)$$

By contrast, the cocondensation of thermally evaporated silicon[8] with trimethylsilane was reported by Skell and Owen to yield only 1,1,1,3,3,3-hexamethyltrisilane **1**.[9]

$$Si + 2HSiMe_3 \rightarrow \underset{\mathbf{1}\ (10\text{–}30\%)}{Me_3SiSiH_2SiMe_3}$$

In the case of a polyvalent atom like silicon that must initiate a multistep reaction sequence to saturate its valence, the task of elucidating the reaction mechanism leading to the observed end products can be formidable, particularly when the state of the initial reactant is unknown. Study of chemically generated species that are potential intermediates can help shed light on complex reactions,[10] and it was with this hope that we set out some years ago to examine the chemistry of divalent silicon species SiR_2.[11]

Indeed the intermediacy of $^{31}SiH_2$ and $^{31}SiHMe$ would neatly explain the two major products in the recoil reactions reported here, since silylene insertions into SiH bonds are well established.[11] Earlier experiments on the reactions of ^{31}Si with silane SiH_4 have, however, raised questions about the involvement of ground-state $^{31}SiH_2$ in product formation,[12] and one must therefore regard Scheme I as only a mechanistic possibility until further experimental data are available.[13]

It is the purpose of this communication to suggest that we are on firmer ground in attributing the formation of products **1** and A to silylene intermediates. A recently discovered rearrangement of silylenes has led to the identification of A and forms the basis for a mechanism that follows a ^{31}Si atom from its initial reactive encounter with a $HSiMe_3$ molecule to **1** and A.

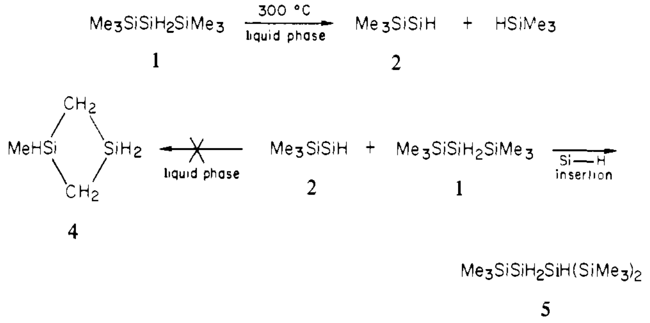
Skell and Owen proposed a pair of consecutive insertions with a (trimethylsilyl)silylene (**2**) intermediate to account for the formation of **1** in the cocondensation of silicon vapor with $HSiMe_3$.[9]

$$Si + H\text{–}SiMe_3 \rightarrow \underset{\mathbf{2}}{H\text{–}Si\text{–}SiMe_3}$$

$$\underset{\mathbf{2}}{Me_3SiSiH} + H\text{–}SiMe_3 \rightarrow \underset{\mathbf{1}}{Me_3SiSiH_2SiMe_3}$$

(Trimethylsilyl)silylene **2** has not otherwise been reported, but the gas-phase rearrangements of methyl(trimethylsilyl)silylene ($Me_3SiSiMe$) and bis(trimethylsilyl)silylene ($(Me_3Si)_2Si$) found recently by Wulff et al.[14] and Chen et al.,[15] respectively, suggest that if **2** is formed in the gas phase, it too should undergo rearrangement according to Scheme II.

Indeed when **2** is generated by gas-phase vacuum-flow pyrolysis of **1** (750 °C, 0.05 torr), a 45% yield of 1-methyl-1,3-disilacyclobutane (**4**) was obtained as the only volatile product detected in addition to $HSiMe_3$.[16] Compound **4** is *not* a product of silicon atom–trimethylsilane cocodensation,[9,17] and it is also absent from the gas-phase reactions of recoiling ^{31}Si atoms and trimethylsilane. Nevertheless [^{31}Si]**2** and [^{31}Si]**3** do appear to be intermediates in the recoil system, diverted by intermolecular reactions prior to the formation of **4**.



