41. *The Preparation of Tetrahydrofurfuryl Bromide and its Reaction with Magnesium.*

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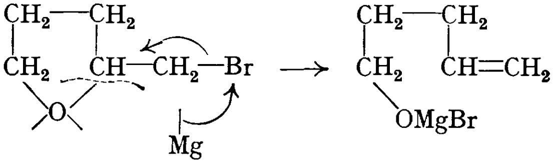
The conversion of tetrahydrofurfuryl alcohol into the bromide has been studied by Dox and Jones (*J. Amer. Chem. Soc.*, 1928, **50**, 2033), Gilman and Brown (*Iowa State Coll. J.*, 1931, **6**, 11), and Paul (*Bull. Soc. chim.*, 1933, **53**, 421), the last claiming a yield of 50%. After many trials we have found conditions under which Paul's method can be employed for the preparation of the bromide in 58—62% yield consistently. Our further use of the reagent forms part of an investigation, an account of which we hope shortly to submit to the Society, but we now comment on the course of its reaction with magnesium.

According to Paul (*loc. cit.*), the reaction in dry ether proceeds normally with formation of a Grignard reagent and, on decomposition with water, tetrahydrosylvane is obtained in 45% yield (allowing for recovered bromide). On the other hand, if the ether is removed and the residue heated for 2 hours at 100—110°, Δ^4-penten-1-ol can be isolated in 50% yield after decomposition of the product with water.

We are unable to confirm this contrast, because in our experience the unsaturated alcohol is the main product when (*a*) highly purified anhydrous ether, (*b*) pure ether saturated with water, (*c*) unpurified ether, or (*d*) ether mixed with one-sixth of its volume of alcohol is used. In (*a*) the temperature was never higher than 50°; tetrahydrosylvane was only formed in traces, if at all, and the amount of recovered bromide was negligibly small (Paul recovered about 30%).

It would appear that hydroxylic compounds are not essential and the mechanism of this interesting decomposition * may be represented by the scheme:



This represents the magnesium as electron-donor to bromine; there are two less acceptable alternatives in which (*a*) the electrons are donated to oxygen, and (*b*) one electron passes from magnesium metal to bromine and one to oxygen.

Experimental.

Tetrahydrofurfuryl Bromide.—A mixture of tetrahydrofurfuryl alcohol (102 g.) and pyridine (5 c.c.) was added dropwise during 2·5—3 hours to one of phosphorus tribromide (96 g.) and pyridine (15 c.c.) with mechanical stirring and maintenance at 0°. Stirring was prolonged one hour, and the mixture kept in the bath until the temperature became that of the room. After 24 hours the almost colourless material was liquefied by cautious heating and distilled, b. p. 60—90°/13 mm.; on redistillation, b. p. 60—65° (nearly all at 61°)/13 mm., $n_D^{18°}$ 1·4880 (yield.

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* The reaction appears to be analogous to that between β-phenoxyethyl bromide and magnesium (Grignard, *Compt. rend.*, 1904, **138**, 1048) which results in the formation of ethylene, phenol, and diphenoxybutane. Our own experiments confirm these observations, but we obtained in addition some phenetole, b.p. 173—174°, after decomposition of the product with water.

104 g. or 63%) (Found : Br, 48·1. Calc. for C_5H_9OBr : Br, 48·5%). The fraction of higher b. p. was isolated by collecting the first distillate at 60—135°/13 mm. (not recommended) or by steam-distilling the original reaction product after the addition of hydrobromic acid (100 c.c.; *d* 1·5), followed by fractionation. In this way 1 : 2 : 5-tribromopentane (*ca.* 5 g.), b. p. 132°/13 mm. (Paul, *loc. cit.*, gives 143°/20 mm.), was obtained (Found : C, 19·7; H, 3·0; Br, 77·4. Calc. for $C_5H_9Br_3$: C, 19·4; H, 2·9; Br, 77·8%).

Reaction with Magnesium.—(a) Reaction was initiated by the addition of a trace of iodine to a mixture of tetrahydrofurfuryl bromide (2 c.c.), magnesium turnings (2·4 g.), and absolute ether (15 c.c.); the remainder of the bromide (total, 16·5 g.), dissolved in dry ether (75 c.c.), was then added gradually so as to maintain a steady rate of reaction, and access of moisture was prevented. After 2 hours the mixture was heated during 3 hours to 40—45° and nearly all the magnesium passed into solution. The cooled product was decomposed with water and dilute hydrochloric acid. The separated and dried ethereal layer was fractionated through an efficient column (the vapour never rose above 37°) and finally a small Vigreux column. Only 0·7 g. was collected from 45—135° and the rise of b. p. was continuous (tetrahydrosylvane has b. p. 82°); the next fraction had b. p. 135—139° (nearly all at 136—137°/745 mm.) (5·3 g.); the amber-coloured residue (3·5—4·0 g.) partly crystallised.

(b) The reaction was initiated as in (a), the same quantities being used; the second portion (50 c.c.) of ether used was, however, previously shaken with water and separated. The reaction was very brisk and was completed at 60—70°. On working up, there were obtained 5·9 g., b. p. 52·5—53°/11 mm. or 137—138·5°/752 mm., and 0·3 c.c., b. p. 56—70°/11 mm.; the residue could not be distilled.

(c) Using ether from the reagent shelf in a similar experiment, completed by heating at 45—50°, we obtained 5·2 g., b. p. 136—138°/750 mm.

(d) The reaction was initiated between magnesium (4·8 g.) and tetrahydrofurfuryl bromide (5 g.) in absolute ether (40 c.c.) and continued by the addition of a mixture of the bromide (28 g.), ether (20 c.c.), and alcohol (10 c.c.); it was finally completed at 40—50°. We isolated 1·1 g., b. p. 85—91°, and 8·8 g., b. p. 135—137°.

The liquid, b. p. 135—137°, obtained in the above experiments contained a trace of halogen; this was removed by a process of refined fractionation (private communication of unpublished method) and then had b. p. 136°/750 mm., $n_D^{15·5}$ 1·4312 (Found : C, 69·1; H, 11·7. Calc. for $C_5H_{10}O$: C, 69·8; H, 11·6%). The phenylurethane had b. p. 183·5°/16 mm. Δ^4-Penten-1-ol has b. p. 138·5—139·5°/766 mm. (Paul, *Ann. Chim.*, 1932, **18**, 334), and its phenylurethane has b. p. 184°/16 mm. (Paul, *Compt. rend.*, 1931, **192**, 1575).

Tetrahydrofurfuryl bromide did not react with zinc filings in boiling absolute alcohol during 5½ hours.

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