Ethylenic Compounds Reactivity: Bromination. XXXVII. Comparison of Alkenes and β-Substituted Styrenes

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The bromination reactivities of *trans*-styrenes $C_6H_5C_\alpha H=C_\beta HR$ (R = alkyl or heteropolar) are related to those of the corresponding alkenes $C_\alpha H_2=C_\beta HR$ by a linear equation with a slope of 0.75. The styrene–ethylene pair lies off this regression. These results imply that the distribution of charge in the transition state is different for both these families. Consideration of log k *vs.* σ^* correlations for styrenes favors a transition state polarity corresponding to that of a carbonium ion with the charge located on C_α.

While the hypothesis that the intermediate in the bromination of ring-substituted styrenes is a carbonium ion (with or without weak Br–C$^+$ interaction) is well supported by data on the reaction products and on the sensitivity of the reaction to substituents on the ring, the case of styrenes with substituents on the double bond is less clear and, in particular, a bromonium ion intermediate or a competition between two carbonium ions has been considered for β,β-dimethylstyrene.[1] Moreover, whereas until now it was generally accepted[2] that the transition state was similar in structure to the intermediate, Yates and Mac Donald[3] propose in a recent study a bromonium-like transition state followed by a carbonium ion intermediate for arylethylenes. The need is thus felt for a direct investigation, therefore based on kinetic measurement, of the nature of the transition state for such compounds. To this end we had studied polar effects on the reactivity of a series of β-substituted styrenes *trans*- C$_6$H$_5$CH=CHR; we now wish to report these results and to compare them with those obtained previously for a set of analogous alkenes CH$_2$=CHR.

Results

To be comparable with previous work[4] the kinetic measurements were performed in methanol. Bromination rate constants follow[5] eq 1 in which k is the rate constant at a

$$k(1 + K[\text{Br}^-]) = k_{\text{Br}_2} + \beta[\text{Br}^-] \quad (1)$$

bromide ion concentration [Br$^-$]; K is the equilibrium constant for the formation of tribromide ion Br$_2^-$ + Br$^-$ $\rightleftarrows$ Br$_3^-$; k_{Br_2} is the rate constant for the addition of molecular bromine; β is a term whose mechanistic interpretation is controversial[6] but is often equated with $Kk_{\text{Br}_3^-}$, where $k_{\text{Br}_3^-}$ is the rate constant for the addition of Br$_3^-$.

Values of k_{Br_2} and $k_{\text{Br}_3^-}$ for different substituents R are listed in Table I. The values of $Q = k_{\text{Br}_2}/k_{\text{Br}_3^-}$ are much greater than unity and are consistent with the idea that Br$_2$ and Br$_3^-$ react simultaneously, the latter being less electrophilic. The value of Q varies very little, so that the following equation is obeyed

$$\log k_{\text{Br}_3^-} = +0.96 \log k_{\text{Br}_2} - 1.48 \quad (2)$$

(correlation coefficient R = 0.995; standard deviation on the slope = 0.04). Thus any reactivity–structure relationship applicable to the reactivity of one of those electrophiles can readily be transposed to the other. It is therefore enough to discuss one series of constants only, and we have chosen k_{Br_2} whose meaning is unambiguous. It should be noted that constancy of Q has already been observed for aliphatic olefins in methanol.[6,7] The Q values, albeit slightly greater for styrenes than for alkenes, are of the same order of magnitude. Rolston and Yates[1] have, on the other hand,

obtained totally different results (Q variable and even less than unity) for the addition of bromine to ring-substituted styrenes in acetic acid. This remark confirms that there is no analogy between Q values measured in different solvents; this disparity was noted previously in a study of the reactivity of aliphatic olefins in methanol and in water.[8]

Discussion

Comparison of Styrenes and Alkenes. Rather than attempt to compare the styrene reactivities directly with a scale of substituent effects, we prefer first of all to relate these data to those of a reference family CH$_2$=CHR, very close to the family in question. In this way the most possible of the extrastructural parameters (nature of the reaction, solvent, temperature) are held constant; thus errors due to faults in external scales of substituent constants are avoided and it is possible to exploit directly mechanistic information available for the reference family. In the present case, studies of the kinetics[9] and the products[10] of the reaction in methanol confirm that a mechanism with a bromonium ion intermediate is of general validity for the CH$_2$=CHR series.

