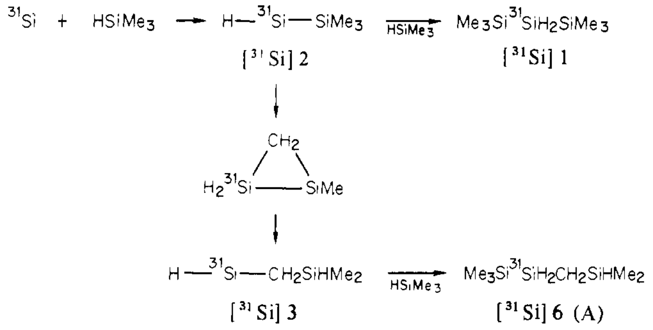
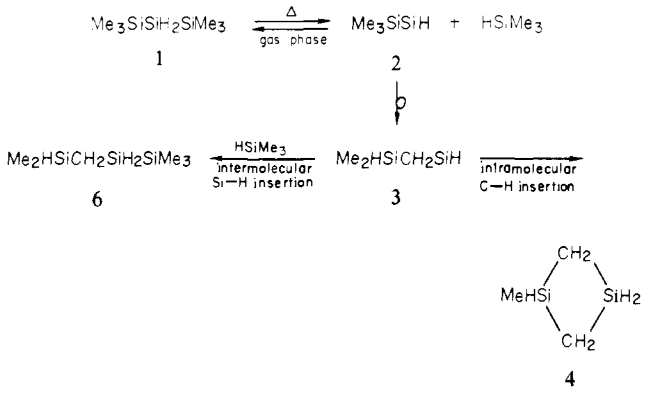
Scheme III



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$_3$Si^{31}SiH$_2$SiMe$_3$, 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: ^{1}H 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$_3$)$_3$Si), 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 $\{[trans\text{-}Ir(CO)(CH_3CN)(PPh_3)_2]_2^{+}\cdot$18-Crown-6$\}[PF_6]_2^{-}\cdot 2CH_2Cl_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.

