CHE84-04049) and the National Institutes of Health (Grant GM-24427) provided financial support for this research. We gratefully acknowledge the many sources of fellowship support noted in ref 1. We thank Professor Robert A. Moss and his associates at Rutgers for supplying the details of the 3-fluoro-3-phenyldiazirine preparation in advance of publication. We thank Dr. Robert J. Rosenthal for assistance with the halodiazirine syntheses.

Trimethylsilyl Accelerated Retro-Diels–Alder Reaction: A Quantitative Measure of the β-Effect

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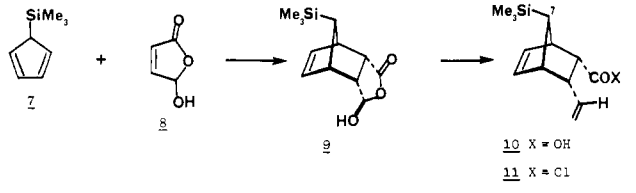
Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47405. *Received August 21, 1986*

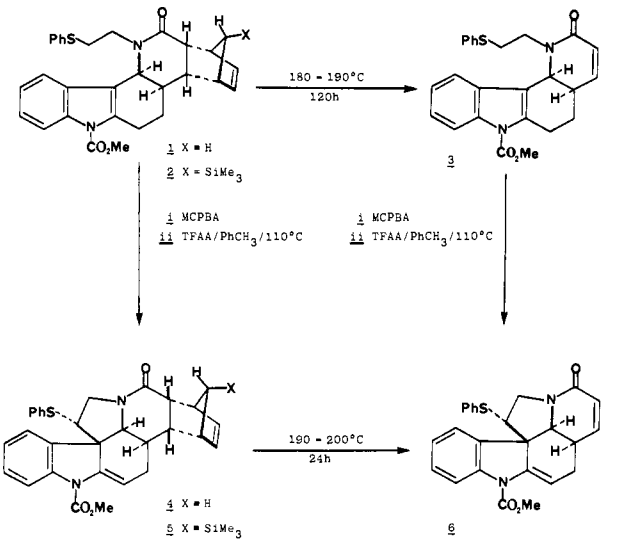
Abstract: The retro-Diels–Alder reaction of **2** proceeds under substantially milder conditions in comparison to its congener, which lacks the trimethylsilyl substituent. When the substrate **14** was used, it was found that the trimethylsilyl group accelerates the retro-Diels–Alder reaction by a factor of approximately 95, relative to the reference **13**. An Arrhenius plot gave E_a, $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$, and $\Delta G^{\ddagger}$.

The retro-Diels–Alder extrusion of cyclopentadiene, as depicted in Scheme I, is part of the strategy we have developed for the synthesis of *aspidosperma*-type indole alkaloids.[1] Heating **1** at 180–190 °C for 120 h (in a sealed tube) resulted in retro-Diels–Alder cyclopentadiene extrusion to give **3** (67%); similarly, heating **4** at 190–200 °C for 24 h gave **6** (>95%). While these extrusions proceed under relatively mild conditions, the reaction times are lengthy. We anticipated that for more highly functionalized sensitive substrates, mild and rapid extrusion conditions would be beneficial. Furan and fulvene Diels–Alder adducts are obvious candidates, except that they are probably too delicate to survive the various electrophilic conditions used in this chemistry and offer other sites of unwanted reactivity. An intriguing solution to this problem, and one of general interest, is to test the following hypothesis, that a trimethylsilyl group trans-coplanar to the C–C bonds which are being broken in the retro-Diels–Alder reaction would lower the activation energy of the extrusion process by virtue of charge stabilization β to the $SiMe_3$ group (Scheme II).[2] The following experiments were conducted to test this idea.

