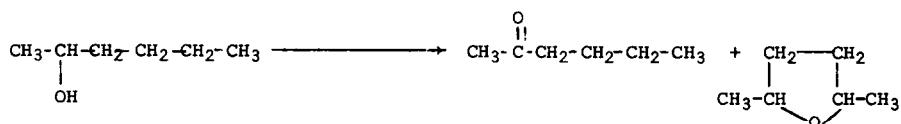


THE OXIDATION OF ALCOHOLS BY BROMINE AND SILVER SALTS

Nina Matheny Roscher and Elizabeth J. Jedziniak
 Department of Chemistry, Douglass College
 Rutgers, The State University, New Brunswick, New Jersey 08903

(Received in USA 17 November 1972; received in UK for publication 13 February 1973)

The alcohol-silver salt-bromine reaction yields tetrahydrofuran derivatives from tertiary alcohols¹ and both ketones and tetrahydrofurans from secondary alcohol systems². The exact mechanism of the tetrahydrofuran forming reaction is the subject of many recent papers³. No mechanisms for the ketone formation have been postulated. Solvent studies^{2b} and silver salt studies^{3a} have indicated that the product of the reaction could be controlled by the reaction conditions. We wish now to report the effect of the acid, one of the products of the reaction, on the other products of the reaction. We find that in the case of organic acids, the strength of the acid is the key to whether ketone or tetrahydrofuran is the oxidation product and to the rate at which the product is formed.



One can control the course of the reaction to change the product from almost all ketone to almost all tetrahydrofuran by changing the acidity of the medium. The implication of this fact on the mechanisms of the reaction to form ketone and to form tetrahydrofuran is not clear at this time.

In order to systematize the study, silver carboxylate salts have been used for the studies on different alcohols. The results reported in this paper for hexan-2-ol, a straight chain alcohol, and menthol, a cyclic alcohol, are representative. Similar observations have been made with other alcohols. With different silver carboxylates the amount of tetrahydrofuran relative to ketone decreases as one progresses in acid strength from silver acetate to silver trichloroacetate and silver trifluoroacetate (See Table).

In addition to the ketone or tetrahydrofuran formed in each case from the alcohol, the acid of the silver salt is also a reaction product. We observed that if the acid is added to

the reaction before the bromine is added, that in fact it is not the silver salt that controls the course of the reaction, but the acid (See Table). In other words while silver acetate gives good yields of tetrahydrofuran, if trifluoroacetic acid is added to the reaction mixture with silver acetate; the tetrahydrofuran formation is suppressed and/or the ketone formation is enhanced. Similarly if solid sodium carbonate is added with silver trifluoroacetate, before the bromine is added, the production of tetrahydrofuran is favored. The effect of a strong acid is observed with both the straight chain and cyclic alcohols.

We find that a strong acid, such as trifluoroacetic acid serves two roles in this reaction. It hinders the formation of tetrahydrofuran, whether it is a product of the reaction or whether it is added to the reaction mixture. In fact not only does it hinder the formation of tetrahydrofuran, but it also favors the production of ketone. Adding trifluoroacetic acid to a silver acetate-bromine-alcohol mixture before the bromine is added hinders tetrahydrofuran formation and increases the production of ketone. Similarly, acid added after the reaction is in progress for a short period of time also hinders tetrahydrofuran formation and increases the production of ketone.

Some workers have experienced difficulties in attempting to use this reaction for large scale synthesis of tetrahydrofurans. Since it has been shown that strong acids hinder tetrahydrofuran formation, it is probable that in a large scale synthesis the build-up of acid as a product also serves to eliminate the tetrahydrofuran formation thus decreasing the yield of the desired product.

Mercuric oxide will generate, from alcohols and bromine, hypobromites that are stable in the dark¹. If mercuric oxide is used to generate the hypobromite, and a silver salt or silver salt and acid are then added, the specificity of the silver salt as illustrated in the Table is maintained. No matter how the hypobromite is generated, the product variation observed with the different silver salts is the same.

Therefore it can be argued that the production of tetrahydrofuran and ketone proceed through the same intermediate, the hypobromite. It is the conversion of this intermediate to product that is influenced by the acid or the anion of the acid.

