

Nature of Alkylidenecarbenes Generated from Alkenyl(phenyl)iodonium Tetrafluoroborates via Base-Induced α -Elimination

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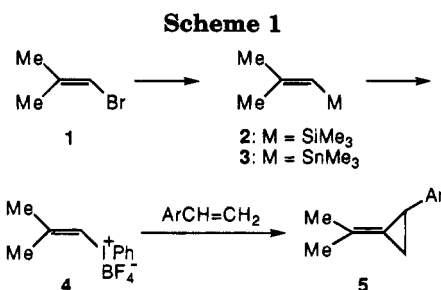
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Alkylidenecarbenes generated from alkenyl(phenyl)iodonium tetrafluoroborates via base-induced α -elimination undergo 1,5-carbon-hydrogen insertion, providing a useful route for the construction of substituted cyclopentenes because of the high regio- and chemoselectivity.¹ A major competing intramolecular process to the insertion of alkylidenecarbenes will be a 1,2-shift of α -substituents, such as H, Cl, Br, I, PhS, PhS(O), aryl, and alkyl groups, yielding rearranged alkynes.

Another possible reaction pathway of alkylidenecarbenes is addition to olefins to give methylenecyclopropanes.² The cycloaddition to olefins has been shown to be a useful tool to define the nature of the carbenic species, the spin multiplicity, and electrophilicity of the alkylidenecarbenes. We have investigated and wish to report the reaction of the alkylidenecarbene, derived from (2-methylpropenyl)(phenyl)iodonium tetrafluoroborate (4), with olefins.

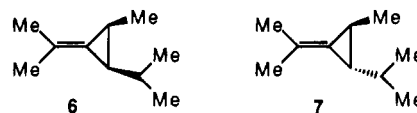
Results and Discussion

The required alkenyliodonium tetrafluoroborate 4 was prepared from the commercially available vinyl bromide 1; reaction of the vinylmagnesium bromide, prepared from 1, with chlorotrimethylsilane gave the vinylsilane 2³ in 40% yield. BF_3 -catalyzed silicon-iodonium exchange reaction⁴ of 2 with iodosylbenzene in dichloromethane at room temperature afforded the vinyliodonium salt 4 as a crystal in 75% yield. Alternatively, the salt 4 was obtained in 98% yield by tin-iodonium exchange reaction of the vinylstannane 3,⁵ prepared from 1 by the reaction of the vinylmagnesium bromide with chlorotrimethylstannane, with iodosylbenzene in the presence of $\text{BF}_3\text{-Et}_2\text{O}$.



The carbenic species derived from 4 via base-induced α -elimination readily undergoes cycloaddition to styrene; when 4 was treated with potassium *tert*-butoxide in the presence of excess amounts of styrene (20 equiv) at 0 °C for 15 min, dimethylmethylenecyclopropane 5 (Ar = Ph) was obtained in 68% yield (Scheme 1). Triethylamine is also effective as a base for a proton abstraction of 4.

To gain some insight into the spin multiplicity of the carbenic species generated from the alkenyliodonium tetrafluoroborate 4, we studied the stereochemistry of the cycloaddition reaction to olefins. It is generally accepted by theoretical calculations⁶ and experimental data⁷ that alkylidenecarbenes possess a singlet ground state with a fairly sizable singlet-triplet energy difference,² which leads to retention of stereochemistry of olefins on the cycloaddition of alkylidenecarbenes. Thus, the alkylidenecarbenic species generated from a variety of progenitors such as *N*-nitrosooxazolidone,^{7a} vinyl triflates,^{7b} and 1-diazo-1-alkenes^{7c} undergo cycloaddition to olefins with retention of stereochemistry. Reaction of 4 with triethylamine in the presence of 10 equiv of *cis*-4-methyl-2-pentene in dichloromethane at 3 °C under nitrogen afforded *cis*-methylenecyclopropane 6 in 28% yield; none of the trans isomer 7 could be detected by analytical capillary GC. Cycloadditions to *trans*-4-methyl-2-pentene under similar conditions gave the trans isomer 7 in 12% yield in more than 99.4% isomeric purity. The observed high stereospecificity of the cycloaddition to the olefins, combined with generation of the free carbene from the alkenyliodonium salt 4 (see below), is consistent with the alkylidenecarbene being produced in a singlet electronic state. The relative rate of the cycloaddition to the *cis* and the *trans* olefins was determined by a competitive experiment ($\text{Et}_3\text{N}/\text{CH}_2\text{Cl}_2/0\text{ }^\circ\text{C}/20\text{ h}$) to be^{7b,8} 5.6:1.



