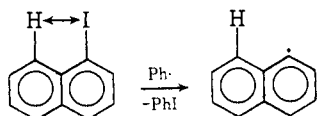
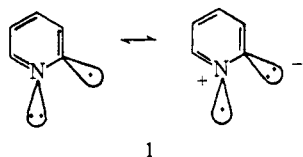


tions and should be reduced for halogen abstractions when electron-withdrawing groups are present on the organic halo compound. However, we prefer to interpret the influence of substituents and electron density on the substrate carbon atom on the rate of halogen abstraction as resulting from a polar effect as discussed above since HMO calculations yield a rather invariant π -electron density of 1.99 ± 0.01 on iodine for all the compounds listed in Table I.

From Table I it can be seen that 1-iodonaphthalene is slightly more reactive than either iodobenzene or 2-iodonaphthalene even though all three have approximately identical calculated electron densities on the carbon of the C-I bond. Even though the difference is not large, this might reflect a slight steric acceleration of iodine abstraction resulting in relief of the 1-8 iodine-hydrogen peri interaction although it is expected that such an interaction would also be reflected by a lower C-Br BDE for the 1 isomer.



2-Iodopyridine is the most reactive compound of the present study possibly as a result of a stabilization of the product 2-pyridyl radical *via* interaction with the lone pair of electrons on nitrogen as depicted in 1. Direct evidence for such an interaction in the 2-pyridyl radical has been obtained from electron spin resonance



studies in which a large (29 ± 1 G) hyperfine interaction

with the nitrogen nucleus was observed.²⁴ The high reactivity of 2-iodopyridine to phenyl radicals is paralleled by the enhanced reactivity of 2-halopyridines with sodium atoms. Both 2-chloro- and 2-bromopyridine react much more rapidly with sodium atoms than do the corresponding 3-chloro- and 3-bromopyridines. The relative rates are 340:1 and 25:1, for the chlorides and bromides, respectively.²⁵ Nevertheless, stabilization of the 2-pyridyl radical as depicted in 1 cannot be of an overwhelming nature since the BDE for 2-bromopyridine is higher than that for bromobenzene and the rate of iodine removal is not significantly greater than the rate anticipated on the basis of a polar effect. If there is a strong resonance interaction with the lone pair of electrons on nitrogen, the observed k_1/k_{Cl} for 2-iodopyridine should be well above the line in Figure 1 while in fact it correlates reasonably well.

Experimental Section

Iodobenzene, 1-iodonaphthalene, 2-iodonaphthalene, 3-iodopyridine, and 2-iodothiophene were commercially available and purified in all cases by either vacuum distillation or recrystallization. 2-Iodopyridine was prepared from 2-aminopyridine by diazotization followed by reaction with potassium iodide.²⁶ 3-Iodothiophene was synthesized from the commercially available bromo compound according to the procedure of Gronowitz and Hakansson.²⁷ 4-Iodopyridine was kindly supplied by Dr. Paul H. Kasai of Union Carbide Corporation.

Kinetic analyses were conducted as described in a previous paper.⁹

Acknowledgment. The authors are indebted to Paul H. Kasai of Union Carbide Corporation for kindly supplying a sample of 4-iodopyridine. Helpful discussions with Andreas A. Zavitsas and William A. Pryor are also gratefully acknowledged.

(24) P. H. Kasai and D. McLeod, Jr., *J. Amer. Chem. Soc.*, **94**, 720 (1972).

(25) E. Warhurst, *Quart. Rev., Chem. Soc.*, **5**, 44 (1951).

(26) J. Halpern and J. P. Maker, *J. Amer. Chem. Soc.*, **87**, 5361 (1965).

(27) S. Gronowitz and R. Hakansson, *Ark. Kemi*, **16**, 309 (1960).

Unsaturated Carbenes from Primary Vinyl Triflates.

I. Method and Scope

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Contribution from the Department of Chemistry, The University of Utah, Salt Lake City, Utah 84112. Received February 8, 1974

Abstract: A variety of primary vinyl triflates, 7-13, containing a hydrogen, dialkyl groups, arylalkyl, or diaryl groups in the β position was prepared from the corresponding aldehydes *via* their silyl enol ethers. Treatment of the dialkyl triflates with *t*-BuOK in a variety of olefins at -20 to $+25^\circ$ afforded methylenecyclopropanes in good yields together with differing amounts of *tert*-butyl vinyl ethers. Whereas similar treatment of β -aryl and β -hydrogen triflates gave only acetylenes as products. Both the olefin adducts as well as the *tert*-butyl vinyl ethers arise from unsaturated carbenes (R)₂C=C: or carbenoids. The methods and scope of unsaturated carbene generation from primary vinyl triflates are discussed.

An enormous amount of work has been reported² in the area of carbene chemistry since the pioneer-

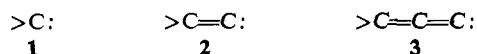
(1) University of Utah Graduate Research Fellow.

(2) For reviews and leading references, see (a) M. Jones, Jr., and R. A. Moss, "Carbenes," Vol. I, Wiley, New York, N. Y., 1973; (b) W. Kirmse, "Carbene Chemistry," 2nd ed, Academic Press, New York,

ing investigations of Doering, Hine, Meerwein, and Skell. Besides the simple carbene itself, 1, there is of

N. Y., 1971; (c) T. L. Gilchrist and C. W. Rees, "Carbenes, Nitrenes and Arynes," Appleton-Century-Crofts, New York, N. Y., 1969; (d) J. Hine, "Divalent Carbon," Ronald Press, New York, N. Y., 1964; (e) D. Bethell, *Advan. Phys. Org. Chem.*, **7**, 153 (1969); (f) R. A. Moss,

course the possibility of unsaturated carbenes. In fact two kinds of unsaturated carbenes have been observed: vinylidene carbenes, **2**, and allenidene carbenes, **3**.



Allenidene carbenes, **3**, have mostly been generated from haloallenes and propargyl halides in the presence of bases.³ On the other hand, vinylidene carbenes, **2**, have been generated by the base decomposition of primary vinyl halides,⁴ deamination of vinylamines,⁵ photofragmentation,⁶ and base decomposition of 5,5-disubstituted *N*-nitrosooxazolidones,⁷ **4**. However, there are known complications and difficulties with most of these techniques. In the case of photofragmentation⁶ less than 5% of the products isolated resulted from the unsaturated carbene. In the case of deamination of vinylamines⁵ the reaction proceeds *via* a vinyl diazonium ion which may decompose *via* alternative pathways (*i.e.*, vinyl cations); furthermore, the reaction is complicated by side products and the difficulty of obtaining precursors. The most elegant and extensive investigations so far involving unsaturated vinylidene carbenes have been carried out by Newman⁷ and coworkers in the base decomposition of nitrosooxazolidones, **4**, and Köbrich^{4a} and coworkers involving primary vinyl halides. However, in the latter case it has been clearly established^{4a} that the reaction proceeds at best *via* a carbenoid and at low temperatures in many instances through the anion, rather than the free carbene. In the former case a complicated pathway, involving several possible intermediates, may be entailed prior to carbene formation. Furthermore, the preparation of the precursor nitrosooxazolidones involves multi-step synthesis and the yields of carbene products are only moderate with several side products.

Hence a generally applicable procedure for the simple generation in good yields of unsaturated carbenes from easily available precursors is readily apparent. It is well known⁸ that a trifluoromethanesulfonate (triflate) is

Chem. Eng. News, 47, 30 (June 16, 1969); (g) G. L. Closs, *Top. Stereochem.*, 3, 194 (1968); (h) B. S. Herold and P. P. Gaspar, *Fortschr. Chem. Forsch.*, 5, 89 (1965); (i) G. G. Roznatev, A. A. Fainzilberg, and S. S. Novikov, *Russ. Chem. Rev.*, 34, 69 (1965); (j) J. A. Bell, *Progr. Phys. Org. Chem.*, 2, 1 (1964); (k) W. B. DeMore and J. W. Benson, *Advan. Photochem.*, 2, 219 (1964); (l) H. M. Frey, *Progr. React. Kinet.*, 2, 131 (1964); (m) E. Chinoporos, *Chem. Rev.*, 7, 153 (1963).

(3) (a) G. F. Hennion, *et al.*, *J. Amer. Chem. Soc.*, 73, 4735 (1951); 75, 1653 (1953); 79, 2142 (1957); (b) H. D. Hartzler, *ibid.*, 83, 4990, 4997 (1961); 86, 526 (1964); 88, 3155 (1966); 93, 4527 (1971); *J. Org. Chem.*, 29, 1311 (1964); (c) V. J. Shiner, *et al.*, *J. Amer. Chem. Soc.*, 84, 2402, 2408 (1962); 89, 622 (1967); (d) W. J. LeNoble, *et al.*, *ibid.*, 92, 568 (1970); (e) H. Reimlinger and R. Paulissen, *Tetrahedron Lett.*, 3143 (1970); D. S. Northington and W. M. Jones, *ibid.*, 312 (1971); (f) T. B. Patrick, *et al.*, *J. Org. Chem.*, 37, 1553 (1972).

