

INVESTIGATION OF FURAN COMPOUNDS

XXX*. INTRAMOLECULAR ALKOXYLATION OF FURFURYL-SUBSTITUTED MONO- AND BICYCLIC ALCOHOLS

A. A. Ponomarev and I. A. Markushina

Kimiya Geterotsiklicheskikh Soedinenii, Vol. 1, No. 2, pp. 195-197, 1965

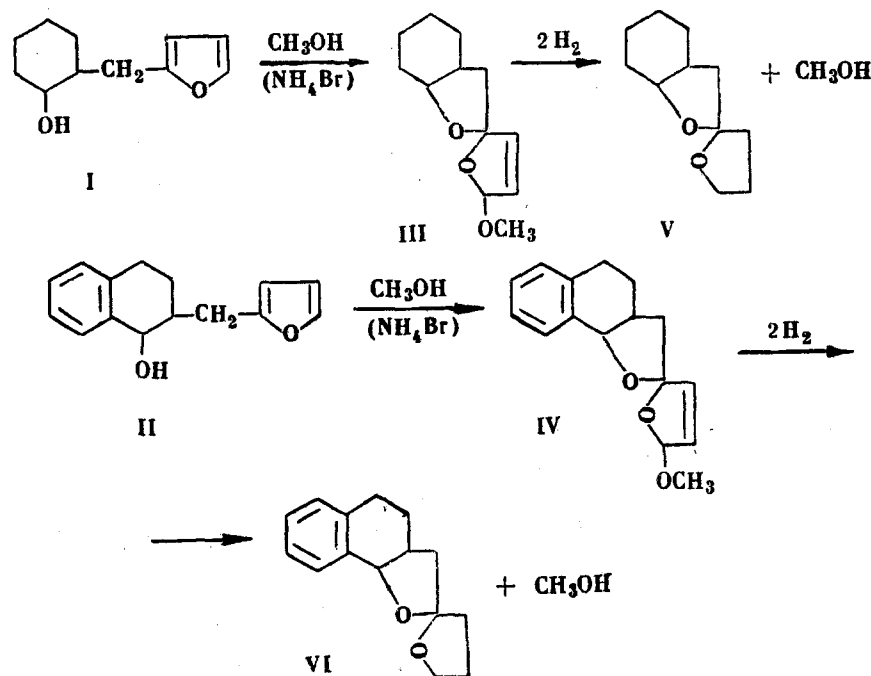
On electrolysis mono- and bicyclic furfuryl-substituted alcohols undergo intramolecular alkoxylation, giving polycyclic spirans. Spiro[perhydrobenzofuran-2, 2-(5'-methoxy, 5'H)furan] and spiro[4H, 5H, 6H, 11H-naphtho-(α, β)-furan-2(3H)][2'-(5'-methoxy, 5'H)furan], hitherto not described, are prepared in this way. On catalytic hydrogenation they give the previously unknown spiro[perhydrobenzofuran-2, 2'-tetrahydrofuran] and spiro[4H, 5H, 6H, 11H-naphtho-(α, β)-furan-2(3H)][2'-tetrahydrofuran].

When methanol solutions of 1-(α -furyl)alkan-3-ols and α, α' -furandialkan-3-ols are electrolyzed, they undergo intramolecular alkoxylation giving compounds of the 2-methoxy-1, 6-dioxaspiro-[4, 4]non-3-ene and 1, 6, 8-trioxadispiro [4. 1. 4. 2]tridec-12-ene [2-4] types.

There were reasons for regarding the new reaction as general and capable of extension to various compounds containing a furan ring and a hydroxyl group situated as in the type example. Accordingly, furfuryl-substituted cyclic alcohols were investigated. Preparatively, the reaction is of interest as offering a new route for synthesis of analogs of a number of naturally occurring substances.

Experiments showed that electrolysis of methanol solutions of 2-furfurylcyclohexanol (I) and 2-furfuryl-1, 2, 3, 4-tetrahydro-1-naphthol (II) also leads to intramolecular alkoxylation with formation of spiro[perhydrobenzofuran-2, 2'-(5-methoxy, 5'H)furan] (III) and spiro[4H, 5H, 6H, 11H-naphtho-(α, β)-furan-2(3H)][2'-(5'-methoxy, 5'H)furan] (IV), in 65% and 56% yields, respectively.

Hydrogenation of compounds III and IV under pressure at 120° using Raney nickel leads to splitting off of the methoxy group and reduction of the double bond, the aromatic ring being unchanged. The products are spiro[perhydrobenzofuran-2, 2'-tetrahydrofuran] (V) and spiro[4H, 5H, 6H, 11H-naphtho-(α, β)-furan-2(3H)][2'-tetrahydrofuran] (VI):



EXPERIMENTAL

Furfurylidene-cyclohexanone and β -furfurylidene- α -tetralone are prepared by the methods described in the literature [5, 6].