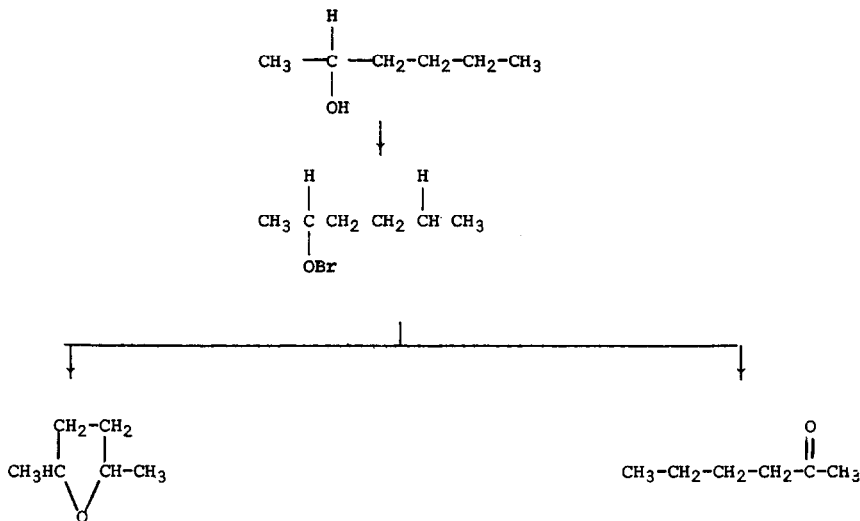
Silver bromide can be observed to form readily whether ketone or tetrahydrofuran is the product of the reaction.

Table
Alcohols with silver compounds, bromine and acids (a)

<u>Alcohol</u>	<u>Silver compound (c)</u>	<u>Acid (d)</u>	<u>Relative yields (b)</u>	
			<u>Tetrahydrofuran (e)</u>	<u>Carbonyl compounds</u>
Hexan-2-ol	Silver acetate	-	87%	13%
Hexan-2-ol	Silver acetate	Acetic acid	85	15
Hexan-2-ol	Silver trifluoroacetate	-	6	94
Hexan-2-ol	Silver acetate	Trifluoroacetic acid	5	95
Hexan-2-ol	Silver trifluoroacetate	Acetic acid	6	94
Hexan-2-ol	Silver trifluoroacetate	Trifluoroacetic acid	10	90
Hexan-2-ol	Silver acetate	Monochloroacetic acid	75	25
Hexan-2-ol	Silver acetate	Dichloroacetic acid	3	97
Hexan-2-ol	Silver acetate	Trichloroacetic acid	5	95
Hexan-2-ol	Silver acetate	Sodium carbonate (f)	69	31
Menthol	Silver acetate	-	69	31
Menthol	Silver trifluoroacetate	-	0	100
Menthol	Silver acetate	Acetic acid	69	31
Menthol	Silver acetate	Monochloroacetic acid	66	34
Menthol	Silver acetate	Dichloroacetic acid	9	91
Menthol	Silver acetate	Trichloroacetic acid	4	96
Menthol	Silver acetate	Trifluoroacetic acid	7	93

(a) Bromine was added to a stirred suspension of the silver compound in hexane and alcohol in the absence of light. The resulting mixture was filtered and the product mixture analyzed by g.l.c. (b) Recovered alcohol varied with each run and was not a function of the silver compound or the acid added. (c) All silver compounds were commercial preparations. (d) The acid was added before the bromine and was equimolar to the alcohol. (e) An average of several determinations ⁺ 3%. (f) Added as a solid before the bromine was added.

The fact that the acid, as well as the silver salt, influences the product formation argues that it is the nature of the gegen-ion, X, and the lability of the hydrogens involved that controls whether the alcohols are oxidized to ketones or to tetrahydrofurans by bromine in the presence of a silver salt.



This research was supported in part by a grant from the Rutgers University Research Council.

References

- R.A. Sneen and N.P. Matheny, J. Amer. Chem. Soc., 1964, 86, 3905,5503;
 - M. Akhtar, P. Hunt and P.B. Dewhurst, J. Amer. Chem. Soc., 1965, 87, 1807;
 - G. Smolinsky and B.I. Feuer, J. Org. Chem., 1965, 30, 3216.
- M. Lj. Mihailovic, Z. Cekovic and J. Stankovic, Chem. Comm., 1969, 981;
 - A. Deluzarche, A. Maillard, P. Rimmelin, F. Schue and J.H. Sommer, Chem. Comm., 1970, 976.
- N.M. Roscher, Chem. Comm., 1971, 474;
 - V. Boido and O.E. Edwards, Can. J. Chem., 49, 2664 (1971);
 - M.M. Green J.G. McGrew II, J.M. Moldowan, J. Amer. Chem. Soc., 93, 6700 (1971).