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THE ADDITION OF 1,2-CYCLOHEXADIENE TO SUBSTITUTED STYRENES.

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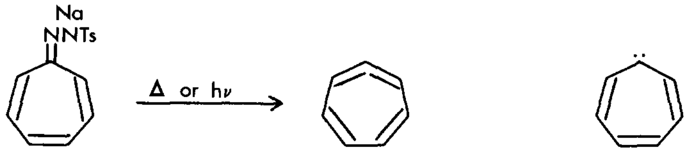
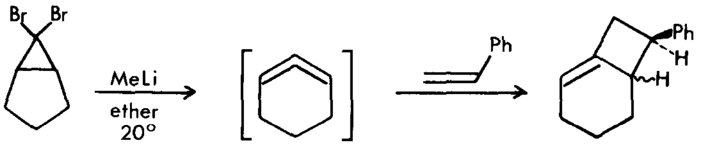
Abstract: 1,2-Cyclohexadiene (4) undergoes addition to a series of substituted styrenes with a Hammett ρ value of +0.79. Deuterium labelling shows the addition is stepwise.

The involvement of 1,2,4,6-cycloheptatetraene (1) in the thermolysis or photolysis of the sodium salt of tropone tosylhydrazone (2) has been indicated by reports from several research groups.[1] We concluded that the previously proposed cycloheptatrienylidene (3) was actually a planar transition state for the interconversion of chiral, nonplanar 1 and its enantiomer.[1c] Since the nucleophilicity of the C_7H_6 intermediate, as shown by its positive Hammett ρ value (+1.0) in its addition to a series of substituted styrenes, was taken as early evidence for the intermediacy of 1,[2] it was decided to study the addition of an authentic strained allene [1,2-cyclohexadiene (4)[3]] to substituted styrenes.



2 1 3

The addition of 4 to styrene itself has been reported to give a 2.2:1 mixture of (*E*) and (*Z*)-5.[3b,4] The Hammett study was conducted by generating 4 in the presence of at least a ten-fold excess of a mixture of styrene and a substituted styrene. Gas chromatographic analysis provided the product ratio.[5] With the knowledge of the starting ratio of styrenes,[5] the relative rates of reaction were calculated according to the formula on the following page. The plot of k_{rel} vs. σ is shown in Figure 1.[6,7]



4 5

$k_{rel} = k_X/k_H = (P_X/P_H)(I_H/I_X)$ where X = sustituted styrene, H =styrene;
(P_X/P_H) = product ratio, (I_H/I_X) = initial styrene ratio

The least-squares ρ value (+0.79) indicates 4 is acting as a nucleophile in its addition to styrene but its small magnitude would indicate a small amount of charge separation in the transition state or, perhaps, that the experiments were being carried out near the isokinetic temperature.[8] The latter point was not checked. The nucleophilic addition of 4 to styrene is consistent with what was found for 1.[2]