With the exception of the particular case of the styrene–ethylene pair which we shall discuss later, the reactivities of the styrenes and the alkenes are linearly related by

$$\log k_{\text{Br}_2}(trans\text{-}C_6H_5CH=CHR) =$$
$$0.75 \log k_{\text{Br}_2}(CH_2=CHR) + 1.62 \quad (3)$$

(R = 0.997; standard deviation on the slope = 0.025). Since the alkenes follow a single reaction mechanism the linearity of the correlation implies that the nature of the effect of R is identical for both families. It has been shown in the case of alkenes that, for the substituents chosen, only their polar effects are involved; steric effects are excluded.[9b] As the value of the slope in (3) expresses the ratio of the sensitivities of each family to the substituent effect, the charge in the case of styrenes must be either lower or further from the substituent R than in the case of alkenes.

We can suggest a bromonium-like transition state with part of the charge delocalized on the carbons for alkenes and for styrenes a carbonium ion-like transition state where the charge is on C_α. In the second case charge is further from the substituent R than in the case of alkenes. To the extent to which the results obtained by Olah, *et al.*, for stable ions in superacid media can be transposed to methanolic media, they support the existence of such structures. According to those authors the alkylethylene bromonium ions are stabilized[11,12] by the resonance forms –C$^+$R^1–CBrR^2– and –CBrR^1–C$^+$R^2–. The interpretation of the ^{13}C nmr data regarding bromine participation in benzylic structures is, however, rather delicate; having found that the bromine atom clearly took part in the stabilization of

Table I
Reactivity of β-Substituted Styrenes, trans-C_6H_5CH=CHR in Methanol at 25°

Compd	R	$k_{Br_2}{}^a$	$k_{Br_3}{}^{-a}$	Q^b
1	$-C_2H_5$	4.29×10^3	1.22×10^2	35
2	$-CH_3{}^c$	3.26×10^3	8.27×10^1	39
3	$-H^d$	1.53×10^3	4.40×10^1	35
4	$-CH_2OH$	1.01×10^3	1.93×10^1	52
5	$-CH_2OCH_3$	2.68×10^2	6.36	42
6	$-CH_2OCOCH_3$	5.59×10	1.28	44
7	$-CH_2Cl$	1.17×10	4.55×10^{-1}	26
8	$-CH(OCOCH_3)_2$	1.41		

^{a} k_{Br_2} and $k_{Br_3}{}^-$ (in M^{-1} sec^{-1}) are calculated by (1) from the rate constants measured at different NaBr concentrations (see Experimental Section). ^{b} $Q = k_{Br_2}/k_{Br_3}{}^-$. ^{c} J.-E. Dubois and M. de Ficquelmont-Loïzos, unpublished results. ^{d} M. de Ficquelmont-Loïzos, Doctoral Thesis No. AO 8355, Paris, 1973.
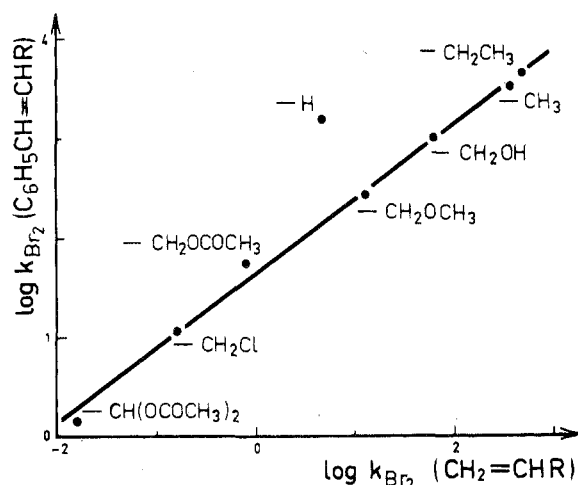

Figure 1. Styrene–alkene correlation. Each point corresponds to a substituent R indicated on the graph. Styrene data are from Table I; alkene data are from Table II and ref 6 and 17.

the ions $ArC^+(CH_3)CH_2Br$,[13] Olah, *et al.*, now conclude that bromine bridging plays only a minor role.[14] We shall now show that our hypothesis is substantiated by consideration of reactivity *vs.* polar effect correlation.

