

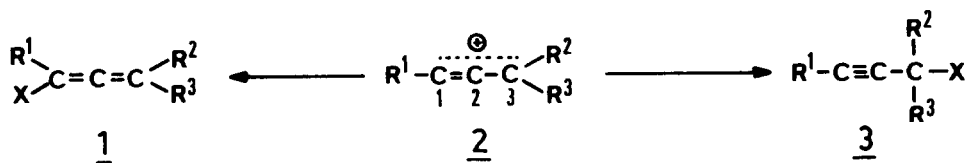
ORIENTATION EFFECTS IN REACTIONS OF ALLENYL CATIONS WITH STYRENE

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Abstract: Allenyl cations, generated *in situ* from allenyl or alkynyl halides and Ag^+ , 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 (2) are ambident electrophiles and react with X^- to yield either allenyl (1) or alkynyl (3) products. Solvolysis studies show that attack at C^3 is generally kinetically preferred, unless R^2 and R^3 are bulky substituents.¹ Since we are interested in employing allenyl cations for organic syntheses,² we have studied their reactions with styrene in order to determine how substituents influence the site of attack.



When solutions of the alkynyl halides 3a - 3e in styrene were treated with silvertrifluoroacetate³ at room temperature and worked up with methanolic KOH, 1:1 products were isolated in 17 - 34% yield (Table 1).⁴ The side products arise from addition of trifluoroacetate to 2.

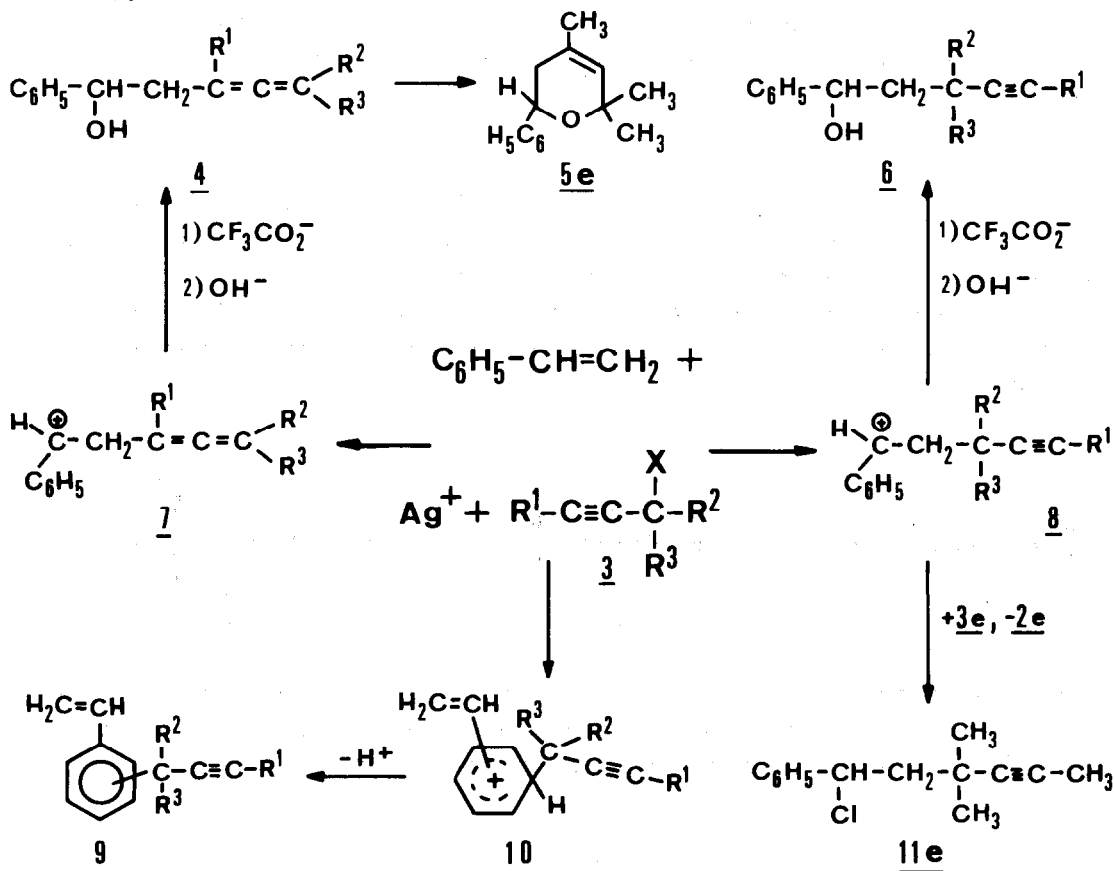
Table 1: Product Ratio of the Reaction of Styrene with Alkynylhalides and AgCF_3CO_2

R^1	R^2	R^3	X	Alkynyl Derivatives	Allenylyl Derivatives	Carbene Adducts	Total Yield of 1:1 Products
<u>a</u> : H	H	H	Br	<u>6a</u> (46%), <u>9a</u> (54%) ^a			20%
<u>b</u> : CH_3	H	H	Br	<u>6b</u> (40%), <u>9b</u> (60%)			34%
<u>c</u> : H	CH_3	H	Br	<u>6c</u> (57%), <u>9c</u> (11%)		<u>13c</u> (32%)	17%
<u>d</u> : H	CH_3	CH_3	Cl	<u>6d</u> (5%)	<u>4d</u> (40%)	<u>13d</u> (55%)	20%
<u>e</u> : CH_3	CH_3	CH_3	Cl	<u>6e</u> (60%), <u>11e</u> (31%)	<u>5e</u> (9%)		17%

a) ortho : meta : para = 54 : 11 : 35⁵

Scheme 1 rationalizes the formation of the reaction products. The homoallynyl alcohol 4d and the acetylenic alcohols 6a - 6e are generated by addition of CF_3CO_2^- to the intermediate benzyl cations 7 and 8, respectively, and subsequent hydrolysis. Alternatively, the benzyl cation 8e can abstract chloride from 3e to yield 11e and the relatively stable trimethylallenylyl cation 2e. Alcohol 4e is not stable under work-up conditions and cyclizes to the dihydropyrene 5e.

Scheme 1



Therefore, isomeric allenyl and alkynyl halides with a low degree of substitution do not react via 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 3a, 3b, and 3c and the preferred formation of allenyl products from 1c. 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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3. On the effect of silver counterion cf. H.M.R. Hoffmann, G.F.P. Kernaghan, and G. Greenwood, J. Chem. Soc. B 1971, 2258.
4. 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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10. Because of better accessibility, 1-bromo-3-methyl-1,2-butadiene and 2-iodo-4-methyl-2,3-pentadiene were employed.
11. β -Ethylnaphtalene can form through cyclization of ortho-15 or its precursor ion and successive hydrogen shifts.

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