Unsaturated Carbenes from Primary Vinyl Triflates. 9. Intramolecular Rearrangement via Free Carbenes[1]

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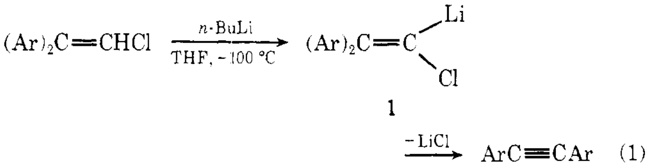
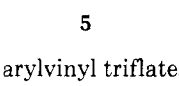
The Fritsch–Buttenberg–Wiechell (FBW) rearrangement of diarylhaloethylenes to diarylacetylenes upon treatment with strong bases has been known since the 1890's.[2,3] Although this rearrangement was recognized as an α-elimination involving a sextet rearrangement by the original discoverers, the exact mechanism and the nature of the intermediate was not firmly established until some 60 years later. By means of elegant C-14 labeling studies, Bothner-By[4] and Curtin and co-workers[5] have shown a strong trans stereochemical requirement for aryl migration and thereby clearly established that the rearrangement proceeds via an organometallic intermediate and carbenoid and not the free unsaturated carbene. Subsequently, Köbrich and co-workers[6] were able to demonstrate the existence and unambiguous involvement of organolithium 1 in these rearrangements in THF at low temperatures (eq 1). Similarly, 1-halo-2-phenylpropene has been shown to give only 1-phenylpropyne upon treatment with strong base.[7] Once again, Köbrich and co-workers[3,8] unambiguously established the carbenoid nature and the involvement of an organolithium compound in this reaction as well.



$$(Ar)_2C{=}CHCl \xrightarrow[\text{THF, -100 °C}]{n\text{-BuLi}} \underset{\mathbf{1}}{(Ar)_2C{=}C\begin{matrix}\diagup Li\\ \diagdown Cl\end{matrix}} \xrightarrow{-LiCl} ArC{\equiv}CAr \quad (1)$$

Recently there has been considerable interest in unsaturated carbenes[9] 2 generated via base-promoted α-elimination from primary vinyl halides 3 or vinyl triflates 4 and base-promoted decomposition of *N*-nitrosooxazolidones 5. Moreover, it has been established that the vinyl halide-derived species is a carbenoid whereas the triflate 4 derived intermediate is in fact the free carbene.[10,11] Furthermore, analogous to the FBW reaction, arylvinyl triflates[12] as well as aryloxazolidones[13] give arylacetylenes as sole products. Hence, it was of interest to examine the mechanism and exact nature of the intermediates in the base-initiated rearrangement of arylvinyl triflates and specifically to ascertain if the reaction proceeds via a carbenoid, analogous to the FBW reaction, or the unencumbered carbene, similar to the behavior of the dialkyl species 2.[10]

$(R)_2C{=}C:$ **2** $(R)_2C{=}CHX$ **3** $(R)_2C{=}CHOSO_2CF_3$ **4**



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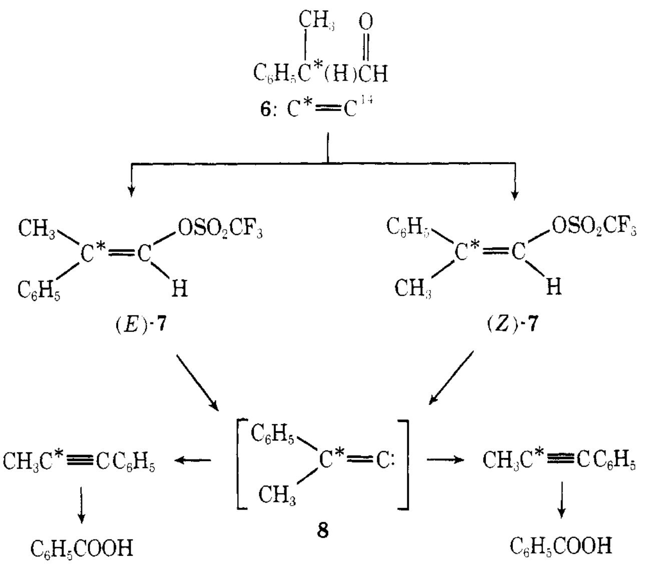
In order to investigate and answer this question, we prepared C-14 labeled (*E*)- and (*Z*)-2-phenylpropenyl triflates 7. Vinyl triflates (*E*)- and (*Z*)-7 were prepared from the corresponding labeled 2-phenylpropanal 6 by known methods and separated by gas chromatography.[12] Labeled 2-phenylpropanal was prepared from the known[14] carbonyl-labeled acetophenone-^{14}C via the procedure of Allen.[15]