Our previous study of stereoselectivity for the intramolecular 1,5-carbon-hydrogen insertions indicates that the

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(8) It has been reported that *cis* alkenes react with 2-methyl-1-propenylidene considerably faster than their *trans* counterparts with a relative reactivity for 2-butene of $k_{\text{cis}}/k_{\text{trans}} = 5.3$.⁹

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Table 1. Relative Reactivity of 4 with Styrenes in the Presence of a Base^a

olefin	$k_{\text{rel}}(\text{Et}_3\text{N})$	$k_{\text{rel}}(\text{KOBU}^t)$
<i>p</i> -MeOC ₆ H ₄ CH=CH ₂	1.52	1.54
<i>p</i> -MeC ₆ H ₄ CH=CH ₂	1.26	1.34
C ₆ H ₅ CH=CH ₂	1.00	1.00
<i>p</i> -ClC ₆ H ₄ CH=CH ₂	0.79	0.84

^a Reactions were carried out in CH₂Cl₂ at 3 °C under nitrogen.**Table 2. ρ Values for the Reaction of 2-Methyl-1-propenylidene with Styrenes**

carbene precursor	reaction condns	ρ	ref
4	Et ₃ N/CH ₂ Cl ₂ /3 °C	-0.56 (σ)	this work
4	KOBu ^t /CH ₂ Cl ₂ /3 °C	-0.55 (σ)	this work
Me ₂ C=CN ₂	KOBu ^t /CH ₂ Cl ₂ /-78 °C	-0.51 (σ)	7c
Me ₂ C=CHOTf	KOBu ^t /-20 °C	-0.75 (σ)	10
Me ₂ C=C(OTf)TMS	R ₄ N ⁺ F ⁻ /0 °C	-0.44 (σ)	2c,7c
Me ₂ C=CHN ₂ Ts	0 °C	-0.71 (σ)	2c,7c
Me ₂ C=CHBr	KOBu ^t /-10 °C	-4.3 (σ^+)	11
Me ₂ C=CBBr ₂	MeLi/-40 °C	-4.3 (σ^+)	11
<i>N</i> -nitroso-oxazolidone	LiOCH ₂ CH ₂ -OEt/40 °C	-3.4 (σ^+)	7a

base-induced α -elimination of alkenyliodonium tetrafluoroborates will involve the free alkylidenecarbene rather than the carbenoid as a reactive intermediate.^{1a} This was further supported by a Hammett study for the cycloaddition of the carbene derived from **4** to ring-substituted styrenes. Relative reactivities toward 2-methyl-1-propenylidene of styrenes were determined by conducting the α -elimination of **4** in large excesses of an equimolar mixture of two styrenes at 3 °C in dichloromethane. The results are summarized in Table 1. Both triethylamine and potassium *tert*-butoxide were used as base for α proton abstraction of **4**. As shown in Table 1, the relative reactivities of substituted styrenes are almost identical regardless of the base used, suggesting that the same reactive species is involved in these cycloadditions.