(4) (a) For a review and leading references, see G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, 6, 41 (1967); (b) M. Tanabe and R. A. Walsch, *J. Amer. Chem. Soc.*, 85, 3522 (1963); (c) H. D. Hartzler, *ibid.*, 86, 527 (1964); (d) D. Y. Curtin and W. H. Richardson, *ibid.*, 81, 4719 (1959); (e) C. R. Hauser and D. Lednicer, *J. Org. Chem.*, 22, 1248 (1957); (f) K. L. Erickson and J. Wolinsky, *J. Amer. Chem. Soc.*, 87, 1142 (1965).

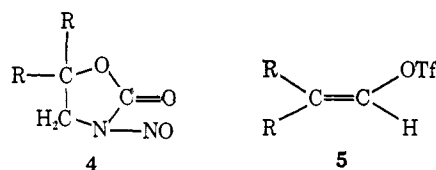
(5) D. Y. Curtin, J. A. Kampmeier, and B. R. O'Connor, *J. Amer. Chem. Soc.*, 87, 863 (1965); D. Y. Curtin, J. A. Kampmeier, and M. L. Farmer, *ibid.*, 87, 874 (1965).

(6) J. C. Gilbert and J. R. Butler, *J. Amer. Chem. Soc.*, 92, 7493 (1970).

(7) (a) M. S. Newman and A. O. M. Okorodudu, *J. Amer. Chem. Soc.*, 90, 4189 (1968); (b) M. S. Newman and T. B. Patrick, *ibid.*, 91, 6461 (1969); (c) M. S. Newman and A. O. M. Okorodudu, *J. Org. Chem.*, 34, 1220 (1969); (d) M. S. Newman and C. D. Beard, *J. Amer. Chem. Soc.*, 91, 5677 (1969); (e) M. S. Newman and T. B. Patrick, *ibid.*, 92, 4312 (1970); (f) M. S. Newman and Z. U. Din, *J. Org. Chem.*, 38, 547 (1973).

(8) (a) R. L. Hansen, *J. Org. Chem.*, 29, 4322 (1965); (b) A. Streitwieser, Jr., C. L. Wilkins, and E. Kiehlmann, *J. Amer. Chem. Soc.*,

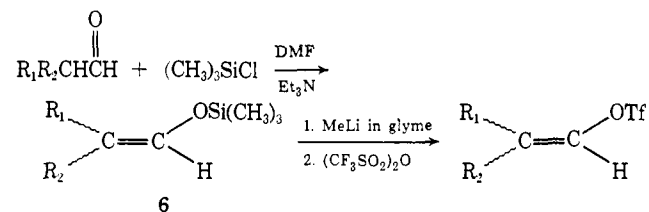
a better leaving group than a tosylate or a halide by a factor of 10⁵–10⁷. Primary vinyl triflates, **5**, therefore



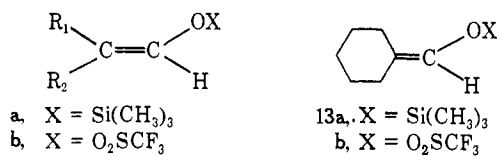
seemed to us to be ideal candidates as progenitors of vinylidene carbenes, **2**. In this paper we report the preparation of such triflates and their use and limitations as precursors of unsaturated carbenes.

Results and Discussion

We first attempted to prepare primary vinyl triflates, **5**, from aldehydes directly in a manner analogous to that employed for the preparation of vinyl triflates from ketones.⁹ However, with the exception of highly enolizable aldehydes such as diphenylacetaldehyde and 9-formylfluorene this proved to be unsuccessful. Primary vinyl triflates may, however, be conveniently and readily obtained in moderate overall yields (35–60%) from the appropriate aldehyde in two steps, by first preparing the trimethylsilyl enol ethers, **6**, according to House¹⁰ and Stork.¹¹ Treatment of these silyl enol ethers with methyl lithium in glyme at low temperature



followed by triflic anhydride gives the desired primary vinyl triflates. Using the appropriate aldehyde, triflates **7b–13b** have been prepared and investigated under



a. X = Si(CH₃)₃

b. X = O₂SCF₃

7. R₁ = R₂ = CH₃

8. R₁ = R₂ = CH₃CH₂

9. R₁ = R₂ = C₆H₅

10E, R₁ = H; R₂ = *n*-C₃H₇

10Z, R₁ = *n*-C₃H₇; R₂ = H

11E, R₁ = CH₃; R₂ = C₆H₅

11Z, R₁ = C₆H₅; R₂ = CH₃

12E, R₁ = CH₃; R₂ = CH₃CH₂

12Z, R₁ = CH₃CH₂; R₂ = CH₃

a variety of conditions as progenitors of unsaturated carbenes, **2**.

A variety of bases such as [(CH₃)₃Si]₂NLi, (C₆H₅)₃C-Na, *n*-BuLi, and NaH was found to give, besides the desired α elimination, various amounts (10–90%) of

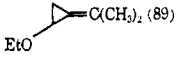
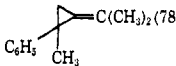

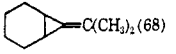
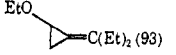
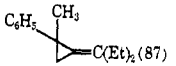

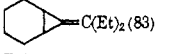
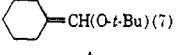
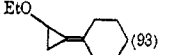

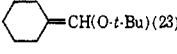
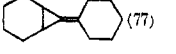




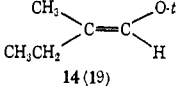
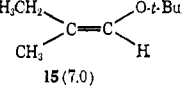
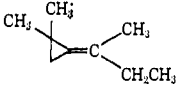
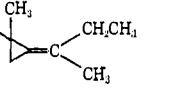
90, 1590 (1968); (c) T. M. Su, W. F. Sliwinski, and P. v. R. Schleyer, *ibid.*, 91, 5386 (1969); (d) S. A. Sherrod, R. G. Bergman, G. L. Gleicher, and D. G. Morris, *ibid.*, 94, 4615 (1972); (e) P. J. Stang and R. Summerville, *ibid.*, 91, 4600 (1969).

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Table I. Reaction of Primary Vinyl Triflates 7b-13b

Rxn	Triflate	Solvent	Rxn cond	Products (rel % yield) ^a
1	7	(EtO)HC=CH ₂	0°, 1 hr	(CH ₃) ₂ C=CH(O- <i>t</i> -Bu) (10) 
2	7	(C ₆ H ₅)CH ₂ C=CH ₂	0°, 1.5 hr	(CH ₃) ₂ C=CH(O- <i>t</i> -Bu) (22) 
3	7		0°, 24 hr	(CH ₃) ₂ C=CH(O- <i>t</i> -Bu) (32) 
4	7	(Et) ₃ SiH	0°, 1.5 hr	(CH ₃) ₂ C=CH(O- <i>t</i> -Bu) (15) (CH ₃) ₂ C=CH[Si(C ₂ H ₅) ₃] (85)
5	8	(EtO)HC=CH ₂	0°, 4 hr	(Et) ₂ C=CH(O- <i>t</i> -Bu) (7) 
6	8	(C ₆ H ₅)CH ₂ C=CH ₂	0°, 4 hr	(Et) ₂ C=CH(O- <i>t</i> -Bu) (13) 
7	8		0°, 4 hr	(Et) ₂ C=CH(O- <i>t</i> -Bu) (17) 
8	13	(EtO)HC=CH ₂	0°, 4 hr	 (7)  (93)
9	13		0°, 20 hr	 (23)  (77)
10	10E + 10Z	(EtO)HC=CH ₂	0°, 3 hr	CH ₃ CH ₂ CH ₂ C≡CH (100)
11	10E + 10Z		0°, 3 hr	CH ₃ CH ₂ CH ₂ C≡CH (100)
12	9	(EtO)HC=CH ₂	0°, 72 hr	C ₆ H ₅ C≡CC ₆ H ₅ (100)
13	9		0°, 72 hr	C ₆ H ₅ C≡CC ₆ H ₅ (100)
14	11E		0°, 2 hr	C ₆ H ₅ C≡CCH ₃ (100)
15	11E	(EtO)HC=CH ₂	0°, 2 hr	C ₆ H ₅ C≡CCH ₃ (100)
16	11Z		0°, 2 hr	C ₆ H ₅ C≡CCH ₃ (100)
17	11Z	(EtO)CH=CH ₂	0°, 2 hr	C ₆ H ₅ C≡CCH ₃ (100)
18	12E	(CH ₃) ₂ C=CH ₂	-20°, 36 hr	 (14) (19) +  (15) (7.0)
				 (16) (42) +  (17) (32)
19	12Z	(CH ₃) ₂ C=CH ₂	-20°, 36 hr	14 (19) + 15 (7.0) + 16 (42) + 17 (32)

^a Uncalibrated relative areas by glc. Besides trace amounts, <1-2%, of unidentified product in some of the reactions, no other peaks (besides solvent) or products were observed. Estimated uncertainty $\pm 2-5\%$.

