

Diels–Alder reactions of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene and 1,1-dimethyl-3,4-diphenyl-1-silacyclopentadiene with maleic anhydride; kinetic measurements

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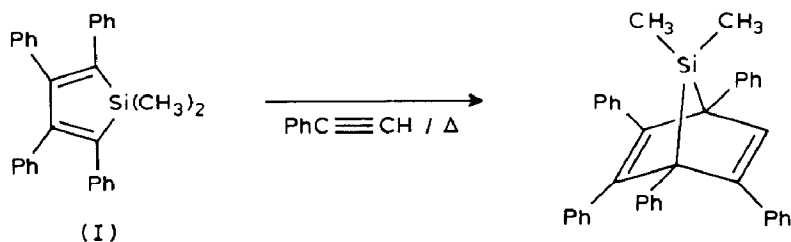
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Abstract

Diels–Alder reactions of 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene and 1,1-dimethyl-3,4-diphenyl-2-silacyclopentadiene with maleic anhydride have been carried out. The rates of these second order reactions have been measured by ^1H FT NMR over a range of temperatures. Arrhenius plots of these data yield the activation parameters for these reactions. The synthesis of 1,1-dimethyl-3,4-diphenyl-1-silacyclopentadiene is reported.

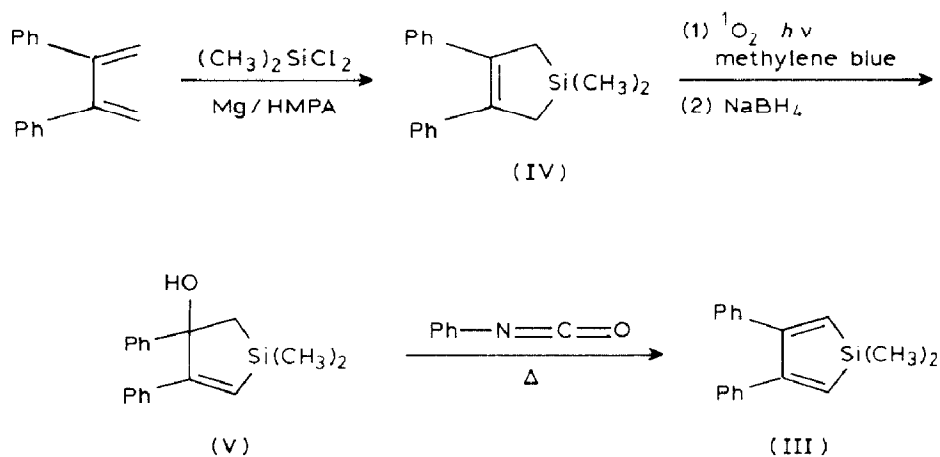
Diels–Alder reactions of siloles (1-silacyclopenta-2,4-dienes) with dieneophiles provide a convenient synthetic route to prepare 7-silanorbornadienes and 7-silanorbornenes [1,2]. For example, 1,1-dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (I) reacts with phenylacetylene to yield 7,7-dimethyl-1,2,3,4,5-pentaphenyl-7-silanorbornadiene.



In addition to the intrinsic interest of such bicyclic compounds, 7-silanorbornadienes have proved useful precursors for the thermal and photochemical generation of silylenes [3,4].

Despite continued interest in such systems, no kinetic measurements for the Diels–Alder reactions of siloles have been reported. We should like to report the first such measurements for reactions of I, 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene (II), and 1,1-dimethyl-3,4-diphenylsilacyclopentadiene (III) with maleic anhydride.