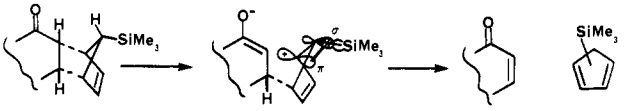
5-(Trimethylsilyl)cyclopentadiene (**7**)[3] reacted with 5-hydroxybutenolide (**8**) at 20 °C to give an 8:1 mixture of Diels–Alder adducts ($SiMe_3$ regioisomers), which on recrystallization gave the pure lactol **9** (78%). Exposure of **9** to $CH_3P^+Ph_3I^-/NaH/Me_2SO$ resulted in the crystalline acid **10** (94%), which was converted into the corresponding acid chloride **11**, using $SOCl_2/Et_2O/DMF$ (catalyst).



Scheme I



Scheme II



The imine **12** was treated with the acid chloride **11** in toluene/*i*-Pr_2NEt/110 °C (identical conditions to those used to give **1**, in the 7-H series) to give **2** (71%) and the α,β-unsaturated lactam **3** (3%). Even under these milder conditions (cf. 180–190 °C for **1** into **3**) a small but readily detectable amount of retro-Diels–Alder reaction has taken place. Heating **2** in toluene/180–190 °C/7 h (sealed tube) gave **3** (ca. 100%). The contrast with the 7-H series, 180–190 °C for 120 h, is dramatic.

Conversion of **2** into **5** with the usual Pummerer conditions ($MCPBA/CH_2Cl_2$ oxidation to the derived sulfoxide, TFAA/110 °C/1.5 h) gave **5** (15%) and the retro-Diels–Alder product **6** (67%). Even conducting the Pummerer reaction at 70 °C gave **6** as the major product. Clearly, the 7-trimethylsilyl group has a substantial accelerating effect. To put this electronic effect on a more quantitative footing, we attempted to study the kinetics of the extrusion process. The *aspidosperma*-type indole alkaloids depicted in Scheme I did not prove to be amenable to first-order

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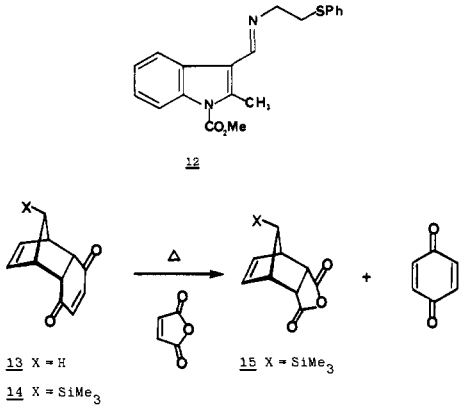
Table I

		13		
temp, °C	59.4	63.9	69.5	78.6
$k \times 10^7$ s^{-1}	4.0	8.0	14.0	55.0
		14		
temp, °C	58.5	64.0	68.0	78.0
$k \times 10^7$ s^{-1}	460.0	848.0	1310.0	3710.0

kinetic analysis, because of the difficulties encountered in quantitatively monitoring the progress of the extrusion process.



In 1939 Wassermann studied the retro-Diels–Alder reaction of **13** and determined the activation energy in benzene as 29 ± 1.5 kcal mol^{-1}.[4] The reaction exhibits a small negative entropy change $\Delta S^{\ddagger} = -3$ eu, which in itself is unusual, but apparently typical of *endo*-cyclopentadiene extrusions.[5] Consequently, the ideal comparison is to measure the thermodynamic parameters for the 7-trimethylsilyl substituted system **14**. The substrate **14** is known and was made from benzoquinone and 5-(trimethylsilyl)cyclopentadiene.[6] The adduct **14** was heated in chlorobenzene at temperatures ranging from 58.5 ± 0.2 °C to 78.0 ± 0.2 °C in the presence of maleic anhydride, and the increase in absorbance at 435 nm (benzoquinone) was measured. Maleic anhydride did not effect the rate of cycloreversion of **13**, nor did it alter the extinction coefficient of benzoquinone at 435 nm. Since maleic anhydride was present in large excess, the kinetic analysis is not complicated by reverse addition of benzoquinone to 5-(trimethylsilyl)cyclopentadiene, which would also result in exo/endo equilibration. The adduct **15** was isolated in these kinetic experiments, demonstrating the 5-(trimethylsilyl)cyclopentadiene is extruded in the retro[$4\pi + 2\pi$]process and that desilylation is *not* taking place. Table I lists the first-order rate constants for **13** and **14**. The trimethylsilyl adduct **14** undergoes the retro-Diels–Alder reaction approximately 95 times as fast as **13** under comparable reaction conditions. When these rate data are used in an Arrhenius plot, the following thermodynamic parameters were obtained: $E_a = 24.8 \pm 1$ kcal mol^{-1}; $\Delta S^{\ddagger} = -5.8 \pm 0.5$ eu; $\Delta H^{\ddagger} = 24.1 \pm 1.2$ kcal mol^{-1}; $\Delta G^{\ddagger} = 26.0 \pm 1.4$ kcal mol^{-1}. Thus, the 7-trimethylsilyl substituent has lowered the Arrhenius activation energy in the extrusion process by approximately 4.2 kcal mol^{-1}, and $\Delta\Delta G^{\ddagger}$ is 3.3 kcal mol^{-1} at 25 °C. In keeping with the literature, the entropy change is a small negative value.