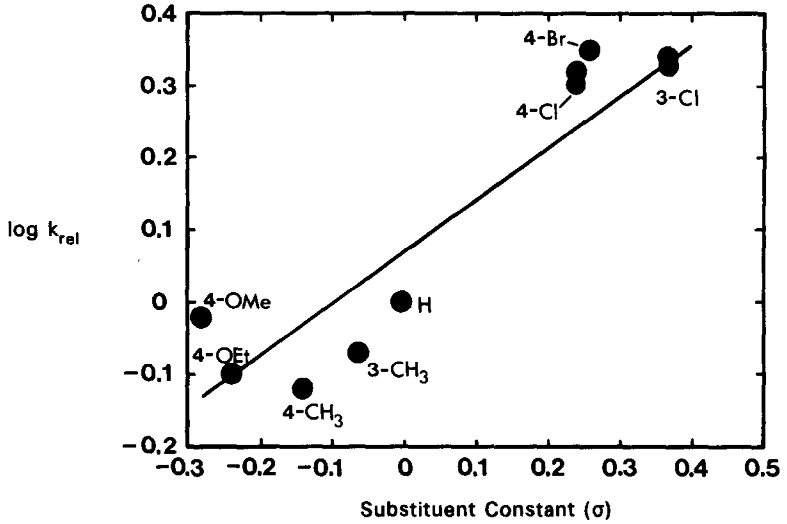
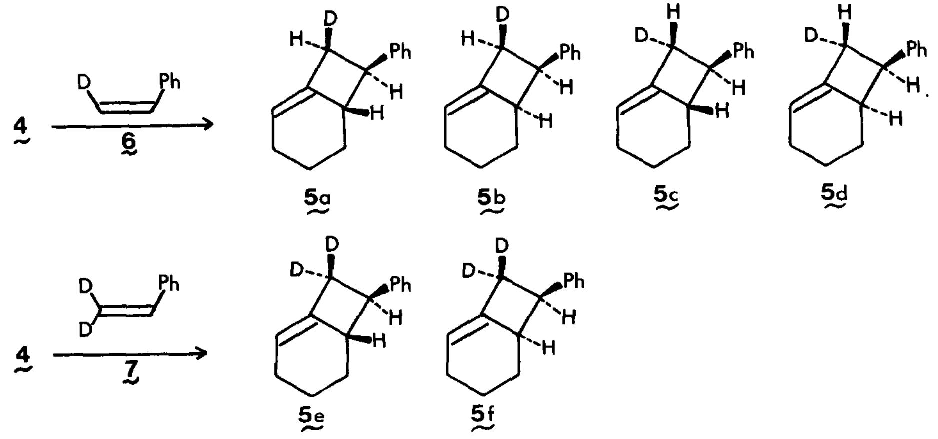
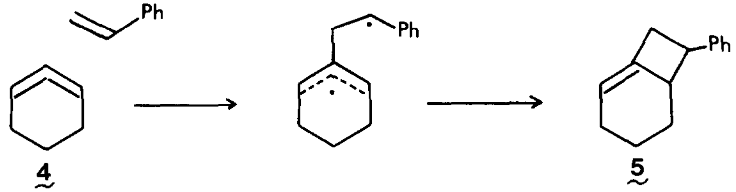


Figure 1. Plot of log k_{rel} vs. σ for the reaction of 4 with substituted styrenes.[6]

The addition of 4 to styrene could occur by a concerted $_{\pi}2_s+(_{\pi}2_s+_{\pi}2_s)$[9] or stepwise mechanism. This was studied with the use of *cis*-β-deuterostyrene (6) and proton-decoupled deuterium (^{2}D) magnetic resonance spectroscopy. If the reaction was concerted, only two ^{2}D resonances due to 5a and 5b should be found. If the reaction was stepwise, four ^{2}D resonances should be observed (5a-d). In order to determine



the chemical shifts of these four types of ^{2}D, the reaction of 4 with β,β′-dideuterostyrene (7) was carried out. This material (5e-f) gave the NMR spectrum shown in Figure 2.[10] The ^{2}D NMR spectrum of the product of 4 with 6 is also shown in Figure 2 and is seen to be essentially identical with the product which has the ^{2}D in all possible positions (5e-f). Thus, the reaction of 4 with styrene is stepwise and probably diradical in character in view of the small ρ value found above. Positive ρ values of the magnitude found in the present work have also been reported for the reaction of alkyl radicals with substituted toluenes.[11]



