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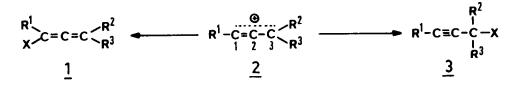
ORIENTATION EFFECTS IN REACTIONS OF ALLENYL CATIONS WITH STYRENE

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Abstract: Allenyl cations, generated <u>in situ</u> from allenyl or alkynyl halides and Ag<sup>+</sup>, attack styrene at the side chain or at the aromatic nucleus. The allenyl/alkynyl product ratio is dependent on the structure of the precursor halide except for highly substituted systems.

Allenyl (= alkynyl) cations ( $\underline{2}$ ) are ambident electrophiles and react with X<sup>-</sup> to yield either allenyl ( $\underline{1}$ ) or alkynyl ( $\underline{3}$ ) products. Solvolysis studies show that attack at C<sup>3</sup> is generally kinetically preferred, unless R<sup>2</sup> and R<sup>3</sup> are bulky substituents.<sup>1</sup> Since we are interested in employing allenyl cations for organic syntheses,<sup>2</sup> we have studied their reactions with styrene in order to determine how substituents influence the site of attack.



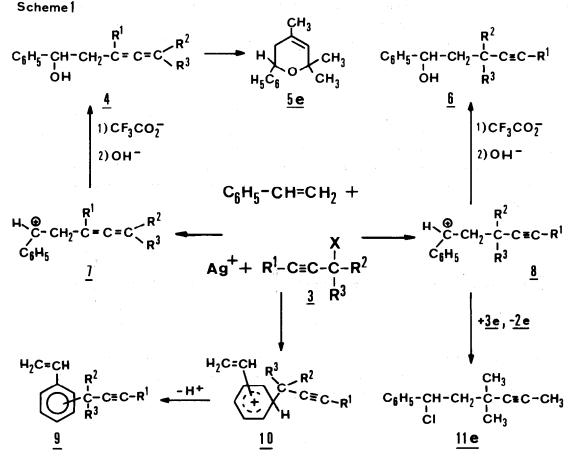
When solutions of the alkynyl halides  $\underline{3a} - \underline{3e}$  in styrene were treated with silvertrifluoroacetate<sup>3</sup> at room temperature and worked up with methanolic KOH, 1:1 products were isolated in 17 - 34% yield (Table 1).<sup>4</sup> The side products arise from addition of trifluoroacetate to <u>2</u>.

R <sup>1</sup>	R <sup>2</sup>	r <sup>3</sup>	х	Alkynyl Derivatives	Allenyl Derivatives	Carbene Adducts	Total Yield of 1:1 Products
<u>a</u> : H	Н	Н	Br	<u>6a</u> (46%), <u>9a</u> (54%) <sup>a</sup>			20%
<u>ь</u> : сн <sub>з</sub>	н	Н	Br	<u>6b</u> (40%), <u>9b</u> (60%)			34%
<u>с</u> : Н	CH3	Н	Br	<u>6c</u> (57%), <u>9c</u> (11%)		<u>13c</u> (32%)	17%
<u>d</u> : Н	CH3	CH3	C1	<u>6d</u> (5%)	<u>4d</u> (40%)	<u>13d</u> (55%)	20%
<u>e</u> : CH <sub>3</sub>	СНЗ	СНЗ	C1	<u>6e</u> (60%), <u>11e</u> (31%)	<u>5e</u> (9%)		17%

Table 1: Product Ratio of the Reaction of Styrene with Alkynylhalides and  $AgCF_{3}CO_{2}$ 

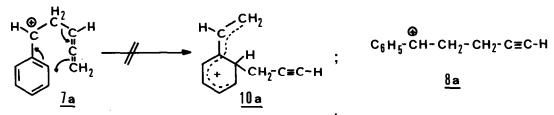
a) ortho : meta : para = 54 : 11 :  $35^5$ 

Scheme 1 rationalizes the formation of the reaction products. The homoallenyl alcohol  $\underline{4d}$  and the acetylenic alcohols  $\underline{6a} - \underline{6e}$  are generated by addition of  $CF_3CO_2^-$  to the intermediate benzyl cations  $\underline{7}$  and  $\underline{8}$ , respectively, and subsequent hydrolysis. Alternatively, the benzyl cation  $\underline{8e}$  can abstract chloride from  $\underline{3e}$  to yield <u>11e</u> and the relatively stable trimethyl-allenyl cation <u>2e</u>. Alcohol  $\underline{4e}$  is not stable under work-up conditions and cyclizes to the dihydropyrane <u>5e</u>.

