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geminal-DEHALOSILYLATION OF α-HALO-β,β-DIMETHYLVINYLTRIMETHYLSILANES: GENERATION OF ISOPROPYLIDENE CARBENE

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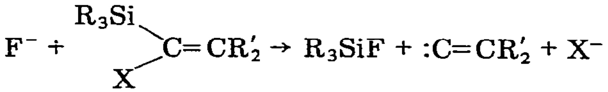
Summary

Treatment of α-chloro- or α-bromo-β,β-dimethylvinyltrimethylsilane with anhydrous tetramethylammonium fluoride (TMAF) in diglyme containing olefins led to isopropylidenecyclopropanes. A stepwise geminal dehalosilylation leading to isopropylidene carbene appears to be involved. The carbene is a species of low electrophilicity (ρ —0.41) and reacts stereospecifically with 2-butene. The substrates α-chloro-β,β-diphenylvinyltrimethylsilane, *E*-1-chloro-1-trimethylsilylpropene and α-chlorovinyltrimethylsilane afford only acetylenes when treated with TMAF.

Introduction

Fluoride ion has been shown to be an effective dehalosilylating agent for both β-haloalkylsilanes [1] and corresponding unsaturated systems such as β-halovinylsilanes [2] and *o*-halophenylsilanes [3]. Thus it seemed possible that similar reactivity might be exhibited by α-halovinylsilanes, in which geminal dehalosilylation would afford unsaturated carbene species (eq. 1). This transformation is of considerable interest from two standpoints: its novelty in organosilicon chemistry and its potential for generating alkylidene carbenes under conditions of low basicity. Prior to our original communication of this work [4], a number of approaches to alkylidene carbene species had been reported [5—8]. Of these, the treatment of primary vinyl trifluoromethanesulfonates with potassium t-butoxide, explored by Stang and co-workers [6], appeared to offer the most desirable combination of substrate availability, mildness of conditions and yields of carbene-olefin adducts. However, even this system was necessarily strongly basic (KO-t-



$$F^- + (R_3Si)(X)C{=}CR'_2 \rightarrow R_3SiF + {:}C{=}CR'_2 + X^- \qquad (1)$$

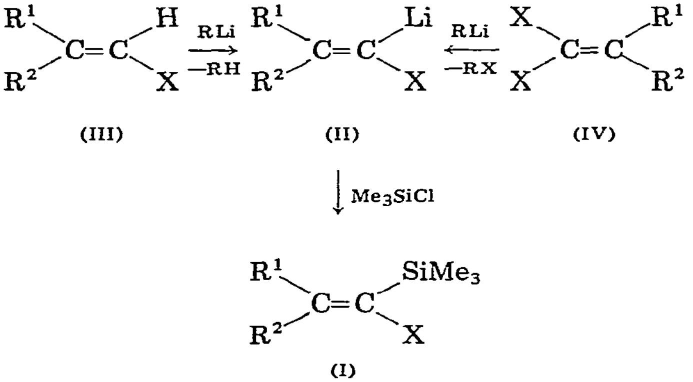
Bu) and, in addition, afforded t-butyl vinyl ether by-products which were not easily separable from the carbene adducts of low-molecular weight olefins *. We report here on our successful attempts to generate and capture isopropylidene carbene ** from the fluoride ion-induced α-elimination of α-halovinylsilanes ***.

Results and discussion

Precursor synthesis

In order to assess the behavior of a variety of substituted methylidene carbenes, a number of β-substituted α-halovinyltrimethylsilanes (Ia—If) were chosen as carbene precursors. Preparation of the known α-chlorovinyltrimethylsilane (Ia) was carried out according to literature procedures [11], but a different approach was devised to obtain Ib—If. In a series of papers, Köbrich and coworkers had explored the synthetic potential of α-halolithium species (II), generated either from metalation of a primary vinyl halide (III) or from metal—halogen exchange of a 1,1-dihaloolefin (IV) [12]. Metalation of III occurs readily when R = aryl [13] or H [14], but proceeds much more slowly for R = alkyl [15], and 1-chloro-2-methylpropene (IIIb) has been identified as not undergoing metalation under these conditions [12]. Since metalation of IIIb would afford IIb, transformable into Ib upon trimethylsilylation, interest focused on this sequence (Scheme 1).

SCHEME 1



Ia, IIa, IIIa: $X = Cl; R^1 = R^2 = H$
Ib, IIb, IIIb: $X = Cl; R^1 = R^2 = CH_3$
Ic, IIc, IIIc: $X = Cl; R^1 = CH_3, R^2 = H$
Id, IId, IIId: $X = Cl; R^1 = H, R^2 = CH_3$
Ie, IIe, IIIe: $X = Cl; R^1 = R^2 = Ph$.
If, IIf, IVf: $X = Br; R^1 = R^2 = CH_3$

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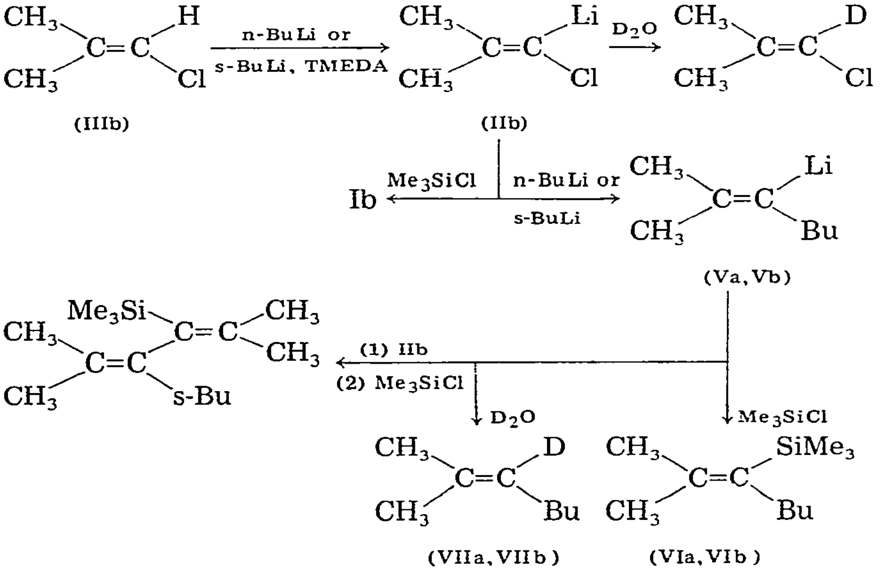
* Recently, major improvements in this approach have been realized using a modification of the basic chemistry reported herein [9].

