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Abstract

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Corresponding Member of the Academy of Sciences of the USSR N. I. SHUIKIN, G. K. VASILEVSKAYA

TAUTOMERISM OF TETRAHYDROFURFURYL BROMIDE UNDER GRIGNARD-SYNTHESIS CONDITIONS

It is known that tetrahydrofuran and tetrahydropyran alcohols, whose hydroxyl group is directly attached to the α-carbon atom of the ring, exist in two tautomeric forms—cyclic and linear (in the form of an oxyaldehyde) ([1,2]). Under ordinary conditions the cyclic form predominates; however, in a number of cases these compounds react in the oxyaldehyde form ([3]):

$$\text{cyclic hemiacetal form} \rightleftarrows \mathrm{CH(O)CH_2CH_2CH_2CH_2OH}$$

It turned out that tetrahydrofurfuryl bromide also exists in both cyclic and linear forms:

$$\text{tetrahydrofurfuryl bromide} \rightleftarrows \mathrm{O{=}CHCH_2CH_2CH_2CH_2Br}$$

Under ordinary conditions the equilibrium is shifted toward the cyclic form; thus, tetrahydrofurfuryl bromide does not give derivatives with hydroxylamine and semicarbazide that are characteristic of the aldehyde group of 5-bromopentanal. However, the presence of an aldehyde group, and consequently the existence of tetrahydrofurfuryl bromide in the tautomeric form of 5-bromopentanal, is revealed in its IR spectrum. In it an absorption band of low intensity at 1715 cm^{-1}, characteristic of the carbonyl group, was observed. In addition, by introducing tetrahydrofurfuryl bromide into the Grignard reaction, it is possible to shift the equilibrium toward formation of 5-bromopentanal and force it to react in this form. Thus, it turned out that the Grignard reagent obtained from tetrahydrofurfuryl bromide (more precisely, from its equilibrium mixture with 5-bromopentanal) reacts with its own carbonyl group. As a result of displacement of the dynamic equilibrium, most of the tetrahydrofurfuryl bromide passes into its tautomer, and the Grignard synthesis proceeds intramolecularly; as a result, after decomposition of the complex formed with water, cyclopentanol was obtained in a yield of 80% of theory:

tetrahydrofurfuryl bromide $\rightleftarrows$ $HCOCH_2CH_2CH_2CH_2Br \xrightarrow{Mg}$ intramolecular Grignard complex $\longrightarrow$ cyclopenty

Experimental section

Tetrahydrofurfuryl bromide was obtained by the action of phosphorus tribromide on tetrahydrofurfuryl alcohol in a yield of 60% of theory ([4]) and had b.p. 59–60° (12 mm), n_D^{20} 1.4862; d_4^{20} 1.4362; MR found 32.25;

calculated: 32.49. Raman spectrum of tetrahydrofurfuryl bromide: ($\Delta\nu$ in cm^{-1}) 2721(2), 293(2sh), 438(1); 502(4); 532(1); 582(2sh); 620(7), 649(10); 659(8); 717(3), 803(1sh); 818(1sh); 872(1sh); 926(8); 1013(1); 1038(1sh); 1095(2sh); 1117(2sh); 1192(1sh); 1220(3); 1250(2); 1318(1sh); 1353(1); 1387(1); 1425(1); 1445(5); 1478(2); 2871(3); 2929(1sh); 2960(4); 2980(3); 3000(2). In the IR spectrum of tetrahydrofurfuryl bromide an absorption band of low intensity was found at 1715 cm^{-1}.

The Grignard reagent from tetrahydrofurfuryl bromide is obtained in the usual way in anhydrous ether. The reaction was initiated with methyl iodide. After the ethereal solution of tetrahydrofurfuryl bromide had been introduced into the flask with Mg, the reaction mixture was cautiously heated for 2 h until the ether boiled gently. During this time all the magnesium passed into solution. The reaction mixture was then cooled and gradually decomposed with water. After removal of the ether and distillation of the reaction product in vacuo, pure cyclopentanol was obtained, in a yield of 80% of theory. It had b.p. 52–54° (12 mm), n_D^{20} 1.4537; d_4^{20} 0.9488. Gas-liquid chromatography proved the identity of the cyclopentanol obtained with an authentic sample. Lit. ([5]): b.p. 139–140°, n_D^{20} 1.4530; d_4^{20} 0.9488.

It has been established that tetrahydrofurfuryl bromide exists in two tautomeric forms: cyclic and linear (carbonyl). It has been shown that, in preparing the Grignard reagent from it, intramolecular cyclization of the linear form occurs to give cyclopentanol, which is formed in a yield of 80% of theory.

N. D. Zelinsky Institute of Organic Chemistry
Academy of Sciences of the USSR

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REFERENCES CITED

[1] R. Paul, *Bull. Soc. chim. France* (5), **1935**, No. 2, 311; J. Colonge, P. Corbet, C. R., **245**, 974 (1957).
[2] C. D. Hurd, W. Saunders, *J. Am. Chem. Soc.*, **74**, 5324 (1952).
[3] J. Colonge, P. Corbet, *Bull. Soc. chim. France*, **1960**, No. 2, 283.
[4] A. A. Ponomarev, *Syntheses and Reactions of Furan Compounds*, Saratov,

1960, p. 205.

[5] C. R. Noller, R. Adams, *J. Am. Chem. Soc.*, **48**, 1084 (1926).

Note: Figure translations are in progress. See original paper for figures.

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