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Mild Generation of Alkylidenecarbenes from (Tosylazo)alkenes and Silylvinyl Triflates. Mode of Decomposition and Nature of the Carbene Intermediates[1,2]

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(Tosylazo)alkenes, $R_2C{=}CHN{=}NTs$, decomposed in olefin–solvent mixtures both under neutral conditions at room temperature and with amine bases present to produce alkylidenecyclopropanes in moderate to good yields. Diazoalkenes, $R_2C{=}C{=}N_2$, were implicated as the intermediates leading to alkylidenecarbenes, $R_2C{=}C:$, in the decompositions. Fluoride-induced α-elimination of trimethylsilyl triflate from $(CH_3)_2C{=}C(OTf)SiMe_3$ at 0 to −20 °C led to high yields of carbene addition to cyclohexene. The nature of the carbene intermediates from the two precursors was examined through their competitive reactivities with styrenes. Hammett correlations of the data gave a $\rho = -0.71$ from the (tosylazo)alkene precursor and a $\rho = -0.44$ from the silylvinyl triflate, values congruous with an electrophilic free carbene as the reacting intermediate from these species.

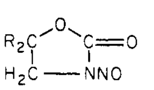
Alkylidenecarbenes 1 have been extensively studied in recent years.[3] Primarily, these carbenes have been formed through the reactions of various compounds with strong bases such as *t*-BuOK or ROLi. The precursors employed most often have been vinyl halides 2,[4] *N*-nitroso-oxazolidones 3,[5] compounds related to 3,[6] and vinyl triflates 4.[7] Recently, Gilbert and co-workers[8] have developed a new and promising basic method of alkylidenecarbene generation that involves the treatment of dimethyl (diazomethyl)phosphonate (5) with *t*-BuOK in the presence of a ketone or aldehyde.

$R_2C{=}C:$

1

$R_2C{=}CHX$

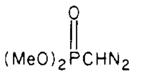
2



3

$R_2C{=}CHOTf$

4, Tf = SO_2CF_3



$(MeO)_2P(O)CHN_2$

5

A number of nonbasic procedures that afford 1 have also been found.[3d] Among the best known are the thermal decomposition of organomercury compound 6 at 150 °C[9] and the treatment of chlorovinylsilane 7 with fluoride anion at 25 °C.[10]

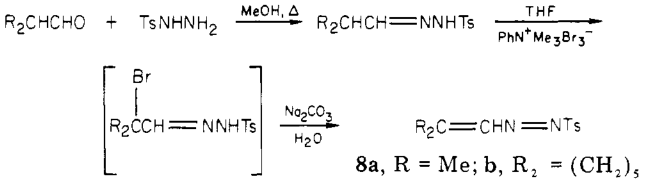
$$(CH_3)_2C{=}C(Br)HgBr/(C_6H_5)_2Hg$$

6

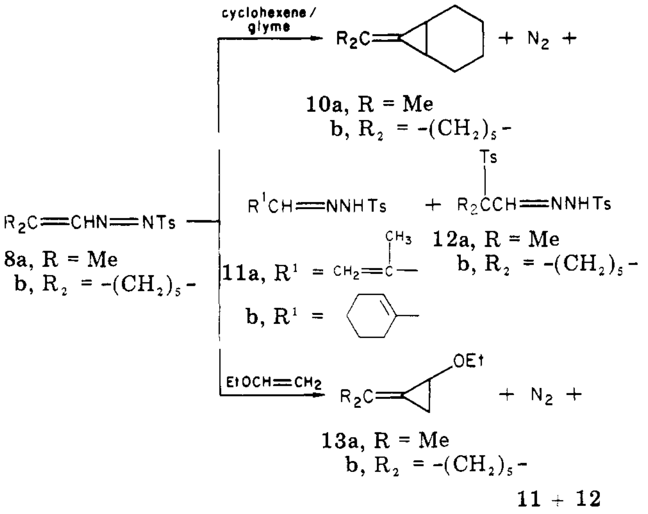
$$(CH_3)_2C{=}C(Cl)SiMe_3$$

7

Scheme I



Scheme II



Among other pursuits, our research efforts have been directed toward finding means of alkylidenecarbene generation that are even milder and more efficacious than those reported to date and that will enable the study of interactions of 1 with a large variety of substrates. We detail here two such mild formations of 1 from (tosylazo)alkenes 8 and silylvinyl triflates 9. In addition, the nature of the intermediates produced from these new precursors is probed through relative reactivity studies.

$$R_2C{=}C(H)N{=}NTs \qquad R_2C{=}C(OTf)SiMe_3$$

8, Ts=p-$CH_3C_6H_4SO_2$ 9

Results and Discussion

Generation from (Tosylazo)alkenes. In 1972 a report appeared on the thermal conversion of (tosylazo)alkene 8 (R = Ph) to diphenylacetylene at 25 °C in which an alkylidenecarbene 1 (R = Ph) was suggested as a possible intermediate.[11] Because alkylidenecarbenes with β-phenyl substitution exclusively rearrange to acetylenes and cannot be trapped intermolecularly,[7] we prepared (tosylazo)al-

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[1] Abstracted in part from the Ph.D. Dissertation of D.P.F., The University of Utah, Salt Lake City, UT, 1982, and the M.S. Thesis of J.A.B., The University of Utah, 1978.

[2] A portion of this work has been published as a preliminary communication: Stang, P. J.; Fox, D. P. *J. Org. Chem.* **1977**, *42*, 1667-9.

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[6] Newman, M. S.; Din, Z. u. *J. Org. Chem.* **1973**, *38*, 547-9.

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[8] Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837-45 and earlier references therein.

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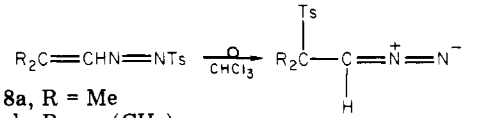
kenes **8a** and **8b** to test for the possible intermediacy of **1**. The synthetic sequence found by Rosini and Baccolini[12] and depicted in Scheme I gave **8a** and **8b** in respective overall yields of 56% and 46%. Slight variations in conditions and procedure were required for the individual preparations (see Experimental Section). Although the decomposition points of **8a** and **8b** are low (<57 °C), they appear to be stable in crystal form for months at −20 °C.

When dissolved in an 85:15 mixture of cyclohexene and glyme or in pure ethyl vinyl ether, **8a** and **8b** decomposed at room temperature in 4–72 h to give several products as shown in Scheme II. Progress of the reactions was monitored through GC analysis, but typically a reaction was complete when the reaction solution, which was originally deep yellow in color, became colorless. Carbene adducts **10a**, **10b**, **13a**, and **13b** were isolated by preparative GC. Tosylhydrazones **11a**, **11b**, **12a**, and **12b** were obtained pure through either fractional recrystallization or preparative TLC of large-scale decompositions of **8a** and **8b** in ethyl vinyl ether. Both pairs of tosylhydrazones arise from processes observed for closely related (tosylazo)alkenes: **11a** and **11b** from spontaneous intramolecular rearrangement of **8a** and **8b**[13] and **12a** and **12b** from 1,4-addition of liberated *p*-toluenesulfinic acid to unreacted **8a** and **8b**.[14]

In addition to spectral evidence and precedence cited above, two additional pieces of evidence for the assignment of structures **11** and **12** were obtained. Tosylhydrazone **11a** was identical spectrally to the tosylhydrazone of 2-methylpropenal prepared independently. Addition of **8a** to an ethanolic solution of *p*-toluenesulfinic acid gave, as major product observed by TLC, a compound with an R_f value identical with that of **12a**.

Yields of adducts **10a** and **10b** were measured for the reactions of **8a** and **8b** in cyclohexene under a variety of conditions. For adduct **10a**, yields ranged from 6% to 30%. Adduct **10b** was formed in 3–50% yield. The influence of changing reaction conditions can be summarized as follows. Lowering the reaction temperature to 5 °C or raising it to 40 °C either decreased the yield or did not significantly improve it. In reactions where solids (Chromosorb W, Celite, or Na_2CO_3) were present in the reaction solution, yields of adducts increased by 20–130% over those that were homogeneous. Reaction rate was also generally increased. The rough surface of the solids may aid in the liberation of nitrogen from a diazo intermediate.[15] Reactions in which Na_2CO_3 was present presumably also had their adduct yields increased through the interception of liberated toluenesulfinic acid by the Na_2CO_3 and not by unconsumed starting material (no **12** was formed). Presence of a homogeneous base, Et_3N, led to the lowest yield of **10b** (3%) and the fastest reaction time (1 h). The primary reaction seen was the base-catalyzed rearrangement of **8b** to **11b**.[13] When glyme was added to cyclohexene to make the solution 15% in glyme, the yield of adduct **10a** increased from 8% in pure cyclohexene[16] to 18% in the cyclohexene–glyme mixture. Increase of polarity of the reaction solution by the addition of an equal volume of chloroform resulted in the lowest yield observed for **10a** (6%); however, the presence of Na_2CO_3 in the chloroform–cyclohexene mixture led to the highest yields of both **10a** and **10b** (30% and 50%, respectively).

