

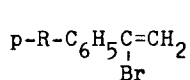
MESOMERIC VINYL CATIONS

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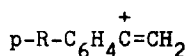
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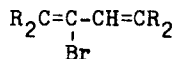
Our earlier finding that vinyl cations 2 are intermediates in the solvolysis of α -bromostyrenes (1) raised the question whether 2-bromo-1,3-butadienes of type 3 would similarly ionize to mesomeric vinyl cations 4 in polar solvents ¹⁾. In these cations the allylic double bond could assume the role of an electron donor. This has now been demonstrated by rate and product studies with the conjugated bromodienes, 2-bromo-4-methyl-1,3-pentadiene (5), trans-(6) and cis-3-bromo-5-methyl-2,4-hexadiene (7), and 3-bromo-2,5-dimethyl-2,4-hexadiene (8) (Table 1) ²⁾.



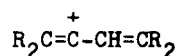
(1)



(2)



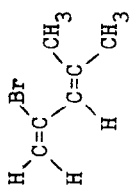
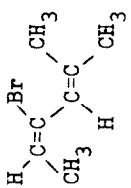
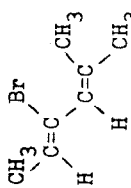
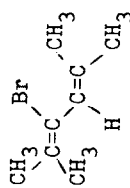
(3)



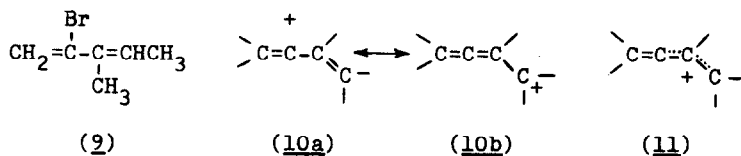
(4)

These compounds show remarkable reactivity as shown by their first order rate constants in 80 vol.% ethanol (Table 1). The rates are insensitive to the addition of four mole equivalents of triethylamine. Furthermore, the rate constant of the bromodiene 5 is increased by a factor of twenty in the more polar solvent 50% ethanol. A mechanism involving the addition of a nucleophile such as HO⁻ or R₃N and subsequent elimination of HBr must therefore be rejected in favour of an ionization mechanism by way of mesomeric vinyl cations 4. The fact that 2-bromo-4-methyl-1,3 pentadiene (5) reacts 23 times faster than p-methoxy- α -bromostyrene (1, R = OCH₃) demonstrates the greater ability of the dimethyl-ethylene group to stabilize an adjacent cationic centre relative to p-methoxy-phenyl.

Table 1. First order rate constants in 80 vol.% ethanol at 100°C ($c = 10^{-3}m$) in the presence of triethylamine ($c = 1.2 \times 10^{-3}m$).

	$k \times 10^4$ (sec^{-1})	E^\ddagger Kcal/mole	S^\ddagger cal/°C	$\lambda_{\text{max}}^{\text{EtOH}}$ nm	$\lambda_{\text{calc.}}^{\text{EtOH}}$ nm	$\epsilon \times 10^3$
 <p>(5)</p>	8.29	23.9	-10.9	227	229	7.5
 <p>(6)</p>	11.1	23.3	-12.1	208	234	8.4
 <p>(7)</p>	4.61	24.9	-9.6	215	234	7.6
 <p>(8)</p>	11.8	26.0	-4.8	210	239	13

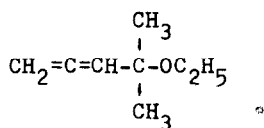
The presence of gem dimethyl groups at C-4 of the butadiene system seems essential for ready ionization since both the cis and trans forms of 2-bromo-3-methyl-1,3-pentadiene (9) react extremely slowly even at 110°. Methyl groups on C-1 exert only a minor influence as deduced from a comparison of the rate constants of 5 with 6, 7 and 8. •



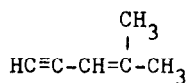
These results are explicable on the basis of structures 10a ↔ 10b or 11 for the intermediate vinyl cation. Maximum overlap of the orbitals involved in the delocalization of positive charge will occur if the planes of the double bonds are perpendicular. The bromodienes should therefore react in a non-planar conformation. Considerable deviation from coplanarity must, however, already be present in the ground state of the bromodienes 6, 7 and 8 since their characteristic diene UV-absorption is shifted to shorter wavelengths by 19 to 29 nm when compared to calculated values (Table 1). Inhibition of diene resonance is also reflected in the relatively low extinction coefficients ϵ (Table 1).

The major cause for the departure from coplanarity is steric hindrance between the C-4 methyl group and the bromine atom and, in the case of the bromodienes 6 and 8, additional hindrance between the C-1 methyl group and the hydrogen atom at C-3. These steric interactions are convincingly revealed in atomic models.

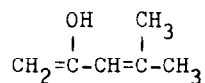
The relatively low reactivity of the bromodienes 7 and 8 can be attributed to steric hindrance to solvation since approach of solvent to the bromine atom is encumbered by the cis methyl group at C-1. The higher activation energies E^\ddagger and the less negative activation entropies S^\ddagger (Table 1) support this conclusion.



(12)



(13)



(14)

The intermediacy of mesomeric vinyl cations in the solvolysis of 5 - 8 is supported by product studies. For example, solvolysis of 5 in 80% ethanol buffered with triethylamine leads to 4-ethoxy-4-methyl-1,2-pentadiene (12) (55%), 2-methyl-pent-2-en-4-yne (13) (29%) and mesityl oxide (16%), the ketotautomer of 2-hydroxy-4-methyl-1,3-pentadiene (14)². The formation of all these compounds can be explained by coordination of solvent to or by proton loss from mesomeric vinyl cations with the charge distribution shown in 10a ↔ 10b.

References

- 1) C.A. Grob and G. Cseh, *Helv. Chim. Acta* 47, 194 (1964).
- 2) The structures of all new compounds were confirmed by elemental and spectral analysis.