In particular, this series of siloles I–III permits quantitative assessment of the effect of aryl substitution on silole reactivity. Siloles I and II and their Diels–Alder adducts with maleic anhydride are known compounds. Silole III was synthesized from 1,1-dimethyl-3,4-diphenyl-1-silacyclopent-3-ene (IV) which was prepared by a dissolving metal reaction between 2,3-diphenyl-1,3-butadiene, dimethyldichlorosilane and magnesium powder in HMPA [5,6]. An ene reaction of IV with photochemically generated singlet oxygen gave 1,1-dimethyl-3-hydroxy-3,4-diphenyl-1-silacyclopent-4-ene (V) after in situ reduction of the corresponding allylic hydroperoxide. Reaction of V with phenyl isocyanate gave the corresponding urethane which undergoes pyrolytic elimination at 80 °C to yield III [7–9].



We have followed the rates of these Diels–Alder reactions of siloles I, II, and III with maleic anhydride by ^1H FT NMR spectroscopy at various temperatures. FIDs were collected at regular time intervals during the reaction. Fourier transform of these FIDs permits integration of the concentrations of the starting materials and products for each series of spectra. A linear relationship exists between $1/[\text{silole}]$ and reaction time as well as between $1/[\text{dienophile}]$ and reaction time. Thus these reactions are second order, first order in each reactant.

The activation parameters for these reactions were determined from plots of the rates of reaction versus the reciprocal of the absolute temperatures (See Table 1).

The energy of activation for the reaction of siloles II and III with maleic anhydride is very close to that observed for the reaction of cyclopentadiene with maleic anhydride (E_a 8.5 kcal/mol) [10]. The large negative entropies of activation values for these reactions are consistent with those previously found for Diels–Alder reactions ($\Delta S^\ddagger$ –30 to –40 eu) [11].

We have also studied the Diels–Alder reaction between silole III and dimethyl fumarate. The activation parameters for this reaction were found to be E_a 16.0 $\pm$ 1.2 kcal/mol, $\Delta H^\ddagger$ 15.2 $\pm$ 1.0 kcal/mol and $\Delta S^\ddagger$ –33.2 $\pm$ 2 eu. For comparison the

Table 1

Activation parameters for Diels–Alder reaction of siloles (I, II, or III) with maleic anhydride

Silole	E_a (kcal/mol)	$\Delta H^\ddagger$ (kcal/mol)	$\Delta S^\ddagger$ (eu)
I	14.4 ± 1.0	13.6 ± 1.0	-34.4 ± 2
II	9.4 ± 0.9	8.8 ± 0.9	-37.1 ± 2
III	8.3 ± 0.8	7.7 ± 0.8	-40.2 ± 2

energy of activation for the Diels–Alder reaction of cyclopentadiene and dimethyl fumarate has been found to be 11.7 kcal/mol [11].

Experimental

^1H and ^{13}C NMR spectra were obtained on a JEOL FX-90 or IBM-Bruker WP-270-SY spectrometer operating in the FT mode. ^{13}C NMR spectra were run with broad band proton decoupling. ^{29}Si NMR spectra were obtained on a Bruker WP-270-SY spectrometer operating in the FT mode. Ten to fifteen percent solutions in chloroform- d_1 were used to obtain ^{29}Si spectra whereas five percent solutions were used for ^1H and ^{13}C NMR spectra. Chloroform was utilized as an internal standard for ^1H , ^{13}C and ^{29}Si NMR spectra. All chemical shifts reported were externally referenced to tetramethylsilane. A DEPT pulse sequence was used to obtain ^{29}Si NMR spectra. This was effective since all the silicon atoms have methyl groups bonded to them [12].

Elemental analysis was performed by Galbraith Laboratories, Knoxville, Tennessee.

All reactions were run under an atmosphere of pre-purified nitrogen. All reagents and solvents were dried over activated 4 Å molecular sieves prior to use.