Reactivity *vs.* Polar Effect Correlation. Reactivity must be related to the polar effect of the substituent *directly* attached to the atom bearing charge in the transition state. In our hypothesis this atom is C_β for alkenes and C_α for styrenes; thus log k_{Br_2} is to be plotted *vs.* $\sigma_R{}^*$ for alkenes and *vs.* $\sigma_{CHBrR}{}^*$ (or more simply $\sigma_{CH_2R}{}^*$)[15] for styrenes. Our preceding results[9b] show that in the case of alkenes a linear relationship is observed between log k_{Br_2} and $\sigma_R{}^*$.

$$\log k_{Br_2} = -3.10\sigma_R{}^* + 8.80 \qquad (4)$$

In the case of the styrene family, if we plot reactivity against $\sigma_R{}^*$, styrene (R = H) lies 1.5 log units above the regression line;[16] if we plot reactivity against $\sigma_{CH_2R}{}^*$, a satisfactory linear relationship including styrene itself is obtained.

$$\log k_{Br_2} = -4.80\sigma_{CH_2R}{}^* + 3.23 \qquad (5)$$

$$(R = 0.982)$$

σ^* values are taken from ref 15a; when necessary a transmission coefficient of 0.43[17] has been applied for heteropolar substituents. If $\sigma_R{}^*$ was linearly related to $\sigma_{CH_2R}{}^*$ for all substituents, the two regressions for styrenes would be equivalent. But the attenuation coefficient of the polar effect for heteropolar substituents is not valid for alkyl ones.[18] This fact can explain why the point corresponding to R = H fits one regression and not the other and conse-

quently why the couple styrene–ethylene lies off correlation 3.

The expected sequence[19] is $|\rho^*|$ (carbonium intermediate) $> |\rho^*|$ (bridged intermediate), since in the second case the charge is dispersed over the atoms making up the bridged ion. This sequence is observed here. The ρ^* value of -4.80 for styrenes is close to the values of ρ and ρ^+ determined for addition reactions with carbonium ion intermediates implying structures XC_6H_4CH=CH_2 or XC_6H_4CH=CHC_6H_4Y very similar to that which we are studying. For the bromination of styrenes[20] and stilbenes,[21] and for the hydration of styrenes,[22] the values of ρ^+ (bromination) and of ρ (hydration) are -4.3, -5.0, and -4.0, respectively. These comparisons confirm the proposal that the polarity of the bromination transition state for β-substituted styrenes is analogous to that of a carbonium ion and not a bromonium ion.

Resonance Contribution of Phenyl Rings. One can compare the β-substituted styrenes with α-methylstyrene, where the methyl substituent is directly attached to the C_α and can only favor the arylcarbonium intermediate, and with *trans*-stilbene, for which carbonium and bromonium ion pathways are of similar importance.[21b] In the case of α-methylstyrene, the benzene ring is no longer in the plane of the C=C double bond[23,24] and this compound can be expected to be of diminished reactivity. The experimentally observed reactivity (log k_{Br_2} = 5.21) is indeed slightly less than the value calculated from eq 5.[25] This difference (0.51 kcal mol^{-1}) is consistent with the angle of rotation given by Suzuki.[23] The resonance contribution to the reactivity of styrene[26] is about 2.2 kcal mol^{-1}. Following a rotation of the benzene ring out of the plane of the double bond through an angle Φ, this contribution is multiplied by the factor[27] $\cos^2 \Phi$. The corresponding energy decrease is 0.65 kcal mol^{-1} which is to be compared with the value of 0.51 kcal mol^{-1} observed. In the case of *trans*-stilbene two identical carbonium ion intermediates are possible but the statistical correction is counterbalanced by the correction due to the presence of a bromonium ion path which is about as important as the carbonium path.[21b] The reactivity of *trans*-stilbene by carbonium ion path is 1.2 log units less than that calculated from eq 5. Both for styrenes and *trans*-stilbene resonance between the ring attached to C_α and the double bond is replaced in the transition state by a greater resonance energy between the ring and the electron deficient C_α. However, in the case of *trans*-stilbene the additional resonance energy existing in the ground state between the double bond and the ring attached to C_β is considerably decreased in the transition state. According to Wheland,[28] comparison of the resonance energies of benzene, styrene, and stilbene suggests that a value of 3–4 kcal mol^{-1} can be attributed to the resonance energy of the double bond with one of the benzene rings. This energy corresponds to 2.2–2.9 log units when expressed in terms of log

Table II
Rate Constants at Different NaBr Concentrations at 25° in MeOH $(M^{-1} \ sec^{-1})$