** No inference as to the state of complexation this species is intended by the use of the term "carbene".

*** Thermolysis of $Me_2C{=}C(Br)HgBr$ has also served as a source of isopropylidene carbene [10].

The use of *N,N,N',N'*-tetramethylethylenediamine (TMEDA) to enhance the kinetic basicity of n-butyllithium [16] proved effective in accelerating the rate of IIIb metalation. Thus, after a 4 h contact time at —100°C addition of D_2O indicated that 43% of IIIb (90% recovery) was deuterated at the 1-position, as determined by NMR analysis. Use of the more potent sec-butyllithium [17] did not noticeably enhance the rate of metalation and led to consumption of IIIb by other pathways. Both organolithium reagents also led to the respective formation of small amounts of VIIa, VIIb, presumably derived from the reaction of the corresponding butyllithium with the carbenoid IIb * (Scheme 2). When IIIb was metalated by n-butyllithium, followed by derivatization with HMPA/trimethylchlorosilane, a 44% yield of Ib was obtained based on the total amount of IIIb employed. In addition, small amounts of VIa were present, which could arise as indicated in Scheme 2. As expected from the metalation studies, reaction of IIIb with sec-butyllithium led to much lower yields of Ib (5%) upon trimethylchlorosilane treatment. Instead, major products were VIb and 2,4-dimethyl-2-hexene; the latter could arise from protonation of unsilylated Vb upon hydrolysis or in situ proton transfer from a co-reactant, and its presence may be indicative of a greater steric impediment to silylation for VIb than for VIa. Several minor products were identified as VIII, which can arise through a series of carbenoid organolithium couplings [7,18,19], and β,β-dimethylvinyltrimethylsilane, whose origin may be small amounts of β,β-dimethylvinyllithium produced by halogen—metal exchange within IIIb **.

SCHEME 2



(Va, VIa, VIIa; Bu = n-butyl; Vb, VIb, VIIb; Bu = s-butyl)

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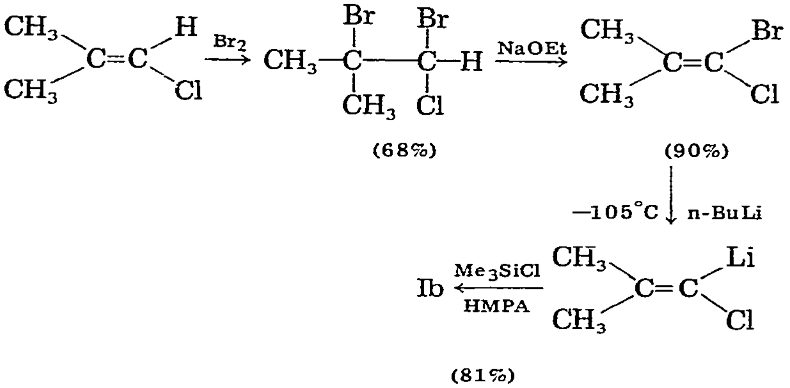
* The ability of carbenoids to react as electrophiles in this sense has been documented [7,18,19].

** Chlorine—lithium exchange in chloroolefins is known to be slower than hydrogen—lithium exchange [7]. Alternatively, Ib may undergo halogen—metal exchange with unreacted IIb if silyation of IIb is slow.

An alternative approach to the synthesis of Ib entailed selective halogen—metal exchange between n-butyllithium and 1-bromo-1-chloro-2-methylpropene, followed by chlorotrimethylsilane derivatization of the intermediate carbenoid at —105°C (Scheme 3). Although all reaction steps in this sequence proceeded in acceptable yields to afford products of high purity, the metalation of IIIb remains the choice for the preparation of Ib because of its directness. The halogen—metal exchange reaction was employed, however, for the synthesis of If, starting with 1,1-dibromo-2-methylpropene (Scheme 1, IVf → IIf → If).

SCHEME 3

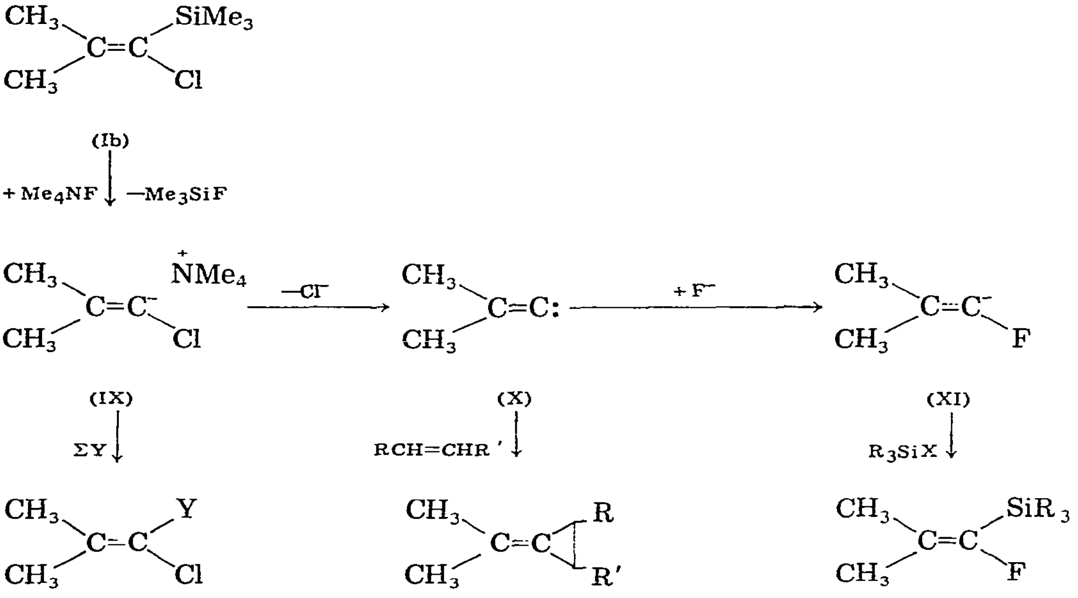


Compounds Ic, Ie were also prepared by the metalation-silylation route. Thus, n-butyllithium/TMEDA treatment of *E*-1-chloropropene (IIIc) gave Ic and similar treatment of 1-chloro-2,2-diphenylethene (IIIe) afforded Ie. However, when IIId was likewise employed, no Id was produced. Instead, an 80% yield of 1-propynyltrimethylsilane was obtained, indicating that an elimination process is favored when vicinal H and Cl are in a *trans* arrangement. This observation is parallel to the known behavior of the isomeric β-chlorostyrenes, in which vicinal dehydrochlorination of the α-(to chlorine)-lithiated *Z*-isomer to lithium phenylacetylide is faster than the corresponding conversion of the α-(to chlorine)-lithiated *E*-isomer [20]. Similar reactivity differences are also exhibited by isomeric α-lithiated chloroethylenes, where that isomer capable of *anti*-dehydrochlorination undergoes conversion to lithium acetylide more easily [7,14].