The kinetic data (Table 2) were obtained on an IBM Bruker FT-WP 270 MHz-SY spectrometer equipped with a variable temperature accessory. The temperature in the probe was controlled by balancing a flow of cold nitrogen gas with a heater. The temperatures was measured by a thermocouple. The temperature was calibrated by measuring the proton chemical shift difference between the C–H and O–H groups of ethylene glycol. Temperatures were reproducible to within 0.5°C and the accuracy was 1°C. Samples for kinetic runs were prepared as follows. A solution which was $2 \times 10^{-2} M$ in the particular silole and $2 \times 10^{-2} M$ in maleic anhydride was prepared in CDCl_3 . 0.25 ml aliquots of this solution were placed in 5 mm NMR tubes which had been dried overnight in an oven at 120°C, purged with argon and cooled. These were sealed under vacuum after a freeze-thaw degassing cycle. FIDs were collected at regular time intervals after thermal equilibration of the sample in the probe. Fourier transform of these FIDs permits integration of the concentration of the starting materials and products for each series of spectra. The rate constants were obtained by a least squares method. An Arrhenius plot gave the activation parameters reported above. The maximum error in the rate constants is approximately $\pm 5\%$.

IR spectra were run on a Perkin–Elmer PE-281 spectrometer. These were taken on neat oils between NaCl plates or on carbon tetrachloride solution in NaCl solution cells.

Table 2

Kinetic data for Diels–Alder reactions of siloles

Silole	Dienophile	Temperature (°C)	k ($\text{mol}^{-1} \times \text{sec}^{-1}$)
III	Maleic anhydride	0	6.14×10^{-3}
		10	1.27×10^{-2}
		20	1.86×10^{-2}
III	Dimethyl fumarate	124	2.90×10^{-3}
		132	4.70×10^{-3}
		147	5.60×10^{-3}
		167	1.35×10^{-2}
II	Maleic anhydride	20	4.60×10^{-3}
		30	7.60×10^{-3}
		40	1.63×10^{-2}
		50	1.72×10^{-2}
		60	3.50×10^{-2}
I	Maleic anhydride	80	2.31×10^{-3}
		100	4.90×10^{-3}
		110	8.47×10^{-3}
		125	1.35×10^{-2}

While silole I and II as well as their Diels–Alder adducts with maleic anhydride are known compounds, we have included both ^{13}C and ^{29}Si NMR data since this information has not been previously reported.

1,1-Dimethyl-2,3,4,5-tetraphenyl-1-silacyclopentadiene (I). Compound I was prepared by the reaction of dimethyldichlorosilane with 1,4-dilithiotetraphenylbutadiene [1,13]. It had the following properties: M.p. 176–178°C (Lit. [14] m.p. 178–181°C); ^{13}C NMR: δ (ppm) –3.93, 125.50, 126.16, 127.36, 127.92, 128.81, 130.00, 138.85, 139.89, 141.88, 154.00; ^{29}Si NMR: δ 8.01 ppm.

1,1-Dimethyl-2,5-diphenyl-1-silacyclopentadiene (II). Compound II was prepared by benzylic bromination of 1,1-dimethyl-2,5-diphenyl-1-silacyclopentane with *N*-bromosuccinimide (NBS) followed by dehydrobromination of *trans*-2,5-dibromo-2,5-diphenyl-1-silacyclopentane by treatment with potassium acetate in refluxing acetonitrile [14,15]. It had the following spectral properties: ^1H NMR: δ (ppm) 0.46 (s, 6H), 7.22–7.33 (m, 12H); ^{13}C NMR: δ (ppm) –2.80, 126.19, 126.89, 128.79, 137.95, 138.87, 144.83; ^{29}Si NMR δ 2.32 ppm.