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(3) G. Stöcklin, "Chemie heiszer Atome", Verlag Chemie, Weinheim, 1969; "Hot Atom Chemistry Status Report", IAEA, Vienna, 1975.

(4) P. P. Gaspar, P. Markusch, J. D. Holten III, and J. J. Frost, *J. Phys. Chem.*, **76**, 1352 (1972).

(5) The fast neutrons do *not* produce recoiling silicon atoms from silicon; thus the trimethylsilane functions solely as the reaction substrate in these experiments.

(6) The small number of recoiling atoms produced in a reaction mixture, typically 10^8, ensures that the only products detected are those in which the radioactive recoil atom incoporates itself by its reactions, thus forming labeled product molecules. These are detected by their radioactive decay, usually by radiochromatographic techniques. Product molecules are identified by comparison of their chromatographic retention times with those of authentic nonradioactive compounds on several different chromatographic columns. At present reactive intermediates cannot be detected directly in recoil experiments because their instantaneous concentrations are too low.

(7) Product yields were determined to an accuracy of ca. ±15%. The location of the ^{31}Si atom indicated in molecules containing nonequivalent silicons is based on the suggested mechanism and on the assumption that silicon scrambling has not occurred. This has been checked by degradation for trisilane from reactions of ^{31}Si atoms in PH_3–SiH_4 mixtures. Within experimental error (±8%) all of the ^{31}Si was in the central position: $SiH_3{}^{31}SiH_2SiH_3$ (G. W. Stewart, M. D. Sefcik, and P. P. Gaspar, unpublished work).

(8) Silicon vapor at 1660 K is reported to consist of 94% Si_1, 3% Si_2, 1.5% Si_3, 1% Si_4 and 1/2% $Si_{>4}$; R. E. Honig, *J. Chem. Phys.*, **22**, 1610 (1954).

(9) P. S. Skell and P. W. Owen, *J. Am. Chem. Soc.*, **89**, 3933 (1967); **94**, 5434 (1972).

(10) P. P. Gaspar, "Recoil Chemistry and Mechanistic Studies with Polyvalent Atoms", in "Recent Developments in Biological and Chemical Research with Short-Lived Isotopes," K. Krohn and J. W. Root, Eds., American Chemical Society, Washington, DC, in press.

(11) P. P. Gaspar, *React. Intermed.*, **1**, 229 (1978); **2**, 335 (1981).

(12) R.-J. Hwang and P. P. Gaspar, *J. Am. Chem. Soc.*, **100**, 6626 (1978).

(13) Competition experiments are under way that compare the selectivity of recoiling silicon atoms with the selectivity of thermally generated SiH_2. Preliminary results indicate that the selectivity in the recoil experiments resembles that of SiH_2: S. Konieczny, S. H. Mo, and P. P. Gaspar, to be published.

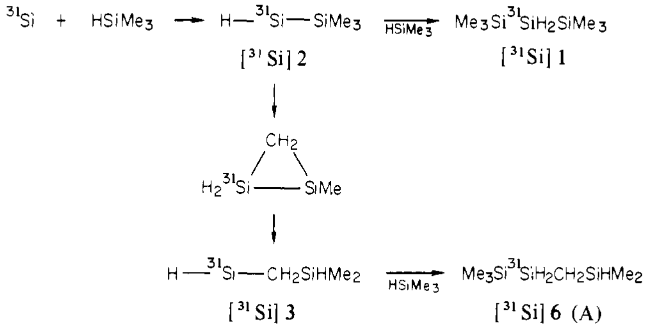
(14) W. D. Wulff, W. F. Goure, and T. J. Barton, *J. Am. Chem. Soc.*, **101**, 486 (1979).

(15) Y.-S. Chen, B. H. Cohen, and P. P. Gaspar, *J. Organomet. Chem.*, **195**, C1 (1980).

(16) Compound **4** has the following spectroscopic characteristics: ^1H NMR (benzene) δ 4.81 (m, 1 H, SiH), 4.63 (quintet of doublets, J = 5 Hz, 2 H, SiH_2), 0.5 to −0.3 (m, 7-H including d at 0.14, CH_2), 0.14 (d, $J_{SiH\text{–}CH_3}$ = 5 Hz, CH_3); mass spectrum, *m/e* 102 (parent and base), 101, 100, 99, 87, 85, 76, 73, 69, 59.

