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THE REACTIONS OF DIHYDROPYRAN AND 2-METHYLDIHYDROPYRAN WITH SOME SCHIFF BASES

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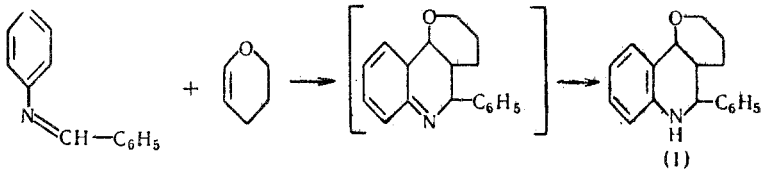
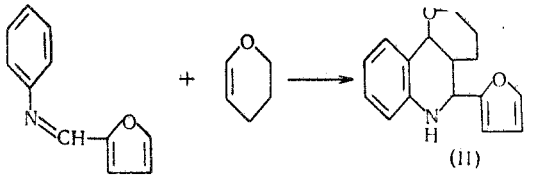
In a previous communication [1] we showed that benzylideneaniline in the presence of BF_3 can react as a diene with some unsaturated compounds containing an activated double bond – ethoxyacetylene, ketene, vinyl ethyl sulfide. The C = C - N = C system of bonds in benzylideneaniline reacts as the diene here.

Further investigation of this reaction showed that compounds such as dihydropyran, dihydrofuran, and their homologs in which the double bond is next to an oxygen atom can participate in the condensation reaction with benzylidene aniline and other Schiff bases having the C = C - N = C bond system in the 1-4 position. From the data obtained in the previous study [1] the reaction scheme for benzylideneaniline and dihydropyran can be represented in the following manner



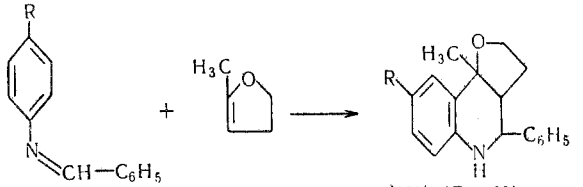
(I)

The adduct formed as a result of the reaction is 2-phenyl-3,4:3',2'-tetrahydropyrano-1,2,3,4-tetrahydroquinoline (I). Furfurylideneaniline and dilydropyran yield 2-(α-furyl)-3,4:3',2'-tetrahydropyrano-1,2,3,4-tetrahydroquinoline (II).



(II)

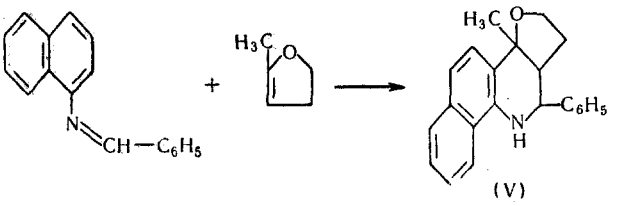
2-Methyl-4,5-dihydrofuran (dihydrosilvan) reacts especially vigorously with Schiff bases. 4-Methyl-2-phenyl-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (III) was obtained by its reaction with benzylideneaniline but 6-methoxy-4-methyl-2-phenyl-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (IV) was obtained with benzylidene-p-anidisine.



R = H, OCH_3

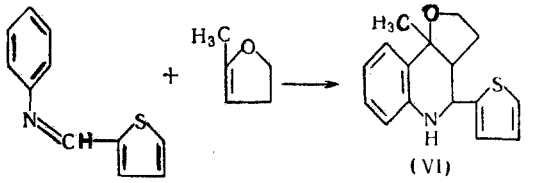
(III) (R = H),
IV) (R = OCH_3)

4-Methyl-2-phenyl-7,8-benzo-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (V) was isolated from the reaction between 2-methyl-4,5-dihydrofuran and benzylidene-α-napthylamine.



(V)

2-Methyl-4,5-dihydrofuran and thienylideneaniline reacted readily to form 4-methyl-2-(α-thienyl)-3,4:3', 2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (VI).



(VI)

The compounds prepared (I)-(VI) were stable crystalline substances which could be distilled under vacuum without decomposition. In all cases only one of the possible stereoisomers was formed which indicates that the reaction was stereospecific as is characteristic of the diene condensation.

EXPERIMENTAL

2-Phenyl-3,4:3',2'-tetrahydropyrano-1,2,3,4-tetrahydroquinoline (I). To a solution of 32 g of benzylideneaniline in 150 ml of absolute ether was added 0.5 ml of BF_3 etherate and then 15 g of dihydropyran was added. The reaction temperature rose from 23 to 28°. The mixture was stirred for 2 h without heating and for 6 h at 38-40°. After this the mixture was washed with 10% NaOH solution and dried over $MgSO_4$. After distilling the reaction products 7.0 g of (I) (14.8% yield) boiling at 183-185° (1.5 mm) was isolated; after crystallization from alcohol white crystals melting at 132-134°.