1,1-Dimethyl-3,4-diphenyl-1-silacyclopent-3-ene. In a 100 ml three-necked round bottomed flask, equipped with a reflux condenser and a Teflon covered magnetic stirring bar, was placed 50 ml of HMPA, freshly distilled from barium oxide, magnesium powder (5.6 g, 0.23 mol), 2,3-diphenyl-1,3-butadiene [16] (20 g, 97 mmol) and dimethyldichlorosilane (35 ml, 0.29 mol). The reaction mixture was heated to reflux. After 10 min a vigorous reaction occurred. The reaction was refluxed for 1 h. Excess dimethyldichlorosilane was removed by evaporation under reduced pressure. The reaction mixture was filtered through a Buchner funnel. The solid was washed several times with ether. The combined organic phase was washed with several 100 ml portions of water. The organic layer was dried over anhydrous magnesium sulfate, filtered and the ether solvent removed by evaporation under reduced pressure. 1,1-Dimethyl-3,4-diphenyl-1-silacyclopent-3-ene was recrystallized from ethanol/methylene chloride (1/1) to give 45 g, (87.8% yield). It had the

following properties: m.p. 76.5–77°C; ^1H NMR: δ (ppm) 0.29 (s, 6H), 1.94 (s, 4H), 7.1 (s, 10H); ^{13}C NMR: δ (ppm) –2.80, 27.07, 126.64, 128.43, 129.51, 139.04, 143.92; ^{29}Si NMR: δ 12.81 ppm. Elemental analysis. Found: C, 81.61; H, 7.83. $\text{C}_{18}\text{H}_{20}\text{Si}$ calcd.: C, 81.76; H, 7.62%.

1,1-Dimethyl-3-hydroxy-3,4-diphenyl-1-silacyclopent-4-ene. A solution of 3 g of 1,1-dimethyl-3,4-diphenyl-1-silacyclopent-3-ene and 10 mg of methylene blue in 100 ml of methanol was placed in a Pyrex tube 1' in length by 3'' in diameter. A fritted gas inlet tube connected to an oxygen tank was inserted into the solution. The Pyrex tube was placed next to a Hanovia 450 W medium pressure mercury lamp which was suspended in a quartz photolysis well. The entire apparatus was cooled to 0°C in a bucket of ice. Oxygen was slowly bubbled through the solution while it was photolyzed for 3 h. At this time, the solution was poured into a 500 ml Erlenmeyer flask containing a 100 ml of aqueous sodium borohydride (2.1 g). This solution was stirred for 12 h. The solution was extracted with pentane. The pentane solution was dried over anhydrous magnesium sulfate, filtered and the solvent removed by evaporation under reduced pressure to give 2.8 g (10 mmol) of the desired alcohol (88% yield). It had the following spectral properties: ^1H NMR: δ (ppm) 0.19 (s, 3H), 0.30 (s, 3H), 1.58 (d of d, 2H, J 2 Hz), 2.4 (br.s, 1H), 6.57 (s, 1H), 7.1–7.6 (m, 10H); ^{13}C NMR: δ (ppm) –1.89, –0.53, 35.06, 86.95, 124.99, 126.69, 127.62, 128.00, 128.15, 128.25, 132.44, 138.99, 148.96, 165.25; ^{29}Si NMR: δ 9.38 ppm; IR: ν 3320, 1560 cm^{-1} .

1,1-Dimethyl-3,4-diphenylsilacyclopenta-2,4-diene. 1,1-Dimethyl-3-hydroxy-3,4-diphenylsilacyclopent-4-ene (3 g, 10.7 mmol) was dissolved in 25 ml of chloroform in a 50 ml three-neck round bottom flask equipped with a reflux condenser. To this was added phenyl isocyanate (1.5 g, 13 mmol). The mixture was refluxed for 12 h. After work-up, 1,1-dimethyl-3,4-diphenylsilacyclopenta-2,4-diene was recrystallized from ethanol/dichloromethane (1/1). In this manner, 2.2 g (78.5% yield) was obtained. It had the following properties: M.p. 96.5–97°C; ^1H NMR: δ (ppm) 0.30 (s, 6H), 6.14 (s, 2H), 7.06–7.23 (m, 10H); ^{13}C NMR: δ (ppm) –4.92, 127.69, 128.29, 128.61, 133.43, 151.78, 161.06; ^{29}Si NMR: δ 2.8 ppm; IR: ν 1600 cm^{-1} . Elemental analysis. Found: C, 81.96; H, 7.08. $\text{C}_{18}\text{H}_{18}\text{Si}$ calcd.: C, 82.38; H, 6.91%.