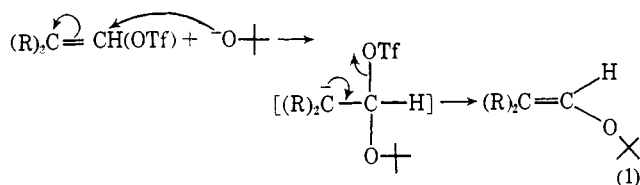
competing nucleophilic attack on sulfur and S-O bond cleavage. Such nucleophilic attack upon sulfur, and the attendant S-O bond cleavage in the presence of strong bases, is a well-known phenomenon.¹² On the other hand, the much softer base *t*-BuOK was found not to result in the undesirable S-O cleavage, and using this base and a variety of olefins as both solvents and trapping agents the results given in Table I were observed. In all instances products were isolated by preparative gc and identified by means of infrared and nmr spectra with the details given in the Experimental Section. In order to determine absolute yields triflate 7 was reacted on a 25-mmol preparative scale with cyclo-

(12) C. A. Bunton and Y. F. Frei, *J. Chem. Soc.*, 1872 (1951); S. Oae, T. Fukumoto, and R. Kiritani, *Bull. Chem. Soc. Jap.*, **36**, 346 (1963); S. Oae and R. Kiritani, *ibid.*, **38**, 765 (1965); R. H. Summerville, C. A. Senkler, P. v. R. Schleyer, T. E. Dueber, and P. J. Stang, *J. Amer. Chem. Soc.*, **96**, 1100 (1974).

hexene and ethyl vinyl ether. In the cyclohexene reaction a 82% yield of combined adduct and *tert*-butyl vinyl ether was actually isolated; the yield of isolated product in the ethyl vinyl ether reaction, again, consisting of the adduct and *tert*-butyl vinyl ether together, was 79%. Clearly carbene generation from primary vinyl triflates is a very high yield reaction. Taking into account the small scale nature of the preparative reactions and the hydrolytic lability of *tert*-butyl vinyl ethers, carbene generation is most likely quantitative. Furthermore reaction occurs rapidly and under very mild conditions. The longer reaction times in Table I were usually due to a matter of convenience rather than necessity. It is not inconceivable that carbene formation and its reaction are virtually instantaneous under these conditions and the limiting factor is the solubility of *t*-BuOK in the olefins employed.

There is little doubt that the olefin adducts observed

in Table I arise *via* the unsaturated carbene or carbenoid, whereas the origin of the *tert*-butyl vinyl ethers might be different. These observed ethers could arise either through the carbenes or *via* a nucleophilic addition-elimination (AdN-E) process¹³ (eq 1). In



order to distinguish between these two possibilities, triflate **7** was reacted in the presence of excess *t*-BuOD. Reaction *via* the AdN-E route should not incorporate deuterium into the *tert*-butyl vinyl ether product whereas reaction *via* the carbene should show deuterium incorporation. Indeed substantial¹⁴ deuterium incorporation was observed in the ether product of triflate **7**, $(CH_3)_3C=C(O-t-Bu)$. The reisolated unreacted triflate **7** showed no deuterium incorporation. Control experiments also demonstrated that the vinylic hydrogen of the product *tert*-butyl vinyl ether does not exchange with *t*-BuOD in the presence of *t*-BuOK under the experimental conditions employed. These results establish that the *tert*-butyl vinyl ether products also arise *via* the unsaturated carbene.¹⁶ Such insertion into the OH bond of alcohols have been observed with certain saturated carbenes.^{2b,17}

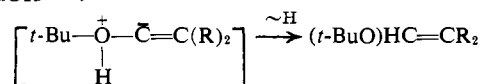
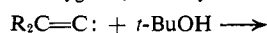
It was of interest to see if besides dialkyl carbenes unsaturated carbenes with one or more β hydrogens and β -aryl groups might also be generated by this technique employing primary vinyl triflates. Therefore triflates **10E** and **10Z** were prepared and a mixture of the two isomers was reacted with *t*-BuOK in cyclohexene and ethyl vinyl ether. In both solvents the sole product observed was 1-pentyne. This product could arise by either an E2 elimination of CF_3SO_3H with *t*-BuO⁻ abstracting the β proton or *via* α elimination, carbene formation, and hydrogen migration. In the former case stereochemistry seems to have little or no effect upon the course of the reaction since elimination seemingly occurs equally well from the *Z* and *E* isomer. Deuterium labeling studies are under way to distinguish between these two possible pathways.

(13) Z. Rappoport, *Advan. Phys. Org. Chem.*, **7**, 1 (1969); G. Modena, *Accounts Chem. Res.*, **4**, 73 (1971); Z. Rappoport and A. Gal, *J. Org. Chem.*, **37**, 1174 (1972).

(14) Using a 12-fold excess of *t*-BuOD, about 90% D by nmr, the product showed 44.0% D-incorporation by mass spectroscopy. Using the relationship¹⁵ of $k_H/k_D = P_yO_x/P_xO_y = k_H/k_D = 0.018 \times 0.56 / 0.0023 \times 0.44$, this would correspond to an isotope effect of $k_H/k_D = 9.9$.

(15) W. von E. Doering and W. A. Henderson, Jr., *J. Amer. Chem. Soc.*, **80**, 5274 (1958); see also ref 2a, pp 153-155.

(16) The carbene itself may react by different pathways to give the observed *tert*-butyl ethers, such as (a) some sort of *direct* insertion of the carbene into the O-H bond, (b) $R_2C=C: + \overset{H^+}{O}C(CH_3)_3 \rightarrow R_2C=C-CH(O^+)H$, (c) attack of the electrophilic carbene upon the oxygen atom and ylide formation



Path b is unlikely as there should be no ready proton source in the presence of excess base. The isotope effect¹⁴ would seem to favor path a over path c. However, it is not our purpose in this paper to establish the exact mechanism of formation of these vinyl ethers only to show that carbenes are involved.

(17) J. A. Kerr, *J. Chem. Soc. A*, 897 (1967).

No olefin adducts or vinyl ether were observed as well in the reaction of the diphenyl triflate **9** or the *E*- and *Z*-phenylmethyl triflates, **11**. In the case of triflate **9** the sole product in either cyclohexene or ethyl vinyl ether was diphenylacetylene and in the case of triflates **11E** and **11Z** the sole product in both solvents was 1-phenylpropyne. Similar results, with sole formation of diarylacetylenes, have been observed in the action of bases under a variety of conditions on β,β -diarylhaloethylenes.¹⁵ In an elegant series of labeling studies with isomeric *cis-trans* starting haloethylenes it was shown¹⁹ that migration of the aryl group *trans* to the leaving halide always predominates in such reactions ruling out the free carbene as an intermediate in these rearrangements.¹⁹

On the other hand, *cis* migration was found^{4a,20} to predominate in the reaction of *E*- and *Z*-2,2-phenylmethyl-1-chloroethylenes with *n*-BuLi at -85° with the *E* isomer being inert under these conditions. Rearrangement and acetylene formation was accompanied by isomerization of the *Z* halide to the *E* halide. This behavior of the halides is in contrast to the observed reaction of the corresponding triflates **11**. In the case of the triflates both the *E* and *Z* isomers react to give only acetylene (rxns 14-17) and no isomerization of starting triflates was observed during the course of the reaction. These results suggest that diaryl and arylalkyl primary triflates react *via* either carbenoids similar to the behavior of the corresponding halides^{4a,21} rather than the free carbenes (*vide infra*), or that intramolecular rearrangement of the free carbenes themselves is faster than the intermolecular trapping of such species by olefins. Interestingly no such migration was observed in any of the dialkyl triflates although we have specifically looked for the products of such rearrangements. That is no 2-butyne or 3-hexyne was observed in any of the reactions of triflate **7** and **8**, respectively, with authentic alkyne used to check for their presence or absence in the gc.