The magnitude of ρ values obtained by a Hammett correlation are summarized in Table 2. Stang and Mangum reported that the free alkylidenecarbene is mildly electrophilic in nature and shows a relatively small negative ρ value,^{2c,10} whereas the carbenoid shows a very large degree of electrophilicity and a large negative ρ value.^{7a,11} Thus, the small ρ values of -0.56 (Et₃N) and -0.55 (KOBu^t) for our system indicate that, as in the case of vinyl triflate- and diazoethene-derived species, alkenyliodonium salt-derived alkylidenecarbenes are mildly electrophilic and the free carbene.

Experimental Section

IR spectra were recorded on a JASCO IRA-1 spectrometer. ¹H NMR spectra were recorded on a JEOL JNM-FX 200 or JNM-GX 400 spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from internal Me₄Si. Mass spectra (MS) were obtained on a JMS-D300 spectrometer. Analytical gas chromatography (GC) was conducted on a Shimadzu GC-14A gas chromatograph with 10% or 20% silicone GE SF-96 on a Chromosorb W-AWDMCS column (3 m) and on a Shimadzu GC-15A gas chromatograph with an 0.25 mm \times 50 m FFS ULBON HR-20M capillary column. Preparative GC was performed on a Shimadzu GC-14A gas chromatograph with 10% or 20% silicone GE SF-96 on a Chromosorb W-AWDMCS column. Thin-layer chromatography (TLC) was carried out on Kieselgel 60 F254 (Merck).

Styrene and substituted styrenes are commercially available and distilled from CaH₂ under nitrogen. Pure *cis*- and *trans*-4-methyl-2-penten-3-ones were purchased from Tokyo Kasei Kogyo Co. and distilled prior to use. Dichloromethane was dried over CaH₂ and distilled. BF₃-Et₂O was distilled from CaH₂ under nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen.

Silicon-Iodonium Exchange Reaction of 2-Methyl-1-(trimethylsilyl)prop-1-ene (2) with Iodosylbenzene. The vinylsilane **2** was prepared in 40% yield from isobutenyl bromide **1** by the reaction of the corresponding vinyl Grignard reagent with trimethylsilyl chloride according to the method developed by Soderquist and Lee.^{3b} To a stirred suspension of iodosylbenzene¹² (5.67 g, 25.8 mmol) and the vinylsilane **2** (2.54 g, 19.8 mmol) in dichloromethane (60 mL) was added dropwise BF₃-Et₂O (4.53 g, 31.9 mmol) at 0 °C in nitrogen, and the mixture was stirred for 2 h at 0 °C and for 4 h at room temperature. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (32 g, 0.30 mol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at -78 °C. Further purification using hexane-diethyl ether gave phenyl-(2-methylprop-1-enyl)iodonium tetrafluoroborate (**4**) (5.12 g, 75%) as colorless prisms: mp 76-79 °C (recrystallized from dichloromethane-diethyl ether); IR (KBr) 3095, 1611, 1445, 1100-1000, 740 cm⁻¹; ¹H NMR (200 MHz, CDCl₃) δ 7.94 (br d, *J* = 8 Hz, 2 H), 7.62 (br t, *J* = 8 Hz, 1 H), 7.48 (br t, *J* = 8 Hz, 2 H), 6.72 (br s, 1 H), 2.23 (d, *J* = 1.2 Hz, 3 H), 2.21 (d, *J* = 0.7 Hz, 3 H). Anal. Calcd for C₁₀H₁₂BF₄I: C, 34.72; H, 3.50. Found: C, 34.72; H, 3.47.

Tin-Iodonium Exchange Reaction of 2-Methyl-1-(trimethylstannyl)prop-1-ene (3) with Iodosylbenzene. The vinylstannane **3** was prepared in high yield from isobutenyl bromide **1** by the reaction of the corresponding vinyl Grignard reagent with trimethylstannyl chloride according to literature procedure.^{5a} To a stirred suspension of iodosylbenzene (2.30 g, 10.5 mmol) and the vinylstannane **3** (1.43 g, 6.53 mmol) in dichloromethane (20 mL) was added dropwise BF₃-Et₂O (1.48 g, 10.5 mmol) at 0 °C in nitrogen, and the mixture was stirred for 1 h at 0 °C and for 2 h at room temperature. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (14.5 g, 0.130 mol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at -78 °C to give the vinyliodonium salt **4** (2.21 g, 98%).

