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NEW METHOD FOR SYNTHESIS OF ACYLALKYLIDENE-2,3-DIHYDROFURANS /2-FURYLIDENEACETOPHENONES/

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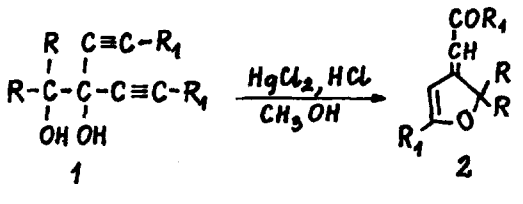
In the course of our investigation on cyclization of acetylene diols under action of mercuric salts [1-3] we have found the new simple way for synthesis of acylalkylidene-2,3-dihydrofurans of general structure /2/.

The compounds of type of alkylidene-2,3-dihydrofurans were so far little known [4,5] and the 3-acylmethylidene-2,3-dihydrofurans were just obtained in 1974 by Mariano and Peters [5] by treating 1-phenyl-4-methyl-4-hydroxypent-2-ene-1-on with diethylamine and subsequentely H_2SO_4 /34.4 % yield/.

Recently we have found that diols /1/ treated with methanolic solution of $HgCl_2$ acidified with hydrochloric acid isomerise to corresponding 2,3-dihydrofurans /2/ in 66 - 85 % yield [6].



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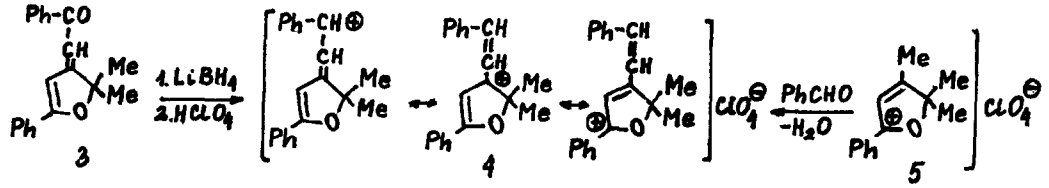
2/R, R_1, % yield are given/: CH_3, C_6H_5, 66,4; CH_3, p-C_6H_4Cl, 84,6; C_6H_5, C_6H_5, 70,0; C_6H_5, p-$C_6H_4CH_3$, 80,0.

Contrary to starting diols /1/ the compounds /2/ are very slightly soluble in cold methanol and precipitate almost completely from solutions forming full-yellow crystals [7].

The structure /3/ has been proved independently on chemical way. In the effect of reduction of /3/ with $LiBH_4$/THF, 20°, 12 h/ followed by treating with $HClO_4$ we have obtained the perchlorate /4/. This material is identical with the perchlorate obtained [8-10] previously by condensation of dihydrofurylium salt /5/ with benzoic aldehyde [11].

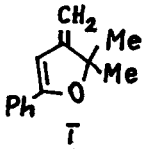


The identity of both perchlorates has been proved by uv and ir spectra.

It seems, that the formation of acylalkylidenedihydrofurans /2/ from diacetylene diols is, at least in case of R_1 = aryl, an universal reaction. The starting so far unknown, diols /1/ are easily accesible in reaction of organic ethynylmagnesium compounds with esters of α-hydroxyacids.

REFERENCES

1. E.D. Venus-Danilova, A. Fabrycy, Zh.Obschch.Khim. 26, 1609 /1956/
2. A. Fabrycy, R. Dobrzeniecka, Zh.Obschch.Khim. 37, 60 /1967/
3. A. Fabrycy, Z. Wichert, Roczniki Chem. 51, /1977/ in presse
4. R.Filler, E. Piasek, L. Mark, J.Org.Chem. 26, 2659 /1961/
5. P.S. Mariano, M. Peters, Tetrahedron Letters 30, 2607 /1974/
6. Satisfactory microanalytical and spectroscopic data were obtained for all new compounds.
7. Another product forming dark-brown crystals with metallic lustre /m.p. 218 - 219°/ precipitated in 8 % yield in case of the diol /1/ R = CH_3, R_1 = C_6H_5. This compound was sparingly soluble in organic solvents and could be easily separated from the main product /2/.
8. A. Fabrycy, Zh.Obschch.Khim. 31, 1548 /1961/
9. A.Fabrycy, Chimia 15, 552 /1961/
10. A. Fabrycy, Roczniki Chem. 40, 1657 /1966/
11. Mariano and Peter described in their paper [5] that reaction of CH_3Li with bullatenone gave unstable 2,2-dimethyl-3-methylene-5-phenyl-2,3-dihydrofuran. /I/ Our previous investigations [8] proved that this compound obtained in reaction of H_2SO_4 with diol II, is completely stable in a saltform. This compound in the form of perchlorate /5/ was used by us for synthesis of a series of colored dihydrofurylium salts [9,10].



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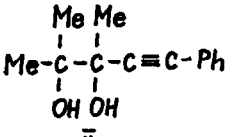

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