Up to this point, scant information had been acquired about the mechanism of decomposition of (tosylazo)alkenes **8a** and **8b**. However, the above data along with several observations that follow provided clues to a probable mechanism. It was discovered that both **8a** and **8b** had different NMR and IR spectra in deuteriochloroform than those recorded in carbon tetrachloride. Specifically for **8a**, three NMR singlets at 2.12, 2.14, and 7.20 ppm in a ratio of 3:3:1 became two singlets at 1.48 and 3.75 ppm in a 6:1 ratio when the solvent was changed from CCl_4 to $CDCl_3$. The signals for the tosyl group remained constant. The major changes in the IR were the rapid disappearance of an absorption at 1635 cm^{-1} and the concomitant appearance of an intense band at 2084 cm^{-1} when the solvent was switched from CCl_4 to $CHCl_3$. Similar spectral changes were seen for **8b**. This spectral data is most congruous with the formation of diazoalkanes **14** from (tosylazo)alkenes **8**. The chemical shift and equivalence of the methyl groups is consistent with structure **14a**. Protons attached to diazo carbons typically have signals from 3 to 5 ppm in the NMR spectrum.[18] Diazo linkages have strong IR absorptions in the vicinity of 2075 cm^{-1}.[18] These conversions of **8** to **14** in $CHCl_3$ were found to be complete and relatively clean by NMR in 2 h at room temperature. Such rearrangements have been observed in closely analogous systems,[19,20] and an α-tosyldiazoalkane has been isolated in good yield and characterized from a $CHCl_3$ solution of a (tosylazo)alkene.[19]

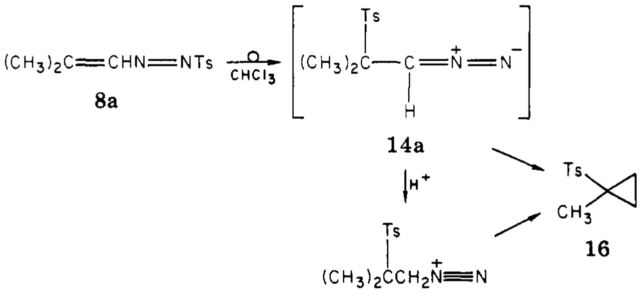


$$R_2C{=}CHN{=}NTs \xrightarrow[\mathrm{CHCl_3}]{\frown} R_2C(Ts){-}CH{=}\overset{+}{N}{=}N^-$$

8a, R = Me
b, R_2 = -$(CH_2)_5$-

14a, R = Me
b, R_2 = -$(CH_2)_5$-

Diazoalkanes typically gave alkyldiazonium salts when treated with acid.[15] When **8a** was treated with an excess of acetic acid 2 h after its dissolution in $CHCl_3$, rapid evolution of nitrogen occurred with the solution becoming colorless in 1 h. The major product observed by NMR[21] was isolated through preparative TLC and determined to be tosylcyclopropane **16**. It could have formed from either **14a** by an intramolecular carbene insertion[20] or from **15**


8a
14a
15
16

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[15] Cowell, G. W.; Ledwith, A. *Q. Rev., Chem. Soc.* **1970**, *24*, 119–67.

[16] Sasaki and co-workers[17] report a similar adduct yield (10%) for the decomposition of [(tosylazo)methylene]adamantane in pure cyclohexene.

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[21] Other signals in the NMR spectrum of the concentrated reaction solution (singlets at δ 1.41, 1.97, and 4.32, in a 6:3:2 ratio) were consistent with $Me_2C(Ts)CH_2OAc$, but the compound was not isolated in sufficient quantity to characterize completely. Even increasing the equivalents of acetic acid from 5 to 20 did not noticeably increase the amount of this ester.

Table I. Carbene Adduct Yields from Reactions of Diazo Intermediates **14**[a] with Base

	solvent[b]	base	temp, °C	time, h	product, yield,[c] %
8a → 14a	Ch:Cy, 1:1	Et_3N	25	15	10a, 32
8a → 14a	Ch:Cy, 1:1	pyridine	25	20	10a, 5
8a → 14a	Ch:Cy, 1:1	DBU	25	20	10a, 36
8a → 14a	Ch:Cy, 1:1	DBU	−15	36	10a, 40
8a → 14a	Ch:Cy, 1:1	none	25	40	10a, 1.5[d]
8b → 14b	Ch:Cy, 1:1	Et_3N	25	20	10b, 57
8b → 14b	Ch:Cy, 1:1	DBU	−15	60	10b, 65

[a] (Tosylazo)alkenes 8 initially dissolved in $CHCl_3$, the resulting solution allowed to stand for 2 h at room temperature, and then cyclohexene and base added to the $CHCl_3$ solution. [b] Ch = chloroform, Cy = cyclohexene. [c] Yields determined by GC. [d] Tosylcyclopropane 16 seen as major product.

by an intramolecular carbenium ion rearrangement.[22,23] The rapid decomposition of **14a** when acetic acid is added seems to favor **15** as the intermediate in this case. Without acid present, decomposition of **14a** was slow (see below).

To determine whether α-tosyldiazoalkanes **14** were intermediates in the thermal decomposition of (tosylazo)alkenes **8** to give alkylidenecarbenes **1**, we performed several experiments. Two hours beyond initial dissolution of either **8a** or **8b** in $CHCl_3$, cyclohexene and a base were added and the solution produced was then stirred. Of several amine bases that were tried (Table I), triethylamine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) proved to be the best. When the addition of cyclohexene and DBU was done at −15 °C, the highest yields of alkylidenecarbene formation from (tosylazo)alkenes **8** were obtained: 40% for carbene adduct **10a** and 65% for **10b**. In contrast to these reactions, introduction of Et_3N to a solution of **8b** in a cyclohexene–glyme mixture resulted mainly in the base-catalyzed rearrangement of **8b** to **11b** and only a 3% yield of **10b** was seen (see above). If only cyclohexene was added to the $CHCl_3$ solution of **14a**, tosylcyclopropane **16** was the major product formed from the slow decomposition of **14a** (see Table I).

On the basis of the preceding results and discussion, a reasonable mechanism can be advanced for the degradation of (tosylazo)alkenes **8** to alkylidenecarbenes **1**. Figure 1 illustrates this mechanism for **8a**. For reactions carried out in the cyclohexene–glyme mixtures, the rearrangement of step a is a major reaction pathway. Adduct **10a** that is produced results from steps b and c. In step c, **8a** acts as a base to generate diazoalkene **17** from **14a**. Tosylhydrazone **12a** comes about through addition of *p*-toluenesulfinic acid to **8a**. When the solvent is changed to $CHCl_3$, step b becomes the dominant pathway of reaction for **8a**. Either a concerted process or the formation of an ion pair followed by rearrangement is probably responsible for the production of **14a** from **8a**.[20] As **8a** is rapidly converted to **14a** in $CHCl_3$, an external base is necessary to form diazoalkene **17**. Indeed, if cyclohexene with no base present in it is added to **14a** in $CHCl_3$, only a 1.5% yield of **10a** is achieved compared to a 40% yield when DBU is present (Table I). In this nonbasic reaction, the major product observed by NMR, tosylcyclopropane **16**, presumably forms as indicated in step e.[20] Generation of isopropylidenecarbene (**18**) from **17** is straightforward and should be extremely rapid even at −15 °C.[8]

An alternate route for the formation of adduct **10a** that does not involve **18** can be envisioned and is depicted in step f of Figure 1. This path was ruled out as follows. **8a** was allowed to convert to **14a** in $CHCl_3$ and then cyclohexene was added. After 40 h, GC analysis revealed a 1.5% yield of **10a**. DBU was then added, and the amount of **10a** was checked at 1- and 40-h intervals after the DBU addition. Only a 0.5% increase in yield was seen at both times, and this increase could easily have resulted from a trace of **14a** still present in solution.