The steric effects of the 7-trimethylsilyl group upon the retro-Diels–Alder process can reasonably be assumed to be negligible, since the C–Si bond length is some 25% longer than the C–C bond.[7] Therefore, we attribute the lowering of activation energy to a polarized transition state (non-concerted), Scheme II, where the $SiMe_3$ group is able to stabilize through hyperconjugation [$(p - \sigma)\pi$] the buildup of cationic character β to it. The ΔE_a value of 4.2 kcal mol^{-1} is therefore a measure of the β-effect.

In summary, the 7-$SiMe_3$ accelerated retro-Diels–Alder process should find useful applications in synthesis, where the dienophilic component needs to be generated under milder conditions than those afforded by conventional cyclopentadiene extrusion.[8]

Experimental Section

8-(Trimethylsilyl)-3-hydroxy-3a,4,7,7a-tetrahydro-4,7-methano-(3*H*)-isobenzofuran-1-one (9). A solution of 5-hydroxybutenolide (**8**) (1.0 g, 10 mM) and 5-(trimethylsilyl)cyclopentadiene (**7**) (1.45 g, 10.5 mM) in dry CH_2Cl_2 (20 mL) was stirred under argon for 48 h. The solvent was evaporated, and the residue was crystallized from EtOAc/hexane to give **9** (1.868 g, 78%): mp 124–125 °C (colorless plates); IR ($CHCl_3$) 3560, 3500–3000, 1760, 1745 (sh), 945, 930, and 830 cm^{-1}; ^{1}H NMR (360 MHz, $CDCl_3$) δ –0.07 (9 H, s), 1.12 (1 H, s), 2.97 (1 H, ddd, J = 8.6, 4.2, and 1.3 Hz), 3.24–3.25 (1 H, m), 3.35–3.57 (1 H, m), 3.42 (1 H, dd, J = 8.6 and 4.7 Hz), 4.20 (1 H, d, J = 5.0 Hz, exchanged by D_2O), 5.19 (1 H, d, J = 3.9 Hz), 6.10–6.16 (2 H, m); ^{13}C NMR (90 MHz, $CDCl_3$) δ –0.35 (q), 47.50 (d), 48.57 (d), 50.77 (d), 51.80 (d), 55.39 (d), 100.32 (d), 134.03 (d), 135.71 (d), 178.13 (s). Anal. Calcd for $C_{12}H_{18}O_3Si$: C, 60.47; H, 7.61. Found: C, 60.37; H, 7.88.