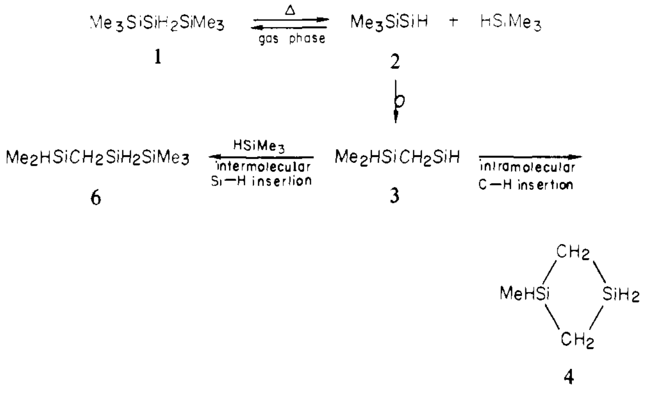
(17) We have repeated the cocondensation of silicon vapor and trimethylsilane using an electrically heated beryllia crucible to evaporate the silicon metal. The only volatile product was **1** (yields up to 24%). A 1% yield of **4** would have been easily detected.

Scheme III



Scheme II includes two intramolecular insertions by a divalent silicon center into C–H bonds. C–H insertion by a silylene has never been realized as an intermolecular process,[11,18] but the intramolecular reaction has been demonstrated by Barton.[14] Si–H insertion by a silylene is much more facile than C–H insertion and can compete even as a bimolecular process when the concentration of trapping reagents is sufficiently high. This has been demonstrated for **2** in the liquid-phase pyrolysis of **1** in which the only silylene reaction product results from attack of unrearranged **2** on its precursor.

The hot-atom experiments are carried out under moderate pressures in the gas phase, where both intramolecular rearrangements and intermolecular insertions by silylenes can occur. This was established by vacuum-flow pyrolysis of **1** in the presence of a large (from 10- to 50-fold) excess in $HSiMe_3$. At low pressures (ca. 0.1 torr) the major product was still **4** (ca. 40% yield) with ca. 3% of a new product **6** from intermolecular trapping of rearranged silylene **3**. When the pressure was increased to ca. 1 torr, 2,2,5-trimethyl-2,3,5-trisilahexane (**6**) was the major product,[19] and the ratio of **6** to **4** was 7.



With the new compound **6** in hand it could be shown[6] that unknown product A from the reactions of recoiling ^{31}Si atoms and $HSiMe_3$ has the structure **6**. While it is possible that $[^{31}Si]$**6** (A) could be formed by other mechanisms, none are at present known, and it is reasonable to believe that the formation of $[^{31}Si]$**6** is diagnostic of the intermediacy of silylene $[^{31}Si]$**3**.

Further evidence comes from the observation that the yield of $[^{31}Si]$**6** (A) increases (from 3 to 6%) and that of $[^{31}Si]$**1** decreases (from 5 to 4%) when the temperature of the hot-atom reaction system is raised from 300 to 403 K. We interpret this temperature effect as being due to an activated process, the rearrangement of **2** to **3**, followed by temperature insensitive trapping of **2** and **3** by trimethylsilane.[20,21] The recoil reaction sequence in Scheme III is in accord with both the formation of $[^{31}Si]$**1** and $[^{31}Si]$**6** and the temperature dependence of their yields.

While other mechanisms including ion–molecule reactions[22] can be written for the formation of $[^{31}Si]$**1**, the complementary yields of $[^{31}Si]$**1** and $[^{31}Si]$**6** observed upon variation of the temperature suggest that a substantial fraction of $[^{31}Si]$**1** is formed from $[^{31}Si]$**2**, the product of insertion of a ^{31}Si atom. There remains the task of determining the electronic state of the silicon atoms that enter scheme III and relating them to the species whose reactions give the major products $H_3{}^{31}SiSiMe_3$ and $MeH_2{}^{31}SiSiMe_3$.