As an initial test of the ability of α-chlorovinyltrimethylsilanes to undergo α-elimination, Ia was treated with anhydrous tetramethylammonium fluoride (TMAF) in diglyme containing ethyl vinyl ether as a carbene scavenger. Complete consumption of Ia occurred within 20 h at 25°C, giving acetylene, fluorotrimethylsilane and a small amount of vinyl chloride as the only volatile products. If it is assumed that elimination did occur to afford an incipient or actual carbene, these results are consistent with the known reactivity of alkylidene carbenes containing a β-hydrogen, in which intramolecular rearrangement to acetylene is fast relative to intermolecular insertion reactions [5]. In order to observe such intermolecular products, the behavior of the dimethyl analogue Ib towards fluoride ion reagents was examined. No reaction occurred between Ib and potassium fluoride in diglyme, even after two days at 80°C. Addition of 18-crown-6 ether, known to enhance the nucleophilicity of fluoride ion [21], resulted in only a 12% consumption of Ib over a period of several more days. Cesium fluoride in diglyme proved marginally more effective, in that 13% of Ib was consumed over a two day period at 25°C. In contrast to these results, the use of TMAF in diglyme led to complete disappearance of Ib in less than a day at 25°C. Moreover, the introduction of a variety of carbenophiles as co-reactants under these conditions afforded isopropylidene adducts in fair to good yields (Table 1). Use of the much stronger base, potassium t-butoxide, converted Ib into products within 1 h at —25°C, but gave a much reduced yield of adduct derived from cyclohexene as the test carbenophile.

Scheme 4 suggests a sequence of events which would account for the products

SCHEME 4



(IIIb) ΣY = HOH, Y = H
(IVg) ΣY = C_2Cl_4, Y = Cl
(IVh) ΣY = $BrCCl_3$, Y = Br

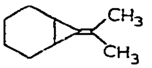
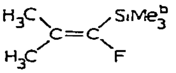
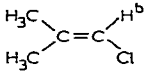
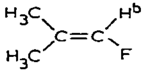
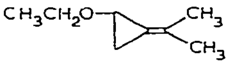
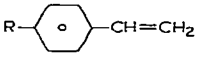
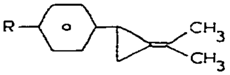
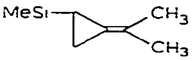
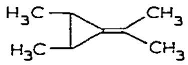
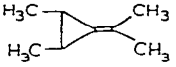
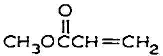
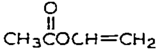
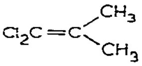
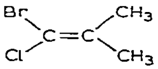
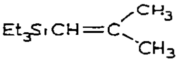
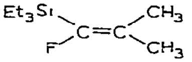
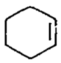
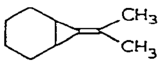
(XIIa) R = R' = $(CH_2)_4$
(XIIb) R = OEt; R' = H
(XIIc) R = Ar; R' = H
(XIId) R = Me_3Si; R' = H
(XIIe) R = R' = CH_3 (*c* and *t*)

(XIIIa) R = Me
(XIIIb) R = Et

observed (Table 1) when Ib was treated with TMAF in the presence of various carbenophiles. Attack of fluoride ion at the silicon of Ib leads to cleavage of the C—Si bond and formation of the charge-separated species IX. Although in principle, Ib could be transformed directly into carbene X, the discrete formation of IX is strongly inferred from the nature of the products obtained in the reactions of Ib and TMAF with water, tetrachloroethylene and bromotrichloromethane. Small amounts of IIIb, the product expected from protonation of IX, were obtained routinely in all reactions and may have arisen from traces of moisture in

TABLE 1

THE REACTION OF $Me_3SiC(Cl)=CMe_2$ WITH Me_4NF [a]

Co-reactant	Products (% yield)
	 (53)  (15)  (7)  (5)
$CH_3CH_2OCH=CH_2$	 (66)
	 [R = H (55), CH_3 (52), CH_3O (48), PhO (56), Cl (24); product from *m*-methylstyrene (47)]
$Me_3SiCH=CH_2$	 (35)
t-$CH_3CH=CHCH_3$	*t*-  (36)
c-$CH_3CH=CHCH_3$	*c*-  (52)
 $CH_3OC(O)CH=CH_2$	None [c]
 $CH_3C(O)OCH=CH_2$	None [c]
$Cl_2C=CCl_2$	 $Cl_2C=C(CH_3)_2$ (80) [d]
$BrCCl_3$	 $BrClC=C(CH_3)_2$ (76) [e]
Et_3SiH	 $Et_3SiCH=C(CH_3)_2$ (65)
Et_3SiF	 $Et_3Si(F)C=C(CH_3)_2$ (21)
	 (71) [f]

[a] In diglyme at 25°C. [b] Obtained in varying amounts with almost all co-reactants. [c] Co-reactant polymerized upon contact with TMAF. [d] Based on 75% conversion of Ib. [e] Based on 16% conversion of Ib. [f] $Me_3SiC(Br)=CMe_2$ instead of Ib.

the TMAF *. Indeed, when Ib was treated with TMAF containing an equivalent amount of water in the presence of cyclohexene, IIIb was obtained in 62% yield, and only 15% of XIIa was formed. Further evidence for the existence of a car-

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* Other, less common, potential proton sources are of course also present, among them being the tetramethylammonium ion, fluorotrimethylsilane and diglyme. The first of these is particularly suspect in this regard, as tetramethylammonium bromide is known to be sufficiently acidic so as to be metalated by phenyllithium [22].

banionic intermediate was afforded by the observation that the dihalides IVg and IVh resulted from the reactions of Ib and TMAF with, respectively, tetrachloroethylene and bromotrichloromethane. An attempt to intercept IX with benzaldehyde failed, however, as consumption of Ib did not occur under these conditions.

Loss of chloride ion from IX would generate the divalent species X, which in contrast to IX, is expected to display electrophilic properties towards co-reactants. Thus, subsequent reaction with olefins afforded XIIa—XIIe and the reaction with triethylsilane gave the expected Si—H insertion product (Table 1). Based on the appearance of 1-fluoro-2-methylpropene and XIIIa in many of the reactions involving Ib and TMAF, fluoride ion can also react with X to afford the α-fluorovinyl carbanion XI; protonation of XI leads to 1-fluoro-2-methylpropene and reaction with the fluorotrimethylsilane generated in situ would give XIIIa. The carbanion XI could in fact be intercepted purposefully, and a run employing Ib, TMAF and fluorotriethylsilane afforded XIIIb as the major product.

