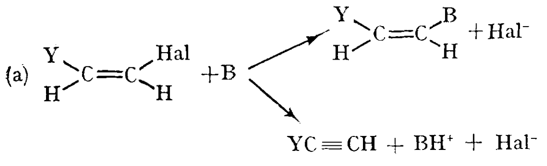
Evidence for a Concerted Process in an Elimination leading to Acetylenes

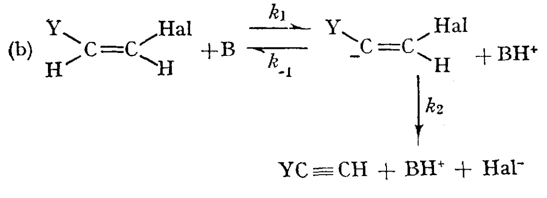
By G. MARCHESE, G. MODENA, and F. NASO
(*Istituto di Chimica Organica, Università di Bari, Italy*)

"ACTIVATED" halogenoethylenes react with nucleophiles by direct substitution often accompanied by an elimination process, particularly when the leaving groups are *trans*-related[1] (Scheme a).

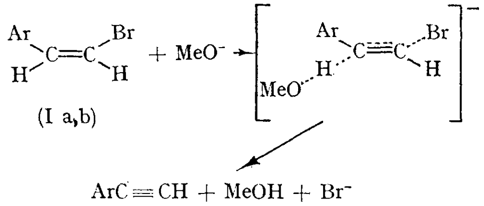


(Y=Electron-withdrawing group)

It is generally accepted,[2] as proved with some examples[3] that the elimination process occurs by a two-step mechanism of the *E*1c*B* type, even when the steric conditions for an *E*2 type mechanism are satisfied (Scheme b).



Nevertheless we have found evidence in favour of a synchronous process in the reactions of *cis*-β-bromo-4-nitrostyrene (Ia) and of *cis*-β-bromo-2,4-dinitrostyrene (Ib) with nethoxide ion in methanol leading to the corresponding acetylenes (IIa, b)[4] (Scheme c).



(IIa,b)

a, Ar = 4-$NO_2-C_6H_4-$;
b, Ar=2,4-$(NO_2)_2-C_6H_3-$

The reactions follow second-order kinetics and the nitrophenylacetylenes are formed in almost quantitative yields. This is in accord with Cristol's results[5] on the reaction of the *cis*-mononitro-derivative (Ia) with NaOH in ethanol and propan-2-ol. The relevant kinetic data are reported in the Table.

The intimate nature of the elimination process has been elucidated by using isotope techniques, which have been successful in studying other systems.[3]

The mononitro- and dinitro-β-bromostyrenes (Ia, b) were allowed to react with MeO^- in MeOD and the reactions were stopped at 5—50% of completion by neutralization of the base. In no

TABLE

Rate constants and energies of activation for the reaction of various β-bromostyrenes with MeO⁻ *in methanol at* 25°C

Styrene	10^4k_2 (sec.$^{-1}$mole^{-1} l.)	E_{act}(kcal./mole)
cis-NO_2–C_6H_4–CH=CHBr	7·10	25·0
cis-4-NO_2–C_6H_4–CD=CHBr	4·00	—
cis-2,4-$(NO_2)_2$–C_6H_3–CH=CHBr	10,650	19·9

case was incorporation of deuterium detected in the unreacted substrates by infrared spectroscopy. The recovered and the starting materials had identical infrared spectra and the characteristic bands of the deuterated bromostyrenes (see below) were absent.

The *cis*-β-bromo-α-deutero-4-nitrostyrene (m.p. 50—51°, mixed m.p.* not depressed) was synthesized by the photoisomerization of the corresponding *trans*-compound, which in turn was prepared by adding DBr to 4-nitrophenylacetylene.

The infrared spectra of the deuterated compounds differed markedly from the protium analogues in the 10·5—15μ region. From infrared and n.m.r. analyses it was possible to estimate a deuterium content at the α-position of 0·7 atom per molecule.

The rate of reaction of the deuterated *cis*-bromonitrostyrene with methoxide ion in methanol at 25·0° was measured. The second-order rate coefficient is $4{\cdot}0 \times 10^{-4}$ sec.$^{-1}$ mole^{-1} l. From it a value of k_H/k_D of 1·8 may be calculated, which becomes 2·2 when allowance is made for the incomplete deuteration at the α-position.

The absence of hydrogen exchange and the observed kinetic isotope effect strongly suggest that in these particular cases the dehydrohalogenation is a concerted process. An *E*1*cB* mechanism would have caused a partial or complete H/D exchange.

The kinetic isotope effect observed, even if smaller than those usually detected in dehydrohalogenations which lead to ethylenes,[6] is unambiguously indicative of the participation of C–H bond breaking in the rate-determining step, and, to our knowledge, it is the first reported case in the dehydrohalogenation of halogenoalkenes. The relatively small value of k_H/k_D suggests that the transition state has an high carbanion character as might be expected in reactions of this kind, since other similar systems react through a fully developed carbanion. Our results, including the observed isotope effect, are also consistent with a two-step process (Scheme b) with $k_2 \gg k_{-1}$. However the concerted mechanism seems to be preferred in agreement with the conclusions reached in the similar case of eliminations leading to olefins.[6]

(*Received, June 6th,* 1966; *Com.* 373.)

---

* With the α-[^{1}H]- compound.

[1] D. E. Jones, R. O. Morris, C. A. Vernon, and R. F. M. White, *J. Chem. Soc.*, 1960, 2349; S. Ghersetti, G. Lugli, G. Melloni, G. Modena, P. E. Todesco, and P. Vivarelli, *ibid.*, 1965, 2227 and previous papers of the series; S. Patai and Z. Rappoport "The Chemistry of Alkenes", ed. S. Patai, Interscience, London, 1964, ch. 8.

[2] G. Köbric, *Angew. Chem. Internat. Edn.*, 1965, **4**, 49, and references therein.

[3] S. Ghersetti, G. Modena, P. E. Todesco, and P. Vivarelli, *Gazzetta*, 1961, **91**, 620; S. I. Miller and W. G. Lee, *J. Amer. Chem. Soc.*, 1959, **81**, 6313.

[4] (Ia), m.p. 50—51°; (IIa), m.p. 149—150° (ref. 5); (Ib), m.p. 80—81°; (IIb), m.p. 95·5—96·5°; uncorrected melting points. Satisfactory analyses were obtained for the new compounds.

[5] S. J. Cristol and W. P. Norris, *J. Amer. Chem. Soc.*, 1954, **76**, 3005; S. J. Cristol, A. Begoon, W. P. Norris, and P. S. Ramey, *ibid.*, p. 4558.

[6] J. F. Bunnett, *Angew. Chem.*, 1962, **74**, 731; D. V. Banthorpe, "Elimination Reactions", ed. E. D. Hughes, Elsevier, London, 1963.