7,7-Dimethyl-5,6-diphenyl-2,3-dicarboxylic anhydride-7-silanorbornene. This compound was prepared by the Diels–Alder reaction of III with maleic anhydride. It had the following spectral properties: ^1H NMR: δ (ppm) –0.84 (s, 3H), –0.26 (s, 3H), 2.60 (t, 2H, J 1.6 Hz), 2.86 (t, 2H, J 1.6 Hz), 6.89–7.12 (m 10H); ^{13}C NMR: δ (ppm) –7.96, –1.51, 41.66, 47.39, 127.20, 128.36, 138.12, 139.09, 173.28; ^{29}Si NMR: δ 45.32 ppm; IR: ν 1740 cm^{-1} . Elemental analysis. Found: C, 73.50; H, 5.70. $\text{C}_{22}\text{H}_{20}\text{SiO}_3$ calcd.: C, 73.30; H, 5.60%.

7,7-Dimethyl-1,4,5,6-tetraphenyl-2,3-dicarboxylic anhydride-7-silanorbornene. This compound was prepared by the Diels–Alder reaction of I with maleic anhydride [17]. It had the following spectral properties: ^1H NMR: δ (ppm) 0.26 (s, 3H), 0.66 (s, 3H), 4.51 (s, 2H), 6.65–7.54 (m, 20H); ^{13}C NMR: δ (ppm) –6.37, –3.28, 50.62, 54.08, 127.38, 127.82, 128.36, 129.34, 130.42, 131.55, 135.83, 136.81, 142.23, 171.91; ^{29}Si NMR: δ 49.87 ppm. Elemental analysis. Found C, 79.23; H, 15.75%. $\text{C}_{34}\text{H}_{28}\text{SiO}_3$ calcd.: C, 79.53; H, 5.66%.

7,7-Dimethyl-1,4-diphenyl-2,3-phthalic anhydride-7-silanorbornene. This compound was prepared by a Diels–Alder reaction of II and maleic anhydride [18]. It had the following spectral properties: ^1H NMR: δ (ppm) 0.46 (s, 3H), 0.12 (s, 3H),

4.36 (s, 2H), 6.55 (s, 2H), 7.26 (m, 10H); ^{13}C NMR: δ (ppm) – 9.06, – 4.32, 50.33, 52.62, 126.33, 126.65, 129.47, 135.94, 139.72, 172.01; ^{29}Si NMR: δ 55.29 ppm; IR: ν 1840 and 1755 cm^{-1} .

trans-2,3-Bis(carbomethoxy)-7,7-dimethyl-5,6-diphenyl-7-silanorbornene. This compound was prepared by a Diels–Alder reaction of III with dimethyl fumarate. It had the following spectral properties: ^1H NMR: δ (ppm) 0.07 (s, 3H), 0.15 (s, 3H), 2.67 (d of d, 1H, J 2.0 Hz), 2.83 (d of d, 1H, J 2.0 Hz), 3.81 (d of d, 1H, J 6 and 2 Hz), 3.98 (d of d, 1H, J 6 and 2 Hz), 3.29 (s, 3H), 3.34 (s, 3H), 6.77–7.10 (m, 10H); ^{13}C NMR: δ (ppm) – 7.76, – 1.01, 41.74, 42.96, 47.56, 48.11, 51.67, 51.74, 126.25, 126.43, 127.87, 128.11, 128.19, 139.20, 139.39, 169.20, 167.64; ^{29}Si NMR: δ 35.09 ppm; IR: ν 1755 cm^{-1} . Elemental analysis. Found: C, 71.10; H, 5.76. $\text{C}_{24}\text{H}_{26}\text{SiO}_4$ calcd.: C, 70.90; H, 5.66%.

Acknowledgements

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