The reaction of α-bromo-β,β-dimethylvinyltrimethylsilane (If) with TMAF was also expected to follow the general pattern of Scheme 4, with the added possibility that substitution of a better leaving group for chlorine would afford X (and subsequent products) in an improved manner. Indeed, when cyclohexene was used as the carbenophile under these conditions, a 71% yield of adduct XIIa was obtained, compared with a 53% yield from the chloro analogue Ib. That the extension of this concept is synthetically fruitful has been shown by Stang and Fox in their work on the compound $Me_3SiC(OTf)=CMe_2$ [9].

All methods for the generation of vinylidene carbenes hitherto reported normally afford products of intramolecular migration (acetylenes) if a β-substituent is either hydrogen or aryl [5]. It was thus of interest to determine whether the present method would (a) follow different behavior relative to aryl migration and (b) show stereochemical selectivity in β-hydrogen migration *. Upon examination, neither possibility was realized. Only diphenylacetylene was obtained from the reaction of the diphenyl substrate Ie with TMAF in the presence of cyclohexene, while behavior comparison of the β-monomethyl substituted compounds Ic, Id was thwarted by our inability to synthesize Id. When Ic was treated with TMAF/cyclohexene, only propyne and *E*-1-chloropropene were formed.

The relative reactivity of isopropylidene carbene generated from $Me_2C=CH$-(OTF) and KO-t-Bu towards *cis*- and *trans*-butene, as well as the stereospecificity of these reactions, have been determined by Stang and Mangum [23]. Inasmuch as the present method for isopropylidene carbene formation differed significantly from that approach, a comparison of corresponding values within the two systems was of interest. The fluoride ion-generated carbene afforded an average *cis/trans* reactivity ratio of 6.1, compared with a value of 3.85 for the KO-t-Bu-derived carbene. Factors which lead to the usually-observed discrimination of carbenes in favor of *cis*-olefins are not well-known. However, the greater selectivity exhibited by the present system (diglyme solvent) may in part arise from greater solvent-complexation of the electrophilic carbene than is available under

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* In a previous system where such differentiation was potentially observable, only acetylenic product was formed [6].

Stang and Mangum's ether-free conditions, as enhanced stability and/or steric requirements can result from such complexation *. Some support for this interpretation is afforded by a comparison of ρ values for the two systems. A Hammett treatment of the relative rates of a series of styrenes with isopropylidene carbene generated from Ib resulted in ρ —0.41 with a correlation coefficient $r = 0.9999$. This value lies in the same range as that for $Me_2C{=}CH(OTf)$-derived isopropylidene carbene (—0.75) [24], but indicates a somewhat lower electrophilicity for the carbene generated under the present conditions. Significantly higher selectivities have been reported for isopropylidene carbene generated from the systems *N*-nitrosooxazolidone/$LiOCH_2CH_2OCH_2CH_3$ (ρ —3.4) [8], $Me_2C{=}CBr_2$/MeLi (ρ —4.3) [25] and $Me_2C{=}CHBr$/KOtBu · HO-t-Bu (ρ —4.3) [25] As has been previously noted [24], these values imply a highly charge-separated transition state for olefin addition, whereas the values ρ —0.41 and ρ —0.75 correspond more closely to a transition state in which bond reorganizations are occurring in a nearly synchronous fashion. Barring significant effects from differences in solvent or cation/anion involvement, the ρ values exhibited by carbenes generated from Ib and other vinyl halides are particularly at odds inasmuch as all these precursors presumably generate $Me_2C{=}C$: in a similar fashion (via a discrete α-halovinyl carbanion). No ready resolution of this disparity comes to mind.

Examination of the isopropylidenecyclopropane adducts (XIIe) obtained from the reaction of Ib and TMAF with pure *cis*- and *trans*-2-butene indicated that cyclopropane formation proceeded with high stereospecificity. Thus, *trans*-olefin afforded 99.8% of *trans*-XIIe and *cis*-olefin gave 99.6% of *cis*-XIIe. Similar values have been reported for triflate-derived isopropylidene carbene [23] and are supportive of a singlet reactive species, in agreement with theoretical predictions [26].

Experimental

General

Infrared (IR) data was obtained on neat films using Beckman IR-8 and Perkin—Elmer 237B spectrophotometers. ^1H NMR spectra were recorded on Varian A-60A or JEOL PFT-100 spectrometers (solvent, internal standard listed sequentially; chloroform taken as δ 7.27 ppm, benzene as δ 7.20 ppm). Analytical and preparative GLC work involved the following stainless steel columns: (A) 8 ft. × 0.25 in. 20% SE-30 (B) 20 ft. × 0.375 in. 25% FFAP.

GLC yields were obtained using internal standards after determination of relative response ratios. Ethereal solvents were distilled from $LiAlH_4$; chlorotrimethylsilane, TMEDA and HMPA were distilled from calcium hydride. Hexane used in metalation runs was rendered olefin-free by treatment with concentrated H_2SO_4. The normality of organolithium reagents was determined by double titration using 1,2-dibromoethane. "Research grade" *cis*-2-butene (99.88 mol%) and *trans*-2-butene (99.75 mol%) were obtained from Phillips Petroleum Co., Bartlesville Oklahoma. Except where noted, all reactions were run under nitrogen.

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* The possibility that the carbene in the present system is salt-complexed (a carbenoid) during further reaction is an additional relevant, but unexplored, factor.

Metalation of 1-chloro-2-methylpropene

A flask equipped with mechanical stirrer, thermometer and jacketed addition funnel was charged with 40 mmol (25 ml) of 1.6 *N* n-BuLi in hexane and cooled to —100°C (ether/liquid N_2). After addition of a mixture of 4.64 g (40 mmol) TMEDA, 120 ml THF and 30 ml ether, 3.60 g (40 mmol) of precooled (—78°C) 1-chloro-2-methylpropene was added slowly. After 4 h at —100°C, 1.04 g (55 mmol) of D_2O in 40 ml THF was added, and the mixture poured into saturated NH_4Cl solution. GLC analysis (column A, 80°C; column B, 60°C) indicated a 90% recovery of 1-chloro-2-methylpropene of which 43% was deuterated at the 1-position (NMR analysis). In addition, 8% of 3-*d*-2-methyl-2-heptene (VIIa) was obtained.