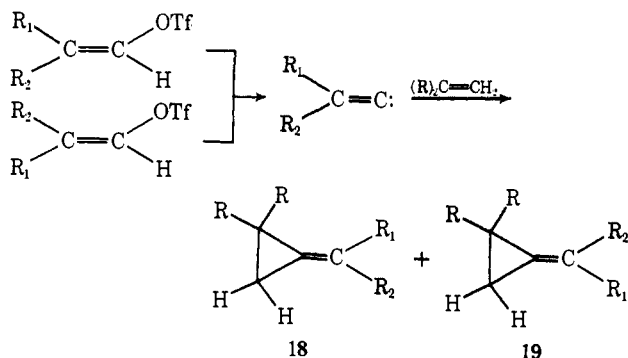
From the data available it is difficult to exactly ascertain whether the reactive intermediate from the base decomposition of primary vinyl triflates is the free carbene or a carbenoid analogous to the species generated in the base decomposition of vinyl halides.^{4a,21} However, some light may be shed on this question by the stereochemical results of addition of unsymmetrical carbenes to unsymmetrical olefins. It is a necessary albeit not sufficient condition for the existence of the free carbene that each one of the two possible pure stereoisomeric vinyl triflates give exactly the same ratio of two possible olefinic adducts, **18** and **19**. Indeed either the pure *E*-ethylmethylvinyl triflate, **12E**, or the pure *Z*-ethylmethyl triflate, **12Z**, gave within experimental

(18) (a) P. Fritsch, *Justus Liebigs Ann. Chem.*, **279**, 319 (1894); W. P. Buttenberg, *ibid.*, **279**, 324 (1894); H. Wiechell, *ibid.*, **279**, 337 (1894). (b) G. Köbrich, *Angew. Chem., Int. Ed. Engl.*, **4**, 49 (1965); (c) G. Köbrich and H. Trapp, *Chem. Ber.*, **99**, 680 (1966).

(19) (a) A. A. Bothner-By, *J. Amer. Chem. Soc.*, **77**, 3293 (1955); (b) D. Y. Curtin, E. W. Flynn, and R. F. Nystrom, *ibid.*, **80**, 4599 (1958); (c) W. Tadros, A. B. Sakla, M. S. Ishak, and E. R. Armanians, *J. Chem. Soc.*, 4218 (1963).

(20) G. Köbrich and F. Ansari, *Chem. Ber.*, **100**, 2011 (1967).

(21) In the case of the species generated from vinyl halides both the halide and the Li (from the RLi generally employed as base) are presumably associated in some manner with the carbene giving rise to a carbenoid. It is much less likely, although not impossible, that either the very weakly nucleophilic triflate anion or the strongly ionic potassium ion would be similarly associated with the carbene generated from vinyl triflates.



error an identical mixture of products with isobutylene. Not only was the ratio of olefinic adducts identical from either starting triflate (rxns 18 and 19) but the ratio of the two possible *tert*-butyl vinyl ether products was also identical, further indicating that both the olefin adducts as well as the *tert*-butyl vinyl ether products in these reactions probably arise from the same intermediate unsaturated carbene.

Finally the unsaturated carbenes generated from primary vinyl triflates readily insert into Si-H bonds in good yields, as typified by the reaction of the dimethyl triflate, 7, with triethylsilane (rxn 4). Such insertions, again in high yields, have also been observed by Newman and Beard^{7d} in the base decomposition of nitroso-oxazolidones, 4.

Summary

In this paper we report the preparation and base decomposition in the presence of olefins of a number of different primary vinyl triflates, 7-13. Dialkyl triflates in the presence of various olefins afford methylenecyclopropanes in good yields together with various amounts of *tert*-butyl vinyl ethers. There is little doubt that the reaction proceeds by α elimination through unsaturated carbenes or carbenoids. The ready availability of primary vinyl triflates from aldehydes and the high yields of products observed under very mild reaction conditions place the base decomposition of such triflates among the best,²² if not the best, sources of unsaturated carbenes, 2. Besides addition to olefins such carbenes also readily insert into Si-H bonds. On the other hand, triflates containing a β hydrogen, either *cis* or *trans* to the leaving group, give only terminal acetylenes as products. Similarly, triflates containing one or more β -phenyl groups give only rearranged alkynes as products.

The exact mechanism of generation, concerted or stepwise, and nature of these unsaturated carbenes, free or carbenoid,²¹ as well as their spin-multiplicity together with further chemistry will be the subject of future papers in this series.

Experimental Section

General. All boiling points and melting points are uncorrected. Nmr spectra were recorded on a Varian Associates A-60 spectrometer and data are given in δ (ppm) relative to internal or external tetramethylsilane (TMS, δ 0) as indicated. All ir spectra were recorded on a Beckman IR5A and are reported in wave numbers

(22) A referee has suggested that the high price of triflic acid makes this an extremely expensive method of unsaturated carbene generation. In fact, at the prevailing price of \$58/900 g. (~\$10/mol) from 3M Co. and the yields of carbenes achieved make this an economically reasonable, if not competitive, procedure aside from its chemical advantages.²¹

(cm⁻¹) calibrated to the 1603-cm⁻¹ line of polystyrene. Mass spectra were recorded on an MS-30 spectrometer. Glc was performed on either a Varian-Aerograph 90P and 920 or Varian Model 1200 Series flame ionization chromatograph with the following columns: A, 0.25 in. \times 5 ft 10% SF-96 on 60-80 Chromosorb W; B, 0.375 in. \times 15 ft 15% SF-96 on 45-60 Chromosorb W; C, 0.125 in. \times 12 ft 5% SF-96 on 100-120 Chromosorb W; D, 0.375 in. \times 15 ft 15% FFAP on 45-60 Chromosorb W; E, 0.375 in. \times 15 ft 15% QF-1 on 45-60 Chromosorb W; F, 0.375 in. \times 25 ft 20% Carbowax 20M on 30-60 Chromosorb W.

Materials. Trifluoromethanesulfonic (triflic) acid²³ was purchased from 3M Co. and converted to the anhydride with P₂O₅.^{9,24} Valeraldehyde, diphenylacetaldehyde, 2-phenylpropanal, cyclohexanecarboxaldehyde, and 2-ethylbutanal were purchased from Aldrich Chemical Co., 2-methylbutanal was purchased from Chemical Samples Co., and isobutyraldehyde from MCB; all were distilled prior to use. Ethyl vinyl ether and α -methylstyrene were purchased from Aldrich Chemical Co. and distilled through a Vigreux column, and the center cut was stored over molecular sieves and used as needed. Reagent grade cyclohexene was distilled from P₂O₅ through a Vigreux column and the center cut was stored over molecular sieves and used as needed. Triethylsilane was purchased from Columbia Organic and used without further purification. Commercial samples of 1,2-dimethoxyethane and triethylamine were distilled from LiAlH₄, and dimethylformamide was distilled from CaH₂ and stored under anhydrous conditions. Aldrich technical grade chlorotrimethylsilane was freshly distilled immediately prior to use. Freshly prepared potassium *tert*-butoxide was doubly sublimed or commercial samples were triply sublimed²⁵ at 165° (0.05 mm) stored under anhydrous conditions, periodically resublimed, and used as needed. Methylolithium was purchased from Alfa Chemical Co. and used after standardization.

General Procedure for the Preparation of Trimethylsilyl Enol Ethers.¹⁰ To a solution of 100 ml of dry dimethylformamide and 60.6 g (0.60 mol) of triethylamine in a 500-ml round-bottom flask were added 32.6 g (0.30 mol) of freshly distilled trimethylchlorosilane and 21.5 g (0.25 mol) of 2-methylbutanal. Upon mixing some light yellow solid formed. The reaction mixture was refluxed with stirring for 12 hr during which time copious amounts of solid (presumably Et₃NHCl) formed. The mixture was allowed to cool; then 200 ml of pentane was added and the entire mixture was washed rapidly with three 300-ml portions of cold saturated NaHCO₃. The combined aqueous NaHCO₃ washes were extracted with two 125-ml portions of pentane. The pentane extracts were combined with the organic layer and washed quickly with two 100-ml portions of cold 1.5 N HCl followed by 100 ml of cold saturated NaHCO₃. The pentane layer was dried over MgSO₄ and the solvent distilled through a short Vigreux column. The residual silyl enol ether was vacuum distilled through a Vigreux column yielding 32.8 g (83%) of >98% pure product consisting of a mixture of silyl enol ethers *E*-12a and *Z*-12a, bp 60-62° (48 mm). Column F at 100° showed the mixture to be 60:40 and it was used without separation: nmr (neat, ext. TMS) δ 0.30 (s, 9 H, SiCH₃), 1.17 (t, 3 H, CH₃), 1.73 (m, 3 H, CH₃), 2.17 (m, 2 H, CH₂), 6.26 (m, 1 H, HC=C); ir (neat) 1678 cm⁻¹ (enol C=C).

2,2-Dimethylsilyl Enol Ether (7a). Isobutyraldehyde (18.0 g, 0.25 mol) gave 30.6 g (85%) of product: bp 114-116° (650 mm); nmr (neat, ext. TMS) δ 0.27 (s, 9 H, SiCH₃), 1.69 (m, 6 H, CH₃C=C), 6.15 (sept., *J* = 1.4 Hz, 1 H, HC=C); ir (neat) 1680 cm⁻¹ (enol C=C).