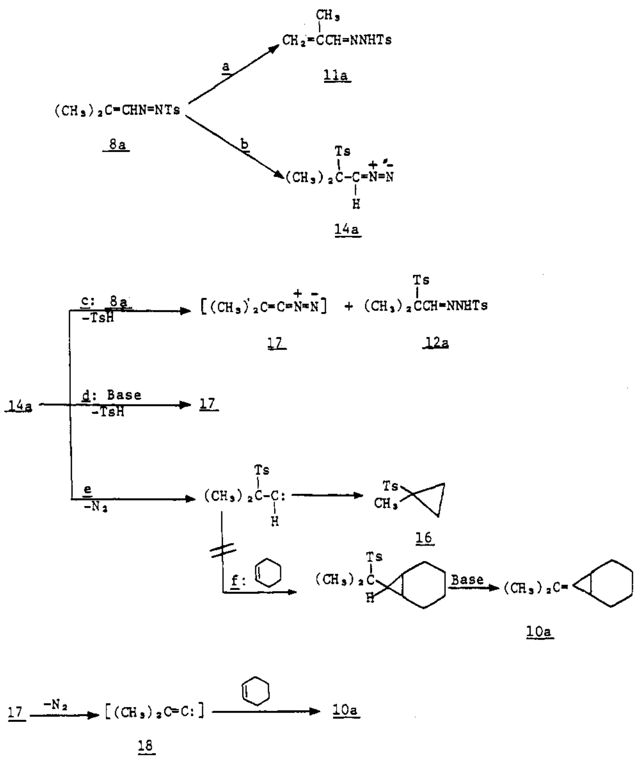

Figure 1. Mechanism of decomposition of (tosylazo)alkene **8a**.

In addition to **8a** and **8b**, (tosylazo)alkene **8c** (R = Br) was prepared by a known procedure.[24] When **8c** was allowed to decompose in cyclohexene at 75 °C for 3 days, no products derived from $Br_2C{=}C{:}$ were found. Small amounts of tribromoethylene and *trans*-1,2-dibromocyclohexane were obtained by preparative GC. The presence of amine bases in the reaction mixture caused rapid tarring. Interestingly, and consistent with the mechanism in Figure 1, **8c** was stable in $CHCl_3$ as observed by IR and did not form any **14c** (R = Br) in 3 days at room temperature.

Generation from Silylvinyl Triflates. A number of reactive intermediates have been generated through fluoride-initiated elimination of a trialkylsilyl group and a leaving group. Examples of intermediates that have been formed in this way are benzyne,[25] quinodimethanes,[26] and

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[22] Friedman, L.; Bayless, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1790–4.

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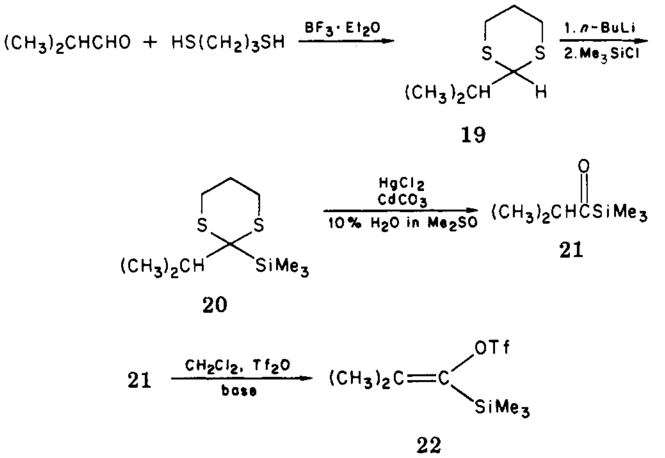
[26] (a) Ito, Y.; Nakatsuka, M.; Saegusa, T. *J. Am. Chem. Soc.* **1980**, *102*, 863–5. (b) Ito, Y.; Miyata, S.; Nakatsuka, M.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 1043–4.

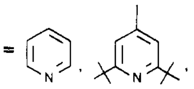
Table II. Relative Reactivities of $(CH_3)_2C{=}C{:}$ with Styrenes $(XC_6H_4CH{=}CH_2)$

	reaction conditions and k_{rel} (substrate/styrene)		
substrate, X =	$(CH_3)_2C{=}CHOTf$ (24), t-BuOK,[a] −20 °C	$(CH_3)_2C{=}CHN{=}NTs$ (8a), 0 °C	$(CH_3)_2C{=}C(OTf)SiMe_3$ (22), $PhCH_2NMe_3F$, 0 °C
p-CH_3O	1.51 ± 0.02	1.51 ± 0.16[b]	1.44 ± 0.06[b]
p-CH_3	1.28 ± 0.04	1.31 ± 0.05	1.19 ± 0.02
H	1.0	1.0	1.0
p-Br	0.63 ± 0.01[c]	0.67 ± 0.05	0.85 ± 0.03

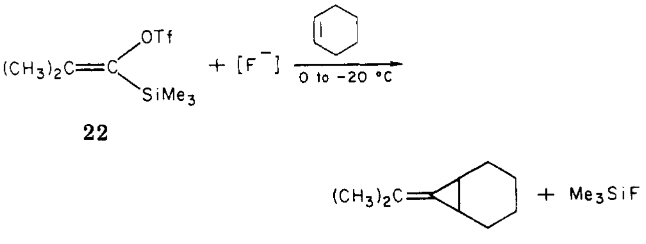
[a] Reference 41. [b] Range/2 for duplicate runs. [c] X = p-Cl.

Scheme III[a]



[a] [base =  $(i\text{-}Bu)_2NCH(i\text{-}Pr)_2$].

Scheme IV[a]



[a] [F⁻] = KF, 18-crown-6; $PhCH_2NMe_3F$, glyme; or 50% KF in H_2O, Aliquat 336.

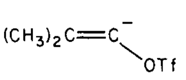
carbenes.[10,27] As mentioned previously, isopropylidenecarbene (**18**) was produced by reaction of fluoride anion with chlorovinylsilane **7**.[10] Replacement of chloride in **7** with triflate, a superior leaving group,[28] was expected to enhance this method further.

Synthesis of the appropriate silylvinyl triflate **22** was accomplished as indicated in Scheme III. Acylsilane **21** was prepared in 54% overall yield with procedures adapted from those of Brook and co-workers[29] and Corey and co-workers.[30] For the conversion of **21** to **22**, several different amine bases can be employed. Use of pyridine[31] gave **22** in 34% yield after 3 days of reaction, while use of N,N-diisobutyl-2,4-dimethyl-3-pentylamine resulted in a 51% yield of **22** after 7 h of reaction. The best yield for triflate **22** was obtained when 2,6-di-*tert*-butyl-4-methylpyridine[32] was employed (78%, 10 h of reaction).[33] With respect to purity, yield, and cost considerations, N,N-diisobutyl-2,4-dimethyl-3-pentylamine is the base of choice for this preparation.

Excellent yields of carbene adduct **10a** were realized when silylvinyl triflate **22** was treated with fluoride anion in a large excess of cyclohexene (Scheme IV). Three sources of fluoride anion were utilized with reaction temperatures running from 0 to −20 °C. Reactions were complete in 1–1.5 h. Yields of **10a** were determined in duplicate for each fluoride source through GC analysis. With 5 equiv of KF and 1.25 equiv of 18-crown-6 in pure cyclohexene at 0 °C, a 92% yield of **10a** was obtained. Use of 0.1 equiv of 18-crown-6 resulted in rapid achievement of 10% reaction, but then the reaction only proceeded slowly, even at room temperature. Reactions with KF and 18-crown-6 are considered solid–liquid phase-transfer catalysis.[34] The lack of exchange observed for fluoride and triflate anions probably arises from the greater solubility of the complex between 18-crown-6 and KOTf in the organic phase than that between 18-crown-6 and KF. Similar difficulties have been noted in related phase-transfer reactions.[35,36]

A yield identical with the 18-crown-6 reaction, 92%, was achieved with benzyltrimethylammonium fluoride (BTAF) in a 17% cyclohexene–83% glyme mixture at −20 °C. A lower percentage of glyme caused a reduction in yield of **10a** (79% yield for 50% glyme). Phase-transfer conditions,[37,38] 50% aqueous KF, cyclohexene, and Aliquat 336 as transfer agent,[39] produced **10a** in 82% yield at 0 °C. As with 18-crown-6, 1 equiv of Aliquat 336 was required for total reaction at low temperature. Of the three fluoride sources employed, BTAF is the best in regards to yield, expense, and mild conditions.[40]

The mechanism of carbene formation from **22** most likely proceeded via attack of fluoride anion on silicon followed closely by expulsion of the triflate group. Fluorotrimethylsilane was collected from the 18-crown-6 reactions and characterized by NMR. The finite existence of intermediate anion **23** was concluded from the production of approximately 2% triflate **24** in the phase-transfer reactions with Aliquat 336.



