BROMINE ATOM CATALYZED ISOMERIZATION OF TERMINAL OLEFINS II THE PROPARGYL BROMIDE-BROMOALLENE SYSTEM Hubert G. Meunier and Paul I. Abell Department of Chemistry, University of Rhode Island Kingston, Rhode Island 02881 (Received in USA 1 June 1967)

The Chemistry of reaction systems in which propargyl and allenic radicals are formed as resonance hybrids has generally indicated that the propargyl radical makes the greater contribution, in that the products are usually related to the propargyl structure.

Caserio and Pratt (1) have worked with this radical system, created by the abstraction of hydrogen from propyne (and also some substituted propynes), using the decomposition of tbutyl hypochlorite as the radical source. The chlorine substituted products are all derived from the propargyl structure, and none from the allenic structure, but the materials balance is not very good, and there may have been some concealed allenic products. Poutsma and Kartch (2) have examined the liquid phase photochlorination of 1-butyne, and found that about one percent of an allenic product was present in the mixture of seven products of the reaction.

The earlier work in this laboratory on the isomerization of terminal olefins by photochemically generated bromine atoms (3) has now been extended to an examination of the hydrogen abstraction from 3-bromopropyne. Abstraction of the propargylic hydrogen

gives a resonance stabilized radical which is mesomeric with an allenic radical, but with the added feature of the presence of a bromine atom in the structure which can assist in stabilization of the radical.

$$HBr \xrightarrow{hV} H \cdot + Br \cdot$$

Br + HC = C - CH₂Br - HBr + HC = C - CHBr
HC = C - CHBr + HC = C = CHBr

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The restoration of a hydrogen atom to these mesomeric radicals has, in our hands, produced a mixture of allenic and propargyl bromides.

HC = C - CHBr

$$HC = C - CHBr$$

 $HC = C - CH_2Br$
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The high reactivity of the allene toward HBr (4), and the non-reversibility of that reaction, traps some of the bromoallene as the HBr addition product.

$$CH_2 = C = CHBr + HBr \rightarrow CH_3 - CBr = CHBr$$

The equilibrium between the propargyl bromide and the bromoallene is established rapidly, but the formation of the 1,2-dibromo-1-propene slowly removes the bromoallene from the equilibrium mixture. Isolation of the bromoallene by gas chromatography and reintroduction, together with HBr into the reaction system recreates the equilibrium, and yields propargyl bromide, residual bromoallene and 1,2-dibromo-1-propene. Little or no addition of hydrogen bromide to the propargyl bromide takes place, but this is not unexpected, since allene has been shown to be a very efficient scavenger of bromine atoms as compared to even very reactive olefins such as isobutylene (4).

By using fairly high temperatures (135-195°C.) and low relative concentrations of HBr, it was possible to measure the propargyl bromide-bromoallene equilibrium constant. These data are shown in Table 1, and plotted in Fig. 1. The ΔH separating propargyl bromide and bromoallene is calculated from the slope to be -1.9 kcal/mole. This leads to values of $\Delta G_{400} \cdot K^{=}$ - 0.83 kcal/mole and $\Delta S_{400} \cdot K^{=}$ -2.7 eu.

The formation of the 1,2-dibromo-1-propene as the sole addition product can be rationalized readily. The addition of the bromine atom to the bromoallene may be expected to take place at the center atom, presuming an analogy with allene itself (3,5,6), to yield a resonance stabilized allyl radical and incorporating the p-orbital overlap of the two bromine atoms. The hydrogen abstraction step will then have the option of taking place at either terminal carbon. That it takes place exclusively at the non-brominated carbon is readily predictable, both on the grounds of steric accessibility and because of the stability



of the vinylic halide which results. The 1,2-dibromo-1-propene may exist in <u>cis</u> and <u>trans</u> forms, but since these readily equilibrate (7), it is not possible to determine which is formed initially. The transition state for hydrogen abstraction from hydrogen bromide is shown in Fig. 2.



As is to be expected from these results, other hydrogen abstracting reagents will also serve to establish the propargyl-allenic radical mesomerism. Experiments with photolyzed HCl and even CF_3I demonstrate that these reagents will accomplish the same thing that HBr does, although with the CF_3I the equilibration is very much slower. The advantage of using HCl is that chain transfer to produce addition of HCl to the bromoallene does not take place, but there seems to be substantially greater formation of decomposition products and/or polymer in the reaction vessel.

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