2,2-Diethylsilyl Enol Ether (8a). 2-Ethylbutanal (25.0 g, 0.25 mol) gave 35.0 g (81%) of product: bp 145-147° (650 mm); nmr (neat, int. TMS) δ 0.12 (s, 9 H, SiCH₃), 0.95 (m, 6 H, CH₂CH₃), 1.96 (m, 4 H, CH₂), 6.00 (b s, 1 H, HC=C); ir (neat) 1665 cm⁻¹ (enol C=C).

2-*n*-Propylsilyl Enol Ether (*E*-10a and *Z*-10a). Valeraldehyde (43.1 g, 0.50 mol) gave 55.3 g (70%) of product: bp 30-34° (15 mm); nmr (neat, ext. TMS) δ 0.34 (s, 9 H, SiCH₃), 1.10 (m, 3 H, CH₃), 1.47 (m, 2 H, CH₂), 2.15 (m, 2 H, CH₂), 4.95 (m, 1 H, β -HC=C), 6.35 (m, 1 H, α -HC=C); ir (neat) 1656 cm⁻¹ (enol C=C).

2,2-Methylphenylsilyl Enol Ether (*E*-11a and *Z*-11a). 2-Phenylpropanal (67.1 g, 0.50 mol) gave 85.5 g (83%) of mixture of isomeric products: bp 67-70° (1.0 mm); nmr *E*-11a (neat, ext. TMS) δ

(23) For information, see Minnesota Mining and Manufacturing Co., Technical Information, "FC-24-Trifluoromethanesulfonic acid."

(24) J. Burdon, I. Farazmand, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.*, 2574 (1957).

(25) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis," Vol. I, Wiley, New York, N. Y., 1967.

0.23 (s, 9 H, SiCH₃), 2.10 (d, $J = 1.4$ Hz, 3 H, CH₃), 6.78 (quart, $J = 1.4$ Hz, 1 H, HC=C), 7.33 (m, 5 H, C₆H₅); *Z*-11a (neat, ext. TMS) δ 0.18 (s, 9 H, SiCH₃), 1.95 (d, $J = 1.4$ Hz, 3 H, CH₃), 6.45 (quart, $J = 1.4$ Hz, 1 H, HC=C), 7.25 (m, 5 H, C₆H₅); ir (neat) 1645 cm⁻¹ (enol C=C).

Silyl Enol Ether 13a. Cyclohexanecarboxaldehyde (34.0 g, 0.3 mol) gave 44 g (80%) of product: bp 75–76° (12 mm); nmr (neat, ext. TMS) δ 0.42 (s, 9 H, SiCH₃), 1.80 (m, 6 H), 2.33 (m, 4 H), 6.29 (m, 1 H, HC=C); ir (neat) 1680 cm⁻¹ (enol C=C).

General Procedure for the Preparation of Triflates from Silyl Enol Ethers. To a 500-ml three-necked flask equipped with a N₂ inlet, addition funnel, magnetic stirrer, and condenser with N₂ outlet was added 46.5 ml of 2.3 *M* CH₃Li in ether (0.107 mol). A stream of N₂ gas and a water bath were used to drive off the ether,²⁶ and to the residual white solid was added 225 ml of dry 1,2-dimethoxyethane, together with a few milligrams of Ph₃CH as indicator. The resulting red solution was cooled to -60° by means of a Dry Ice-acetone bath and to it was added 15.8 g (0.10 mol) of the mixture of silyl enol ethers *E*- and *Z*-12a in an equal volume of glyme over a period of 0.5 hr. After the addition was complete, the reaction mixture was stirred for 1.5 hr and allowed to warm to -30°. At the end of this period the light pink solution was recooled to -75° and 32.4 g (0.115 mol) of triflic anhydride was added dropwise over a period of 0.5 hr, at which time the solution turned light yellow. After re-packing of the cold bath the solution was stirred and allowed to warm to room temperature overnight. The reaction mixture was diluted with 250 ml of pentane and extracted with 100 ml of 20% NaHSO₃. The aqueous layer was back extracted with two 150-ml portions of pentane. The combined organic layer was dried over MgSO₄ and the solvent distilled off through a Vigreux column. The residual dark brown liquid was vacuum distilled yielding 13.5 g (62%) of product, bp 67–69° (45 mm), consisting of a 60:40 mixture of the *E* and *Z* triflates 12b.²⁷ The isomers were readily separated on column E at 100°; nmr, *E*-12b (CCl₄, int. TMS) δ 1.09 (trip, $J = 7.0$ Hz, 3 H, CH₃), 1.80 (b s, 3 H, CH₃), 2.10 (quart., $J = 7.0$ Hz, 2 H, CH₂), 6.50 (b s, 1 H, HC=C); ir (CCl₄) 1720 and 1680 (enol C=C), 1248, 1213, 1147, 1020, and 864 cm⁻¹; mass spectrum 218 (M⁺, 23), 73 (10), 69 (64), 67 (11), 57 (45), 55 (19), 53 (18), 43 (100), 41 (85). *Z*-12b nmr (CCl₄, int. TMS) δ 1.10 (trip, $J = 7.5$ Hz, 3 H, CH₃), 1.71 (d, $J = 1.7$ Hz, 3 H, CH₃), 2.27 (quart, $J = 7.5$ Hz, 2 H, CH₂), 6.43 (b s, 1 H, HC=C); ir (CCl₄) 1680 (enol C=C), 1251, 1211, 1150, 1030, and 865 cm⁻¹; mass spectrum 218 (M⁺, 13), 69 (58), 67 (11), 57 (38), 55 (17), 53 (16), 43 (100), 41 (77).

2,2-Dimethyl Triflate (7b). Silyl enol ether 7a (43.2 g, 0.30 mol) gave 32 g (52%) of product: bp 63–66° (72 mm); nmr (neat, ext. TMS) δ 1.65 (b s, 6 H, CH₃), 6.40 (b s, 1 H, HC=C); ir (neat) 1690 (enol C=C), 1220, 1142, 1000 cm⁻¹; mass spectrum 204 (M⁺, 23), 125 (14), 69 (37), 59 (37), 45 (100), 43 (62), 41 (35).

2,2-Diethyl Triflate (8b). Silyl enol ether 8a (8.6 g, 0.05 mol) gave 7.2 g (62%) of product: bp 78–80° (45 mm); nmr (neat, int. TMS) δ 1.03 (t, $J = 7.2$ Hz, 6 H, CH₃), 2.17 (overlap, quart., $J = 7.2$ Hz, 4 H, CH₂), 6.44 (b s, 1 H, HC=C); ir (neat) 1670 (enol C=C), 1215, 1150, 945 cm⁻¹; mass spectrum 232 (M⁺, 8.4), 69 (11), 57 (15), 55 (16), 43 (100), 41 (29), 39 (9).

2-*n*-Propyl Triflate (*E*- and *Z*-10b). Silyl enol ethers 10b (5.1 g, 0.032 mol) gave 2.82 g (40.5%) of product; bp 71–73° (48 mm), consisting of a 60:40 mixture of the *E* and *Z* isomers, respectively, that was separated into the pure isomers by preparative gc on column A at 85°: nmr *E*-10b (CCl₄, int. TMS) δ 0.94 (t, $J = 6.5$ Hz, 3 H, CH₃), 1.46 (m, 2 H, CH₂), 2.07 (m, 2 H, CH₂), 5.75 (t d, $^3J = 12$ Hz, $^4J = 7.1$ Hz, 1 H, β -HC=C), 6.55 (d, $J = 12$ Hz, 1 H, α -HC=C); ir (neat) 1660 (enol C=C), 1208, 1195, 992, 935 cm⁻¹, mass spectrum

218 (M⁺, 7.8), 125 (49.9), 69 (100), 68 (17), 67 (14), 59 (78), 57 (15), 55 (23), 43 (12), 42 (32), 41 (35); for *Z*-10b nmr (CCl₄, int. TMS) δ 0.93 (t, $J = 6.5$ Hz, 3 H, CH₃), 1.47 (m, 2 H, CH₂), 2.22 (m, 2 H, CH₂), 5.25 (t d, $^3J = 5.5$ Hz, $^4J = 7.5$ Hz, 1 H, β -HC=C), 6.55 (d, $J = 5.5$ Hz, 1 H, α -HC=C); ir (neat) 1665 (enol C=C), 1215, 1145, 990, 955 cm⁻¹; mass spectrum 218 (M⁺, 4.7), 125 (42), 85 (10), 69 (100), 68 (25), 67 (20), 59 (59), 57 (19), 55 (24), 43 (13), 42 (39), 41 (36).

