

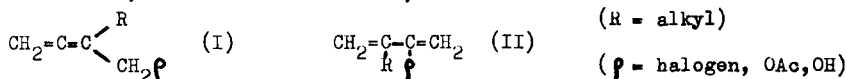
PROOF OF A RADICAL MECHANISM IN THE PHOTOCHEMICAL REARRANGEMENT OF α -ALLENIC HALIDES

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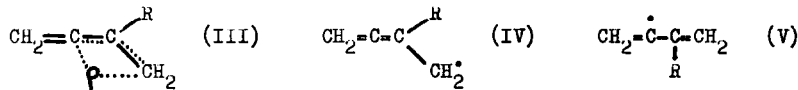
The liquid-phase rearrangement of 1.2 dienes (I) to 1.3 dienes (II) can be catalyzed by Cu dust, Cu⁺, Zn²⁺, etc..^(1,2). It can also be achieved thermally at temperatures ranging from 80-130°C (ρ = Br) to 350-400°C (ρ = Cl)^(2,3,4) and photochemically^(4,5).



The Cu-catalyzed rearrangement of (I) proceeds through a free-radical mechanism, as shown by the ESR spectrum of (I) (R = Et, ρ = Br, T = 114°C), where radicals appear in excess of 10^{18} ml^{-1} (2), whereas none are detected in the ESR spectrum of the isomeric (II), although the polymerization of (II) could be expected to produce substantial amounts of free radicals. Conversely the thermal rearrangement of (I) to (II) shows some evidence of competition between an ionic and a free-radical mechanism^(3,4).

The main experimental features of the photochemical (I) \rightarrow (II) rearrangement have been previously described^(4,5). The rate depends on the nature of ρ , but not on R, bromides rearranging faster than chlorides. The photochemical primary process of C- ρ bond-splitting is the rate-determining step as (contrary to the thermal rearrangement which exhibits a very high temperature coefficient) the temperature coefficient here is only $1.05^{\pm 0.03}$.

This photorearrangement can either involve an internal complex such as (III) or a radical such as (IV), which could rearrange to (V)⁽⁵⁾.



The available data on the spectra of (I) and (II), as well as those on the photorearrangement kinetics, do not allow to discriminate between these mechanisms. We have obtained evidence of a free-radical mechanism by inducing the rearrangement in a mixture of two competing (I) compounds, differing by both the nature of R and ρ . In one case we used 1-chloro 2-ethyl buta-2.3 diene and 1-bromo 2-n.butyl buta-2.3 diene. An internal-complex mechanism would give at most four compounds, the two reactants and two products which would be 2-chloro 3-ethyl buta-1.3 diene and 2-bromo 3-n.butyl buta-1.3 diene.



In the case where photolysis would result in a radical splitting all fragments could recombine in a nearly random fashion. Actually molecular halogens and hydrocarbons are never detected in the products in any significant amounts, and there is no need to consider

possible products other than halogeno-allenes or halogeno-1.3 dienes. A radical mechanism could therefore produce at most four (I) compounds (two reactants plus the two compounds from halogen interchange) and four (II) compounds (random recombination of two 1.3 dienyl radicals with atomic chlorine or bromine).

As the rearrangement rate is much smaller for chlorides than for bromides a great excess of (I) chlorides was used in the mixtures. We always identified at least five of the eight possible compounds, which is sufficient proof of a free-radical mechanism.

EXPERIMENTAL The allenic (I) compounds were prepared as previously described by us⁽⁶⁾. The chlorides were substantially pure, the bromides had usually a 3-10% content in isomeric (II) due to some thermal rearrangement occurring even at room-temperature. They were irradiated with a Philips SP 500 lamp at 32°C (dry boiling pentane solution, .4 M) in a Suprasil vessel. Continuous bubbling of pentane-saturated nitrogen in the solution ensured stirring while maintaining a constant volume. Small samples could be drawn through a capillary tap. It was checked with interference filters that no wavelength above 2400Å could induce any photolysis. The reaction progress was followed by measuring the $\nu_{C=C=C}$ 1950cm⁻¹ band-area. Samples were analyzed by VPC (10% DEGS on W Chromosorb carefully silanized, temperature 80-110°C). Each chromatographic experiment was repeated as two of us have shown that α -allenic bromides can rearrange on VPC columns⁽⁷⁾, through a thermal phenomenon (which can be avoided by low-temperature operation) and the effect of active sites in the packing-material (reduced by an alkaline silanizing reagent such as HMDS at the cost of a slightly reduced efficiency of the column). All VPC and spectral data were checked with samples independently prepared. Spectrophotometric estimations from the integrated band-intensities had to be restricted to the allenes (I) as the 1.3 dienes (II) polymerize partly.

In the above conditions a mixture of 1-chloro 2-n.butyl buta-2.3 diene and 1-bromo 2-ethyl buta-2.3 diene (3/1 molar ratio) gives the two "normal" rearrangement products plus 2-chloro 3-ethyl buta-1.3 diene and its dimer, in quantities amounting to a 50-60% exchange. No exchanged allene is found.

With a mixture of 1-chloro 2-ethyl buta-2.3 diene and 1-bromo 2-n.butyl buta-2.3 diene (1/1 to 10/1 molar ratios), the free-radical exchange ratio is smaller but it is always possible to detect at least 5% of 2-bromo 3-ethyl buta-1.3 diene in addition to the 2-chloro 3-ethyl- and 2-bromo 3-n.butyl buta-1.3 dienes.

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