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SOLVOLYSIS OF ALLENYL BROMIDE IN AQUEOUS ETHANOL

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It is well known that allylic halides are more reactive under solvolytic conditions than their saturated counterparts, due to the delocalization of the positive charge in the developing carbonium ion over the π - system.[1] It has also been known for some time that vinyl bromide and alkylvinyl halides in general are highly unreactive, even in the presence of silver salts, under solvolytic conditions.[2] In view of the current interest in vinyl cations[3] it was therefore of special interest to investigate the solvolytic behavior of allenyl bromide, the "unsaturated" analog of the allylic system, and inquire about the possible stabilization of the developing vinyl cation by the allenyl double bond.

Bromoallene was prepared by the cuprous bromide catalyzed isomerization[4] of commercial propargyl bromide followed by a spinning band distillation: (bp 72-73°), nmr (CCl_4) δ 4.93 (d, 2, δ = 6.1Hz) δ 5.98 (t, 1, δ = 6.1Hz). Rates were measured in duplicate or triplicate in 50% aqueous ethanol in sealed tubes, by potentiometric titration of aliquots with NaOH on a Metrohm E436 Potentiograph. Good pseudo first-order rates were obtained up to about 83-88% reaction, after which the rates fell off presumably due to the slow electrophilic addition[5] of the HBr formed to unreacted starting material or to products. The results, together with related data, are given in Table I.

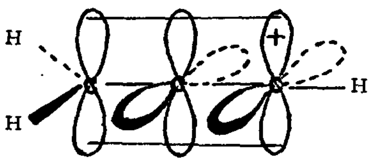
TABLE I

Summary of Solvolysis Rates of Allenyl and Propargyl Bromide in 50% Aqueous Ethanol

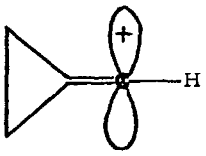
Substrate (a)	Temp. °C	k_1 sec^{-1} (b)	$\Delta H^{\ddagger}$	$\Delta S^{\ddagger}$
$CH_2=C=CHBr$	25.0 (c)	2.6×10^{-11}	24.9 kcal/mole	-23.4 e.u.
"	140.0	$(4.46 \pm .65) \times 10^{-6}$		
"	150.0	$(7.57 \pm .98) \times 10^{-6}$		
"	160.0	$(1.88 \pm .25) \times 10^{-5}$		
"	160.0 (d)	$(1.07 \pm .12) \times 10^{-5}$		
$CH\equiv C\text{-}CH_2Br$	25.0 (a)	1.1×10^{-7}	20.7 kcal/mole	-20.9 e.u.
"	100.0	$(1.47 \pm .15) \times 10^{-4}$		
"	120.0	$(6.35 \pm .65) \times 10^{-4}$		

(a) About 0.028-0.032 M is substrate. (b) Rate constants were obtained by using a non-linear least-squares program (LSKIN1 - D. F. DeTar and C.E. DeTar, Computer Programs for Chemistry, V.1, Benjamin Inc., New York, 1969) (c) Extrapolated (d) 60% Aqueous ethanol.

It is evident from the data in Table I that allenyl bromide, unlike simple alkyl vinyl halides, does, in fact, react under solvolytic conditions. Furthermore, the solvent "m" value of 0.44 for the allenyl system is comparable to the 0.455 "m" value of the allylic system.[1] The solvolytic reactivity of allenyl bromide is probably due to the stabilization of the vinyl cation by the allenyl double bond as shown in structure I. Similar behavior



I



II

with comparable reactivity was observed by Bässler and Hanack[6] in the solvolysis of bromomethylenecyclopropane; where the stabilization arises from overlap of the empty orbital with the cyclopropane ring, II, a phenomenon well known in ordinary carbonium ion chemistry.[7]