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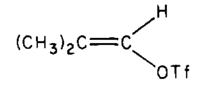

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Table III. Selectivity of $(CH_3)_2C{=}C{:}$ toward Styrenes as a Function of Precursors

precursor, reaction conditions	ρ	r	k_{rel} (cyclohexene/styrene)	ref
$(CH_3)_2C{=}CHOTf$ (**24**), *t*-BuOK, −20 °C	−0.75 ± 0.04[a] (σ)	0.99	1.74 ± 0.14[b]	41
$(CH_3)_2C{=}CHN{=}NTs$ (**8a**), 0 °C	−0.71 ± 0.02 (σ)	0.99	1.84 ± 0.17	this work
$(CH_3)_2C{=}C(OTf)SiMe_3$ (**22**), $PhCH_2NMe_3F$, 0 °C	−0.44 ± 0.07 (σ)	0.98	2.67 ± 0.10	this work
$(CH_3)_2C{=}C(Cl)SiMe_3$ (**7**), Me_4NF, 25 °C	−0.41 (σ)	0.99		10
$(CH_3)_2C{=}CHBr$ (**25**), *t*-BuOK, −10 °C	−4.3 (σ^+)			42
$(CH_3)_2C{=}CBr_2$ (**26**), MeLi, −40 °C	−4.3 (σ^+)			42
N-nitrosooxazolidone (**3**, R = Me), $LiOCH_2CH_2OEt$, 40 °C	−3.4 (σ^+)		0.16	43
Ad=CHBr (**27**),[c] *t*-BuOK, 18-crown-6, 100 °C			2.50	17
Ad=CHN=NTs (**28**), 25 °C			2.08	17

[a] Standard deviation of the slope. [b] Range/2 for duplicate runs. [c] Ad = adamantylidene.

Nature of the Intermediates. With several techniques for generating alkylidenecarbenes in hand, it was of interest to determine the nature of the intermediates involved in each through relative reactivity studies. Such studies should indicate if significant differences exist between these intermediates. As isopropylidenecarbene (**18**) selectivity toward a series of substituted styrenes has been determined for several different generation methods, both by us and others, Hammett analyses were also carried out for the carbenes from (tosylazo)alkene **8a** and silylvinyl triflate **22**. Procedures essentially the same as those reported earlier[41] were employed to determine the selectivities and ρ values given here. Table II details these selectivities along with those found earlier for the carbene from triflate **24**.[41] In Table III are compiled the ρ values obtained for isopropylidenecarbene from precursors reported both here and elsewhere, correlation coefficients (r) where known, and k_{rel} determined for cyclohexene–styrene with the various systems.

From the data in Tables II and III, important information can be gained about intermediates derived from the respective precursors. Significant differences exist between the first two methods of carbene generation in Table II, both in terms of mechanism and reaction conditions. For **24**, an α-elimination mechanism is involved and a metal ion, K^+, and a strong base are present during the reaction, whereas no metal or strong base is present and a diazoalkene intermediate has been implicated in the decomposition of **8a** (see above). Leaving groups are also considerably disparate: triflate anion when **24** is employed and nitrogen when **8a** is used. The fact that nearly identical selectivities are produced with either triflate **24** or (tosylazo)alkene **8a** strongly indicates that *the reacting intermediate in each case is a free carbene.*

The relative reactivities of the carbene derived from silylvinyl triflate **22** are very close to those obtained with triflate **24** and (tosylazo)alkene **8a**. Two explanations can be put forth for the slight differences in the relative reactivities and ρ values. First, experimental error can readily account for the small discrepancies seen. Only three relative rates were determined for each precursor, and the standard deviation of the slope for **22** is the largest of all three precursors. Even for the lowest deviation, ±0.02 for **8a**, the true value of ρ lies between −0.5 and −0.9 at the 99% confidence level. Therefore, the ρ of −0.44 obtained with **22** is certainly within experimental error of the other two values, −0.71 and −0.75. Second, there exists a fundamental difference in the reaction mediums employed in the reactions of **24**, **8a**, and **22**. For **24** and **8a**, the medium is the styrenes, while glyme is involved in the selectivity reactions of **22**. Interestingly, chlorovinylsilane **7** as carbene precursor gives a ρ of −0.41, which is almost identical with that for **22**, −0.44. Diglyme is present in the reactions of **7**. Perhaps glyme and diglyme complex with the free carbene and slightly alter its reactivity and selectivity.[44] Such behavior would not be unexpected as these solvents have available lone pairs on the oxygens and alkylidenecarbenes are electrophilic.[41] In fact, a closely related solvent, tetrahydrofuran, has been found to complex with isopropylidenecarbene, and this complexation led to an isolable product.[45] Further experimental study may be necessary to more accurately assess the role of ether solvents, if any, in alkylidenecarbene reactions.

In regards to the other systems in Table III, the ρ values determined with vinyl halide **25**, dibromoalkene **26**, and *N*-nitrosooxazolidone **3** (R = Me) remain anomalies. The fact that relative reactivities obtained with **3** (R = Me) for several other alkenes (except for styrene) match closely those found with triflate **24**[46] is particularly puzzling. Styrene seems to be significantly more reactive than cyclohexene with the carbene generated from **3** (R = Me), in substantial disagreement with the corresponding rates acquired through the use of precursors **24**, **8a**, and **22**. New data procured with vinyl halide **27** and (tosylazo)alkene **28**[17] seem to substantiate the k_{rel} values for cyclohexene–styrene obtained with **24**, **8a**, and **22** (Table III).

In any case, the ρ values for **24**, **8a**, **22**, and **7** are clearly more consistent with an electrophilic free carbene as the reacting intermediate formed from these precursors. The magnitudes of the values are similar to those for dihalocarbenes[41,47] and indicate that the addition of alkylidenecarbenes to olefins is concerted and has only a slightly polarized transition state.

In summary, two new methods of generating alkylidenecarbenes have been presented. The first was the thermal or basic decomposition of (tosylazo)alkenes. Diazoalkenes were found to be involved as intermediates in the decompositions. Yields of carbene adducts obtained were moderate, but the thermal degradation represents an essentially neutral procedure for the production of alkylidenecarbenes. With the second technique, reaction of fluoride anion with a silylvinyl triflate, conditions were mild and the yields of alkylidenecarbene addition to cyclohexene are the highest

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reported to date. Since our initial report,[2] this method has been successfully used with base-sensitive systems, i.e., isonitriles,[48] enethiols,[49] and isocyanates.[50] Further work along this line continues. Finally, the alkylidenecarbenes formed from the new precursors were shown through selectivity studies to be both electrophilic and free.

Experimental Section

General Methods. All boiling and melting points are uncorrected. Analytical weights were measured on a Mettler H33AR or H18 balance. Infrared spectra were recorded on a Beckman IR5A, Beckman Acculab 3, or Perkin-Elmer 298 infrared spectrometer and are reported in wavenumbers (cm^{-1}) calibrated to the 1602-cm^{-1} absorption of polystyrene. ^1H NMR spectra were recorded on a Varian A-60, EM-360, or EM-390 spectrometer, and all values are given in δ (ppm) relative to internal tetramethylsilane (Me_4Si, δ 0) except where indicated. Mass spectra were recorded on a Varian MAT-112 gas chromatograph-mass spectrometer equipped with GC columns containing either 1% SE-30 or 1% OV-17 as stationary phase. Mass spectra are reported as m/z (relative intensity). Ultraviolet spectra were obtained on a Cary 14 or Cary 17 spectrometer. Analytical and preparative TLC were done on silica gel (Merck silica gel 60 F-254 with 0.2-mm thickness). Preparative GC was accomplished on a Varian Aerograph 90-P or 920 gas chromatograph. Analytical GC was carried out on a Hewlett-Packard 700 flame-ionization gas chromatograph connected to a Hewlett-Packard 3370B integrator or a Hewlett-Packard 5710A flame-ionization gas chromatograph connected to a Hewlett-Packard 3380A integrator. Columns used in this work are as follows: A, 0.25 in. × 5 ft 15% SF-96 on 45–60 Chromosorb W; B, 0.25 in. × 6 ft 10% SF-96 on 60–80 Chromosorb W; C, 0.125 in. × 6 ft 10% UCW-982 on 80–100 Chromosorb W; D, 0.125 in. × 10 ft 10% Apiezon J on 100–120 Chromosorb W; E, 0.125 in. × 15 ft 10% Carbowax 20M on 100–120 Chromosorb W; F, 0.125 in. × 20 in. 10% UCW-982 on 80–100 Chromosorb W. Relative reactivities were calculated as previously described for 2-methyl-1-propenyl triflate (**24**).[41]