(±)-(2,3-*endo*)-7-*anti*-(Trimethylsilyl)-3-ethenylbicyclo[2.2.1]hept-5-ene-2-carboxylic Acid (10) (X = OH). To a solution of triphenylphosphonium methiodide (900 mg, 2.23 mM) in dry Me_2SO (3 mL), a solution of dimsyl sodium [prepared from NaH (106 mg) in Me_2SO (3 mL) warmed 1 h at 70 °C, then cooled to 20 °C] was added dropwise. After 1 h at 20 °C, a solution of the lactol **9** (177 mg, 0.74 mM) in Me_2SO (0.5 mL) was added, and the mixture was stirred at 20 °C for 2 h. The above mixture was poured into water (20 mL), acidified with 2 N HCl, and extracted with ether (3 × 10 mL). The dried extract ($MgSO_4$) was evaporated under reduced pressure, and the residue was chromatographed over silica gel (eluting with Et_2O/petrol) to give **10** (X = OH) (165 mg, 94%): mp 83–85 °C (from petrol); IR ($CHCl_3$) 3500–2400, 1695, 1235, 850, and 830 cm^{-1}; ^{1}H NMR (360 MHz $CDCl_3$) δ –0.08 (9 H, s), 1.08 (1 H, s), 2.90 (1 H, br s), 3.16–3.18 (3 H, s), 4.94 (1 H, dd, J = 9.9 and 1.9 Hz), 5.11 (1 H, dd, J = 16.9 and 1.9 Hz), 5.33–5.40 (1 H, m), 6.05 (1 H, dd, J = 5.3 and 2.9 Hz), 6.24 (1 H, dd, J = 5.3 and 2.5 Hz), 10.6 (1 H, br s); ^{13}C NMR (90 MHz, $CDCl_3$) δ –0.25 (q), 48.58 (d), 51.68 (d), 51.76 (d), 51.95 (d), 52.19 (d), 115.71 (t), 133.85 (d), 135.98 (d), 139.56 (d), 179.39 (s). Anal. Calcd for $C_{13}H_{20}O_2Si$: C, 66.05; H, 8.53. Found: C, 65.97; H, 8.37.

Hexacyclic Adduct 2. The above acid (180 mg, 0.76 mM) was treated with freshly distilled thionyl chloride (100 μL, 1.51 mM) and DMF (3 μL) in dry ether (3 mL). The solution was evaporated in vacuo to give **11** (X = Cl). The acid chloride **11**, in dry toluene (1.5 mL), was added to a solution of the imine **12** [prepared from 1-carbomethoxy-2-methyl-3-formylindole (138 mg, 0.635 mM) and 2-(phenylthio)ethylamine (198 mg, 0.64 mM)] in dry toluene (6 mL, 0.11 M) containing i-Pr_2NEt (146 μL, 0.83 mM; 1.1 equiv vs. **11**) at 0 °C. The above mixture was warmed to 20 °C over 1 h and then heated at reflux (110 °C) for 2 h. The mixture was cooled to 20 °C, washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated to give a brown foam. The crude product was chromatographed over silica gel eluting with EtOAc/petrol to give **2** (257 mg, 71%): mp 158–160 °C (from MeOH); IR ($CHCl_3$) 1730, 1625, 1440, 1330, 845 cm^{-1}; UV (EtOH) 207, 258, 296 nm (ϵ 40 000, 21 400, and 4 800); ^{1}H NMR (300 MHz, $CDCl_3$) δ –0.10 (9 H, s), 0.89 (1 H, br s), 1.81–2.05 (2 H, m), 2.20–2.31 (1 H, m), 2.33–2.41 (1 H, m), 2.43 and 2.49 (2 H, d of ABq, J = 9.0 and 4.5 Hz), 2.91–3.06 (2 H, m), 3.15–3.20 (2 H, m), 3.32–3.39 (2 H, m), 4.02 (3 H, s), 4.47 (1 H, br s), 4.75 (1 H, m), 6.04 (1 H, br s), 6.22 (1 H, dd,

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(i) X = H; 22.8 (ii) X = t-Bu; 28.1 (iii) X = SiMe3; 20.5

sponsible for the observed acceleration in the Retro-Diels–Alder process.