The same procedure was applied to the metalation of 3.37 g (37.4 mmol) 1-chloro-2-methylpropene using 37.4 mmol of 1.2 *N* sec-BuLi in hexane, 4.05 g TMEDA 120 ml THF, and 30 ml ether and 30 ml of hexane. After 3.25 h at —100°C, D_2O quench gave 43% of recovered 1-chloro-2-methylpropene which was 30% deuterated at the 1-position, and 17% of 3-*d*-2,4-dimethyl-2-hexene (VIIB).

α-Chloro-β,β-dimethylvinyltrimethylsilane (Ib)

A. From the metalation of 1-chloro-2-methylpropene. A flask equipped with thermometer, mechanical stirrer and jacketed addition funnel was immersed in a —78°C cooling bath and charged with 125 ml (200 mmol) of 1.6 *N* n-butyllithium in hexane, followed by addition of a precooled (—78°C) mixture of 23.5 (203 mmol) TMEDA, 500 ml THF and 125 ml ether. The mixture was further cooled to —100°C and 25.8 g (287 mmol) of precooled (—78°C) 1-chloro-2-methylpropene added. After stirring at —100°C for 4 h, 22.5 g (208 mmol) of precooled (—78°C) chlorotrimethylsilane in 25 ml THF was slowly added, followed after 0.5 h by precooled HMPA * (10 ml) in 20 ml THF. The reaction mixture was held at —100°C for an additional 0.5 h and then allowed to spontaneously rise to room temperature. After addition to saturated NH_4Cl solution, the organic phase was washed with water to constant volume, dried ($MgSO_4$), and fractionated using an 8" adiabatic Widmar column to give 14.2 g (44%) ** of Ib [4], b.p. 161—162°C/760 mmHg; ${}^1H$ NMR (CCl_4, PhH): δ 0.16 (9 H, s), 1.77 (3 H, s), 1.82 ppm (3 H, s). GLC analysis (column A, 110°C) indicated a purity of 99.9%. As a forerun, 1.60 g (4.6%) of α-n-butyl-β,β-dimethylvinyltrimethylsilane (VIa) was also obtained, b.p. 106—108°C/5 mmHg (Found: C, 71.67; H, 12.86. $C_{11}H_{24}Si$ calcd.: C, 71.65; H, 13.12%). IR: 6.20m, 6.9m, 7.1w, 7.23m, 7.30m, 8.00s, 9.25w, 11.60s, 12.0s, 13.2s, 14.6m, 16.2 μm, ${}^1H$ NMR (CCl_4, PhH): δ 0.06 (9 H, s), 0.9—1.8 (7 H, m), 1.64 (3 H, s), 1.74 (3 H, s), 2.0—2.4 ppm (2 H, m).

The same general procedure was applied to the metalation of 10.8 g (120 mmol) 1-chloro-2-methylpropene using 120 mmol of 1.2 *N* sec-BuLi in hexane, 14 g TMEDA, 170 ml THF and 42 ml ether. After 4 h at —100°C, silylation using 13 g (133 mmol) chlorotrimethylsilane in 15 ml THF and then a mixture

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* A much lower yield of Ib (ca. 10%) is obtained if HMPA is omitted.

** Although longer metalation times may have led to higher conversions, the tedium of temperature maintenance led to acceptance of these results.

of 15 ml HMPA in 15 ml THF led to the formation of only 5% Ib, together with 36% α-sec-butyl-β,β-dimethylvinyltrimethylsilane (VIb), 25% 2,4-dimethyl-2-hexene [27], 8% β,β-dimethylvinyltrimethylsilane (XIV) [28] and 7% 3-sec-butyl-2,5-dimethyl-4-trimethylsilylhexa-2,4-diene (VIII).

VIb. Found: C, 71.81; H, 13.31. $C_{11}H_{24}Si$ calcd.: C, 71.65; H, 13.12%. IR: 6.25m, 6.86m, 7.28m, 8.00s, 8.15m, 11.50s, 12.0s, 13.2s, 14.8m, 15.7 nm. ^{1}H NMR (CCl_4, PhH): δ 0.13 (9 H, s), 0.60—1.58 (8 H, m), 1.68 (3 H, s), 1.77 (3 H, s), 2.55 ppm (1 H, sextet).

XIV. IR: 6.16m, 6.92m, 7.29m, 8.00s, 8.70w, 11.48s, 12.0s, 13.0w, 13.4w, 14.5m nm.

VIII. Found: C, 75.46; H, 12.38. $C_{15}H_{30}Si$ calcd.: C, 75.54; H, 12.67%. IR: 6.25w, 6.90m, 7.33m, 8.01s, 8.18w, 10.91w, 11.46m, 12.0s, 13.3m, 14.2m μm. ^{1}H NMR ($CDCl_3$, PhH): δ 0.24 (9 H, s), 0.9—1.3 (8 H, m), 1.57 (3 H, s), 1.71 (3 H, s), 1.82 (3 H, s), 1.98 (3 H, s), 2.44 ppm (1 H, m).

B. From halogen metal exchange of 1-bromo-1-chloro-2-methylpropene. Pre cooled (—78°C) n-butyllithium in hexane (2.5 *N*, 45 ml, 113 mmol) was added dropwise to a mixture of 16.9 (100 mmol) 1-bromo-1-chloro-2-methylpropene, 240 ml THF, 60 ml ether and 60 ml pentane cooled to —105°C over 1.5 h. After an additional hour of stirring at —105°C, 12.2 g (113 mmol) chlorotrimethylsilane in 30 ml THF was added, followed 0.5 h later by 12 ml HMPA in 25 ml THF. The mixture was allowed to warm spontaneously to room temperature over 12 h and worked up. Fractionation afforded 13.1 g (81%) of Ib, b.p. 160—162°C/760 mmHg, in 99.9% purity.

1,2-Dibromo-1-chloro-2-methylpropane.

A stirred solution of 50.0 g (553 mmol) 1-chloro-2-methylpropene and 32.0 g (405 mmol) pyridine in 250 ml CH_2Cl_2 was treated dropwise with a solution of 64.0 g (400 mmol) bromine in 100 ml CH_2Cl_2. After 12 h, the reaction mixture was washed with water (3×), dilute HCl and $NaHCO_3$ solution. Distillation of the dried and concentrated organic phase afforded 67.5 g (68%) of 1,2-dibromo-1-chloro-2-methylpropane, b.p. 62—63°C/6 mmHg in 99% purity. Found: C, 19.12; H, 2.84. $C_4H_7Br_2Cl$ calcd.: C, 19.19; H, 2.82%. IR: 6.88m, 7.19m, 7.28m, 8.5w, 9.09s, 10.35m, 12.13m, 13.07m, 13.29s, 13.62m nm. ^{1}H NMR (CCl_4, TMS): δ 1.98 (6 H, s), 5.98 ppm (1 H, s).