Acknowledgment. We thank the United States Department of Energy for support and encouragement. This is Technical Report COO-1713-102. We are grateful to John Hood and the staff of the Washington University cyclotron for neutron irradiations and Professor Robert T. Conlin for advice and assistance.

Registry No. 1, 5089-32-7; **2**, 80540-71-2; **4**, 80540-80-3; 6, 80540-72-3; $^{31}SiH_4$, 22206-61-7; $H_3{}^{31}SiSiMe_3$, 80540-73-4; $MeH_2{}^{31}SiSiMe_3$, 80540-74-5; $Me_3Si^{31}SiH_2SiMe_3$, 80540-75-6; A, 80540-76-7.

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(18) The claim has been made that $SiCl_2$ undergoes intermolecular C–H insertion: E. A. Chernyshev, N. G. Komalenkova, and S. A. Bashkirova, *Usp. Khim.*, **45**, 1782 (1976).

(19) **6** has the following spectroscopic characteristics: ^1H NMR (benzene) δ 3.96 (m, 1 H, SiH), 3.55 (t, 2 H, $J_{CH_2-SiH_2}$ = 5 Hz, SiH_2), 0.06 (s, 9 H, $(CH_3)_3Si$), 0.03 (d, 6 H, J_{SiH-CH_3} = 4 Hz), −0.30 (m, 2 H, CH_2); mass spectrum, *m/e* 176 (parent), 102, 73 (base), 59, 45, 43.

(20) Since reactions of recoiling atoms occurring above threshold should proceed at rates insensitive to the ambient temperature, it is only the later steps in a sequence of reactions initiated by a recoiling atom that may be expected to display a temperature dependence. These later steps involve intermediates that can be collisionally deexcited to the point that they behave like thermally generated species. We have demonstrated in experiments with inert moderator gases that the primary reactions of recoiling ^{31}Si atoms with $HSiMe_3$ involve kinetically excited atoms.

(21) That Si–H insertion by $SiMe_2$ has no energy barrier has recently been shown: I. M. T. Davidson, F. T. Lawrence, and N. A. Ostah, *J. Chem. Soc., Chem. Commun.*, 859 (1980); I. M. T. Davidson and N. A. Ostah, *J. Organomet. Chem.*, 206, 149 (1981).

(22) G. W. Stewart, J. M. S. Henis, and P. P. Gaspar, *J. Chem. Phys.*, **58**, 890 (1973).

Coronation of Ligating Acetonitrile by 18-Crown-6. X-ray Crystal Structure of $\{[\textit{trans}\text{-Ir(CO)(CH}_3\text{CN)(PPh}_3)_2]_2{}^+\cdot\text{18-Crown-6}\}[\text{PF}_6]_2{}^-\cdot 2\text{CH}_2\text{Cl}_2$

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In common with a number[1] of CH-acidic compounds, acetonitrile forms[2,3] a crystalline derivative with 18-crown-6 (18C6). Unfortunately, the guest–host stoichiometry varies[2] between different crops of crystals, and no X-ray crystal structure of a complex has so far appeared in the literature. However, we

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(1) The crystal structures of (a) a 1:1 complex of dimethylacetylenedicarboxylate with 18-crown-6 (Goldberg, I. *Acta Crystallogr. Sect. B* **1975**, *B31*, 754) and (b) a 2:1 complex of malonodinitrile with 18-crown-6 (Kaufmann, R.; Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *Chem. Ber.* **1977**, *110*, 2249) have been determined.

(2) Gokel, G. W.; Cram, D. J.; Liotta, C. L.; Harris, H. P.; Cook, F. L. *J. Org. Chem.* **1974**, *39*, 2445.

(3) El Basynony, A.; Klimes, J.; Knöchel, A.; Dehler, J.; Rudolph. G. *Z. Naturforsch. B* **1976**, *31B*, 1192.