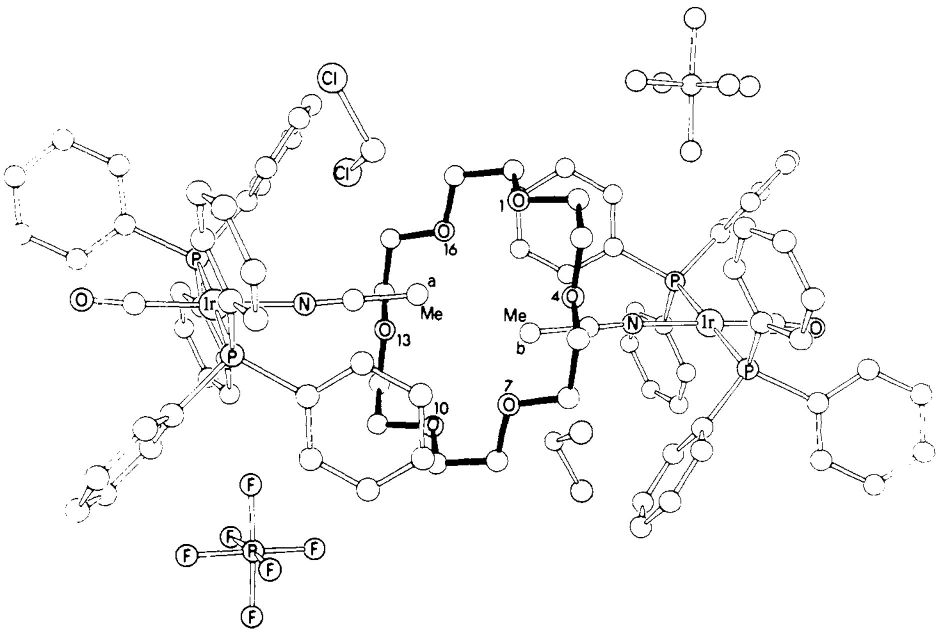

Figure 1. Crystal structure of $\{[trans\text{-Ir(CO)(CH}_3\text{CN)(PPh}_3)_2]_2{}^+\cdot 18\text{C}6\}[\text{PF}_6]_2{}^-\cdot 2\text{CH}_2\text{Cl}_2$. Structural parameters are as follows. Bond distances: C–C, 1.45–1.49 Å; C–O, 1.36–1.43 Å. Bond angles at O: 112; 114°. Torsional angles: |O–C–C–O|, 67.1–68.9°; |C–C–O–C|, 174.9–179.5°. Hydrogen bond distances R(C···O), Å (angles (θ, deg) between COC planes and the C(Me$_a$)O vectors): O(1), 3.24 (7); O(7), 3.26 (9); O(13), 3.38 (12). The positions of the methyl hydrogens have not yet been established: it is assumed that the C(Me$_a$)–H bonds are directed toward O(1), O(7), and O(13) and the C(Me$_b$)–H bonds toward O(4), O(10), and O(16). Distance R[C(Me$_a$)–C(Me$_b$)], 3.93 Å. Ir–CO/NCCH$_3$ geometries—bond distances: Ir—C, 1.81 Å; C≡O, 1.14 Å; Ir—N, 2.06 Å, N≡C, 1.12 Å; C—C (Me), 1.49 Å. bond angles: Ir–C–O, 176°; Ir–N–C, 175°; N–C–C (Me), 179°.

reasoned that because nitrile coordination to a transition metal (M) involves the generation of a formal positive charge at the donor nitrogen atom $[\text{CH}_3\text{—C}{\equiv}\text{N}^+{:}{\rightarrow}\text{M}^-]$, ligating CH_3CN molecules should be rendered more CH acidic by coordination to M. Furthermore, in view of the demonstrated ability of both aquo[4] and ammine[5] ligands associated with transition and post-transition-metal complexes to form crystalline adducts with crown ethers by utilizing O—H··O and N—H··O hydrogen bonds, respectively, it seemed likely that an appropriate complex containing a CH_3CN ligand might form a crystalline adduct with 18C6 as a result of C—H··O hydrogen bonding. This communication describes (i) the isolation of a crystalline adduct (2:1 guest–host) formed between the $[trans\text{-Ir(CO)(CH}_3\text{CN)(PPh}_3)_2]^+$ cation[6] and 18C6 and (ii) the determination of its structure by X-ray crystallography.

Hexane was added to a solution of $[trans\text{-Ir(CO)(CH}_3\text{CN)(PPh}_3)_2]^+[\text{PF}_6]^-$ (0.16 mmol) and 18C6 (0.16 mmol) in CH_2Cl_2 (5 mL) until crystallization started to occur.[7] After 1 h at room temperature, the 2:1 adduct (54%, mp 128 °C) containing 2 mol of CH_2Cl_2 of solvation was isolated.[8] Any charge transfer from 18C6 to the complex should be reflected in shifts to lower frequencies of both nitrile and carbonyl stretching frequencies in the IR spectrum, compared with those exhibited by the free complex. Although ν(CN) shows a small decrease (from 2295 cm^{-1} in the free complex to[8] 2285 cm^{-1}) in the solid-state IR spectrum of the 2:1 adduct, ν(CO) actually increases (from 1980 cm^{-1} in the complex to 2000 cm^{-1}) on adduct formation. The ^{1}H NMR spectrum of the free complex in CD_2Cl_2 is virtually identical (the methyl singlet for the CH_3CN ligand appears at δ 1.45) with that observed[8] for the 2:1 adduct, apart from the absence of the singlet for the methylene protons in 18C6. This observation is consistent with the marked dissociation of the adduct in solution.

