

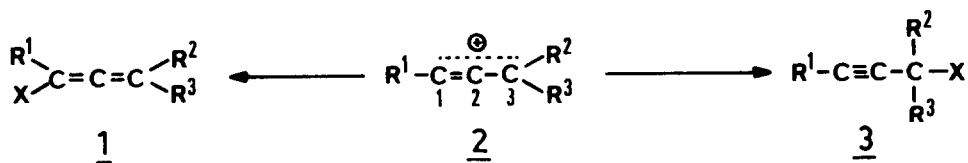
ORIENTATION EFFECTS IN REACTIONS OF ALLENYL CATIONS WITH STYRENE

Herbert Mayr*, Bärbel Grubmüller, and Inge K. Halberstadt

Institut für Organische Chemie der Universität Erlangen-Nürnberg
Henkestr. 42, D-8520 Erlangen

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.

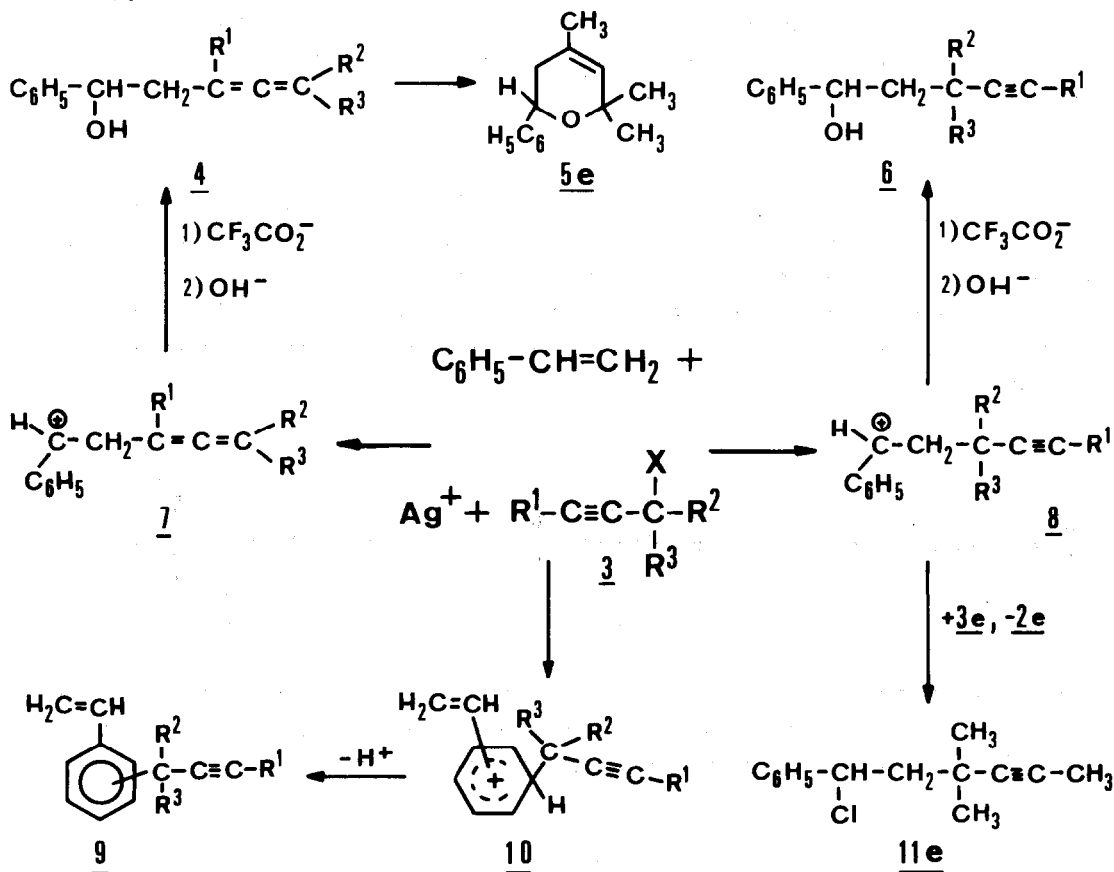
Table 1: Product Ratio of the Reaction of Styrene with Alkynylhalides and AgCF_3CO_2