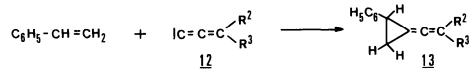


The observation of ring substituted styrenes  $\underline{9a} - \underline{9c}$  was unexpected, since electrophilic attack at styrene usually occurs at the side chain. $\overline{}^{6}$  Formation of these products through a Cope type rearrangement (Scheme 2) can be excluded: Generation of <u>7a</u> from 5-chloro-5phenyl-1,2-pentadiene and  $AgCF_3CO_2$  gave exclusively the homoallenyl alcohol <u>4a</u> after hydrolysis. Kinetic product control is thus confirmed. Since the benzenium ion 10a (paraisomer) is 17 kcal/mol less stable than the benzyl cation 8a according to MINDO/3 calculations,<sup>7</sup> 8 and 10 must be formed <u>via</u> an early transition state, so that their large energy difference has little effect on the activation energy.

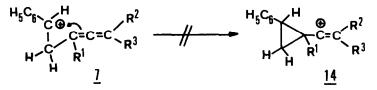
## Scheme 2



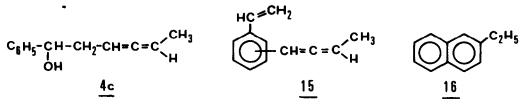
Deprotonation of initially formed allenyl cations (2,  $R^1$  = H) to vinylidene carbenes (12) and the cycloaddition reactions of the latter with styrene  $\frac{1}{8}$  account for the formation of the vinylidene cyclopropanes 13.



An alternative mechanism, homoallenyl rearrangement  $\underline{7} \rightarrow \underline{14}^9$  can be excluded, since directly generated 7c did not give cyclopropyl compounds under these conditions. Furthermore cyclopropyl ketones arising from trifluoroacetate addition to 14 have never been observed.



The alkynyl halides 3d and 3e can be replaced by their allenyl isomers 1 as starting materials without changing the allenyl/alkynyl product ratio significantly.<sup>10</sup> In contrast, 1-bromo-1,2-butadiene (1c) gave predominantly the allenyl derivatives 4c (27%), 15 (17%), and 16 (10%),<sup>11</sup> whereas the products obtained from 3c were only formed in minor amounts, 14% 6c, 20% 10c, and 2% 13c. Bromo- and iodopropadiene did not react under these conditions



Therefore, isomeric allenyl and alkynyl halides with a low degree of substitution do not react <u>via</u> common intermediates. The structure of the starting halides is largely retained in the reaction products, as shown by the exclusive formation of alkynyl products from <u>3a</u>, <u>3b</u>, and <u>3c</u> and the preferred formation of allenyl products from <u>1c</u>. Nucleophilic assistance of CX cleavage by styrene or ion pairing may account for this effect. The reactions of the di- and trimethylsubstituted systems, however, can proceed with complete propargyl-allenyl rearrangements.

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## References and Notes:

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- All compounds shown in Table 1 were separated by layer chromatography and identified by spectroscopic methods.
- 5. The isomer ratio was determined by catalytic hydrogenation and gaschromatographic comparison with authentic ethylpropylbenzenes.
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- Because of better accessibility, 1-bromo-3-methyl-1,2-butadiene and 2-iodo-4-methyl-2,3-pentadiene were employed.
- β-Ethylnaphtalene can form through cyclization of ortho-<u>15</u> or its precursor ion and successive hydrogen shifts.

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