The solid-state structure of the 2:1 adduct was determined by X-ray analysis.[9] Figure 1 reveals that the iridium complex cations and the CH_2Cl_2 molecules are related by a crystallographic center of symmetry located at the center of the 18C6 ring which adopts the ubiquitous conformation where the sequence of torsional angles

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[6] Reed, C. A.; Roper, W. R. *J. Chem. Soc., Dalton Trans.* **1973**, 1365.

[7] Attempts to prepare a crystalline adduct between 18C6 and $[trans\text{-Ir(CO)(NH}_3\text{)(PPh}_3)_2]^+[\text{PF}_6]^-$ were unsuccessful. In addition, ^{1}H NMR spectroscopy in CD_2Cl_2 solution demonstrated that the broad singlet observed at δ 2.10 for the NH_3 protons was unaffected on addition of 18C6 to the solution. The absence of an interaction in solution between the NH_3 ligand and 18C6 was confirmed by IR spectroscopy (CH_2Cl_2). Inspection of space-filling molecular models of the $[trans\text{-Ir(CO)(NH}_3\text{)(PPh}_3)_2]^+$ cation and 18C6 reveals that the bulky PPh_3 ligands on the metal prohibit 18C6 from approaching to within interactive distance of the NH_3 ligand. However, replacement of the NH_3 ligand by the more elongated CH_3CN ligand leaves the CH_3 group well exposed to interact with 18C6.

[8] IR (Nujol): ν(CN) 2285 (w), (CO) 2000 (s), (CO) 1120 (s), (PF) 820 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.46–7.70 (m, 60 H, 4PPh$_3$), 5.30 (s, CH_2Cl_2), 3.55 (s, 24 H, 12OCH$_2$), 1.46 (s, 6 H, 2CH$_3$CN). Integration of the signals in the spectrum indicates that the adduct has 2:1 (guest:host) stoichiometry. This conclusion was confirmed by a satisfactory elemental analysis (Anal. Calcd for $C_{78}H_{66}O_2N_2P_4Ir\cdot C_{12}H_{24}O_6\cdot P_2F_{12}\cdot C_2H_4Cl_4$: C, 48.1; H, 4.1; N, 1.2. Found: C, 48.2; H, 4.2; N, 1.2) and X-ray crystallography.

[9] Crystals of $\{[trans\text{-Ir(CO)(CH}_3\text{CN)(PPh}_3)_2]_2{}^+\cdot 18\text{C}6\}[\text{PF}_6]_2{}^-\cdot 2\text{CH}_2\text{Cl}_2$ are triclinic with $a = 19.767$ (1) Å, $b = 11.048$ (1) Å, $c = 11.799$ (1) Å, $\alpha = 73.92°$, $\beta = 101.75°$, $\gamma = 96.46°$, $U = 2420$ Å^3, space group $P\bar{1}$, $Z = 2$, μ(Cu Kα) ≈ 77 cm^{-1}. Of the 4981 independent reflections ($\theta \leq 50°$) measured on a diffractometer using Cu Kα radiation, 440 were classified as unobserved. The structure was solved by the heavy-atom method, and the absorption corrected data refined anisotropically to give a current $R = 0.044$.

[10] Vögtle, F.; Weber, E. In "The Chemistry of The Functional Groups. Supplement E, The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups, and their Sulphur Analogues"; Patai, S., Ed.; Wiley: Chichester, 1980; p 59.

[11] (a) Dale, J. *Isr. J. Chem.* **1980**, *20*, 3. (b) Bovill, M.; Chadwick, D. J.; Sutherland, I. O.; Watkin, D. *J. Chem. Soc., Perkin Trans. 2* **1980**, *1529*.