Reaction of the Vinyliodonium Salt 4 with Styrenes. To a mixture of potassium *tert*-butoxide (27 mg, 0.24 mmol) and styrene (455 mg, 4.36 mmol) was added the vinyliodonium tetrafluoroborate **4** (74 mg, 0.22 mmol) at 0 °C under nitrogen, and the mixture was stirred for 15 min at 0 °C. After the addition of water, the reaction mixture was extracted with pentane. Analytical GC using a column of 10% silicone GE SF-96 (130 °C) with tridecane as internal standard showed the formation of 1-(1-methylethylidene)-2-phenylcyclopropane (**5**) (Ar = Ph)^{7b} in 68% yield. A pure sample of **5** (Ar = Ph) was obtained by preparative GC (10% silicone GE SF-96, 1 m). The other *para*-substituted adducts **5** (Ar = *p*-MeOC₆H₄, *p*-MeC₆H₄, and *p*-ClC₆H₄)^{7b} were prepared in a similar manner. **5** (Ar = Ph): IR (CHCl₃) 2980, 1780, 1605, 1500, 1450, 1370, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.24 (t, *J* = 7.3 Hz, 2 H), 7.14 (t, *J* = 7.3 Hz, 1 H), 7.08 (d, *J* = 7.3 Hz, 2 H), 2.56 (m, 1 H), 1.91 (m, 3 H), 1.79 (m, 3 H), 1.67 (m, 1 H), 1.07 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 142.9, 128.3, 126.2, 125.4, 122.8, 119.9, 22.3, 22.2, 20.4, 15.1; MS *m/z* 158 (M⁺), 143, 128, 115, 91; HRMS calcd for C₁₂H₁₄ (M⁺) 158.1095, found 158.1079. **5** (Ar = *p*-MeOC₆H₄): ¹H NMR (400 MHz, CDCl₃) δ 7.01 (d, *J* = 8.8 Hz, 2 H), 6.79 (d, *J* = 8.8 Hz, 2 H), 3.77 (s, 3 H), 2.52 (m, 1 H), 1.90 (m, 3 H), 1.80 (m, 3 H), 1.60 (m, 1 H), 0.99 (m, 1 H); ¹³C NMR (100 MHz, CDCl₃) δ 157.6, 134.8, 127.2, 122.7, 119.9, 113.7, 55.2, 22.3, 22.2, 19.6, 14.7; MS *m/z* 188 (M⁺), 173, 157; HRMS calcd for C₁₃H₁₆O (M⁺) 188.1201, found 188.1184. **5** (Ar = *p*-MeC₆H₄): ¹H NMR (400

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MHz, CDCl_3) δ 7.05 (d, J = 7.8 Hz, 2 H), 6.98 (d, J = 7.8 Hz, 2 H), 2.53 (m, 1 H), 2.30 (s, 3 H), 1.90 (m, 3 H), 1.79 (m, 3 H), 1.63 (m, 1 H), 1.03 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.8, 134.9, 129.0, 126.1, 122.6, 120.0, 22.3, 22.2, 21.0, 20.1, 14.9; MS m/z 172 (M^+), 157, 142; HRMS calcd for $\text{C}_{13}\text{H}_{16}$ (M^+) 172.1253, found 172.1259. **5** (Ar = *p*- ClC_6H_4): ^1H NMR (400 MHz, CDCl_3) δ 7.20 (d, J = 8.5 Hz, 2 H), 7.00 (d, J = 8.5 Hz, 2 H), 2.52 (m, 1 H), 1.90 (m, 3 H), 1.77 (m, 3 H), 1.68 (m, 1 H), 1.05 (m, 1 H); ^{13}C NMR (100 MHz, CDCl_3) δ 141.5, 130.9, 128.3, 127.5, 123.3, 119.5, 22.2, 22.1, 19.8, 15.3.

