

BROMOHYDRIN FORMATION IN DIMETHYL SULFOXIDE

THE REACTION OF CONJUGATED DIENES

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(Received in USA 31 January 1972; received in UK for publication 7 February 1972)

Allylic cations and their resonance forms have traditionally been invoked to explain the generation of 1,2- and 1,4-adducts which result from addition of electrophilic reagents to conjugated dienes.¹

It has become quite clear, however, that in some cases the presence of the second double bond does not provide the expected resonance stabilization. Thus, for example, more activation energy is required to form the chloronium (or related) ion in the ionic chlorination of butadiene than in 1-butene, suggesting that the additional double bond is deactivating and implying little delocalization of positive charge onto carbon.² In another case, the bromination of butadiene in methanol, similar lack of charge distribution is suggested as the reason for the relative amounts of 1,2- and 1,4-addition products (15:1) obtained.³

Additionally, in the general case,⁴ the reaction of electrophiles with butadiene is complicated by the following factors: (1) the 1,2-adducts are known to be the kinetic products of the reaction and to rearrange to the 1,4-adducts; (2) the allylic cation is secondary on one end while primary on the other, thus, perhaps, apparently prejudicing nonallylic contribution (1,2-addition) and; (3) the geometry of the overall process cannot be determined.

Bromohydrin formation in dimethyl sulfoxide (DMSO) utilizing N-bromosuccinimide (NBS) as the source of positive bromine does not suffer the same drawbacks since the bromohydrins

cannot equilibrate and they are formed by the attack of DMSO, a potent nucleophile, on the bromonium or carbonium ion.⁵ In addition, the utilization of dienes which are potentially secondary on either end of the allylic system and in which the geometry of the overall process can be determined mitigates the remaining problems.

The TABLE presents a series of dienes which have been treated with NBS in moist DMSO under the usual neutral conditions.⁵ It is quite clear from these results that the regio- and stereospecific nature of the addition of the elements HOBr has been preserved even in the presence of the additional double bond with the bromine becoming attached to the least hindered terminal carbon atom.

The data permit the following conclusions: (1) A symmetrical, or nearly so, brominium ion cannot be involved even in these secondary systems (TABLE, Compounds 1 and 2) since this would have resulted in formation of two bromohydrins (i.e. 4,5 and 5,4); (2) Extensive charge delocalization from bromine onto carbon cannot obtain (if the orbital on carbon remains coplanar with the orbitals of the π system) since this would provide two similar secondary cations either of which could lead to bromohydrin (TABLE, Compounds 3-4 and 6); (3) Where a choice is presented (TABLE, Compound 5), terminal attack at a more substituted double bond leading to a tertiary (and allylic) cation is preferred over attack at a less substituted double bond leading to a secondary (and allylic) cation; (4) Some bridging must be present to account for the stereospecific nature of the process or the reaction is consummated before rotation can occur (TABLE, Compounds 1 and 2), and; (5) Steric effects hinder the reaction extensively, presumably by prohibiting initial attack of the electrophile (TABLE, Compound 7).

Therefore, we picture the reaction path as one involving rapid collapse of the solvent shell DMSO onto an ion which is partially bridged at the allylic end, deriving some stabilization from its allylic nature but the majority from the bromine bridge.

We are currently endeavoring to adjust the system to change the relative stabilities of the potential sites of attack.

PRODUCTS RESULTING FROM THE REACTION OF A SERIES OF CONJUGATED DIENES WITH NBS IN MOIST DMSO

TABLE

<u>DIENE</u>	<u>PRODUCT</u>	<u>YIELD (%)^a</u>
E,E-2,4-hexadiene (1)	erythro-5-bromo-4-hydroxy-E-2-hexene	93
Z,Z-2,4-hexadiene (2)	threo-5-bromo-4-hydroxy-Z-2-hexene	94
E-1,3-pentadiene (3)	5-bromo-4-hydroxy-E-2-pentene	95
Z-1,3-pentadiene (4)	5-bromo-4-hydroxy-Z-2-pentene	94
2-methyl-1,3-butadiene (5)	4-bromo-3-hydroxy-3-methyl-1-butene	94
Z-3-methyl-1,3-pentadiene (6)	Z-5-bromo-4-hydroxy-3-methyl-2-pentene	93
2,4-dimethyl-2,3-hexadiene (7)	no reaction	--

(a) The yields expressed are the average of two (2) or more runs and were obtained from gas liquid partition chromatography (glpc) and proton magnetic resonance (pmr) integration. Isolated yields, after distillation were 10-12% lower in each case. The products reported were accompanied by 3-4% unreacted diene and a small quantity (2-3%) of another product whose behavior, in each case, was similar to that of dibromide. The minor products are currently under investigation.

References

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An anonymous referee has correctly pointed out that the slower rate for butadiene could be due to an unfavorable A value (no temperature study having been reported) and that, therefore, strictly speaking, $\Delta\Delta F$ rather than $\Delta\Delta E_a$ is involved.
- (3) V.L. Heasley and P.H. Chamberlain, J. Org. Chem., 35, 539 (1970).
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