It is interesting to note that the allenyl cation, I, is a resonance form of the propargyl cation $CH{\equiv}\overset{+}{C}{-}CH_2 \longleftrightarrow \overset{+}{C}H{=}C{=}CH_2$. Hence in analogy to the known radical behavior of allenyl and propargyl substrates[8] there should be a common intermediate in the solvolysis of allenyl and propargyl bromide. The existence and importance of such resonance hybrids has been demonstrated by nmr spectral studies of alkynylcarbonium ions in strong acid media.[9] The 4×10^3 difference in solvolytic reactivity between the allenyl and propargyl bromide is probably due to both differences in ground state energies between the two species as a result of the stronger carbon-halogen bond[10] in the sp^2-hybridized allenyl bromide relative to the sp^3-hybridized C-Br bond in propargyl bromide, as well as differences in transition state geometries.

The products expected from such a solvolytic reaction in aqueous solvents should be propargyl alcohol and acrolein. However, control experiments demonstrated that neither expected product survives under the reaction conditions and no products other than polymeric material were isolated.

Finally it should be pointed out that the behavior of allenyl bromide under solvolytic conditions is markedly different from the behavior of allenyl halides in the presence of strong bases such as NaOH and t-BuOK where they react via an unsaturated carbene, $>C{=}C{=}C:$, intermediate.[11] The solvolytic reactivity of the parent allenyl bromide resembles much more the solvolytic behavior of triarylhaloallenes, which have been convincingly shown[12] to proceed via a resonance stabilized vinyl cation similar to I.

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References

1. A. Streitwieser, Jr., Chem. Reviews, 56, 571 (1956); R. H. DeWolfe and W. G. Young, ibid., 56, 753 (1956).

2. R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "Systematic Identification of Organic Compounds," J. Wiley and Sons Inc., New York, 1964.

3. M. Hanack, Acc. Chem. Res., 3, 209 (1970).

4. T. L. Jacobs and W. F. Brill, J. Am. Chem. Soc., 75, 1314 (1953).

5. R. C. Fahey, "Topics in Stereochemistry," V. 3, E. Eliel and N. L. Allinger, Eds., Interscience, New York, 1968.

6. T. Bässler and M. Hanack, Tetrahedron Lett., 0000 (1971).

7. R. Breslow in "Molecular Rearrangements," Vol. 1, P. de Mayo, Ed., Interscience Publishers, 1963; N.C. Deno, Prog. Phys. Org. Chem., 2, 129 (1964); G. W. Van Dine and P. von R. Schleyer, J. Am. Chem. Soc., 88, 2321 (1966); M. Hanack and H. J. Schneider, Angew. Chem. Int. Ed. Engl., 6, 666 (1967); H. G. Richey in "Carbonium Ions" Vol. III, G. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1971.

8. M. L. Poutsma, Tetrahedron Lett., 2925 (1969).

9. H. G. Richey, Jr., and J. M. Richey, "Carbonium Ions," V. 2, G. A. Olah and P. v. R. Schleyer, Eds., Wiley-Interscience, New York, 1970, pp. 931-949.

10. W. Moffit, Proc. Roy. Soc., A 202, 548 (1950); J. D. Roberts and V. C. Chambers, J. Am. Chem. Soc., 73, 5034 (1951); L. L. Miller and D. A. Kaufman, ibid., 90, 7282 (1968).

11. G. F. Hennion and D. E. Maloney, J. Am. Chem. Soc., 73, 4735 (1951); V. J. Shiner, Jr., and J. W. Wilson, ibid., 84, 2402 (1962); H. D. Hartzler, ibid., 83, 4990, 4997 (1961); J. Org. Chem., 29, 1311 (1964); V. J. Shiner, Jr., and J. S. Humphrey, Jr., J. Am. Chem. Soc., 89, 622 (1967); W. J. LeNoble, et.al., ibid., 92, 5681 (1970).

12. M. D. Schiavelli, S. C. Hixon, and H. W. Moran, J. Am. Chem. Soc., 92, 1082 (1970).