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J = 5.4 and 3.0 Hz), 7.14-7.41 (8 H, m), 8.10 (1 H, d, J = 8.4 Hz). Conducting the above reaction on a 2.88 mM scale gave **2** (1.037 g, 76% after recrystallization from MeOH). Anal. Calcd for $C_{33}H_{38}N_2O_3SSi$: C, 69.43; H, 6.71; N, 4.91. Found: C, 69.24, H, 6.74; N, 4.96. Further elution gave **3** (9 mg, 3%), whose ^1H NMR spectrum was identical with an authentic sample of **3**.[1]

Pummerer Reaction on 2 and the Formation of (±)-2,3,6,7-Tetrahydro-1-carbomethoxy-11-β-(phenylthio)-20,21-dinoraspidospermidin-8-one (6). A solution of MCPBA (17 mg, 83 μM) in CH_2Cl_2 (1 mL) was added over 0.5 h to a stirred solution of **2** (47 mg, 82.3 μM) in CH_2Cl_2 (1.5 mL) and 10% aqueous $NaHCO_3$ (1.5 mL) at 0 °C. The CH_2Cl_2 layer was separated and the aqueous phase extracted with CH_2Cl_2 (2 mL); the combined extracts were dried ($MgSO_4$) and evaporated to give the derived sulfoxide (58 mg, 100%) as a mixture of diastereoisomers (1:1). To a solution of the above sulfoxides in CH_2Cl_2 (1 mL) at 0 °C was added trifluoroacetic anhydride (26 μL, 184 μM), and the mixture was maintained at 20 °C for 1 h. The mixture was evaporated and toluene (2 mL) added to the residue. After the solution was heated at reflux (ca. 110 °C) for 1 h, the mixture was washed with saturated aqueous $NaHCO_3$, dried ($MgSO_4$), and evaporated in vacuo to give a brown glass (41 mg), which was chromatographed over silica gel (4 g) eluting with EtOAc to give **5** (7 mg, 15%): mp 174-176 °C (from EtOAc/hexane); IR ($CHCl_3$) 1710, 1615, 1440, and 1370 cm^{-1}; ^1H NMR (360 MHz, $CDCl_3$) δ -0.10 (9 H, s), 1.06 (1 H, s), 2.01-2.06 (2 H, m), 2.49 (1 H, dd, J = 9.0 and 3.3 Hz), 2.94 (1 H, dd, J = 9.0 and 4.2 Hz), 3.07 (1 H, m), 3.08 (1 H, d, J = 12.0 Hz), 3.13 (1 H, d, J = 6.0 Hz), 3.17 (1 H, d, J = 12.0 Hz), 3.44 (1 H, br s), 3.89 (3 H, s), 4.09 (1 H, d, J = 5.0 Hz), 4.61 (1 H, dd, J = 10.8 and 5.6 Hz), 6.07 (1 H, dd, J = 5.5 and 3.0 Hz), 6.32 (1 H, br s), 7.11-7.17 (7 H, m), 7.37 (1 H, ddd, J = 8.0, 6.0, and 3.0 Hz), 7.84 (1 H, br d, J = 8.0 Hz). Anal. Calcd for $C_{33}H_{36}N_2O_3SSi$: C, 69.68; H, 6.38; N, 4.93. Found: C, 69.49; H, 6.34; N, 4.94. Further elution gave **6** (22 mg, 67%) identical with an authentic sample. The ratio of **5** to **6** varies with the reaction time and the reaction temperature. For example, conducting the Pummerer reaction in benzene at 70 °C for 1.5 h gave **5** (41%) and **6** (53%).

Retro-Diels-Alder Reaction of Adducts 2 and 5. A degassed (freeze-thaw, 0.1 Torr) solution of **2** (8.3 mg) in toluene (1 mL), contained in a resealable Carius tube, was heated at 180-190 °C for 7 h. Evaporation of the mixture gave **3** (ca. 100%), identical with an authentic sample. Similar treatment of **5** (8.0 mg) at 120 °C for 0.5 h gave **6** (ca. 100%), identical with an authentic sample.