1-Bromo-1-chloro-2-methylpropene

A solution of 24.7 g (100 mmol) 1,2-dibromo-1-chloro-2-methylpropene in 40 ml ethanol was added over 10 min at 0°C to a solution of sodium ethoxide prepared from 2.8 g (120 mmol) sodium and 50 ml absolute ethanol. After 30 min at room temperature, GLC analysis showed complete consumption of dibromide. After a water and pentane work-up, distillation (7 in. Vigreux column) gave 15.1 g (90%) of 1-bromo-1-chloro-2-methylpropene, b.p. 129—130°C/760 mmHg, in 99.5% purity. Found: C, 28.17; H, 3.37. C_4H_6BrCl calcd.: C, 28.35; H, 3.57%. IR: 6.15 w, 6.92w, 7.29w, 8.18w, 9.23m, 11.45s, 11.82 nm. ^{1}H NMR (CCl_4, TMS): δ 1.79 ppm (s).

Tetramethylammonium fluoride

A modification of Urban and Dötzer's method [29] was used to prepare anhydrous tetramethylammonium fluoride. All steps were carried out under dry (Anhydrone) nitrogen or in a dry box. Anhydrous tetramethylammonium chloride (J.T. Baker Chemical Co.) was recrystallized from anhydrous methanol and dried over P_2O_5 at 160°C and 2 mmHg for 5 days (Found: C, 43.72; H, 11.23; N, 12.50. $C_4H_{12}NCl$ calcd.: C, 43.84; H, 11.04; N, 12.78%). A solution of 10.4 g (95.7 mmol) Me_4NCl in 25 ml anhydrous methanol was added by syringe to a solution of sodium methoxide in methanol prepared from 2.2 g (95.7 mmol) sodium metal and 45 ml anhydrous methanol. A mildly exothermic reaction occurred which deposited white salts immediately. These were removed by filtration through a glass frit (medium), and the filtrate concentrated under reduced pressure to half volume. After a one-day storage period (dessicator), additional solid was removed (fine glass filter) to afford a 2.2 *N* solution of tetramethylammonium methoxide (HCl titration).

A solution of anhydrous HF [30] in methanol was prepared as follows. Commercial HF was transferred by polyethylene (PE) tubing and condensed in a 250 ml PE bottle containing 40 ml SbF_5 (3 parts HF to 1 part SbF_5). The SbF_5 (98% purity, Ventron Corp.) was manipulated by PE syringe in a glove bag. Reevaporation of HF from this mixture was aided by mild heating, affording about 9 ml of anhydrous liquid HF as condensate in a PE tube. This was evaporated into 100 ml anhydrous methanol in a PE bottle to afford a solution determined by NaOH titration to be 4.15 *N* in HF.

Upon addition of 93 mmol HF in methanol (22.5 ml of a 4.15 *N* solution) to 93 mmol Me_4NOMe in methanol (43 ml of a 2.2 *N* solution) via PE syringe, an exothermic reaction occurred immediately accompanied by a small amount of white precipitate. After filtration, methanol was removed from the filtrate under 1 mmHg pressure with gradual heating to 160°C. A white fluoride was thus obtained. Found: C, 50.63; H, 12.71; N, 15.59. $C_4H_{12}NF$ calcd.: C, 51.58; H, 12.99; N, 15.04%. The differential in carbon values indicates a maximum water content of 11 mol percent. A qualitative test for the presence of chloride ion was negative.

Reaction of α-chloro-β,β-dimethylvinylsilane (Ib) with alkali metal fluorides and KO-t-Bu

A mixture of 1.08 g (6.7 mmol) Ib, 1.84 g (32 mmol) KF, 10 ml cyclohexene and 15 ml diglyme was stirred at 80°C for 2 days. No consumption of Ib occurred. Addition of 1.26 g (5.2 mmol) 18-crown-6 ether in 5 ml cyclohexene was followed by an additional 16 h at 80°C. Only 12% of Ib was consumed at this point and no further consumption occurred over an additional 3 day period. In a similar reaction, a mixture of 1.1 g Ib, 2.1 g (14 mmol) CsF, 8 ml cyclohexene and 8 ml diglyme led to a 13% consumption of Ib after 2 days at 25°C.

A flask equipped with septum inlet was charged with 1.89 g (17 mmol) KO-t-Bu (triply sublimed), 12.5 ml diglyme and 20 ml cyclohexene. After the flask was wax-sealed, it was cooled to −25°C and 2.16 g (13.4 mmol) Ib was added dropwise by syringe. After 1 h, almost complete consumption of Ib was noted. Analysis after work-up indicated a 97% conversion of Ib and the formation of XIIa in 23% yield.

Reaction of α-chloro-β,β-dimethylvinyltrimethylsilane with tetramethylammonium fluoride

A. With olefins. A number of olefins were employed to trap the vinylidene carbene generated in these reactions (Table 1). The reaction employing cyclohexene is illustrative of the general procedure.

A flask with septum-sealed side arm was charged with 1.28 g (13.7 mmol) Me_4NF in a dry box and the flask sealed with wax. There was then added 6 ml diflyme, 14 ml cyclohexene and 2.00 g (1.23 mmol) of Ib by syringe, and the mixture stirred at 25°C for 3 days (GLC analysis showed complete consumption of Ib after 21 h). The reaction mixture was worked up by exhaustive water extraction. GLC analysis (column A, 90°C) showed a 53% yield of 7-isopropylidenebicyclo[4.1.0]heptane (XIIa) [6], 15% α-fluoro-β,β-dimethylvinyltrimethylsilane (XIIIa), 7% 1-chloro-2-methylpropene and 5% 1-fluoro-2-methylpropene. The aqueous phase afforded 1.53 g (87%) AgCl upon $AgNO_3$ treatment. Fluorotrimethylsilane was also identified as a component of the reaction mixture before hydrolysis.

XIIIa. Found: C, 57.71; H, 10.58. $C_7H_{15}SiF$ calcd.: C, 57.48; H, 10.34%. IR: 6.05w, 6.9m, 7.08m, 7.21m, 7.28m, 8.00s, 9.55s, 9.70s, 10.44w, 11.28m, 11.90s, 13.18s, 14.38m 15.70s nm. ^1H NMR (CCl_4, PhH): δ 0.05 (9 H, s), 1.49 and 1.54 ppm (6 H, 2 overlapped doublets, J 3 and 4 Hz).