Materials. Chlorotrimethylsilane (Aldrich) and *N*,*N*-diisobutyl-2,4-dimethyl-3-pentylamine (Fluka) were distilled from CaH_2. Triethylamine was distilled from $LiAlH_4$ (Alfa) and 1,2-dimethoxyethane (glyme, Aldrich or Ansul) and tetrahydrofuran were distilled from either $LiAlH_4$ with triphenylmethane as indicator or from potassium benzophenone ketyl. Isobutyraldehyde (MCB) and cyclohexanecarboxaldehyde (Aldrich) were distilled prior to use. Cyclohexene (Baker) was distilled under N_2 from either CaH_2 or Na. The cyclohexene was stored under N_2 or over Na. Styrene (Aldrich) and *p*-bromostyrene (Aldrich) were fractionally distilled under vacuum to >98% purity. The other two styrenes, *p*-methylstyrene and *p*-methoxystyrene, were prepared according to the procedure of Walling and Wolfstirn.[51] Triflic acid (3M) was converted to triflic anhydride by the method of Anderson.[52] Recrystallization[53] was utilized to purify tosylhydrazine (Aldrich). Dry KF was obtained through preliminary drying of commercial anhydrous KF in a 180 °C oven for several hours followed by overnight heating at 100 °C in vacuo. The following materials were all used as received: $HgCl_2$ (Alfa 99.5% minimum), $CdCO_3$ (Alfa), 18-crown-6 (Dupont), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU, Aldrich), Aliquat 336 (General Mills), Chromosorb W (Johns-Manville), and Celite (Baker 503). Known procedures were used to prepare 2-methylpropenal,[54] phenyltrimethylammonium perbromide,[55,56] benzyltrimethylammonium fluoride,[57] and *p*-toluenesulfinic acid.[58] Three of the adducts of isopropylidenecarbene addition to styrenes, 2-phenyl-2-isopropylidenecyclopropane, 2-*p*-tolyl-1-isopropylidenecyclopropane, and 2-(*p*-methoxyphenyl)-1-isopropylidenecyclopropane, were made as previously described[41] and were utilized for GC identification of products in the relative reactivity studies reported here.

2-Methylpropenal Tosylhydrazone (11a). General Procedure. A solution of 5.3 g (0.029 mol) of recrystallized tosylhydrazine in 30 mL of MeOH was warmed to 38 °C, and 2.0 g (0.029 mol) of 2-methylpropenal in 4 mL of MeOH was added dropwise over a 10-min period. After the aldehyde addition, the reaction temperature was kept at 45 °C for 20 min. Slow crystallization was induced through cooling of the light yellow reaction solution in a dry ice–isopropyl alcohol bath. The product was isolated by vacuum filtration and dried in vacuo to yield 5.7 g (84%) of white needles of **11a**: mp 123–125 °C dec; IR ($CHCl_3$) 3200 (NH), 1597, 1380, 1360, 1172, 1067, 1040, 918, 840, 820 cm^{-1}; NMR ($CDCl_3$) δ 1.82 (s, 3, $CH_3C{=}C$), 2.38 (s, 3, CH_3Ar), 5.17 (br s, 1, $HC{=}C$), 5.33 (br s, 1, $HC{=}C$), 7.20 (s, 1, $HC{=}N$), 7.60 (m, 4, ArH), 8.55 (s, 1, NH).

Cyclohexanecarboxaldehyde Tosylhydrazone. Cyclohexanecarboxaldehyde (11.2 g, 0.1 mol) gave, after one recrystallization of initial product from methanol, 22.1 g (79%) of tosylhydrazone: mp 97–98 °C dec [lit.[12] mp 99–100 °C]; IR (Nujol) 3226 (NH), 1595, 1330, 1319, 1163, 1071, 813 cm^{-1}.

Isobutyraldehyde Tosylhydrazone. Isobutyraldehyde (9.5 g, 0.13 mol) gave 23.6 g (76%) of tosylhydrazone: mp 98–99 °C dec [lit.[59] mp 98–100 °C]; IR (Nujol) 3215 (NH), 1595, 1351, 1316, 1163, 1015, 810 cm^{-1}; NMR (Me_2SO-d_6) δ 0.90 (d, 6, Me_2C), 2.37 (s, 3, $ArCH_3$), 1.9–2.6 (m, 1, Me_2CH), 7.20 (d, 1, $HC{=}N$), 7.57 (m, 4, ArH), 10.85 (s, 1, NH).

[(Tosylazo)methylene]cyclohexane (8b). During a 15-min period, phenyltrimethylammonium perbromide (1.50 g, 4 mmol) was added with a porcelain spatula to a solution under nitrogen of 1.12 g (4 mmol) of cyclohexanecarboxaldehyde tosylhydrazone in 40 mL of THF. The orange color of the perbromide was discharged and a white salt precipitated. After addition was complete, the reaction mixture was allowed to stir for 15 min, and then 160 mL of ice-cold ether was added to the light yellow solution. The organic mixture was shaken with 30 mL of cold saturated Na_2CO_3 whereupon a bright yellow color appeared in the organic layer. The organic layer was washed with 20 mL of cold saturated brine and then dried for 0.5 h at 0 °C with a large amount of Na_2SO_4. A bulb-to-bulb distillation at 0 °C (10 mm) was used to reduce the organic solution to approximately 35 mL. Addition of 35 mL of pentane followed by cooling of the solution to −20 °C by a dry ice–CCl_4 bath caused the remaining water to solidify. The organic mixture was decanted off the ice crystals, and an additional 100 mL of pentane was added. Slow crystallization resulted upon cooling of the mixture at −30 °C for 2 days. The dense, yellow crystals were removed by vacuum filtration and dried in vacuo for 0.5 h at 0 °C to yield 0.65 g (58%) of **8b**: mp 56–57 °C dec [lit.[12] mp 54–55 °C dec]; UV max (*n*-heptane) 284 nm (ϵ 22 000), 228 (12 800), 421 (106) [lit.[12] max (*n*-hexane) 280 (15 000), 420 (80)]; IR (CCl_4) 2940, 2860, 1626, 1441, 1354, 1170, 1144, 1091, 674 cm^{-1}; NMR (CCl_4) δ 1.70 (br s, 6, β- and γ-cyclohexyl), 2.47 (m, 2, α-cyclohexyl), 2.53 (s, 3, $ArCH_3$), 2.69 (m, 2, α-cyclohexyl), 7.12 (s, 1, $HC{=}C$), 7.71 (m, 4, ArH).

1-(Tosylazo)-2-methylpropene (8a). The procedure given above for (tosylazo)alkene **8b** was followed with the following differences. Initial reaction of isobutyraldehyde tosylhydrazone (1.2 g, 5 mmol) with the perbromide was carried out at −20 °C instead of at room temperature. After the volume of the ether–THF mixture had been reduced to approximately 40 mL, 135 mL of pentane was added in one portion. When the mixture was cooled to −20 °C with a dry ice–CCl_4 bath, rapid crystallization of product occurred. Crystallization was completed with a dry ice–isopropyl alcohol bath. Filtration and in-vacuo drying as before gave 0.7 g (59%) of powdery yellow **8a**: mp 44–45 °C dec; UV max (*n*-heptane) 276 nm (ϵ 17 900), 227 (12 800), 418 (104); IR (CCl_4) 1637, 1435, 1359, 1173, 1142, 1094, 686 cm^{-1}; NMR (CCl_4)

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δ 2.12 (s, 3, $CH_3C{=}C$), 2.14 (s, 3, $CH_3C{=}C$), 2.54 (s, 3, $ArCH_3$), 7.20 (m, 1, $HC{=}C$), 7.73 (m, 4, ArH).

Isobutyryltrimethylsilane (21). A three-step synthesis was employed to prepare **21**. Following the general procedure outlined by Corey and co-workers,[30] 2-isopropyl-1,3-dithiane (**19**) and 2-isopropyl-2-trimethylsilyl-1,3-dithiane (**20**) were prepared in respective isolated yields of 72% and 88%. Ketone **21** was synthesized from **20** according to a procedure recommended by Brook and co-workers[29] for volatile acylsilanes and described in the following. To a three-necked, 3-L flask equipped with a mechanical stirrer and protected from light with aluminum foil were added 345 g (2 mol) of $CdCO_3$, 1.5 L of 10% H_2O in Me_2SO, and 93.6 g (0.4 mol) of **20**. The system was connected to an oil bubbler, and 543 g (2 mol) of $HgCl_2$ was added in two portions to the stirring solution. Vigorous gas evolution was observed for 15 min. Stirring was continued for 6 h, and the flask was then fitted for distillation with a 40-cm Vigreux column. Distillation at 120 mm was carried out until no more organic material distilled. About 125 mL of a two-phase system was collected. The aqueous portion was washed with three 50-mL portions of pentane, and the organic material was then dried with $MgSO_4$. Fractional distillation through a short Vigreux column gave 48.8 g (85%) of **21**, a faintly yellow-green liquid with a camphoraceous odor: bp 74–75 °C (70 mm) [lit.[60] bp 120–130 °C]; IR (neat) 1639 (C=O), 1458, 1250, 990, 864, 840, 753, 694 cm^{-1}; NMR (neat, external Me_4Si) δ −0.17 (s, 9, $SiMe_3$), 0.58 (d, 6, Me_2C), 2.57 (m, 1, $HCMe_2$).

