

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

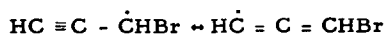
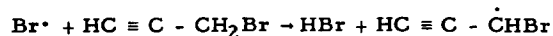
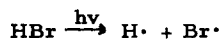
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The Chemistry of reaction systems in which propargyl and allenic radicals are formed as resonance hybrids has generally indicated that the propargyl radical makes the greater contribution, in that the products are usually related to the propargyl structure.



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 t-butyl 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.





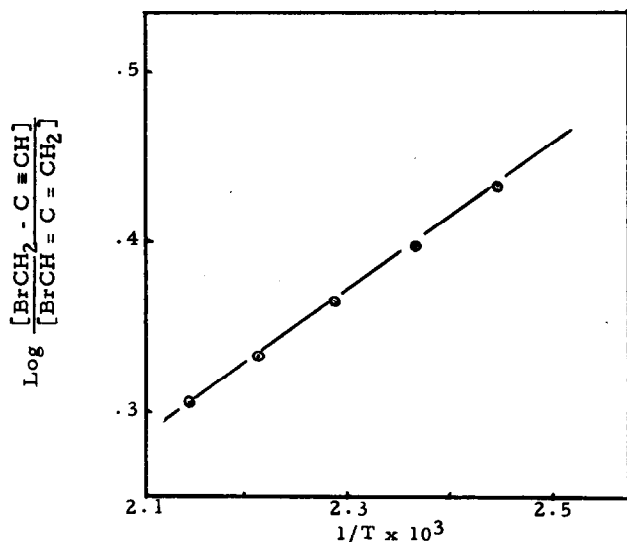


TABLE 1

| Temp.<br>°C. | $K = \frac{[\text{BrCH}_2 - \text{C} \equiv \text{CH}]}{[\text{BrCH} = \text{C} = \text{CH}_2]}$ |
|--------------|--|
| 135          | 2.69   |
| 150          | 2.48   |
| 165          | 2.30   |
| 180          | 2.13   |
| 195          | 2.00   |

Fig. 1 -- Arrhenius Plot, Equilibration of 3-Bromopropyne

of the vinylic halide which results. The 1,2-dibromo-1-propene may exist in cis and trans 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.

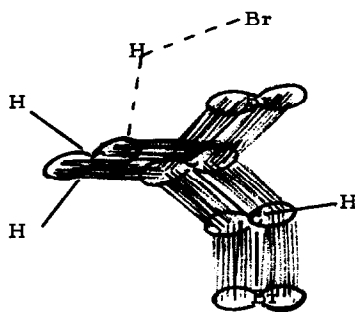


Fig. 2

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  $\text{CF}_3\text{I}$  demonstrate that these reagents will accomplish the same thing that HBr does, although with the  $\text{CF}_3\text{I}$  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.

#### REFERENCES

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