The Dark Reaction of Alcohols with Silver Compounds and Bromine[1]

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Summary Improved yields of tetrahydrofuran derivatives can be obtained from a variety of alcohols, on treatment of the alcohol with bromine in the presence of a silver salt, by the correct selection of the silver salt used as the reagent.

THE preparation of tetrahydrofuran derivatives from tertiary alcohols by the reaction of bromine with the alcohol in the absence of light and in the presence of silver oxide has been reported previously.[2] Systems in which the reaction is geometrically favoured, such as stereoidal alcohols where 1,3-diaxial interaction is favourable, gave the best yields. Recently, Mihailovic and his co-workers[3] reported the extension of the use of the silver oxide–bromine reagent to primary and secondary aliphatic alcohols with an unactivated γ carbon atom. Tetrahydrofuran derivatives are produced in good yields. Sommer and his co-workers[4] have suggested recently that the yields can be further improved by the addition of tetrahydrofuran to the reaction mixture. Their data suggest that the reaction is solvent sensitive and provide support for the original thesis[2a] that the transition state is ionic.

TABLE 1

4-Methylpentan-2-ol with silver compounds and bromine[a]

	Relative yield[c]	
Silver compound[b]	Tetrahydrofuran	Carbonyl compounds
Silver carbonate	90 ± 3%	10 ± 3%
Silver acetate	95 ± 3	4 ± 3
Silver sulphate	93 ± 7	7 ± 7
Silver nitrate	65 ± 13	35 ± 13
Silver oxide	3 ± 4	97 ± 3
Silver trifluoroacetate[d] . .	0	100

[a] Bromine was added to a stirred suspension of the silver compound in pentane and alcohol. The resulting mixture was filtered and the product mixture analysed by g.l.c. The reported yields are an average of a minimum of five runs. [b] All silver compounds were commercial preparations. Silver oxide was also prepared as described (ref. 3). No difference was observed in the product ratio. [c] Recovered alcohol varied with each run and was not a function of the silver compound. There was complete reaction in some silver carbonate runs. [d] Estimated error 3%.

TABLE 2

Alcohols with silver compounds and bromine[a]

		Relative yields	
Alcohol	Silver compounds[c]	Tetrahydrofuran	Carbonyl compounds
Octan-2-ol	Silver carbonate	98 ± 3%	2 ± 3%
Octan-2-ol	Silver acetate	82 ± 3	18 ± 3
Octan-2-ol	Silver oxide	7 ± 3	94 ± 3
Octan-2-ol	Silver oxide[d]	42	58
2,6-Dimethylhexan-4-ol . .	Silver carbonate	89 ± 3	11 ± 3
2,6-Dimethylhexan-4-ol . .	Silver acetate	98 ± 2	2 ± 2
2,6-Dimethylhexan-4-ol . .	Silver oxide	15 ± 6	85 ± 6
Cholestan-6β-ol[e]	Silver acetate	>99	<1
Cholestan-6β-ol[e]	Silver oxide	<1	>99

[a] Bromine was added to a stirred suspension of the silver compound in pentane and alcohol in the absence of light. The resulting mixture was filtered and the product mixture analysed by g.l.c. [b] Recovered alcohol varied with each run and was not a function of the silver compound. [c] All silver compounds were commercial preparations. [d] This run was carried out in the presence of light. [e] The product mixture was analysed by column chromatography.

The present work supports their data, and also shows that yields of tetrahydrofuran can be greatly improved by careful selection of the silver salt used as the reagent. In fact, it is shown that silver oxide is one of the poorest silver compounds to use as a reagent for this reaction.

The reaction was studied using pentane as solvent at room temperature with an average reaction time of 0·5 h. All reactions are carried out in the dark room with a red light as the only illumination.

We have studied the conversion of 4-methylpentan-2-ol into 2,4-dimethyltetrahydrofuran and 4-methylpentan-2-one under conditions identical except for the identity of the silver compound and have found the ratio of the products changes as the silver compound is changed (Table 1). For example, we find that silver oxide, together with silver trifluoroacetate, gives mainly ketone as product, whereas silver carbonate and silver acetate give mainly the tetrahydrofuran derivative as product. With 4-methylpentan-2-ol silver nitrate lacks specificity, giving both the tetrahydrofuran derivative and the ketone, with a slight preference for the tetrahydrofuran derivative.

The change in product with different silver compounds is not limited to the 4-methylpentan-2-ol system, as shown by studies of other alcohols with selected silver compounds (Table 2). A similar preference for the formation of a tetrahydrofuran derivative is observed with both silver carbonate and silver acetate, whereas silver oxide leads predominately to ketone formation.

The reason for this change in product with change in the anion of the silver compound is not clear. However, our results are not inconsistent with an ion-pair transition state in which the anion plays an important role.

Light improves the yield of the tetrahydrofuran derivative, as the work of Mihailovic[3] and Sommer[4] suggests. It is possible, however, that the increase in the tetrahydrofuran derivative is from a competing photochemical reaction[5] where the silver compound generates a hypobromite which breaks down photochemically rather than by the reaction of the alcohol with the silver compound–bromine reagent that occurs in the absence of light.

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[5] Unpublished data.