2,2-Methylphenyl Triflate (*E* and *Z*-11b). Silyl enol ethers 11b (10.3 g, 0.05 mol) gave 9.4 g (70.5%) of product, bp 41–42° (0.1 mm), consisting of a 85:15 mixture of the *E* and *Z* isomers, respectively, that was separated into the pure isomers by preparative gc on column B at 160°: nmr *E*-11b (CCl₄, ext. TMS) δ 2.44 (d, $J = 1.6$ Hz, 3 H, CH₃), 7.22 (m, 1 H, HC=C), 7.68 (m, 5 H, C₆H₅); *Z*-11b nmr (CCl₄, ext. TMS) δ 2.32 (d, $J = 1.64$ Hz, 3 H, CH₃), 7.01 (m, 1 H, HC=C), 7.68 (m, 5 H, C₆H₅); ir for mixture of *E* and *Z* (neat) 1652 (enol C=C), 1215, 1145, 942, 755, 697 cm⁻¹; mass spectrum *E* and *Z* 266 (M⁺, 13), 133 (44), 121 (32), 119 (95), 117 (100), 105 (98), 103 (17), 84 (18), 82 (28), 79 (20), 77 (27), 69 (12), 51 (11), 49 (9), 47 (28), 43 (17).

Triflate (13b). Silyl enol ether 13a (14.7 g, 0.08 mol) gave 12.3 g (63%) of product: bp 83–86° (18–19 mm); nmr (neat, int. TMS) δ 1.58 (b s, 6 H), 2.20 (m, 4 H), 6.45 (b s, 1 H, HC=C); ir (neat) 1670 (enol C=C), 1205, 1145, 1005 cm⁻¹; mass spectrum 244 (M⁺, 12), 94 (12), 93 (100), 91 (24), 81 (30), 79 (19), 77 (21), 69 (30), 67 (55), 57 (17), 55 (55), 53 (12), 43 (21), 41 (35).

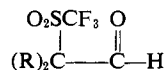
2,2-Diphenyl Triflate (9b). To a 50-ml erlenmeyer flask containing 20 ml of dry pyridine was added 4.0 g (0.02 mol) of diphenylacetaldehyde, closed with a serum cap and cooled to -70° in a Dry Ice-acetone bath. To this solution was added 5.8 g (0.021 mol) of triflic anhydride by means of a syringe, resulting in a white precipitate which turned yellow then red upon standing. The reaction mixture was kept at -20° for 24 hr and then at 0° for 4 days. The entire mixture was poured into 300 ml of ice-water, stirred, and extracted with five 100-ml portions of ether. The combined ether extracts were washed with two 50-ml portions of 10% HCl followed by 50 ml of distilled water and then dried over MgSO₄ and the solvent evaporated. The residue was vacuum distilled yielding 5.3 g (79%) of product: bp 107–109° (0.4 mm); nmr (neat, int. TMS) δ 6.99 (s, 1 H, HC=C), 7.27 (m, 10 H, C₆H₅); ir (neat) 1650 (enol C=C), 1215, 1145, and 952 cm⁻¹; mass spectrum 328 (M⁺, 18), 195 (40), 182 (15), 178 (23), 168 (14), 167 (100), 165 (55), 152 (36), 105 (62), 77 (33), 76 (12), 69 (9), 51 (11).

General Procedure for the Reaction of Primary Vinyl Triflates with *t*-BuOK in Olefins. Into a dry 25-ml round-bottom flask equipped with a magnetic stirrer and serum cap were added 1.5–7.5 mmol of *t*-BuOK (10–50% excess) and 10–20 ml of the appropriate olefin solvent and the mixture was precooled to -20°. To the stirred cold mixture was added 1.0–5.0 mmol of the appropriate triflate with the aid of a syringe and the mixture allowed to warm up to the indicated reaction temperature. Stirring was maintained at the appropriate temperature for the periods indicated in Table I. In most cases the mixture turned slightly yellow to yellow-brown as the reaction proceeded. In the case of nonvolatile solvents (cyclohexene, α -methylstyrene) the reaction mixture was analyzed directly by gc and the products were collected by preparative glc. In the case of the more volatile solvents (isobutylene) an equal volume of pentane was added to the reaction mixture, the volatile solvent was allowed to evaporate at room temperature, and the residual pentane solution was analyzed directly by gc.

Reaction of Triflate 7b with Ethyl Vinyl Ether (Rxn 1). Triflate 7b (5.0 mmol) was reacted in 15 ml of solvent containing 7.5 mmol of base for 1 hr at 0°. The mixture was analyzed on column A at 75° and found to contain 10% of *tert*-butyl vinyl ether, 89% of adduct, and 1% of an unidentified product. The vinyl ether and adduct were collected by preparative gc on column A at 75°. For (CH₃)₂C=CHO-*t*-Bu; nmr (CCl₄, int. TMS) δ 1.22 (s, 9 H, *t*-Bu), 1.55 (s, 3 H, CH₃), 1.57 (s, 3 H, CH₃), 5.94 (m, 1 H, HC=C); ir (CCl₄) 1684 (enol C=C), 1153 cm⁻¹ (C—O); mass spectrum 128 (M⁺, 16), 72 (78), 59 (18), 57 (100), 43 (19), 41 (31); for adduct, nmr (neat, int. TMS) δ 1.08 (m, 2 H), 1.11 (t, $J = 6.8$ Hz, 3 H, CH₃), 1.80 (m, 6 H, 2CH₃C=C), 3.48 (quart., $J = 6.8$ Hz, 2 H, CH₂), 3.61 (m, 1 H); ir (neat) 1782 (C=C), 1124 cm⁻¹ (C—O); mass spectrum 126 (M⁺, 0.9), 111 (83), 97 (31), 83 (9), 79 (15), 69 (37), 67 (32), 55 (28), 53 (16), 43 (32), 41 (100), 39 (23).

Reaction of Triflate 7b with α -Methylstyrene (Rxn 2). Triflate 7b (5.0 mmol) was reacted in 15 ml of solvent containing 7.5 mmol of base for 1.5 hr at 0°. The mixture was analyzed on column A at 110° and found to contain 22% of the *tert*-butyl vinyl ether and 78% of the adduct. The adduct was collected on column A at

(26) It is important to drive off all the ether as well as to maintain the temperature cold throughout the reaction in order to minimize C-alkylation and sulfone



formation. We have found in several preparations where ether drive off was incomplete and/or the reaction carried out above 0° that as much as 10–50% C-alkylation occurred. The small amounts of sulfone formed are readily washed out by the NaHSO₃ washing.

(27) Assignment of isomers was based upon chemical shift; for the *E* isomer the β -methyl and vinylic proton both were at slightly lower field, as expected due to van der Waals deshielding,²⁸ than for the corresponding *Z* isomer.

(28) P. Laszlo and P. J. Stang, "Organic Spectroscopy Principles and Application," Harper and Row, New York, N. Y., 1971.

110°: nmr (neat, int. TMS) δ 1.23 (m, 2 H, cyclopropane), 1.48 (s, 3 H, CH₃), 1.80 (m, 6 H, 2CH₂C=C), 7.18 (m, 5 H, C₆H₅); ir (neat) 1779 (C=C), 1600 (C=C), 763, and 698 cm⁻¹; mass spectrum 157 (100), 143 (15), 142 (51), 141 (20), 130 (10), 129 (42), 128 (26), 115 (29), 91 (12), 77 (18).

Reaction of Triflate 7b with Cyclohexene (Rxn 3). Triflate 7b (5.0 mmol) was reacted in 20 ml of solvent containing 6.0 mmol of base for 24 hr at 0°. The mixture was analyzed on column A at 80° and found to contain 32% of the *tert*-butyl vinyl ether and 68% of the adduct. The adduct was collected on column A at 80°: nmr (neat, int. TMS) δ 1.20 (m, ~3 H), 1.51 (m, ~4 H), 1.77 (m, ~9 H); ir (neat) 1776 cm⁻¹ (C=C); mass spectrum 136 (M⁺, 62), 121 (93), 107 (42), 94 (33), 93 (100), 91 (47), 85 (27), 81 (31), 79 (67), 77 (39), 67 (77), 55 (36), 43 (31), 41 (68).

Reaction of Triflate 7b with Triethylsilane (Rxn 4). Triflate 7b (5.0 mmol) was reacted in 10 ml of solvent containing 6.0 mmol of base for 1.5 hr at 0°. The mixture was analyzed on column A at 130° and found to contain 15% of the *tert*-butyl vinyl ether and 85% of the vinylsilane. The vinylsilane was collected on column A at 120°: nmr (CCl₄, ext. TMS) δ 1.28 (m, 15 H, 3 Et), 2.22 (s, 3 H, CH₃), 2.32 (s, 3 H, CH₃), 5.58 (b s, 1 H, HC=C): ir (neat) 1621 (enol C=C), 1012, 845, 801, and 751 cm⁻¹.