Scheme I



Reaction of each pure (*E*)- and (*Z*)- triflate with 50% excess *t*-BuOK in a mixture of dry pentane and glyme for 24 h at −20 °C gave phenylpropyne[16] as the sole product collected by preparative gas chromatography, respectively. In order to determine the location of the C-14 label, and hence the stereochemical requirements of this rearrangement, the product phenylpropyne from each reaction was oxidized[17] to benzoic acid by $KMnO_4$ as shown in Scheme I. The resultant benzoic acids were assayed along with the respective precursor acetylenes and triflates.[18] The complete lack of activity in *both* acids indicates that the alkyne products had to arise via a nonstereoselective process and hence a common intermediate derived from the two isomeric starting triflates. Since prior control experiments[12] had established that the starting isomeric vinyl triflates do not interconvert, these results are only compatible with a free carbene intermediate, 8, rather than a carbenoid. Either a carbenoid or some type of organometallic intermediate would have been expected to show a stereochemical preference for migration and hence an unequal distribution of labels in the resulting alkynes as has been observed by Bothner-By[4] and Curtin[5] in the FBW reaction.

Hence, analogous to the behavior of the alkylidene carbenes as a function of progenitors,[10] there is a clear-cut difference in the intramolecular rearrangement of aryl-substituted unsaturated carbenes; with the reaction proceeding via a carbenoid in the case of arylvinyl halides and most likely the free carbene in the case of arylvinyl triflates.[20]

Experimental Section

Preparation of ^{14}C Labeled 2-Phenylpropanal (6). Carbonyl-labeled acetophenone-^{14}C,[14] 27.7 g (231 mm), was converted to phenylmethylglycidic ester in 62% yield and used in the preparation of 6 to give 12.5 g (65%) of product[16] according to Allen.[15]

Preparation of (*E*)- and (*Z*)-7 Vinyl Triflates. Carbon-14 labeled 2-phenylpropanal, (6) 11.8 g (88 mm), was converted to a mixture of the isomeric (*E*)- and (*Z*)-vinyl triflates 7 via their silyl enol ethers in 50% overall yield according to procedures previously reported.[12] The *E* and *Z* isomers were separated by preparative GC on a 15 ft by 0.375 in. 15% QF-1 column at 130 °C and identified by spectral means.[12,16]

Reaction of (*E*)- and (*Z*)-7 Vinyl Triflates. Each pure isomer was reacted according to the following general procedure. To a 5-mL round-bottom flask, equipped with a magnetic stirring bar and a serum cap, were added 0.269 g (2.4 mm) of sublimed *t*-BuOK and 1.5 mL of an 80:20 mixture of dry pentane and glyme. The reaction mixture was cooled in a dry ice–acetone bath and 0.425 g (1.6 mm) of the pure triflate, dissolved in 1.0 mL of the above pentane–glyme

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mixture, was added over a 15-min period. The mixture was allowed to warm to −20 °C and stirred for 24 h. At the end of this period, the dark-orange reaction mixture was poured into 10 mL of pentane and washed with four 1-mL portions of H_2O, the aqueous layer back-extracted with 10 mL of pentane, and the combined pentane solution was dried over $MgSO_4$. The pentane was distilled and the product phenylpropyne[16] was collected by preparative GC on the above column in 56% yield (104 mg).

Oxidation of Phenylpropyne to Benzoic Acid. The product phenylpropyne from each pure isomeric vinyl triflate was oxidized according to the following general procedure.[17] Into a 25-mL round-bottom flask equipped with a magnetic stirring bar and reflux condenser was added 4 mL of H_2O, 0.41 g (2.6 mmol) of $KMnO_4$, and 38 mg of Na_2CO_3 followed by 75 mg (0.65 mmol) of the phenylpropyne. The entire mixture was stirred for 1 h at room temperature and then refluxed for about 3 h until the purple color had completely vanished. After cooling, 0.5 mL of 50% H_2SO_4 was slowly added, the mixture was refluxed for 0.5 h and then cooled, and the brown MnO_2 was decomposed with $NaHSO_3$. The solution was made strongly acidic by the addition of 0.5 mL of 50% H_2SO_4 and after cooling in an ice bath the white precipitate was filtered. The filtrate was washed with cold water and the crystals allowed to air dry. The resulting benzoic acid was doubly sublimed to yield 35 mg (44%) of product which was assayed[18] for radioactivity along with each precursor phenylpropyne and vinyl triflate.

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Registry No.—6, 64188-89-2; (*E*)-7, 64162-87-4; (*Z*)-7, 64162-86-3; phenylpropyne-^{14}C, 64162-88-5; acetophenone-^{14}C, 5821-66-9; ethyl phenylmethylglyudate, 64162-89-6.