[12] Exceptions are provided by the adducts of (i) benzenesulfonamide and 18C6 (2:1 guest–host) (Knöchel, A.; Kopf, J.; Oehler, J.; Rudolph, G. *J. Chem. Soc., Chem. Commun.* **1978**, 595) and (ii) urea and 18C6 (5:1 guest–host) (Harkema, S.; van Hummel, G.J.; Daasvatn, K.; Reinhoudt, D.N. *J. Chem. Soc., Chem. Commun.* **1981**, 368) where a conformation with the sequence of torsional angles (O–C, C–C, C–O, etc. in the symmetrically independent portions of the ring reading $ag^+aag^+ag^+g^+a$ is adopted. (iii) Also in the 1:1 adduct of NaSCN and 18C6 (Dobler, M.; Dunitz, J.D.; Seiler, P. *Acta Crystallogr., Sect. B* **1974**, *B30*, 2741) the macrocyclic ring adopts a highly irregular conformation. For detailed discussions of the conformational behavior of 18C6, see ref 11.

(O–C, C–C, C–O, etc.) in the symmetrically independent portions of the ring read ag^+aag^-a. This conformation characterizes[10,11] the vast majority[12] of 18C6 adducts. The structural parameters associated with the six-point binding site are summarized in the caption to Figure 1. The angles ($\theta = 7, 9, 12°$) of approach of the C(Me)O vectors to the associated COC planes indicate an almost trigonal geometry ($\theta = 0°$) for the C—H··O hydrogen bonds rather than a tetrahedral one ($\theta \simeq 55°$).

The coronation of an acetonitrile ligand in the [*trans*–Ir(CO)(CH_3CN)(PPh_3)$_2$]$^+$ cation by 18-crown-6 provides an elegant example[13,14] of second-sphere coordination[15] of a transition-metal complex by a crown ether in the solid state.

Acknowledgment. This research was supported by grants from the Science Research Council in the United Kingdom.

Registry No. {[*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]$_2^+$·18C6}[PF_6]$_2^-$·2CH_2Cl_2, 80434-43-1; [*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]$^+$[PF_6]$^-$, 80434-42-0.

Supplementary Material Available: A table of atomic positional and thermal parameters for {[*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]$_2^+$·18-crown-6}[PF_6]$_2^-$·2CH_2Cl_2 (2 pages). Ordering information is given on any current masthead page.

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(13) Copper iodide reacts (Hardt, H. D.; Stoll, H.-J. *Z. Anorg. Allg. Chem.* **1978**, *442*, 221) in acetonitrile solution with dibenzo-18-crown-6 (DB18C6) to form a crystalline adduct [$(CuI)_4(CH_3CN)_4$·DB18C6] which exhibits fluorescence thermochromism. In addition, the luminescence spectra of the adduct is red shifted at 298 K. This has been interpreted by the authors in terms of an unspecified interaction between the crown and the acetonitrilecopper iodide.

(14) Small rate enhancements in the reaction of [*trans*-Co($H_2NCH_2CH_2NH_2$)$_2$(CH_3CN)(NO_2)]$^{2+}$[ClO_4]$_2^-$ with D_2O at pD 4.4 in the presence of either 18-crown-6 or 15-crown-5 to give [*trans*-Co($H_2NCH_2CH_2NH_2$)$_2$(D_2O)(NO_2)]$^{2+}$[ClO_4]$_2^-$ have been ascribed (Blackmer, G. L.; Nordyke, M. D.; Vickrey, T. M.; Bartsch, R. A.; Holwerda, R. A. *Inorg. Chem.* **1978**, *17*, 3310) to complexation by the crown ethers of the cobalt-bound acetonitrile through the acidic methyl group C–H bonds. It should be recognized, however, that the crown ethers will probably interact (cf. ref 4 and 5) more strongly with (a) the $H_2NCH_2CH_2NH_2$ ligands by N—H··O hydrogen bond formation in the reactant and product complexes and (b) the D_2O ligand by O—D··O hydrogen bond formation in the product complex. In the present investigatiion, we have found that 18C6 promotes the displacement of CH_3CN by Cl^- ion. Thus, on adding excess of solid NaCl to {[*trans*-Ir(CO)(CH_3CN)(PPh_3)$_2$]$_2^+$·18C6}[PF_6]$_2^-$ in CH_2Cl_2, a mixture of [Ir(CO)(CH_3CN)(PPh_3)$_2$]$^+$[PF_6]$^-$, Ir(CO)(PPh_3)$_2$Cl, and (presumably) [Na·18C6]$^+$[PF_6]$^-$ is formed; addition of a further 1 equiv of 18C6 results in complete conversion to Ir(CO)(PPh_3)$_2$Cl. The driving force for this reaction is clearly solubilization of NaCl in CH_2Cl_2 by 18C6 since addition of NaCl to a MeOH solution of [Ir(CO)(CH_3CN)(PPh_3)$_2$]$^+$[PF_6]$^-$ precipitates Ir(CO)(PPh_3)$_2$Cl quantitatively even in the absence of the crown ether.