Reaction of Triflate 8b with Ethyl Vinyl Ether (Rxn 5). Triflate 8b (3.0 mmol) was reacted in 20 ml of solvent containing 4.0 mmol of base for 4 hr at 0°. The mixture was analyzed on column C at 118° and found to contain 7% of the *tert*-butyl vinyl ether and 93% of the adduct. The ether and adduct were collected on column A at 100°. For (Et)₂C=CHO-*t*-Bu, nmr (CCl₄, ext. TMS) δ 1.36 (m, 6 H, 2CH₃), 1.60 (s, 9 H, *t*-Bu), 2.40 (m, 4 H, 2CH₂), 6.33 (b s, 1 H, HC=C); ir (neat) 1667 (C=C), 1153 cm⁻¹ (C—O); for adduct, nmr (neat, int. TMS) δ 1.08 (m, 11 H), 2.22 (q, *J* = 7.5 Hz, 4 H), 3.34 (q, *J* = 7.0 Hz, 2 H), 3.58 (m, 1 H); ir (neat) 1773 (C=C), 1127 cm⁻¹ (C—O); mass spectrum 154 (M⁺, 2), 139 (18), 125 (85), 111 (22), 109 (15), 97 (45), 95 (14), 93 (21), 91 (20), 83 (29), 81 (30), 79 (35), 77 (16), 69 (28), 67 (30), 57 (21), 56 (15), 55 (100), 43 (63), 41 (59).

Reaction of Triflate 8b with α -Methylstyrene (Rxn 6). Triflate 8b (3.0 mmol) was reacted in 20 ml of solvent containing 4.0 mmol of base for 4 hr at 0°. The mixture was analyzed on column A at 152° and found to contain 13% of the *tert*-butyl vinyl ether and 87% of the adduct. The adduct was collected on column A at 145°: nmr (neat, int. TMS) δ 0.95 (t, *J* = 7.0 Hz, 3 H, CH₃), 1.12 (t, *J* = 7.0 Hz, 3 H, CH₃), 1.30 (m, 2 H), 1.51 (s, 3 H, CH₃), 2.20 (m, 4 H, 2CH₂), 7.15 (m, 5 H, C₆H₅); ir (neat) 1779 (C=C), 1600 (C=C), 763, and 696 cm⁻¹.

Reaction of Triflate 8b with Cyclohexene (Rxn 7). Triflate 8b (5.0 mmol) was reacted in 20 ml of solvent containing 7.5 mmol of base for 4 hr at 0°. The mixture was analyzed on column C at 91° and found to contain 17% of the *tert*-butyl vinyl ether and 83% of the adduct. The adduct was collected on column A at 120°: nmr (neat, ext. TMS) δ 1.36 (t, *J* = 7.10 Hz, 6 H, 2CH₃), 1.76 (m, 10 H), 2.46 (q, *J* = 7.0 Hz, 4 H, 2CH₂); ir (neat) 1764 cm⁻¹ (C=C); mass spectrum 164 (M⁺, 46), 149 (17.9), 136 (19.1), 135 (88.2), 121 (34.1), 107 (70.6), 95 (27.7), 93 (100), 91 (50.8), 81 (58.8), 79 (82.4), 67 (42.3).

Reaction of Triflate 13b with Ethyl Vinyl Ether (Rxn 8). Triflate 13b (4.0 mmol) was reacted in 15 ml of solvent containing 6.1 mmol of base for 4 hr at 0°. The mixture was analyzed on column A at 140° and found to contain 7% of *tert*-butyl vinyl ether and 93% of the adduct. The ether and adduct were collected on column A at 130° for A (Table I) nmr (CCl₄, int. TMS) δ 1.22 (s, 9 H, *t*-Bu), 1.52 (m, 6 H), 2.03 (m, 4 H), 5.95 (m, 1 H, HC=C); ir (CCl₄) 1678 (enol C=C) and 1141 cm⁻¹ (C—O); for adduct nmr (neat, int. TMS) δ 1.08 (m, 2 H), 1.13 (t, *J* = 6.5 Hz, 3 H, CH₃), 1.57 (b s, 6 H), 2.28 (b s, 4 H), 3.50 (quart, *J* = 6.5 Hz, 2 H, CH₂), 3.67 (m, 1 H); ir (neat) 1779 (C=C) and 1121 cm⁻¹ (C—O); mass spectrum 166 (M⁺, 15), 151 (21), 138 (12), 137 (46), 123 (56), 120 (11), 119 (18), 110 (31), 109 (57), 107 (23), 105 (33), 97 (17), 96 (14), 95 (68), 94 (14), 93 (50), 92 (33), 91 (88), 83 (20), 81 (61), 80 (21), 79 (98), 78 (14), 77 (38), 69 (19), 67 (100), 55 (58), 41 (59).

Reaction of Triflate 13b with Cyclohexene (Rxn 9). Triflate 13b (4.0 mmol) was reacted in 15 ml of solvent containing 6.1 mmol of base for 20 hr at 0°. The mixture was analyzed on column A at 155° and found to contain 23% of the *tert*-butyl ether and 77% of the adduct. The adduct was collected on column A at 140°: nmr (neat, int. TMS) δ 1.25 (m, 4 H), 1.57 (b s, 12 H), 2.25 (b s, 4 H); ir (neat) 1782 cm⁻¹ (C=C); mass spectrum 176 (M⁺, 27.1), 148 (17), 147 (27), 134 (21), 133 (34), 120 (10), 119 (28), 108 (18), 107 (22), 106 (12), 105 (38), 95 (29), 94 (39), 93 (59), 92 (25), 91 (86), 81 (35), 80 (34), 79 (100), 78 (14), 77 (35), 73 (18), 67 (42).

Reaction of Triflates E-10b and Z-10b with Ethyl Vinyl Ether (Rxn 10). A mixture of the *E* and *Z* triflates 10b (3.5 mmol) was reacted in 15 ml of solvent containing 4.3 mmol of base for 3 hr at 0°. The mixture was analyzed on column D at 80° and found to contain only 1-pentyne which was collected: nmr (CCl₄, int. TMS) δ 1.00 (trip, *J* = 7.0 Hz, 3 H), 1.50 (m, 2 H, CH₂), 1.78 (t, *J* = 2.9 Hz, 1 H, HC=C), 2.13 (m, 2 H); ir (CCl₄) 3311 (HC=C) and 2123 cm⁻¹ (C=C).

Reaction of Triflates E-10b and Z-10b with Cyclohexene (Rxn 11). A mixture of the *E* and *Z* triflates 10b (3.5 mmol) was reacted in 15 ml of solvent containing 4.3 mmol of base for 3 hr at 0°. The reaction mixture was analyzed on column D at 80° and found to contain only 1-pentyne.

Reaction of Triflate 9b with Ethyl Vinyl Ether (Rxn 12). Triflate 9b (1.0 mmol) was reacted in 10 ml of solvent containing 1.5 mmol of base for 72 hr at 0°. The mixture was analyzed on column A at 196° and found to contain only diphenylacetylene by coinjection with authentic sample as well as spectral comparison with authentic sample.

Reaction of Triflate 9b with Cyclohexene (Rxn 13). Triflate 9b (1.0 mmol) was reacted in 10 ml of solvent containing 1.5 mmol of base for 72 hr at 0°. The mixture was analyzed on column A at 196° and found to contain only diphenylacetylene.

Reaction of Triflate E-11b with Ethyl Vinyl Ether (Rxn 14). Triflate E-11b (5.0 mmol) was reacted in 15 ml of solvent containing 7.5 mmol of base for 72 hr at 0°. The mixture was analyzed on column A at 90° and found to contain only 1-phenylpropyne by coinjection with authentic sample and spectral comparison with authentic sample. The progress of the reaction was monitored by gc and no interconversion of *E* to *Z* isomer was observed.

Reaction of Triflate E-11b with Cyclohexene (Rxn 15). Triflate E-11b (5.0 mmol) was reacted in 15 ml of solvent containing 7.5 mmol of base for 72 hr at 0°. The mixture was analyzed on column A at 90° and found to contain only 1-phenylpropyne.

Reaction of Triflate Z-11b with Ethyl Vinyl Ether (Rxn 16). Triflate Z-11b (5.0 mmol) was reacted in 15 ml of solvent containing 7.5 mmol of base for 72 hr at 0°. The mixture was analyzed on column A at 90° and found to contain only 1-phenylpropyne by coinjection and spectral comparison with authentic sample. The progress of the reaction was monitored by gc and no interconversion of the *Z* to *E* isomer was observed.