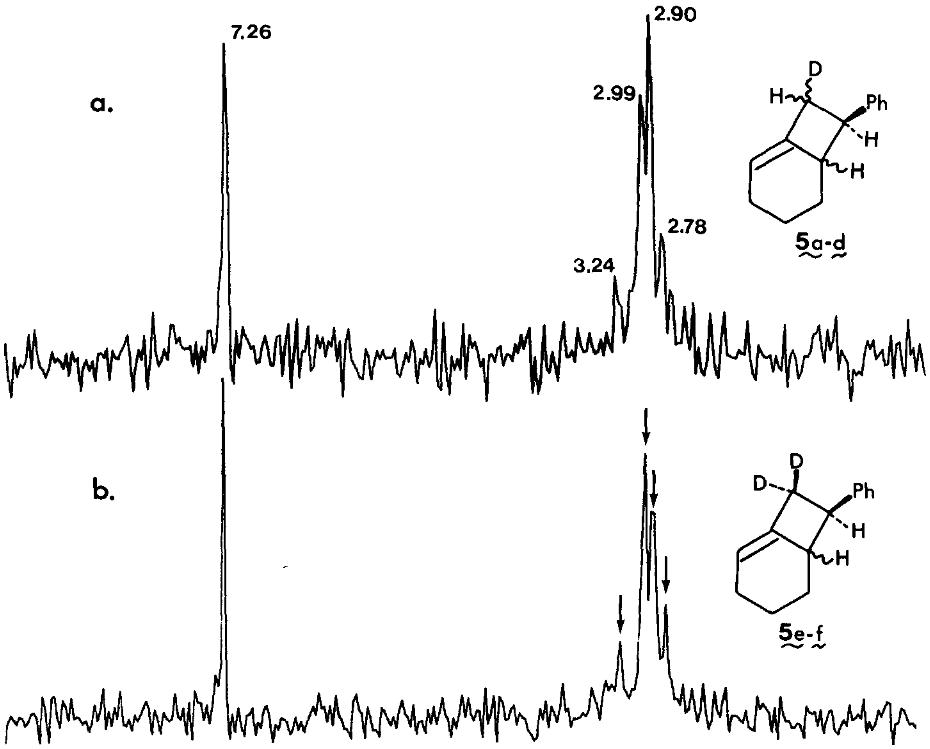


Figure 2. Proton-decoupled ^{2}D NMR spectra (61.4 MHz) of 5 derived from 6 (a) and from 7 (b).[10] The solvent was $CHCl_3$. The chemical shifts are reported in δ units and are measured relative to the internal standard $CDCl_3$ which was set at 7.26 ppm.

Acknowledgment

Financial support from a Murdock Charitable Trust Grant of the Research Corporation and University of Montana Faculty and Graduate Student Research Grants is sincerely appreciated. We also thank the MONTS-NSF project (ISP-8011449) for funds which were used in the purchase of a 270 MHz NMR spectrometer which was used in this project. The ^{2}D NMR spectra were recorded at the South Carolina Magnetic Resonance Laboratory (NSF CHE-8207445). We thank Mr. Darren Hollenbaugh for conducting experiments which showed that 4-(N,N-dimethylamino)styrene should not be used in this study.

References and Footnotes

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4. The formation of the mixture of (*E*) and (*Z*)-**5** does *not* demand a stepwise mechanism.

5. The pure adducts were individually prepared and used to calibrate the detector response of the gas chromatograph. The styrene ratios did not change significantly throughout the reaction as determined by GLPC. The amounts of the *E* and *Z* product from a given styrene were combined for the calculation of k_{rel}.

6. The substituent constants (σ) were taken from J. March, "Advanced Organic Chemistry," 3rd. Ed., Wiley-Interscience, New York, p. 244 (1985). The values of k_{rel} are 2.13 and 2.08 (3-chloro), 2.22 (4-bromo), 2.00 and 2.11 (4-chloro), 0.85 (3-methyl), 0.76 (4-methyl), 0.80 (4-ethoxy), and 0.95 (4-methoxy).

7. Attempts to extend the plot with 4-(N,N-dimethylamino)styrene failed since the generation of 4 by the above method formed methyl bromide which reacted to produce the N,N,N-trimethylammonium substituted styrene.

8. For a discussion of the isokinetic point, see T. H. Lowery and K. S. Richardson, "Mechanism and Theory in Organic Chemistry," 2nd Ed., Harper and Row, New York, p. 142 (1981).

9. D. J. Pasto, *J. Am. Chem. Soc.*, **101**, 37 (1979).

10. The spectra were obtained without lock and using the lock coil for observation. The ^{2}D NMR spectra were also taken at 13.7 MHz using a lithium chloride lock. These spectra showed the 2.78 and 3.24 ppm peaks as shoulders on a strong peak at about 2.93 ppm.

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