Found: C 81.55; 81.33; H 7.20; 7.19; N 5.40; 5.04%. $C_{18}H_{19}NO$. Calc: C 81.47; H 7.22; N 5.28%. All other experiments were carried out similarly.

2-(α-Furyl)-3,4:3',2'-tetrahydropyrano-1,2,3,4-tetrahydroquinoline (II). To a solution of 9.8 g of furfurylideneaniline in 50 ml of absolute benzene was added 0.3 ml of BF_3 etherate and 4.8 g of dihydropyran and the mixture was heated at 50° for 4 h. There was obtained 3.3 g of (II) (22.8% yield) boiling at 175-190° (0.2 mm) which after recrystallization from hexane and then from alcohol gave white crystals melting at 152.5-153.5°.

Found: C 74.68; 74.84; H 6.54; 6.68; N 5.67; 5.78%. $C_{16}H_{17}NO_2$. Calc: C 75.27; H 6.71; N 5.49%.

4-Methyl-2-phenyl-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (III). To a solution of 25 g of benzylideneaniline in 100 ml of benzene containing 0.5 ml of BF_3 etherate was added 12 g of 2-methyl-4,5-dihydrofuran. The temperature of the mixture spontaneously rose from 18.5 to 64°. The mixture was stirred without heating for 3 h. After distilling off solvent a crystalline residue was obtained; from this 30.2 g of (III) (81.3% yield) as white crystals melting at 139-139.5° was separated by crystallization from alcohol.

Found: C 80.96; 81.18; H 7.59; 7.41; N5.63; 5.48%. $C_{18}H_{19}NO$. Calc: C81.47; H 7.22; N 5.22%.

6-Methoxy-4-methyl-2-phenyl-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (IV). To a solution of 19.5 g of benzylidine-p-anisidine in 100 ml of benzene containing 0.25 ml of BF_3 etherate was added 8.7 g of 2-methyl-4,5-dihydrofuran. The reaction began rapidly and the temperature in the reaction mixture rose spontaneously from 18 to 47°. The mixture was stirred for 3 h. After distilling off solvent crystalline residue was obtained. After recrystallization from alcohol 18.7 g (70.3% yield) of crystals was obtained; IV was isolated melting at 149-151.5° after a second recrystallization.

Found: C 77.12; 76.88; H 7.22; 7.36%. $C_{19}H_{21}NO_2$. Calc: C 77.26; H 7.17; N 4.74%. In addition, crystals melting at 131-133° apparently an isomer of (IV) were isolated from the mother liquors. Found: C 77.90; 77.70; H 7.05; 7.18%.

4-Methyl-2-phenyl-7,8-benzo-3,4:3',2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (V). To a solution of 23 g of benzylidene-α-naphthylamine in 125 ml of benzene containing 0.5 ml of BF_3 etherate was added 9 g of 2-methyl-4,5-dihydrofuran. The reaction mixture was observed to heat from 18.5 to 49°. The mixture was stirred for 4 h and worked up by the general method. A fraction boiling at 220-230° (0.2 mm) was obtained by vacuum distillation; this solid glassy mass weighed 19.2 g (61%). Crystalline (V) melting at 145-147.5° was obtained by recrystallization from alcohol. Found: C 83.36; 83.28; H 6.78; 6.70% $C_{22}H_{21}NO$. Calc: C 83.77; H 6.71%.

4-Methyl-2-(α-thienyl)-3,4:3'2'-tetrahydrofurano-1,2,3,4-tetrahydroquinoline (VI). To a solution of 10 g of thienylideneaniline in 50 ml of benzene was added 0.25 ml of BF_3 etherate and then 4.7 g of 2-methyl-4,5-dihydropyran. The reaction mixture temperature rose from 22.5 to 49°. After being stirred for 1.5 h the mixture was worked up in the usual manner. After distilling off solvent a crystalline material was obtained from which 9 g of (VI) (61.50% yield) was isolated by recrystallization from alcohol; these white crystals melted at 142.5-144°.

Found: C 71.54; 71.34; H 6.31; 6.50; N 5.21; 5.14% $C_{16}H_{17}NOS$. Calc: C 70.82; H 6.31; N 5.16%.

SUMMARY

Schiff bases such as benzylideneaniline, benzylidene-p-anisidine, benzylidene-α-naphthylamine, and thienylideneaniline react in the presence of BF_3 with dihydropyran and 2-methyl-4,5-dihydrofuran by diene addition to form 1,2,3,4-tetrahydroquinoline derivatives as adducts.

LITERATURE CITED

1. L. S. Povarov, V. I. Grigos and B. M. Mikhailov, Izv. AN SSSR. Ser. khim. 1963, 2039.