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A Diels–Alder Route to Pyridone and Piperidone Derivatives

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The Diels–Alder reaction is one of the most versatile routes for the construction of carbocycles.[1] Appropriate selection of dienes and dienophiles allows for a wide range of structural and functional variations in the adducts. In this respect, the recent availability of highly functionalized dienes has considerably widened the scope of the reaction.[2]

Relatively few dienophiles incorporating heteroatoms in the conjugated system have found use in synthesis.[3] At the beginning of these studies, we noticed, in particular, that 1- and 2-aza-1,3-dienes had almost not been explored for their reactivity as enophiles.[4–6] We expected significant synthetic potential for 2-aza-1,3-dienes **1** provided that one could force them to interact with the 4π electron system of the diene rather than with the n electrons of the nitrogen. The few available studies on 2-aza-1,3-dienes have indeed shown that they are able to undergo [4 + 2] cycloadditions with conventional electron-poor dienophiles.

Our own studies[5] have been mainly concerned with 2-aza-1,3-dienes bearing a substituted amino group at position 1. This conferred higher reactivity on the diene in its reactions with electrophilic dienophiles. Further, the amino group in the adducts was amenable to elimination. As shown in Scheme I, *conformational factors play a significant role in determining the reaction site for the dienophile.* Thus **1a**, which mainly exists in the s-cis conformation,[7] readily reacts with ethyl propiolate in acetonitrile at 60 °C to give, after spontaneous aromatization, the known pyridine **2** in 50% yield. In the case of **1b**, the s-cis conformation is no longer available,[7] and *no cycloadduct* could be obtained with ethyl propiolate under a variety of experimental conditions. Although the diene quickly disappeared, no characterizable products were obtained.

With these observations in mind, it became obvious that 2-aza-1,3-dienes such as **3** fulfill all structural requirements to react successfully with electrophilic dienophiles. The presence of trialkylsilyloxy group at position 3 should further enhance the reactivity of the π system[8] and permits introduction of a masked lactam function.

The required dienes **3a** and **3b** were conveniently prepared by enol silylation of the readily available imides **4a**[9] and **4b** with *tert*-butyldimethylsilyl triflate[10] in ether containing 2.2 equiv of triethylamine: **3a**, 86%; bp 74 °C (6.10^{-2} torr); NMR ($CDCl_3$)

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(3) Reviews: (a) Lora-Tamayo, M.; Madronero R. In "1,4-Cycloaddition Reactions"; Hamer, J., Ed.; Academic Press: New York, 1967; Chapter 5, pp 127–142. (b) Lora-Tamayo, M.; Soto, J. L. *Ibid.*; Chapter 7, pp 180–204. (c) Colonge, J.; Descotes, G. *Ibid.*; Chapter 9, pp 217–254. (d) Pfundt, G.; Schenck, G. O. *Ibid.*; Chapter 11, pp 346–418.

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(7) Especially noteworthy for configurational assignment is the coupling between C-3 and H-1 in the ^{13}C NMR spectra of **1a** and **1b**. For **1a**, $J_{trans} = 11.9$ Hz; for **1b**, $J_{cis} = 7.8$ Hz. E.g., see: Vogeli, U.; von Philipsborn, W. *Org. Magn. Reson.* **1975**, *7*, 617.

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