Isopropylidene carbene adducts obtained from other olefins employed are listed in Table 1. Adducts to *cis*- and *trans*-butenes [23], ethyl vinyl ether [6], substituted styrenes [6] and vinyltrimethylsilane [4] have been reported previously and were identified by spectral comparison. Additional characterization data are as follows: Isopropylidene(trimethylsilyl)cyclopropane (XIId). IR: 3.26w, 3.33s, 3.35s, 3.38m, 3.40m, 3.46m, 6.88m, 7.29m, 7.99s, 8.45w, 9.84m, 10.08w, 10.50w, 11.33m, 11.53m, 11.98vs, 13.3m, 14.4m, 15.1m nm.

Isopropylidene(*p*-phenoxyphenyl)cyclopropane. Found: C, 86.11; H, 7.11. $C_{18}H_{18}O$ calcd.: C, 86.36; H, 7.25%. IR: 6.26s, 6.64s, 6.72s, 7.30w, 8.1vs nm. ^1H NMR (CCl_4, TMS): δ 0.8—1.4 (2 H, m), 1.85 (6 H, m), 2.5 (1 H, m), 7.0 ppm (9 H, m).

Isopropylidene(*m*-tolyl)cyclopropane. Found: C, 90.90; H, 9.13. $C_{13}H_{16}$ calcd.: C, 90.64; H, 9.36%. IR: 6.20s, 6.28w, 6.70m, 6.88m, 7.29m, 8.32m, 12.80s, 14.29s nm. ^1H NMR ($CDCl_3$, TMS): δ 0.8—1.7 (2 H, m), 1.7—2.0 (6 H, m), 2.26 (3 H, s), 2.3—2.65 (1 H, m), 6.7—7.1 ppm (4 H, m).

When 1.42 g (9.0 mmol) of Ib was allowed to react with 0.93 g (10.0 mmol) TMAF in a mixture of 0.18 g (10.0 mmol) H_2O, 8 ml diglyme and 8 ml cyclohexene for 72 h at 25°C, 72% of Ib was consumed. GLC analysis showed a 14% yield of XIIa and 62% 1-chloro-2-methylpropene.

B. With other co-reactants. Reactions were run essentially as in part A, except that cyclohexene was replaced by an approximately equal volume of other co-reactants. In this way, triethylsilane afforded, after 18 h at 25°C, 65% of triethyl(2-methylpropenyl)silane [6] and 8% 1-chloro-2-propene. Tetrachloroethylene gave, after 64 h, 80% IVg [31] (authentic sample prepared by the method of Rabinowitz and Marcus [32]) based on 75% consumption of Ib. After 3 days at 25°C, bromotrichloromethane gave 76% of IVh based on a 16% consumption of Ib, along with the disproportionation products CCl_4, Br_2CCl_2 and CBr_4. The reaction with triethylfluorosilane afforded after 64 h, 21% of a compound tentatively identified as α-fluoro-β,β-dimethylvinyltrimethylsilane (XIIIb). Satisfactory analysis could not be obtained, the best values found being C, 64.74; H, 11.24. $C_{10}H_{21}SiF$ calcd.: C, 63.77; H, 11.24%. However, spectral data were consistent with the proposed structure. IR: 6.05w, 6.82m, 7.05m, 7.23w, 8.03m, 9.5—10.0 m, 13.56s, 13.8s, 14.17s nm. ^{1}H NMR (CCl_4, PhH): δ 0.40—1.16 (15 H, m), 1.62 ppm (6 H, apparent triplet, J 4 Hz).

The addition of 10 ml benzaldehyde to a mixture of 0.72 g (7.7 mmol) TMAF and 15 ml diglyme resulted in a brown mixture which was treated with 0.81 g (5.0 mmol) Ib. After 1 day at 25°C GLC analysis showed no consumption of Ib.

When a mixture of 1.13 g (7.0 mmol) Ib, 0.88 g (9.5 mmol) TMAF and 6 ml diglyme (no added carbenophile) was allowed to react for 24 h at 25°C, total consumption of Ib occurred. GLC analysis showed no evidence for possible insertion products of diglyme. A parallel reaction employing THF in place of diglyme gave identical results; 7% of 1-chloro-2-methylpropene and 17% 1-fluoro-2-methylpropene were present.

α-Bromo-β,β-dimethylvinyltrimethylsilane (If)

A mixture of 12.3 g (57.7 mmol) 1,1-dibromo-2-methylpropene [33], 120 ml THF, 30 ml ether and 15 ml pentane was cooled to —105°C and treated with a precooled (—78°C) sample of n-butyllithium in hexane (26.5 ml, 2.5 *N*, 66.3 mmol) over 10 min. After an additional 50 min at —105°C solutions of 7.2 g (66 mmol) chlorotrimethylsilane in 15 ml THF and 10 ml HMPA in 15 ml THF were added in sequence, and the mixture allowed to slowly warm to 25°C. After work-up, distillation (7 in. vigreux) gave 9.6 g (80%) of If [34], b.p. 90—92°C/40 mmHg, of 99.6% purity. Found: C, 40.65; H. 7.21. $C_7H_{15}BrSi$ calcd.: C, 40.58; H, 7.30%. IR: 6.20m, 6.92m, 7.10m, 7.32m, 8.00s, 11.23s, 11.9s, 13.2s, 14.5m nm. ^{1}H NMR (CCl_4, PhH): δ 0.18 (9 H, s), 1.80 (3 H, s), 1.87 ppm (3 H, s).

Reaction of α-bromo-β,β-dimethylvinyltrimethylsilane (If) with tetramethylammonium fluoride

A mixture of 0.73 g (3.5 mmol) If, 0.47 g (5.1 mmol) TMAF, 8 ml cyclohexene and 4 ml diglyme was stirred in a sealed flask at 25°C for 2 days. Analysis after work-up showed complete consumption of If and the formation of XIIa in 71% yield.