Retro-Diels-Alder Reaction of 14 in the Presence of Maleic anhyride. A mixture of the adduct **14** (22 mg, 0.09 mM) and maleic anhydride (12 mg, 0.122 mM) in dry $CHCl_3$ (3 mL) was stirred at 70 °C for 3 h. The mixture was cooled and evaporated, and the residue was recrystallized from hexane/CH_2Cl_2 to give **15** (15 mg, 71%): mp 98-99 °C, NMR (90 MHz, $CDCl_3$) δ -0.05 (9 H, s), 1.24 (1 H, s), 3.62 (4 H, m), 6.26 (2 H, m).

Kinetics. The recrystallized adduct **14** (0.7-1.5 mM) and freshly sublimed maleic anhydride (2.0-4.3 mM) were dissolved in chlorobenzene (100 mL), and the solution was placed in a refluxing solvent bath (temp ±0.2 °C) and equilibrated while being magnetically stirred. Aliquots (3 mL) were removed and cooled in ice-water. Analysis of each aliquot was carried out with a Perkin-Elmer 330 spectrometer, observing the increase in absorbance at 435 nm for the benzoquinone chromophore.

Data were obtained over the first 3 to 5 half-lives, with infinity absorbance recorded after at least 10 half-lives. The reaction displayed clean first-order kinetics over 1 to 2 half-lives, and the slope of the log ($A_\infty - A_t$) vs. time curve was obtained by least-squares analysis enabling the first-order rate constant to be calculated.

A control rate run was carried out to determine the effect, if any, of added maleic anhydride on the rate of cycloreversion of **13**. Data obtained at 78 °C were comparable to those obtained by Wasserman and Khambata [3.1×10^{-4} min^{-1}, 3.3×10^{-4} min^{-1} vs. 3.3×10^{-4} min^{-1} (lit.[4])].

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[4]Paracyclophane Intercepted

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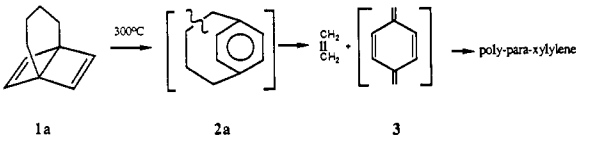
Abstract: Irradiation (254 nm) of 1,4-tetramethylene(Dewar benzene) (**1a**) at -20 °C in THF leads to [4]paracyclophane (**2a**). In the absence of acid, **2a** polymerizes immediately. In the presence of CF_3COOH, adducts **6** and **7** are formed by protonation of **2a** at a bridgehead carbon atom to give the benzenonium ion **9a**, followed by addition of a nucleophile, i.e., CF_3COO^- or THF, respectively, at the other bridgehead carbon, leading to a bridged 1,4-dihydrobenzene. The corresponding methanol adduct **8** is formed on irradiation of **1a** in methanol solution in the presence of CF_3COOH. The difference in behavior between **2a** and its higher homologue is discussed on the basis of calculated charge densities.

Small [n]cyclophanes[1] continue to receive considerable interest. It has been shown that reducing the length of their oligomethylene bridge forces the benzene ring into a nonplanar, boat-type geometry. Surprisingly, this change appears to hardly impair the aromatic delocalization.[2] On the other hand, the increasing strain clearly manifests itself in a rapid decrease of thermal stability. This is convincingly demonstrated by the instability of the shortest member of the homologous family of [n]paracyclophanes, the recently prepared [5]paracyclophane (**2b**).[3] This hydrocarbon

Scheme I



1a 2a 3

is thermally unstable above 0 °C and polymerizes;[3a] substitution of the aromatic ring by electron-withdrawing groups increases the thermal stability somewhat, but still the half-lives are not more than several hours at room temperature.[3b-d] Reasonable, though not complete stability is encountered only with the next higher homologue [6]paracyclophane (**2c**).[4] Extrapolating the homologous series in the opposite direction, one expects a dramatic decrease in stability for [4]paracyclophane (**2a**) for which MNDO

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