2-Furfurylcyclohexanol and 2-furfuryl-1, 2, 3, 4-tetrahydro-naphthol are prepared by hydrogenating furfurylidene-cyclohexanone and β -furfurylidene- α -tetralone over copper-chromium catalyst at 120°/120 atm. Yields 78% and 87%, respectively.

* For Part XXIX see [1].

2-Furfurylcyclohexanol: bp 117-118° (5 mm), n_D^{20} 1.5071, d_4^{20} 1.069, MR_D 50.20, calculated: 50.83. Found: C 73.28; 73.05; H 9.32; 9.39%, calculated for $C_{11}H_{16}O_2$: C 73.30; H 8.95%.

2-Furfuryl-1,2,3,4-tetrahydro-1-naphthol bp 141-142° (1 mm), d_4^{25} 1.1436, n_D^{25} 1.5688, MR_D 65.38; calculated: 65.70. Found: C 79.20; 79.04; H 6.81; 6.86%, calculated for $C_{15}H_{16}O_2$: C 78.92; H 7.07%.

An electrolyzer with a nickel cathode and carbon anode [7, 8] is used to electrolyze solutions of furfuryl-substituted mono- and bicyclic alcohols.

Spiro[perhydrobenzofuran-2,2'-(5'methoxy,5'H)furan] (III). 54 g freshly distilled 2-furfurylcyclohexanol are dissolved in 225 ml methanol and placed in the electrolyzer. The electrolyte is ammonium bromide. The temperature in the electrolyzer is -12°. The current is 2-4 a, voltage 14-20 v. When electrolysis is finished, the solution is treated with sodium methoxide (1.2 g sodium metal in 20 ml methanol), the methanol and ammonia evaporated off on a water bath under reduced pressure, the precipitate of sodium bromide filtered off and washed with ether. After evaporating off the ether the residue is vacuum-distilled. The yield is 65% on the material, and 62% on the current, bp 120-124° (3 mm), d_4^{20} 1.0881, n_D^{20} 1.4862, MR_D 55.51, calculated: 55.48. Found: C 68.82; 68.48; H 8.77; 8.81%, calculated for $C_{12}H_{18}O_3$: C 68.55; H 8.63%.

The alcohol (II) is similarly methoxylated. Yield 56% on the material, and 51% on the current, bp 153-165° (1 mm), d_4^{25} 1.1695, n_D^{25} 1.5548, MR_D 70.87, calculated: 70.35. Found: C 74.62; 74.79; H 7.33; 7.18%, calculated for $C_{16}H_{18}O_3$: C 74.39; H 7.03%.

Spiro[perhydrobenzofuran-2,2'-tetrahydrofuran] (V). 30 g spiran III, 35 ml anhydrous alcohol, and 2 g Raney nickel are charged into a 150-ml rotating steel autoclave. Initial hydrogen pressure 110 atm, temperature 120°. Seven liters hydrogen are absorbed. When hydrogenation has ended, the reaction mixture is freed from catalyst and solvent, and the residue vacuum-distilled. Yield 88%, bp 94-95° (4 mm), d_4^{20} 1.0384, n_D^{20} 1.4834, MR_D 50.16, calculated: 49.68. Found: C 72.67; 72.74; H 9.85; 9.73%, calculated for $C_{11}H_{18}O_2$: C 72.49; H 9.96%.

Spiran VI is obtained by a method similar to that used for methoxy compound IV, yield 72%, bp 147-154° (2 mm), d_4^{20} 1.1298, n_D^{20} 1.5502, MR_D 64.96, calculated: 64.56. Found: C 78.46; 78.53; H 7.98; 8.12%, calculated for $C_{15}H_{18}O_2$: C 78.22; H 7.88%.

REFERENCES

1. A. A. Ponomarev and I. A. Markushina, KhGS, no. 1, 43, 1965.
2. A. A. Ponomarev and I. A. Markushina, DAN, 126, 99, 1959.
3. A. A. Ponomarev and I. A. Markushina, ZhOKh, 31, 554, 1961.
4. A. A. Ponomarev and I. A. Markushina, ZhOKh, 33, 3957, 1963.
5. Organic Syntheses [Russian translation], no. 7, IL, Moscow, 49, 1956.
6. A. Dunlop and F. Peters, The Furans, 476, 1953.
7. A. A. Ponomarev and I. A. Markushina, Uch. Zap. SGU, 71, 135, 1959.
8. A. A. Ponomarev and I. A. Markushina, ZhOKh, 30, 976, 1960.

30 November 1963

Chernyshevskii Saratov State University