Tetrahedron Letters No.27, pp. 3127-3130, 1968. Pergamon Press. Printed in Great Britain.

ACETOLYSIS OF 4-BROMOBUTYL-1,1-d_2 p-NITROBENZENESULFONATE. EVIDENCE FOR 1,4-BROMINE PARTICIPATION AND THE EXISTENCE OF A 5-MEMBERED CYCLIC BROMONIUM ION DURING ACETOLYSIS.

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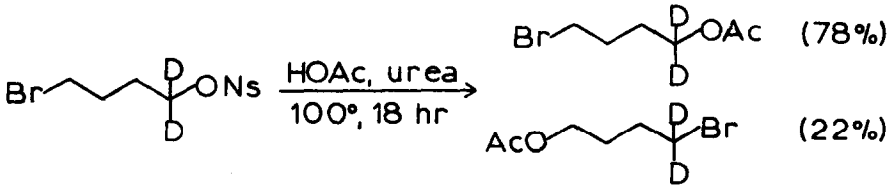
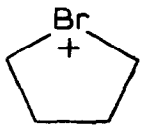
(Received in USA 7 March 1968; received in UK for publication 8 April 1968)

We wish to report that acetolysis of 4-bromobutyl-1,1-d_2 p-nitrobenzenesulfonate leads to 78% of the unrearranged product, 4-bromobutyl-1,1-d_2 acetate, and 22% of the rearranged product, 4-bromobutyl-4,4-d_2 acetate.



These results strongly support 1,4-bromine participation during the ionization of a primary alkyl arenesulfonate,* and the existence of a 5-membered cyclic bromonium ion (free or part of an ion pair) as a discrete intermediate.



Glpc analysis of the products of the acetolysis of light 4-bromobutyl p-nitrobenzenesulfonate at 100° for 18 hr showed that >85% 4-bromobutyl acetate was produced. 4-bromobutanol-1,1-d_2 was prepared by the reduction of ethyl 4-bromobutyrate with lithium aluminum deuteride. The nmr spectrum of the distilled product showed a two-proton triplet at 3.45 δ for hydrogens α to the bromine but no significant proton signal at 3.60 δ for hydrogens α to the hydroxy group. The alcohol was converted to the p-nitrobenzenesulfonate by treatment with p-nitrobenzenesulfonyl chloride according to the

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*Peterson has recently obtained evidence for 1,4- and 1,5-halogen participation during the solvolysis of primary alkyl arenesulfonates (1,2).

procedure of Streitwieser (3). The nmr spectrum of the recrystallized p-nitrobenzenesulfonate (mp 62.0-62.5°) showed no significant signal at 4.25 δ due to protons α to the p-nitrobenzenesulfonate group.

A quantity of 132 mg (0.39 mmole) of the dideuterated p-nitrobenzenesulfonate was dissolved in 4.5 ml of acetic acid that contained 46 mg (9 mmole) of urea. The nonnucleophilic base urea was used to neutralize the strong arenesulfonic acid produced instead of the traditionally used sodium acetate in order to avoid direct displacement of the primary arenesulfonate by acetate ion (4). The mixture was heated at 100° in a sealed tube for 18 hr. The sealed tube was cooled and opened, and 27.0 mg (0.21 mmole) of napthalene, the internal nmr standard, was added. The solution was extracted with ether in the usual manner (4). Most of the ether was removed by distillation and the products and standard were dissolved in 1 ml of carbon tetrachloride. An nmr spectrum of this solution gave peaks at δ 1.15 (t, 12 integration units), 1.80 and 1.95 (m and s, 180 i.u.) 3.45 (rough t, 44 i.u.), 4.0 (rough t, 10 i.u.), and 7.55 (m, 138 i.u.). This spectrum was consistent with that of a mixture of naphthalene, 4-bromobutyl-1,1-d_2 acetate, 4-bromobutyl-4,4-d_2 acetate, and a trace of ethyl ether. The peak at 1.15 δ was due to the methyl of ethyl ether which means that 8 i.u. of the peak at 3.45 δ was due to the methylene group of the ethyl ether. The ratio of $-CH_2Br$ hydrogens to $-CH_2OAc$ hydrogens was (44 - 8):10. Thus the ratio of 4-bromobutyl-1,1-d_2 acetate to 4-bromobutyl-4,4-d_2 acetate produced was 36:10. Comparison of the area of the napthalene signal to those of the acetate signals indicated that 78% of the theoretical amount of acetates was recovered.

Migration of the bromine atom is most reasonably accounted for by participation of the bromine during ionization of the arenesulfonate to form a 5-membered cyclic bromonium ion (or ion pair) as an intermediate. The existence of the 5-membered bromonium ion as an intermediate and not just a transition state is favored since complete migration of the bromine

leads to a primary ion that cannot be any lower in energy than the initially formed ion and therefore the driving force for bromine participation must be the formation of a stable bromonium ion.

The fact that only 22% of the rearranged acetate was obtained means that either the arenesulfonate reacts equally by two pathways, one involving direct displacement by acetic acid and the other involving bromine participation, or the arenesulfonate reacts exclusively to form the bromonium ion but unsymmetrical solvation due to the presence of the leaving group results in unequal formation of the two acetates. It is possible that a secondary deuterium isotope effect could lead to an unequal formation of the two acetates, but it is unreasonable that this effect would favor the formation of one isomer by a factor of three.

Much experimental evidence exists that makes halonium ions reasonable intermediates. Evidence for 5-membered cyclic halonium ions during cationic solvent addition reactions and solvolyses of secondary alkyl arenesulfonates has been presented recently by Peterson (5). Olah has observed 3-membered cyclic halonium ions by nmr (6,7) and McLafferty and Djerassi presented mass spectral evidence for the existence of 5-membered cyclic halonium ions in the gas phase (8,9). Indeed diaryl iodonium, bromonium, and chloronium ions are stable enough to be isolated (10,11).

It should be noted that rate data (12) itself cannot be used to substantiate the direct involvement of the bromine since the exact inductive effect of the bromine is unknown (5,12) and even if this is known, participation by the solvent shell of the halogen could account for a rate acceleration.

Acknowledgement. Helpful discussions with Professors James A. Marshall and Paul E. Peterson are gratefully acknowledged.

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