When the amounts of $HgCl_2$ and $CdCO_3$ were lowered from those reported above to 2.2 and 1.2 equiv, respectively, acylsilane **21** was produced in 70–75% yield from 30 g of **20**.[61]

1-Trimethylsilyl-2-methyl-1-propenyl Triflate (22). Into a 250-mL Erlenmeyer flask equipped with a serum stopper were placed 150 mL of CH_2Cl_2 and 17.2 g (0.061 mol) of triflic anhydride. The flask was cooled to 0 °C with an ice bath, and 14.5 g (0.064 mol) of *N*,*N*-diisobutyl-2,4-dimethyl-3-pentylamine followed by 8.0 g (0.056 mol) of acylsilane **21** were each added dropwise via a syringe to the stirring solution. The progress of the reaction was monitored on column C at 100 °C. When a product to ketone ratio of 91:9 was seen (3 h at 0 °C and 4 h at room temperature), solvent was removed from the gold solution with a rotary evaporator and 500 mL of pentane was added to the yellow semisolid mixture. A white solid (20.9 g) precipitated and was removed by suction filtration. (The free amine can be recovered from this triflic acid salt.) The organic solution was extracted with three 250-mL portions of ice-cold 1 N HCl and then with three 100-mL portions of water. The organic mixture was dried with a mixture of Na_2CO_3 and $MgSO_4$. After removal of the pentane with a rotary evaporator, the light yellow residue was distilled through a short Vigreux column to give 7.74 g (51%) of pure **22**: IR (neat) 1629 (C=C), 1406, 1387, 1250, 1202, 1143, 946, 881, 846 cm^{-1}; NMR (C_6H_6, external Me_4Si) δ −0.37 (s, 9, $SiMe_3$), 0.82 (s, 3, $CH_3C{=}C$), 1.08 (s, 3, $CH_3C{=}C$); (CCl_4, external Me_4Si) δ −0.05 (s, 9, $SiMe_3$), 1.57 (s, 6, $Me_2C{=}C$); mass spectrum *m/z* (relative intensity) 261 ($M^+ - CH_3$, 3), 207 (14), 93 (10), 77 (48), 75 (23), 73 (100), 54 (47), 53 (14); chemical ionization (isobutane) 261 (8), 223 (14)8, 207 (20), 128 (14), 127 (M^+ − OTf, 100), 81 (11).

2-(*p*-Bromophenyl)-1-isopropylidenecyclopropane. This cyclopropane was prepared in identical manner to the syntheses of the other related styrene adducts.[41] Treatment of 2-methyl-1-propenyl triflate (**24**, 1.5 g, 7.5 mmol) with 0.84 g (7.5 mmol) of potassium *tert*-butoxide in a mixture of 4.0 g of *p*-bromostyrene and 5 mL of glyme gave, after workup and isolation by preparative GC on column B at 145 °C, pure 2-(*p*-bromophenyl)-1-isopropylidenecyclopropane: IR (neat) 3075, 2940, 1725 (C=C), 1495, 1075, 820 cm^{-1}; NMR (CCl_4, external Me_4Si) δ 0.80 (m, 1, cyclopropyl), 1.50 (m, 1, cyclopropyl), 2.25 (m, 1, cyclopropyl), 1.58 (s, 3, CH_3), 1.72 (s, 3, CH_3), 6.86 (m, 4, aromatic).

Thermal Decomposition of (Tosylazo)alkene 8a in Ethyl Vinyl Ether. To a 50-mL, round-bottomed flask connected to an oil bubbler and protected from light with aluminum foil were added a small quantity of powdered glass and a bright yellow solution of 0.8 g (3.4 mmol) of **8a** in 25 mL of ethyl vinyl ether. (Stock bottles of (tosylazo)alkenes were kept at −78 °C during weighing of a reaction sample. Weighed samples were immediately dissolved in the reaction solvent.) Evolution of gas ceased after 2.5 h of reaction at room temperature. Following 3.5 h of reaction, a trace of white solid was present in the light yellow reaction mixture. Analysis of the mixture on column A at 80 °C revealed that one major volatile product had formed. Analysis of the mixture by TLC on silica gel showed that two additional major products were present in approximately equal amounts with respective R_f values of 0.43 and 0.59 (ether). The reaction flask was cooled to −78 °C, and the white powder that precipitated was removed by vacuum filtration. TLC analysis showed the solid was mainly the component with the low R_f value, and it was recrystallized from ethyl vinyl ether to give tosylhydrazone **12a**, which was identified by spectral means.

Ethyl vinyl ether was removed from the original reaction mixture with a rotary evaporator. The yellow, gummy residue was washed with 2 mL of pentane. Adduct **13a** was isolated from the pentane wash with column A at 80 °C and was spectrally identical with an authentic[7] sample. The yellow, gummy residue left after the pentane wash was dissolved in 10 mL of ether, and the ether solution was cooled to −40 °C and then filtered. Following removal of the ether from the filtered solution with a rotary evaporator, 6 mL of a 1:1 mixture of ether and pentane was added to the yellow residue. The solvent mixture was poured off the residue that would not dissolve. Analysis of the decanted liquid through TLC analysis showed it to contain mainly the component with the high R_f value. Preparative TLC on silica gel with 25% ether in $CHCl_3$ gave tosylhydrazone **11a**, which was identical spectrally with **11a** independently prepared from 2-methylpropenal (see above).

For 2-methyl-2-tosylpropenal tosylhydrazone (**12a**): mp 131–133 °C dec; IR ($CHCl_3$) 3190 (NH), 1600, 1370, 1324, 1308, 1294, 1170, 1137, 1090, 1067 cm^{-1}; NMR ($CDCl_3$) δ 1.38 (s, 6, Me_2C), 2.37 (s, 3, CH_3Ar), 2.39 (s, 3, CH_3Ar), 7.00–7.76 (m, 9, HC=N, aromatic), 9.00 (s, 1, NH).

Thermal Decomposition of (Tosylazo)alkene 8b in Ethyl Vinyl Ether. Reaction of (tosylazo)alkene **8b** (0.6 g, 2.2 mmol) was essentially carried out as detailed above for **8a**. Adduct **13b** was isolated from the pentane wash with column A at 130 °C and was spectrally identical with an authentic[7] sample. Tosylhydrazones **11b** and **12b** were isolated in similar fashion as were **11a** and **12a** (see above) and were identified by spectral means.

For 1-tosylcyclohexanecarboxaldehyde tosylhydrazone (**12b**): mp 144–146 °C dec; IR ($CHCl_3$) 3190 (NH), 1597, 1370, 1320, 1290, 1172, 1145, 1095, 1070 cm^{-1}; NMR ($CDCl_3$) δ 1.01, 1.46, 1.90 (m, 11, cyclohexyl), 2.37 (s, 3, CH_3Ar), 2.39 (s, 3, CH_3Ar), 7.0–7.8 (m, 9, HC=N, aromatic), 9.16 (br s, 1, NH). For 1-cyclohexenecarboxaldehyde tosylhydrazone (**11b**): mp 106–108 °C dec; IR (Nujol) 3225 (NH), 1639, 1600, 1434, 1360, 1340, 1319, 1302, 1166, 1087, 950, 927, 821, 706, 681 cm^{-1}; NMR ($CDCl_3$) δ 1.55 (m, 4, cyclohexyl), 2.07 (m, 4, cyclohexyl), 2.37 (s, 3, CH_3Ar), 5.92 (br s, 1, HC=C), 7.18 (s, 1, HC=N), 7.58 (m, 4, aromatic), 8.48 (s, 1, NH).

Thermal Decomposition of (Tosylazo)alkene 8a in Cyclohexene and Glyme. With the standard setup given above, evolution of N_2 from a solution of 0.8 g (3.4 mmol) of **8a** in a mixture of 21 mL of cyclohexene and 4 mL of glyme ceased after 24 h of reaction at room temperature. Analysis of the mixture by TLC showed the presence of tosylhydrazones **11a** and **12a** in roughly equal amounts. Solvent was removed from the light yellow reaction mixture with a rotary evaporator, and the oily, yellow residue was washed with 2 mL of pentane. Adduct **10a** was isolated from the pentane wash on column A at 90 °C and was spectrally identical with authentic[7] material.

Thermal Decomposition of (Tosylazo)alkene 8b in Cyclohexene and Glyme. (Tosylazo)alkene **8b** (0.6 g, 2.2 mmol) was treated as described above for **8a**. After 32 h of reaction at room temperature, tosylhydrazones **11b** and **12b** were observed through TLC analysis. Carbene adduct **10b** was obtained from column A at 140 °C and was spectrally identical with an authentic[7] sample.