R	NaBr 0.05	NaBr 0.10	NaBr 0.20
	A. β-R-Substituted Styrenes		
$-C_2H_5$	5.46×10^2	3.45×10^2	2.37×10^2
$-CH_2OH$	1.18×10^2	7.33×10^1	4.62×10^1
$-CH_2OCH_3$	3.28×10^1	2.04×10^1	1.35×10^1
$-CH_2OCOCH_3$	6.78	4.22	2.77
$-CH_2Cl$	1.58	1.06	7.62×10^{-1}

	0.05	0.10	0.20	k_{Br_2}	$k_{Br_3^-}$
	B. Others				
$C_6H_5C(CH_3)=CH_2{}^a$	1.85×10^4	1.09×10^4	6.77×10^3	1.62×10^5	2.39×10^3
$CH_2=CHCH_2OCH_3{}^b$	1.98	1.38	1.06	1.31×10	7.17×10^{-1}
$CH_2=CH_2{}^c$				4.65	

Registry no. [a] 98-83-9. [b] 627-40-7. [c] 74-85-1.

k, and this is compatible with the deviation observed, since this energy is not reduced completely to zero in the transition state.

In a recent study on the bromination of 1,2-disubstituted ethylenes, Yates and Mac Donald[3] find that steric constraints in cis isomers are increased in the transition state. They propose, therefore, for all the compounds studied including those with a phenyl substituent that the transition state is bromonium ion like. A similar dichotomy between steric and polar data has already been noted in a related addition reaction, the Prins reaction of β-methyl styrenes.[29] It seems that in order to reconcile the two sets of data it is necessary to abandon pure carbonium and bromonium ions as transition state models and to adopt a more flexible representation. Currently available results on the bromination of α-arylethylenes suggest that the transition state has the following characteristics: polarity analogous to that of an α-aryl α-bromocarbonium ion, but spatial layout analogous to that of the CTCE[30] which precedes the transition state along the reaction coordinate, without free rotation about the BrC–C+ bond.

Experimental Section

Chemicals. Compounds 5, 6, and 8 were prepared as described previously.[31-33] Other compounds were obtained commercially. Compounds were purified by vapor-phase chromatography on $AgNO_3$ or DEGS columns except for ethylene which was used without further purification, compounds 4 and 7 which were distilled at reduced pressure, and compound 8 which was recrystallized from petroleum ether. Methanol was dried by distillation over Mg and was then twice distilled over Br_2.

Kinetic Measurements. Except for α-methylstyrene where the couloamperometric method[34] was used the rate constants were determined by potentiometry[35,36] at different Br^- concentrations (Table II). The variation of the potential E of the electrode Pt, $Br_2|Br^-$ relative to a calomel reference electrode is measured as a function of time. Bromine is produced in the medium by electrolysis of NaBr. Initial Br_2 concentrations are in the range 2×10^{-5}–1×10^{-4} M. Pseudo-first-order conditions are obtained by using an olefin/bromine ratio greater than 20. The rate constants are calculated by the expression $k_2 = -78.2 \ dE/[(a - b)dt]$, where a and b are the initial concentrations of olefin and bromine and E is the emf in millivolts. The standard deviation (between different determinations and the mean value) is in all cases less than 2.5%. The rate constants k_{Br_2} and $k_{Br_3^-}$ are calculated from eq 1 by the least-squares method applied to all the experimental data (not mean values). The standard deviation is about 2% on k_{Br_2} and about 3% on $k_{Br_3^-}$.

The rate constant k_{Br_2} is particularly small for ethylene and compound 8 and was determined directly in the absence of NaBr by titration. The bromine is neutralized by a buffered As_2O_3 solution and the back titration by electrolytically generated I_2 is performed amperometrically. The measurements can in this case be falsified by the production of Br^- during the reaction (formation of solvent incorporated product). In view of the concentrations used the amount of Br^- produced on the end of the reaction could

be as much as 4×10^{-4} M. This would correspond to a rate constant at most 7% less than k_{Br_2}. However, no indication of any regular curvature can be seen in the log $[(a - x)/(b - x)]$ vs. time plots and the systematic error of the experimental value relative to k_{Br_2} is very probably much less than 7%. These two rate constants are slightly less reproducible than those measured by potentiometry: the standard deviation is 3.6 and 4.8% respectively for ethylene and compound 8. The constants are, however, obtained without extrapolation. Whereas in all other cases the initial olefin concentration is determined by weighing, the ethylene concentration is determined indirectly. If there is excess Br_2 the initial ethylene concentration is reckoned to be the difference between the initial and final Br_2 concentrations; if there is excess ethylene a methanolic ethylene solution is titrated against Br_2.