Reaction of Triflate Z-11b with Cyclohexene (Rxn 17). Triflate Z-11b (5.0 mmol) was reacted in 15 ml of solvent containing 7.5 mmol of base for 72 hr at 0°. The mixture was analyzed on column A at 90° and found to contain only 1-phenylpropyne.

Reaction of Triflate E-12b with Isobutylene (Rxn 18). Triflate E-12b (0.3 mmol) was reacted in 1.0 ml of solvent containing 0.44 mmol of base for 36 hr at -20°. The mixture was analyzed on column F at 75° and found to contain four products: **14** (18.8 ± 0.2%), **15** (7.3 ± 0.2%), **16** (42.1 ± 0.3%), and **17** (31.8 ± 0.3%). The products were collected on column F at 85°. For **14** nmr (CCl₄, int. TMS) δ 0.98 (t, *J* = 7.3 Hz, 3 H, CH₃), 1.22 (s, 9 H, *t*-Bu), 1.55 (m, 3 H, CH₃), 1.95 (q, *J* = 7.3 Hz, 2 H, CH₂), 6.00 (m, 1 H, HC=C); ir (CCl₄) 1672 (C=C) and 1148 cm⁻¹ (C—O); for **15** nmr (CCl₄, int. TMS) δ 0.93 (t, *J* = 7.2 Hz, 3 H, CH₃), 1.22 (s, 9 H, *t*-Bu), 1.53 (m, 3 H, CH₃), 2.05 (q, *J* = 7.2 Hz, 2 H, CH₂), 5.93 (b s, 1 H, HC=C); ir (CCl₄) 1675 (C=C) and 1148 cm⁻¹ (C—O); for **16** nmr (CCl₄, int. TMS) δ 0.88 (m, 2 H), 1.05 (m, 3 H, CH₃), 1.15 (s, 6 H, 2 ring CH₃), 1.77 (m, 3 H, CH₂), 2.13 (m, 2 H, CH₂); ir (CCl₄) 1782 cm⁻¹ (C=C); for **17** nmr (CCl₄, int. TMS) δ 0.77 (m, 2 H), 1.06 (m, 3 H, CH₃), 1.15 (s, 6 H, 2 ring CH₃), 1.75 (m, 3 H, CH₃), 2.13 (m, 2 H, CH₂); ir (CCl₄) 1779 cm⁻¹ (C=C). The isomers²⁹ were assigned on the basis of chemical shift and van der Waals deshielding effects.²⁸

Reaction of Triflate Z-12b with Isobutylene (Rxn 19). This reaction was carried out in an identical manner with reaction 18 just described resulting in: **14** (18.8 ± 0.1%), **15** (7.7 ± 0.2%), **16** (41.6 ± 0.3%), **17** (32.0 ± 0.3%).

Preparative Scale Reaction of Triflate 7b with Cyclohexene. To a 100-ml round-bottom flask equipped with a magnetic stirring bar were added 3.4 g (0.03 mol) of *t*-BuOK and 60 ml of cyclohexene and the solution was cooled to -20°. To the cooled mixture was added 5.1 g (0.025 mol) of dimethylvinyl triflate **7b** in 15 ml of cyclohexene over a period of 15 min. The tightly stoppered re-

(29) It should be emphasized that the conclusions are independent of the accuracy of the assignment of product isomers (as well as starting isomers) as long as identical ratios were obtained from either pure starting triflate, which was within experimental error the case.

action mixture was allowed to stir at 0° for 24 hr, during which time the mixture turned orange. At the end of this period the reaction mixture was extracted with 10 ml of H₂O, the aqueous layer was back extracted with three 25 ml portions of pentane, and the combined organic fraction was dried over MgSO₄. The solvents (pentane and cyclohexene) were slowly distilled off at atmospheric pressure through a small Vigreux column. The residue was vacuum distilled yielding two fractions, a forecut 1.1 g, bp 65–80° (45 mm), and a main fraction, 2.8 g, bp 81–83° (45 mm). The forecut was found to contain by gc on column A solvent (mostly cyclohexene) and 19% of the desired products whereas the main cut contained 90% of the desired products (*tert*-butyl vinyl ether and adduct) and 10% of solvent, for an overall yield of 2.7 g (82%) of carbene products. In such a small scale preparation it was impossible to obtain solvent free products by distillation alone without substantial loss in yield.

Preparative Scale Reaction of Triflate 7b with Ethyl Vinyl Ether. To a 100-ml round-bottom flask equipped with a magnetic stirring bar was added 3.5 g (0.031 mol) of *t*-BuOK and 70 ml of ethyl vinyl ether. This reaction mixture together with 5.1 g (0.025 mol) of the pure triflate 7b in a 10-ml addition funnel was allowed to cool to –20° in a cold room. After temperature equilibration the triflate was added to the solvent mixture over a period of 15–20 min during which time the entire mixture turned light yellow and viscous. The mixture was allowed to warm to 0°, stirred for 16 hr and then washed with about 7 ml of cold water. The water was back extracted with two 15-ml portions of ether and the combined organic portion dried over MgSO₄. After removal of solvent through a small Vigreux column at atmospheric pressure the residue was vacuum distilled yielding two fractions, a forecut, 1.2 g, bp 50–61° (50 mm), and a main fraction, 2.4 g, bp 62–67° (50 mm). Gas chromatography (column A at 75°) showed the forecut to be 66.6% solvent and 33.3% product and the maincut to be 88% products (*tert*-butyl vinyl ether and adduct) and 12% solvent for an

overall yield of 2.5 g (79%). Once again due to the small scale nature of the reaction it proved to be impossible to obtain solvent free products by distillation alone without substantial loss in yield.

Reaction of Triflate 7b with *t*-BuOD. To a 10-ml round-bottom flask equipped with a magnetic stirring bar were added 0.168 g (1.5 mmol) of *t*-BuOK and 0.75 g (10 mmol) of *t*-BuOD (90% D by nmr). The stoppered flask was allowed to cool to –20°; then 0.408 g (2.0 mmol) of triflate 7b in 5.0 ml of pentane was added and the solution stirred at 0° for 48 hr. At the end of this period both the unreacted triflate as well as the product *tert*-butyl vinyl ether were collected by preparative gc on column B at 80° and analyzed for deuterium content by both nmr and mass spectroscopy. The recovered triflate was found to contain no deuterium (<1%) within the limits of detection of nmr and mass spectroscopy, whereas the product *tert*-butyl vinyl ether (CH₃)₂C=CH(D)O-*t*-Bu was found to contain 55% H (45% D) by nmr integration and 43.8% D by mass spectroscopy.

Reaction of (CH₃)₂C=CHO-*t*-Bu with *t*-BuOD. To a 5-ml round-bottom flask equipped with a magnetic stirring bar was added 0.084 g (0.75 mmol) of *t*-BuOK and 0.375 g (5.0 mmol) of *t*-BuOD (99% D by nmr) in 1.5 ml. of dry pentane. The flask was cooled to –20° and 0.13 g (1.0 mmol) of *tert*-butyl isobutenyl ether in 1.0 ml of dry pentane was added. The solution was stirred at 0° for 48 hr. At the end of this period the ether was reisolated by preparative gc on column B at 80°. The recovered ether was found to contain no deuterium (<1%) within the limits of detection of nmr and mass spectroscopy.

Acknowledgments. Financial support by the Research Corporation and the University of Utah Research Committee are gratefully acknowledged. We thank Mr. Briant G. Herzog for the preparation of silyl enol ethers 7a and 13a.

Magnetic Circular Dichroism Studies. XXVII.¹ Electronic Structure of Ring-Halogenated Difluorophenylcarbenium Ions

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Abstract: The electronic structure of ring-halogenated difluorophenylcarbenium ions has been investigated by magnetic circular dichroism and absorption spectroscopy. The trends in the observed wavelength shifts for the two lowest excited states, some of which are quite large, are mostly accounted for by considering the benzyl cation self-consistent orbitals and assuming a first-order mesomeric effect.

Carbocations² are important intermediates in many organic chemical reactions, particularly isomerization, polymerization, surface catalytic reactions, and Friedel–Crafts reactions of hydrocarbons.

Early studies of carbocations were hindered by the fact that much of this work utilized concentrated sulfuric acid which, in addition to the carbocations, also produced decomposition products or allowed side reactions (sulfonation). By using highly acidic superacids and low nucleophilicity solvent systems (such as SO₂ and SO₂ClF) at low temperature, Olah and others³

have been able to measure the physical properties (nmr, ir, uv, Raman, and ESCA) of many carbocations, a series of studies which have produced significant contributions to the understanding of organic ion chemistry. Here we wish to focus attention on absorption spectroscopy, and its more selective counterpart magnetic circular dichroism (MCD) spectroscopy.⁴

Previous optical studies on carbocations^{3b} have been handicapped by the above mentioned experimental difficulties and by the fact that overlapping bands occur

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