Thermal Decomposition of (Tosylazo)alkene 8c in Cyclohexene. An orange solution of 1 g (2.7 mmol) of **8c**[24] and 0.84 g (4.1 mmol) of 2,6-di-*tert*-butyl-4-methylpyridine[32] in 25 mL of cyclohexene was heated to 75 °C under nitrogen, and after 72 h the reaction solution was yellow and had a considerable amount

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[60] Jones, P. R.; West, R. *J. Am. Chem. Soc.* **1968**, *90*, 6978–82.

[61] Treptow, W.; Stang, P. J., The University of Utah, unpublished data, 1978.

of brown solid in it. Analysis of the mixture on column C at 115 °C showed it to contain a small amount of two volatile products in an approximate 1:1 ratio. A 50-mL portion of pentane was added to the reaction mixiture, and the resulting solution was filtered. The organic mixture was extracted with four 20-mL portions of cold 1.5 N HCl to remove the pyridine base. The acid washes were back-extracted with three 20-mL portions of pentane. Following concentration of the organic mixture with a rotary evaporator, the volatile products were obtained from the residue with column A at 110 °C. The product with the shorter retention time gave spectra consistent for tribromoethylene. In particular, its mass spectrum had mass ions at *m/z* 262, 264, 266, and 268 in roughly a 1:3:3:1 ratio. The other volatile product was determined to be *trans*-1,2-dibromocyclohexane through spectral comparison with the reaction product of bromine addition to a CCl_4 solution of cyclohexene.

Reaction of (Tosylazo)alkene 8a with *p*-Toluenesulfinic Acid. A solution of 62 mg (0.4 mmol) of *p*-toluenesulfinic acid in 2 mL of ethanol was added to 24 mg (0.1 mmol) of **8a**, and the solution was immediately swirled in a dry ice–isopropyl alcohol bath. After several minutes of periodic swirling at room temperature and in the dry ice bath to control the reaction, the reaction solution was colorless. Tosylhydrazone **12a** was found to be the major product through TLC comparison with isolated **12a** (see above). A small amount of tosylhydrazone **11a** was also seen through TLC analysis.

Isomerization of (Tosylazo)alkenes 8a–c in $CHCl_3$. (Tosylazo)alkene **8a** in CCl_4 gave the expected spectra (see above). When **8a** was dissolved in $CHCl_3$, the initial bright yellow solution became fluorescent yellow-green after 2 h at room temperature. Major changes were also observed through spectral analysis. Spectral data were consistent for the formation of 2-tosyl-2-methyl-1-diazopropane (**14a**): IR ($CHCl_3$) 2084 ($C{=}N_2$) cm^{-1}; NMR ($CDCl_3$) δ 1.48 (s, 6, Me_2C), 2.51 (s, 3, CH_3Ar), 3.75 (s, 1, $HC{=}N_2$), 7.73 (m, 4, ArH). In the NMR spectrum, the rearrangement of **8a** to **14a** appeared to be extremely clean and complete in 2 h. With time (8 h), the diazo absorption in the IR disappeared and a new strong absorption at 1730 cm^{-1} appeared. (Tosylazo)alkene **8b** also underwent a similar conversion in $CHCl_3$ to give 1-tosyl-1-(diazomethylene)cyclohexane (**14b**): IR ($CHCl_3$) 2082 ($C{=}N_2$) cm^{-1}; NMR ($CDCl_3$) δ 1.60 (m, 10, cyclohexyl), 2.48 (s, 3, CH_3Ar), 3.52 (s, 1, $HC{=}N_2$), 7.60 (m, 4, ArH).

A small amount of **8c** was dissolved in $CHCl_3$, and IR spectra were recorded at intervals of 0 h, 20 h, 3 days, and 12 days after initial dissolution. Very little change was observed from the initial spectrum, and no absorption was observed in the diazo absorption region.

Reaction of (Tosylazo)alkene 8a with Acetic Acid. A solution of 50 mg (0.21 mmol) of **8a** in 1 mL of $CHCl_3$ was allowed to stand in the dark for 2 h at room temperature. The yellow-green solution was then poured into a stirring solution of 252 mg (4.2 mmol) of acetic acid in 0.6 mL of $CHCl_3$. Evolution of N_2 was rapid, and the reaction solution was colorless after 1 h. Volume of the solution was increased to 10 mL with $CHCl_3$, and the resulting mixture was washed with three 2-mL portions of saturated Na_2CO_3 and then dried over K_2CO_3. After concentration on a rotary evaporator, analysis of the mixture on column F at 150 °C showed one major volatile product. The major product (R_f 0.32) along with other products (R_f 0.21 and 0.17) were seen through TLC analysis on silica gel with *n*-hexane–ethyl acetate (3:1) as developing solvent. Preparative TLC was utilized to obtain the major product, 1-tosyl-1-methylcyclopropane (**16**): IR ($CHCl_3$) 1600, 1313, 1302, 1140, 1087, 1040, 1020 cm^{-1}; NMR ($CDCl_3$) δ 0.80 (m, 2, cyclopropyl), 1.37 (s, 3, CH_3), 1.61 (m, 2, cyclopropyl), 2.51 (s, 3, CH_3Ar), 7.74 (m, 4, ArH); mass spectrum, *m/z* (relative intensity) 155 (100), 82 (40), 65 (77), 64 (13), 63 (25), 57 (20), 56 (21), 55 (100, M^+ − Ts), chemical ionization (isobutane) 210 (M^+, 100).

Before TLC isolation of **16**, an NMR of the $CHCl_3$ solution of reaction products revealed the presence of **16** but also had additional singlets at 1.41, 1.97, and 4.32 ppm in a 6:3:2 ratio. The signals suggest the presence of 2-tosyl-2-methylpropyl acetate. Not enough of this product (~15% of total products) was obtained to completely characterize.

Yield Determinations with (Tosylazo)alkenes 8a and 8b. General Procedure I. To either a 5-mL ampule or a 1-dram glass vial were added a bright yellow solution of 25 mg (0.105 mmol) of **8a** and 8.2 mg (0.0525 mmol) of *n*-undecane as internal GC standard in 1–4 mL of solvent. The amount of solvent was dependent on the solubility of the (tosylazo)alkene. **8b** (28 mg, 0.1 mmol) and 8.5 mg (0.05 mmol) of *n*-dodecane as an internal GC standard were also employed. Yields of carbene adducts **10a** and **10b** and the effects of differing reaction conditions on these yields are discussed in the text. Surfaces employed for the heterogeneous reactions were either inert surfaces (Chromosorb W or Celite, ~40 mg/1.5 mL of solvent) or powdered anhydrous Na_2CO_3 (2 molar equiv). Reaction progress was monitored and yield was determined on column C at 100 °C for **10a** and on column C at 150 °C for **10b**. Reactions were usually complete when the reaction solution became colorless. Adducts **10a** and **10b** were the only significant volatile products.

Yield Determinations with (Tosylazo)alkenes 8a and 8b. General Procedure II. A bright yellow solution of 25 mg (0.105 mmol) of **8a** in 0.5 mL of $CHCl_3$ was allowed to stand for 2 h in the dark at room temperature. To the yellow-green reaction mixture (see above for spectral analysis) were then added a solution of both 8.2 mg (0.0525 mmol) of *n*-undecane as internal GC standard and 1.1 equiv of amine base in 0.5 mL of cyclohexene and a stirring bar. **8b** (28 mg, 0.1 mmol) and 8.5 mg (0.05 mmol) of *n*-dodecane were employed. Table I details the bases used, the reaction conditions, and the yields found for adducts **10a** and **10b**. Production of adducts was followed and yields were determined as in General Procedure I. Varying amounts of a high-boilingproduct, 1-tosyl-1-methylcyclopropane (**16**), were seen in the reactions of **8a**, both on column F at 150 °C and through TLC analysis on silica gel. (Small amounts of high-boiling products were seen in reactions of **8b**, but they were not isolated or identified.) Adducts **10a** and **10b** were isolated from the respective Et_3N reactions of **8a** and **8b** through preparative GC (column A at 100 °C for **10a** and column A at 150 °C for **10b**) and both were identical with authentic[7] material by spectral comparison.

Control Reaction of (Tosylazo)alkene 8a in $CHCl_3$. The reaction was set up as described above in General Procedure II except that no amine base was added initially. After being stirred for 40 h at room temperature, the reaction solution was colorless and analysis on column C at 100 °C indicated that a 1.5% yield of carbene adduct **10a** had been formed. The solution was then treated with 17.6 mg (0.12 mmol) of DBU at room temperature. Yield of **10a** was found to be 2% at both 1-h and 40-h intervals following DBU addition.