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

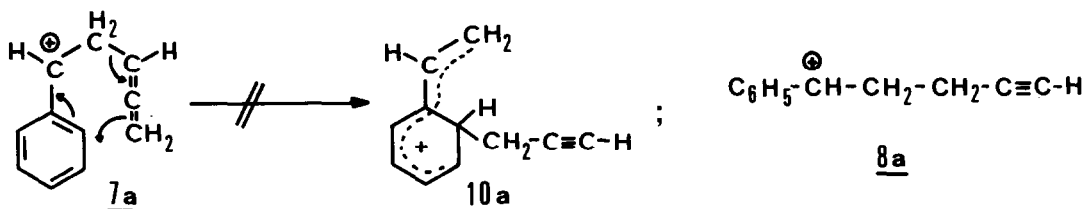
Scheme 1 rationalizes the formation of the reaction products. The homoallenyl alcohol 4d and the acetylenic alcohols 6a - 6e are generated by addition of CF_3CO_2^- to the intermediate benzyl cations 7 and 8, respectively, and subsequent hydrolysis. Alternatively, the benzyl cation 8e can abstract chloride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

Scheme 1

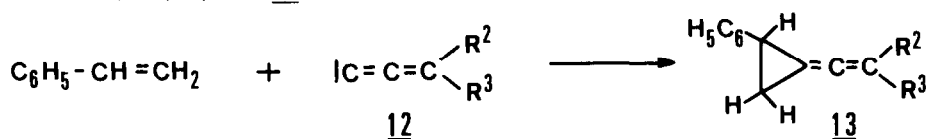


The observation of ring substituted styrenes 9a - 9c was unexpected, since electrophilic attack at styrene usually occurs at the side chain.⁶ Formation of these products through a Cope type rearrangement (Scheme 2) can be excluded: Generation of 7a from 5-chloro-5-phenyl-1,2-pentadiene and AgCF_3CO_2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

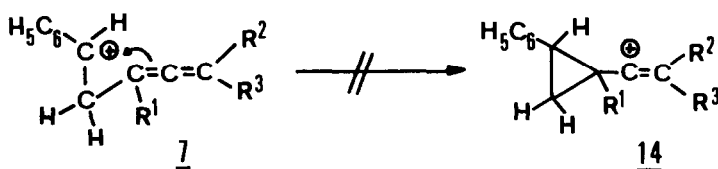
Scheme 2



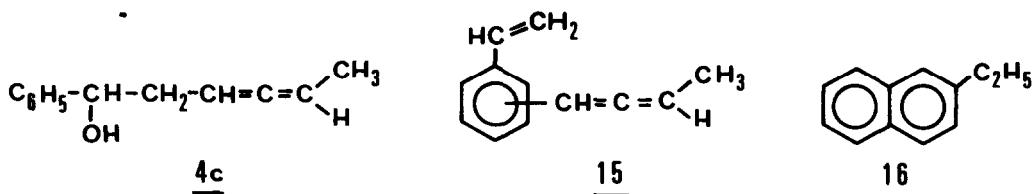
Deprotonation of initially formed allenyl cations (2, $\text{R}^1 = \text{H}$) to vinylidene carbenes (12) and the cycloaddition reactions of the latter with styrene⁸ account for the formation of the vinylidene cyclopropanes 13.



An alternative mechanism, homoallenyl rearrangement 7 \rightarrow 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.¹⁰ In contrast, 1-bromo-1,2-butadiene (1c) gave predominantly the allenyl derivatives 4c (27%), 15 (17%), and 16 (10%),¹¹ 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 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.

Support of this work by the Deutsche Forschungsgemeinschaft is gratefully acknowledged. We thank Prof. P.v.R. Schleyer for discussions.

References and Notes:

1. M.D. Schiavelli, T.C. Germroth, and J.W. Stubbs, J. Org. Chem., 41, 681 (1976) and references cited therein.
2. H. Mayr and B. Grubmüller, Angew. Chem., 90, 129 (1978); Int. Ed. Engl., 17, 130 (1978).
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.
6. G.A. Olah in "Friedel Crafts and Related Reactions", Vol I, G.A. Olah, Ed., Interscience, New York, 1963, p. 903.
7. R.C. Bingham, M.J.S. Dewar, and D.H. Lo, J. Am. Chem. Soc., 97, 1285 (1975).
8. H.D. Hartzler, J. Am. Chem. Soc., 83, 4990 (1961); P.J. Stang, Chem. Rev., 78, 383 (1978).
9. M. Hanack and J. Häffner, Tetrahedron Lett., 1964, 2191; Chem. Ber., 99, 1077 (1966); M. Bertrand and M. Santelli, Tetrahedron Lett., 1969, 2511, 2515.
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.

(Received in Germany 7 March 1979)