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(18) C-14 assay was done according to B. M. Tolbert and W. E. Siri, "Techniques in Organic Chemistry", A. Weissberger, Ed., 3rd ed, Vol. 1, part IV, Interscience, New York, N.Y., 1960, pp 3431–3432. The starting aldehyde **6** *had an activity of* 4.60 ± 0.05 *mCi/mol, the resultant triflates*[19] 4.33 ± 0.12 mCi/mol, the alkyne from (*E*)-**7** 4.63 ± 0.06 mCi/mol, and from (*Z*)-**7** 4.57 ± 0.03 mCi/mol; the benzoic acids from both series had less than 0.5% activity.

(19) Fluorine interferes with this method of assay, hence, the lower precision and activity of the triflates.

(20) The possible rapid equilibration of (*E*)- and (*Z*)-carbenoids prior to rearrangement can not be ruled out, nor easily probed experimentally. The possibility of a *large* difference in migratory aptitude (in favor of phenyl) overwhelming any tendency toward stereochemical selectivity can be ruled out by the observation of alkyl migration and acetylene formation in certain dialkylvinyl triflates $R(CH_3)C = CHOTf$ under similar conditions.[21]

(21) Unpublished observations, D. P. Fox.

Reaction of Pentafluorosulfur Bromide with *cis*- and *trans*-1,2-Difluoroethylene

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The incorporation of pentafluorosulfur groups into hydrocarbons was first accomplished by Case et al. in reactions of pentafluorosulfur chloride with olefins and chloroolefins under free-radical conditions.[1] Similar results were later obtained by Gard and coworkers in reactions with pentafluorosulfur bromide with olefins, but under more facile conditions.[2] In some recent work in this laboratory, we have also noted a distinct difference in the reactivity of SF_5Cl and SF_5Br toward olefins,[3] as well as in the ability of SF_5Br itself to add to various substituted olefins.[4] Such behavior has prompted an investigation into the mechanism by which SF_5Br adds to unsaturated systems.

We have found that pentafluorosulfur bromide reacts with *cis*- and *trans*-1,2-difluoroethylene to give the erythro and threo forms of the addition product $SF_5CHFCHFBr$. The relative amounts of conformers produced are very similar for each olefin and are essentially identical for reactions carried out in the presence or absence of light as shown in Table I. This indicates that the reactions are not stereospecific and suggests that they are occurring via the same radical intermediate in all systems. Dehydrobromination of the addition products yields a mixture of *cis*- and *trans*-$SF_5CF{=}CFH$.

Structural assignments of the erythro and threo diastereomers have been made on the basis of a comparison of vicinal fluorine coupling constants obtained from proton-decoupling experiments in the C–F region of the fluorine NMR spectra. In one compound, a multiplet was found to collapse to two overlapping pentets arising from coupling between the vicinal fluorine atoms and between one of these fluorines and the SF_4 group. The second multiplet in the same spectrum collapsed to two doublets that were formed from coupling between vicinal fluorines and between one of the fluorine atoms and the axial fluorine in the SF_5 group. From these data, the vicinal fluorine coupling constant in this compound was determined to be 37 Hz. Similar proton decoupling in the second compound resulted in a vicinal fluorine coupling of 13 Hz. The larger coupling constant was assigned to the trans arrangement of the fluorine atoms found in the erythro structure **1a,** in accordance with the Karplus rule that relates the size of the coupling constant to the dihedral angle between coupled species.[5] Similarly, the smaller F–F coupling constant was assigned to the gauche arrangement of fluorine atoms in the threo compound in **1b.** Additional fluorine and proton NMR data are contained in Table II.

Dehydrobromination of the *erythro*- and *threo*-$SF_5CHFCHFBr$ diastereomers yielded mixtures of *cis*- and *trans*-$SF_5CF{=}CFH$. The predominant formation of the cis isomer from the erythro compound and the trans isomer from the threo compound is consistent with an antiperiplanar arrangement of the hydrogen and bromine atoms to be eliminated. The presence of a second isomer in each reaction, as indicated by a cis–trans ratio of 4:1 for erythro and 0.4:1.0 for threo, suggested that some syn elimination was occurring as well. The trans olefin underwent isomerization to the more stable cis form in good yields (77%) at 125 °C. This isomerization is consistent with previous work that has shown the *cis*-1-fluoro-2-haloolefins to be more stable than the trans isomer.[6] Structural assignments of the olefins are based on the greater intensity of the olefin-stretching vibration in the infrared spectrum, as expected, for the less symmetrical cis