α-Substituent Effect of a Triple Bond on a Vinyl Cation

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Summary Solvolysis of 2-bromobut-1-en-3-yne (**2**) and 1-halogenobuta-1,2,3-trienes (**3**) shows that incorporation of a triple bond in an α-aryl-stabilized vinyl cation system destabilizes the cation owing to a larger inductive effect of the triple bond compared with its π-conjugative effect and that the difference in rates of reaction of (**2**) and (**3a**) can be ascribed to a difference in their ground-state energies.

The only member of the family of stabilized vinyl cations remaining unknown is the α-ethynylvinyl cation (**1**),[1] although we have already detected one example of the cation (**1**) in the solvolysis of butatrienyl halides.[2] Calculations show that the parent vinyl cation is stabilized to a similar extent by a triple bond and a methyl group, compared with much greater stabilization by a double bond.[3]

We now report the effect of incorporation of a triple bond in an α-(*p*-methoxyphenyl)vinyl cation system. 2-Bromo-1,1-diphenyl-4-(*p*-methoxyphenyl)but-1-en-3-yne (**2**) and the 4,4-diphenyl-1-halogeno-1-(*p*-methoxyphenyl)buta-1,2,3-trienes (**3**) were solvolysed in aqueous ethanol buffered with sodium hydroxide.

Table Rates of solvolysis of (**2**), (**3**), and (**7**) in aqueous ethanol buffered with sodium hydroxide[a]

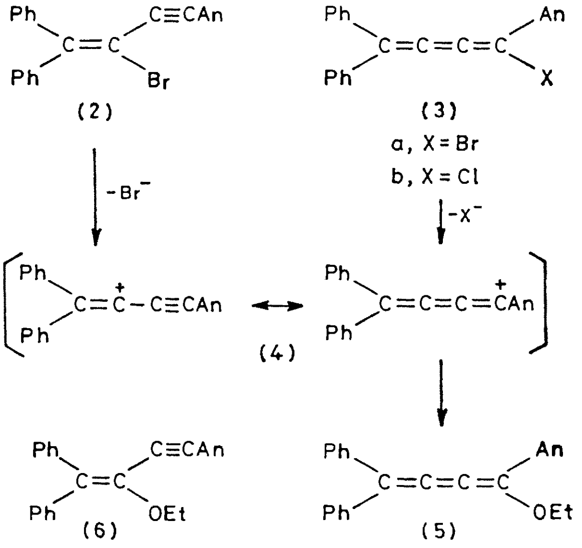
Compound	Solvent composition[b]	Temp /°C	$10^5 \times$ Rate/s^{-1}
(**2**)	80%	140	1·86
	70%	140	3·94
(**3a**)	80%	140	2000[c]
"	"	110	186
"	"	100	83·6
"	"	90	33·3
"	"	80	12·2
"	70%	100	197
"	"	90	82·1
(**3b**)	70%	100	6·30
(**7**)	80%	139·8	77·0[d]

[a] Reactions were followed by potentiometric titration of halide ion. [b] % of EtOH in EtOH–H_2O. [c] Extrapolated from data at lower temperatures. [d] From ref. 4.

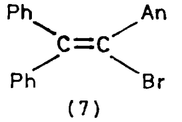
The kinetic results are shown in the Table. The reaction obeyed first-order kinetics. Solvent effects were observed for (**2**) [*m* (25 °C)† = 0·76] and (**3**) [*m* (25 °C)† = 0·78] and a leaving group effect was observed for (**3**) (k_{Br}/k_{Cl}‡ = 31).

The reaction products could not be determined in detail. However, the butatriene (**5**)§ was isolated in 40% yield from the reaction of (**3a**) in 80% aqueous ethanol at 120 °C for 1 h, and it was also detected by i.r. and u.v. spectroscopy in the crude mixture obtained on heating of (**2**) in 70% aqueous ethanol at 150 °C for 22 h. This shows that there is most probably a common reactive intermediate (**4**). The isolation of (**5**), together with the results in ref. 2, demonstrates that the cation (**1**) shows ambident reactivity. Compound (**5**) arises from attack by solvent on a terminal positive carbon atom; the ether (**6**) arising from attack on an internal carbon atom was not detected, but in the intramolecular cyclization reported in ref. 2 an internal positive carbon atom of (**1**) was exclusively attacked by a methoxy-group.

(**1**)



(**2**) (**3**) a, X = Br b, X = Cl (**4**) (**6**) (**5**)



(**7**)

An = *p*-$MeOC_6H_4$

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† *m* values were calculated from a plot of log *k* vs. Grunwald–Winstein's *Y* parameter, and the relationship $m_1T_1 = m_2T_2$. *m* (25 °C) = 0·5—0·76 for tris (*p*-methoxyphenyl)vinyl halides in ref. 4.

‡ k_{Br}/k_{Cl} = 58 for tris (*p*-methoxyphenyl)vinyl halides in ref. 4.

§ M.p. 125—128 °C; δ ($CDCl_3$, $SiMe_4$) 1·44 (3H, t, *J* 7 Hz), 3·76 (3H, s), 4·21 (2H, q, *J* 7 Hz), and 6·7—7·6 (14H, m); ν_{max} (Nujol) 2050 cm^{-1} (C=C=C=C); λ_{max} (EtOH) 260 and 410 nm; *m/e* 354 (M^+).

The ratio of the rates of reaction of (**7**) compared with (**2**) (41 : 1) implies that the inductive effect of the triple bond is larger than its π-conjugative effect on formation of the vinyl cation (**4**). In contrast, the ratio of the rates of reaction of (**3a**) compared with (**2**) (*ca.* 1000 : 1) was largely due to the energy gap between the ground state of (**2**) and (**3**), because the reactive intermediate (**4**) in the reactions of both was considered to be the same. The energy gap was calculated as 5·5 kcal mol^{-1}, which is reasonable from consideration of the fact that there are no instances of the rearrangement of but-1-en-3-ynes to buta-1,2,3-trienes, but there is evidence for the reverse transformation.[5]

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[1] P. J. Stang, Z. Rappoport, M. Hanack, and L. R. Subramanian, 'Vinyl Cations,' Academic Press, New York, 1979.

[2] S. Kobayashi, T. Sonoda, and H. Taniguchi, *Chem. Letters*, 1977, 163.

[3] Y. Apeloig, P. v. R. Schleyer, and J. A. Pople, *J. Org. Chem.*, 1977, **42**, 3004.

[4] Z. Rappoport and A. Gal, *J. Amer. Chem. Soc.*, 1969, **91**, 5246.

[5] H. Fischer in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, London, 1964, Ch. 13.