α-Chloro-β,β-diphenylvinyltrimethylsilane (Ie)

The procedure of Köbrich and Trapp [13] was used for tne metalation of 1-chloro-2,2-diphenylethane [35,36], A mechanically-stirred mixture of 8.56 g (40 mmol) 1-chloro-2,2-diphenylethene, 64 ml THF, 16 ml ether and 16 ml pentane was cooled to —100°C and treated with precooled (—78°C) n-butyllithium in hexane (20 ml, 2.5 *N*, 50 mmol) over 1 h. After another 25 min at —100°C, sequential addition of chlorotrimethylsilane (4.88 g, 45 mmol) in 15 ml THF and 10 ml HMPA in 10 ml THF was carried out. After allowing the reaction mixture to warm to 25°C, work-up followed by short-path distillation gave 8.1 g (71%) of Ie, b.p. 111—112°C/0.2 mmHg, in 99% purity, and 1.2 (17%) of diphenylacetylene. Found (Ie): C, 71.29; H, 6.58; Cl, 12.35. $C_{17}H_{19}ClSi$ calcd.: C, 71.18, H, 6.68; Cl, 12.35%. IR: 6.35w, 6.70m, 6.92m, 7.10w, 8.00s, 9.30w, 9.70w, 10.40m, 11.0w, 11.60s, 11.9s, 12.30m, 12.60w, 13.18s, 13.53s, 14.4s, 15.74m nm. ^{1}H NMR ($CDCl_3$, $CHCl_3$): δ 0.32 (9 H, s), 7.54 ppm (10 H, m).

E-1-Chloro-1-trimethylsilylpropene (Ic)

Precooled n-butyllithium in hexane (53 ml, 2.5 *N*, 132 mmol) was added to a mixture of 9.1 g (120 mmol) *E*-1-chloropropene, 18.5 g (160 mmol) TMEDA, 240 ml THF, 60 ml ether and 30 ml hexane at —105°C over 45 min. After an additional 2.5 h at —105°C, 13.0 g (120 mmol) chlorotrimethylsilane was added, followed 45 min later by 10 ml HMPA in 20 ml THF. Thirty min later, the mixture was allowed to warm to 25°C. Work-up and distillation (Widmer column) afforded 11.3 g (64%) of Ic, b.p. 139—140°C/760 mmHg, in 98% purity. Found: C, 48.33; H, 8.75. $C_6H_{13}ClSi$ calcd.: C, 48.46; H, 8.81%. IR: 6.2w, 6.92m, 7.08m, 7.25w, 7.70w, 7.99s, 11.5s, 11.9s, 12.4(sh), 13.2s, 14.4m, 15.8s nm. ^1H NMR (CCl_4, TMS): δ 0.15 (9 H, s), 1.65 (3 H, d), 6.34 ppm (1 H, q).

Z-1-Chloro-1-trimethylsilylpropene (Id) (attempted)

A procedure identical to that used for the preparation of *E*-1-chloro-1-trimethylsilylpropene was employed starting with *Z*-1-chloropropene. Only 1-propynyltrimethylsilane was obtained in 80% yield (based on the n-butyllithium employed).

Reaction of Ia with TMAF

A mixture of 0.73 g (5.4 mmol) Ia, 0.5 g (5 mmol) TMAF, 0.8 g ethyl vinyl ether and 20 ml diglyme was stirred at 25°C for 20 h. Ia was completely consumed. GLC analysis indicated the presence of acetylene, fluorotrimethylsilane, and a small amount of vinyl chloride. No carbene-olefin adduct was present.

Reaction of Ie with TMAF

A mixture of 0.93 g (10.0 mmol) TMAF, 12.5 ml diglyme, 7 ml cyclohexene and 1.89 g (6.6 mmol) Ie was stirred at 25°C in a sealed flask for 16 h. Complete consumption of Ie had occurred, and diphenylacetylene was present in 88% yield. No cyclohexene-carbene adduct was observed by GLC.

Reaction of Ic with TMAF

A mixture of 0.58 g (3.9 mmol) Ic, 0.54 g (5.8 mmol) TMAF, 8 ml cyclohexene and 4 ml diglyme was stirred at 25°C for one day. At this time, no Ic remained; the reaction mixture consisted of a 55/45 mixture of, respectively, propyne and *E*-1-chloropropene. No cyclohexene-carbene adduct was observed by GLC.

Relative reactivity determination (2-butenes)

The stereospecificity of the isopropylidene carbene-butene addition reaction was determined by allowing TMAF, Ib and the respective pure 2-butene (1/1/6) to react in diglyme for 44 h at room temperature. Duplicate runs gave 32% (36%) of *trans*-XIIe in greater than 99.5% (99.5%) isomeric purity from *trans*-2-butene and 53% (52%) of *cis*-XIIe in greater than 99.5% (99.5%) isomeric purity from *cis*-2-butene (Column A, 80°C). Both *trans*- and *cis*-XIIe were independently stirred with excess TMAF in diglyme for 2 days with no change in isomeric purity.

For relative rate determinations, mixtures of *cis*- and *trans*-2-butene were prepared by vacuum system manipulation and amounts transferred calculated from volume and pressure data. In duplicate runs, these mixtures were then allowed to react with Ib and TMAF in diglyme for 44 h at 24.0 ± 0.6°C. The relative reactivity k_c/k_t was calculated as equal to P_cO_t/P_tO_c, where P and O refer, respectively, to the mole fractions of adduct product and starting olefin [37] Data were obtained as follows:

Ib (mmol)	TMAF (mmol)	Diglyme (ml)	2-Butene (mmol)		Adduct (% yield)		k_c/k_t
			cis	*trans*	*cis*	*trans*	
9.2	10.6	8.0	19.4	20.0	40.3	7.0	5.9
4.1	4.7	5.0	10.3	9.8	41.2	6.3	6.2

Relative reactivity determination (styrenes)

Following the general procedure, mixtures of styrene and a given substituted styrene were allowed to react with Ib and TMAF in 8 ml diglyme for 24—48 h at 25.0 ± 0.5°C. Substituted styrenes were prepared by standard procedures [38] and the amounts used for relative reactivity studies corrected for purity: *p*-methoxystyrene (95.0%), *p*-methylstyrene (99.9%), *m*-methylstyrene (98.2%), *p*-phenoxystyrene (88.3%) and styrene (99.9%). *p*-Chlorostyrene was also examined but partially polymerized under the reaction conditions. Relative reactivities we were calculated as for 2-butenes, and data obtained as follows:

Substituted styrene	Ib (mmol)	TMAF (mmol)	Styrenes (mmol)		Adducts (% yield)		k_X/k_H
			X	H	X	H	
X = *p*-PhO	4.83	5.7	5.32	13.77	16.33	31.11	1.357
X = *p*-CH_3O	4.81	5.5	10.71	12.87	24.41	22.72	1.290
X = *p*-CH_3	3.97	5.3	15.11	17.92	24.70	24.82	1.180
X = *m*-CH_3	4.01	4.7	10.85	14.55	20.81	26.06	1.072

A computer fit * of the data according to the relationship log $(k_X/k_H) = \rho\sigma$ [37] afforded a value of ρ —0.41 with correlation coefficient, r 0.9999.

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