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Reaction of Carbethoxynitrene with Allenes[1]

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Carbethoxynitrene, from base-catalyzed α elimination of N-(p-nitrobenzenesulfonoxy)urethane (9), reacts with allene and 1,1-dimethylallene to produce 1,2-cycloaddition products. Tetramethylallene fails to produce an adduct with the nitrene. The results appear to be most consistent with a cycloaddition mechanism in which the initial step is reaction of triplet nitrene with a terminal carbon atom of the allenic moiety. The thermal isomerization of 2-isopropylidene-N-carbethoxyaziridine (14) to 2-ethoxy-5,5-dimethyl-4-methylene-2-oxazoline (5b) is described.

The reaction of various types of carbenes or carbenoids with allenes has been investigated and proceeds in an unexceptional fashion to yield methylenecyclopropanes regardless of whether the divalent carbon species is in a singlet or triplet spin state.[2,3] In view of the recent interest in the chemistry of nitrenes,[5] isoelectronic analogs of carbenes, it is somewhat surprising that the corresponding reaction of this species with allenes has received only cursory examination. Thus, the sole reported investigation of this type of reaction is that of Bleiholder and Shechter in which they studied the thermally induced reaction of ethyl azidoformate (1) with tetramethylallene (2) and the photochemically initiated reaction of 1 with 1,1-dimethylallene (3).[6] The thermal process afforded the triazoline 4 (38%) and the isopropylideneoxazoline 5a (29%) as addition products;

4

5   6

a, R = CH₃
b, R = H

the photochemical reaction produced the methyleneoxazoline 5b (47%) as the only reported product. The N-carbethoxyaziridines, 6, products that might have been anticipated if allenes were to behave toward nitrenes as do carbenes, were not observed in either experiment.

Whereas photolysis of 4 was found to yield 5a (43%), thermolysis did not promote this transformation; thus 5a potentially represented a primary product of reaction of carbethoxynitrene with tetramethylallene. Two mechanistic pathways for formation of 5a appeared to be reasonable, viz., 1,3-dipolar cycloaddition of the nitrene to tetramethylallene to generate 5a directly (eq 1) or 1,2 cycloaddition

5a   (1)
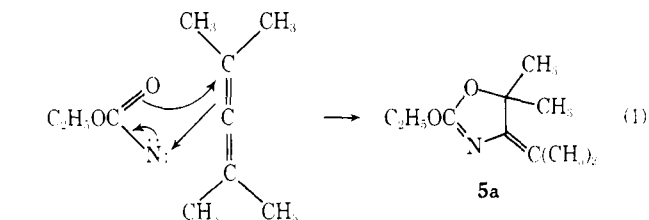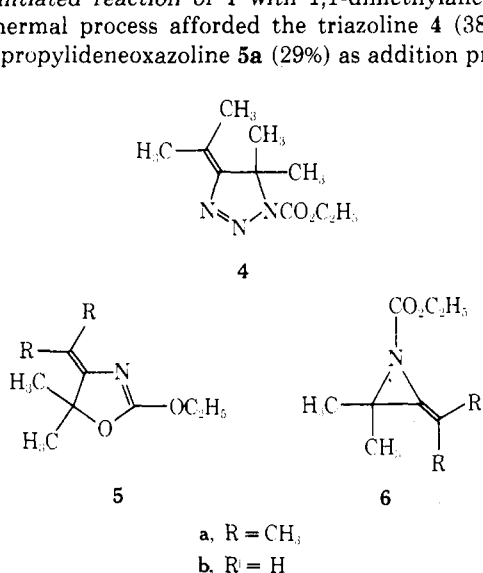
between the nitrene and the allene to produce 6a, which in turn underwent a [1,3]-sigmatropic isomerization to 5a (eq 2). Since the pathway involving 1,3-dipolar cycloaddition was without precedent in nitrene chemistry, Bleiholder and Shechter favored the second alternative (eq 2), a suitable analogy for the rearrangement of 6a being the reported thermal conversion of the aziridine 7 to the oxazoline 8 (eq 3).[7]

We have reinvestigated the reaction of carbethoxynitrene with allenes under conditions more conducive not only to isolation of alkylideneaziridines, should they be formed, but also to the extension of such studies to triplet