Competition Experiments Using Triethylamine. In a 10-mL oven-dried two-necked round-bottomed flask fitted with a nitrogen balloon, a rubber septum, and a magnetic stirring bar were placed the vinylidonium tetrafluoroborate **4** (60 mg, 0.17 mmol) and a mixture of styrenes (4.3 mmol of each styrene), and 1.0 mL of dichloromethane was added. The mixture was cooled to 3 °C. Triethylamine (21 mg, 0.21 mmol) was added, and the reaction mixture was stirred for 4 h at 3 °C. After the addition of water, the reaction mixture was extracted with dichloromethane. The organic solution was analyzed by GC using a column of 10% silicone GE SF-96 with tridecane as internal standard. The yields of dimethylmethylenecyclopropanes were 60–70%. All reactions were performed at least twice, and relative reactivities are reported in Table 1.

Competition Experiments Using Potassium *tert*-Butoxide. In a 10-mL oven-dried two-necked round-bottomed flask fitted with a nitrogen balloon, a rubber septum, and a magnetic stirring bar were placed potassium *tert*-butoxide (13 mg, 0.11 mmol) and a mixture of styrenes (2.4 mmol of each styrene), and the mixture was cooled to 3 °C. A solution of the vinylidonium tetrafluoroborate **4** (33 mg, 0.095 mmol) in 0.5 mL of dichloromethane was added dropwise, and the reaction mixture was stirred for 4 h at 3 °C. After the addition of water, the reaction mixture was extracted with dichloromethane. The organic solution was analyzed by GC as described above. The

yields of dimethylmethylenecyclopropanes were 49–69%. All reactions were performed at least twice, and relative reactivities are reported in Table 1.

Reaction of the Vinylidonium Salt **4 with *cis*-4-Methyl-2-pentene.** To a solution of the vinylidonium tetrafluoroborate **4** (35 mg, 0.10 mmol) and *cis*-4-methyl-2-pentene (84 mg, 1.0 mmol) in 1.0 mL of dichloromethane was added triethylamine (12 mg, 0.12 mmol) at 3 °C under nitrogen, and the mixture was stirred for 20 h at 3 °C. After the addition of water, the reaction mixture was analyzed by GC using a column of 20% silicone GE SF-96 (70 °C) with nonane as internal standard. The GC showed the formation of *cis*-1-(1-methylethylidene)-2-isopropyl-3-methylcyclopropane (**6**) in 28% yield. The isomeric purity of **6** was determined to be more than 99.7% by analytical capillary GC using FFS ULBON HR-20M (70 °C). Preparative GC (20% Silicone GE SF-96, 3 m) afforded the pure cyclopropane **6**.^{7a,c,e}

Reaction of the Vinylidonium Salt **4 with *trans*-4-Methyl-2-pentene.** To a solution of the vinylidonium tetrafluoroborate **4** (35 mg, 0.10 mmol) and *trans*-4-methyl-2-pentene (84 mg, 1.0 mmol) in 1.0 mL of dichloromethane was added triethylamine (12 mg, 0.12 mmol) at 3 °C under nitrogen, and the mixture was stirred for 20 h at 3 °C. After the addition of water, the reaction mixture was analyzed by GC using a column of 20% silicone. The GC showed the formation of *trans*-1-(1-methylethylidene)-2-isopropyl-3-methylcyclopropane (**7**) in 12% yield. The isomeric purity of **7** was determined to be more than 99.4% by analytical capillary GC using FFS ULBON HR-20M (70 °C). Preparative GC (20% Silicone GE SF-96, 3 m) afforded the pure cyclopropane **7**.^{7a,c}

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