Reaction of Triflate 22 with KF and 18-Crown-6 in Cyclohexene. General Procedure. To each of two 5-mL, round-bottomed flasks equipped with a stirring bar and a serum cap were added 29 mg (0.5 mmol) of KF and a solution of 33 mg (0.125 mmol) of 18-crown-6 and 15.6 mg (0.1 mmol) of *n*-undecane as internal GC standard in 2 mL of cyclohexene. Each reaction flask was cooled to 0 °C under nitrogen, and a solution of 27.6 mg (0.1 mmol) of triflate **22** in 0.5 mL of cyclohexene was added dropwise via a syringe to each rapidly stirring reaction mixture. After addition was complete, the syringe was washed with an additional 0.5 mL of cyclohexene. Analysis of each colorless mixture on column C at 100 °C showed that reaction was complete after 1.5 h. For the two reactions, an average yield of 92.3 ± 0.1% for the formation of adduct **10a** was determined.

Following GC analysis, the two reaction solutions were combined, and a bulb-to-bulb distillation was carried out. Pot temperature was increased to a final temperature of 65 °C, and all volatile material was collected in a receiver cooled to −78 °C. The presence of fluorotrimethylsilane in the distillate was indicated by a doublet in the ^{1}H NMR spectrum at δ 0.06 relative to $CHCl_3$ with a $J_{H\text{-}F} = 7.20$ Hz [lit.[62] $J_{H\text{-}F} = 7.15 \pm 0.08$ Hz]. Solvent was then removed from the reaction mixtures with a rotary evaporator, and the residue was taken up in pentane. Adduct **10a** was obtained from this residue on column A at 100 °C. Spectra obtained with this sample were identical with that of authentic[7] material.

Reaction of Triflate 22 with KF and 10% 18-Crown-6 in Cyclohexene. Triflate **22** (55.2 mg, 0.2 mmol) was treated with 5.3 mg (0.02 mmol) of 18-crown-6 and 17.4 mg (0.3 mmol) of KF

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Table IV. Compositions of Styrene Mixtures and GC Analysis Conditions for Relative Reactivity Studies

reactant	substrate X[a]	O_H/O_X[b]	analysis column	analysis temp, °C
8a	p-CH_3O	1.52	D	130–190
8a	p-CH_3	1.29	D	138
8a	p-Br	0.78	E	160–195
8a	cyclohexene	1.23	C	85–135
22	p-CH_3O	1.52	D	130–190
22	p-CH_3	1.65	D	160
22	p-Br	0.76	E	130
22	cyclohexene	1.49	C	85–125

[a] $XC_6H_4CH{=}CH_2$ for styrene substrates. [b] Mole ratio for styrene/substrate.

in 6 mL of a 1:1 mixture of cyclohexene and glyme. After 3 h at 0 °C, reaction was found to be only 11% complete by GC analysis. Further reaction at room temperature for 12 h increased the amount of adduct **10a** to 25% of theoretical.

Reaction of Triflate 22 with $PhCH_2NMe_3F$ in Cyclohexene and Glyme. A 5-mL portion of pentane was added under nitrogen to 0.1014 g of a 25% dispersion of powdered $PhCH_2NMe_3F$ (25.4 mg, 0.15 mmol) in mineral oil, and the resulting mixture was stirred for several minutes. The salt was allowed to settle, and then the pentane was removed with a syringe through a serum stopper. This procedure was repeated twice, and then the residual pentane was removed with a stream of N_2. Reaction of triflate **22** (27.6 mg, 0.1 mmol) with this fluoride source was carried out at −20 °C in 3 mL of a 5:1 mixture of glyme and cyclohexene. As before, reaction was found to be complete after 1.5 h of vigorous stirring, and adduct **10a** was found to have formed in 91.7 ± 0.2% yield (from duplicate runs). A reaction set up as above with a 1:1 mixture of cyclohexene and glyme and a reaction temperature of 0 °C gave 79% of adduct **10a**.

Reaction of Triflate 22 with Aqueous KF and Aliquat 336 in Cyclohexene. Triflate **22** (27.6 mg, 0.1 mmol) was reacted at 0 °C in a two-phase system consisting of 58 mg of 50% aqueous KF (29 mg, 0.5 mmol of KF) and a solution of 76 mg (0.15 mmol) of Aliquat 336[39] in 3 mL of cyclohexene. Vigorous and turbulent stirring was maintained during the reaction to achieve good interaction of the two phases. Again, no **22** remained after 1.5 h of reaction. An average yield of 82.1 ± 0.4% was observed for adduct **10a** from duplicate runs. Further analysis of each mixture on column C at 70–100 °C revealed the presence of 2-methyl-1-propenyl triflate (**24**) in 2.3 ± 0.3% yield.

Reaction of Triflate 22 with Aqueous KF and 10% Aliquat 336 in Cyclohexene. The procedure described above was used except that 5.0 mg (0.01 mmol) of Aliquat 336 and room temperature were used for this reaction. After 1 h of vigorous stirring, adduct **10a** had been formed in 8% yield. The yield increased to 11% after 40 h. Addition of 55.5 mg (0.11 mmol) of Aliquat 336 followed by 0.5 h of reaction resulted in the formation of **10a** in 74% yield.

General Procedures for the Selectivity Experiments. The following was used for the reactions of (tosylazo)alkene **8a**. A solution of 0.050 g (0.21 mmol) of **8a** in 1 mL of the appropriate styrene mixture was allowed to stand at 0 °C until reaction was complete, usually about 3 days. Direct analysis of the mixture was then carried out on a gas chromatograph. The results of multiple injections of duplicate runs are listed in Tables II and III. Table IV gives the composition of the styrene mixtures used and the conditions of GC analysis.

For reactions of silylvinyl triflate **22**, a suspension of benzyltrimethylammonium fluoride (25 mg, 0.15 mmol), 0.5 mL of glyme, and 0.5 mL of the appropriate sytrene mixture was cooled to 0 °C, and triflate **22** (24 mg, 0.087 mmol) was added. After vigorous mixing, the solution was allowed to stand for 24 h at 0 °C before direct GC analysis. As for **8a**, results and conditions are given in Tables II–IV.

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Registry No. **8a**, 62618-93-3; **8b**, 42449-08-1; **10a**, 53282-47-6; **10b**, 19690-02-9; **11a**, 87185-17-9; **11b**, 87185-15-7; **12a**, 87189-83-1; **12b**, 87185-14-6; **16**, 87185-16-8; **21**, 56583-93-8; **22**, 73876-87-6; p-$CH_3OC_6H_4CH{=}CH_2$, 637-69-4; p-$CH_3C_6H_4CH{=}CH_2$, 622-97-9; $C_6H_5CH{=}CH_2$, 100-42-5; p-$BrC_6H_4CH{=}CH_2$, 2039-82-9; $(CH_3)_2C{=}C{:}$, 26265-75-8; cyclohexanecarboxaldehyde tosylhydrazone, 34266-29-0; isobutyraldehyde tosylhydrazone, 20208-71-3; 2-(p-bromophenyl)-1-isopropylidenecyclopropane, 87185-13-5.

Site of Attack of a Carbene on Alkylbenzenes, Naphthalene, and Thiophene and the Norcaradiene–Cycloheptatriene Equilibration

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Upon thermolysis at 40–50 °C, 5-(diazomethyl)-1,4-diphenyl-1,2,3-triazole (1) reacts with p-ethyltoluene, p-cymene, p-*tert*-butyltoluene, p-diisopropylbenzene, durene, and naphthalene to give a mixture of carbene-derived cycloheptatriene/norcaradiene products; attack is favored adjacent to the more highly branched substituent. Decomposition of 1 in p-diisopropylbenzene afforded a tropilidene and a C–H insertion product in a ca. 1:1 ratio. Naphthalene was attacked at the 1,2-position to form a norcaradiene and at the 2,3-position to form a cycloheptatriene. Thiophene was attacked only at the 2,3-position, with formation of a cyclopropanothiophene. The kinetics of the thermal rearrangement of the product from 4-*tert*-butyltoluene to an isomeric cycloheptatriene were first order; E_a = 24.90 ± 0.4 kcal/mol, and $\Delta S^{\ddagger}$ = 14.5 eu. The NMR spectrum of the isomer showed the presence of rotamers and conformers with high energy barriers between them, such that they are individually recognizable at room temperature.

Introduction

In previous articles[2] we have demonstrated that the position and number of alkyl substituents on an aromatic substrate influence the site selectivity of carbene addition, as well as the structure of the product, norcaradiene (NCD) or cycloheptatriene (CHT). In the present study, the effect of branching and number of the alkyl substituents and of benzo fusion on the structure of the product and site selectivity has been investigated. 5-(Diazomethyl)-1,4-diphenyl-1,2,3-triazole (**1**) affords a favorable opportunity

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[1] In part from the doctoral dissertation of C.D.B.

[2] Bedford, C. D.; Bruckmann, E. M.; Smith, P. A. S. *J. Org. Chem.* 1981, *46*, 679.

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