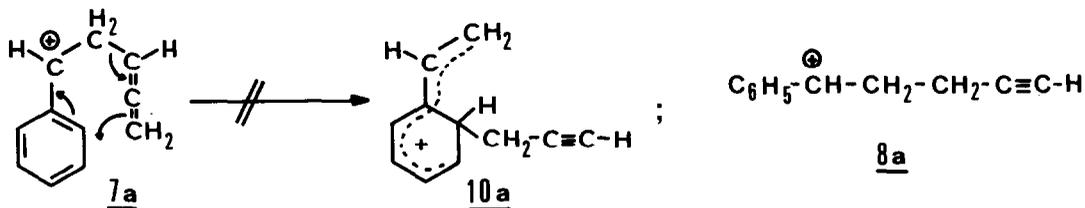
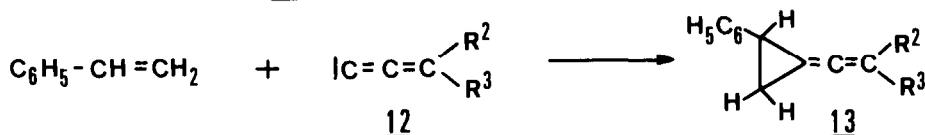


The observation of ring substituted styrenes 9a - 9c was unexpected, since electrophilic attack at styrene usually occurs at the side chain.⁶ Formation of these products through a Cope type rearrangement (Scheme 2) can be excluded: Generation of 7a from 5-chloro-5-phenyl-1,2-pentadiene and AgCF_3CO_2 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.

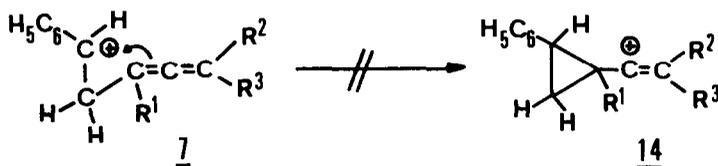
Scheme 2



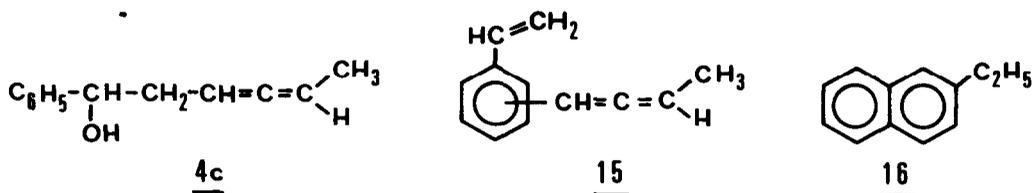
Deprotonation of initially formed allenyl cations (2, $\text{R}^1 = \text{H}$) to vinylidene carbenes (12) and the cycloaddition reactions of the latter with styrene⁸ account for the formation of the vinylidene cyclopropanes 13.



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.

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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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