Stereochemical and Kinetic Aspects of the Formation of Allenes and Acetylenes by Dehydrobromination

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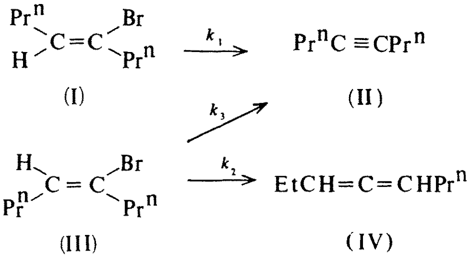
THE yields of allenes from base-promoted dehydrohalogenation of vinyl halides are generally low and the products are often contaminated with isomeric acetylenes.[1] The mechanism of these reactions is unclear since, in most cases, the stereochemistry is unknown and it has not been established whether interconversion of allenes and acetylenes occurs under the reaction conditions.[2]

It has been established that *anti*-elimination of hydrogen halide from *trans*†-vinyl halides to give acetylenes is much faster than *syn*-elimination from the corresponding *cis*-vinyl halide.[3] We report results which provide evidence for the mechanism of the formation of allenes and which also extend the implications of preferred *anti*- over *syn*-periplanar elimination.



Base = NaOMe–MeOH–Me_2SO

trans-4-Bromo-oct-4-ene[4] (I) was dehydrobrominated at 25° under *E*2 conditions [1·0 N-NaOMe in 15% (v/v) MeOH–Me_2SO] to give oct-4-yne (II) in quantitative yield. In contrast *cis*-4-bromo-oct-4-ene‡ (III) underwent dehydrobromination under similar conditions [0·9N-NaOMe in 20% (v/v) MeOH–Me_2SO at 80°) to give a single product in >85% yield. On the basis of its spectral properties (i.r.,[5] n.m.r., and mass), and synthesis[6] of authentic material, this was identified as octa-3,4-diene (IV).

It is therefore apparent that for (III) the (presumably *anti*) dehydrobromination to form an allene is much faster than *syn*-elimination to produce an acetylene. This stereochemical aspect of the formation of allenes from vinyl halides does not appear to have been previously demonstrated.[1,7]

A reasonably quantitative determination of the relative rates of three different elimination processes (k_1, k_2, and k_3) was made as follows. The value of k_1/k_2 was determined by the competitive dehydrobromination at 25° of solutions of (I) and (III) [0·0018M and 0·0037M, respectively, in 0·078 N-NaOMe in 15% (v/v) MeOH-Me_2SO] to be 43·8 ± 2·5.§ The value of k_2/k_3, determined under similar conditions by the dehydrobromination at 25° of solutions of (III) [0·0015M in 0·985N-NaOMe in 15% (v/v) MeOH-Me_2SO], was found to be 1500 ± 300.§ Thus the ratio of *anti*- to *syn*-periplanar elimination (k_1/k_3) is (6·6 ± 1·4) × 10^4 (which corresponds

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† In this context we refer to *trans* and *cis* with respect to the hydrogen and halogen atoms.

‡ In our hands (III) (as well as *cis*-3-bromohex-3-ene and *cis*-5-bromodec-5-ene) generally contained *ca.* 15% of the *trans*-isomer when prepared by the published procedure (ref. 4).

§ By employing appropriate control experiments we have established that there was no significant interconversion of (I) and (III) (K. E. Harwell and L. F. Hatch, *J. Amer. Chem. Soc.*, 1955, **77**, 1682) or of (II) and (IV) (ref. 2) under the reaction conditions.

to $\Delta\Delta G^{\ddagger}{}_{(25^\circ)} = -6{\cdot}6 \pm 0{\cdot}2$ kcal./mole)[8] and is in the range of rate ratios observed for other halogenoalkenes.[3]

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[5] A. A. Petrov, T. V. Yakovleva, and V. A. Kormer, *Optics and Spectroscopy*, 1959, **7**, 170.

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[8] For a treatment of the standard deviations see H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry", 2nd edn., D. Van Nostrand, Princeton, 1956, p. 515.