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Substituted Dihydrofurans Synthesis

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Abstract

In the interphase catalysis conditions C-alkenylation of the symmetric β-diketones by methylene group in presence of K_2CO_3/DMCO has been realized, on result of which the products of intramolecular heterocyclization – substituted dihydrofurans have been received.

Key words: *interphase catalysis, intramolecular heterocyclization, energy stabilization*

Introduction

β-dicarbonyl compounds as bifunctional reagents are convenient syntones for furans and tetrahydrofurans «designing».

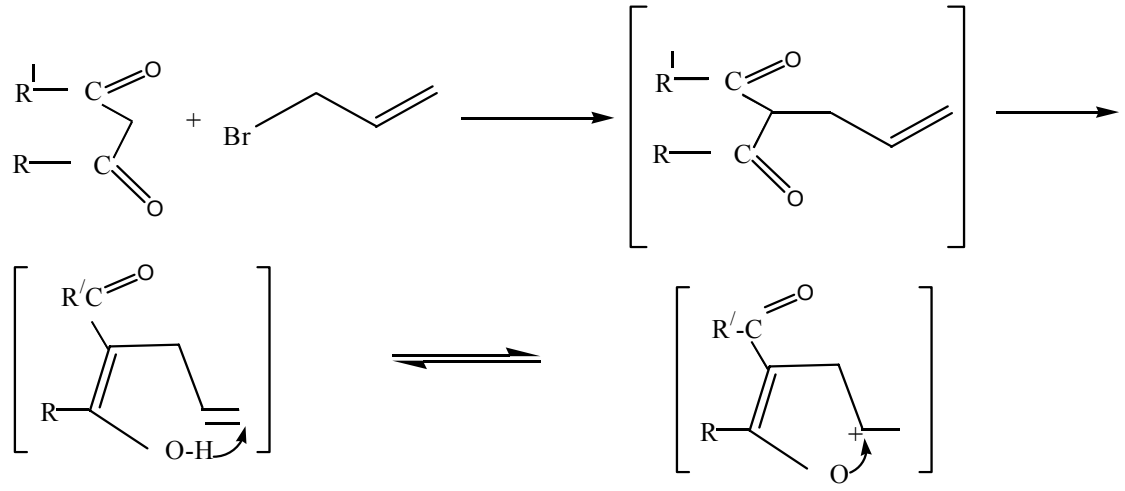
There are some works in technical publications dedicated to interaction of different alkylhalogens with compounds containing the active methylene group. The interest to this reaction is due to the fact that it is one of the synthesis method of dihydrofurans derivatives finding application in fine organic synthesis for production of physiologically active substances. However known in literature synthesis methods under action of strong alkalis (alcoholates and alkaline metals hydroxides) have some shortcomings. The essential shortcoming is formation of C-and O-isomers, influence of the solvent on reactions direction is not considered in detail [1-4], number of the published works is not enough.

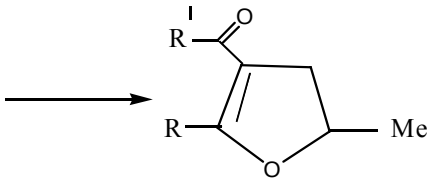
In this connection the convenient preparative cycloalkylation method of active methylene compounds by unsaturated C_3- halogens using the available alkalis as the condensing agents, precisely potassium carbonate, has been developed by us.

With the purpose of C-alkenylation by methylene group reactions of allylbromide with β-dicarbonyl compounds (acetylacetone, dimedone, dibenzoilmethane, malone ether) have been investigated and corresponding substituted dihydrofurans have been received.

In has been achieved that equimolar interaction of initial substances in the system K_2CO_3/DMCO leads to formation with yield up to 75% exclusively of the products of intramolecular cyclization of intermediately forming C_3-alkenylation products: 2,5-methyl-3-acetyl-[4-5]-dihydrofuran (I), 2-phenyl-3-benzoil-5- methyl-[4-5] dihydrofuran (II), 2,6,6-trimethyl-[2,3]-dihydrofuro [8,9-d]- cyclohexane-4(III) and 2-etoxi-3-etoxicarbonyl-5-methyl-[4-5]-dihydrofuran (IV).

It is obviously, the mechanism of considered reaction is contained in initial substitution of one of the hydrogen atoms of methylene group on allyl group, subsequent enolization of the forming 2-allylsubstituted 1,3-diketone (to that the alkali medium and power stabilization at the expense of double bond conjugation is conductive) with the following prototropic izomerization and ring closure of heterocycle.





(I-IV)

R= R/=Me (I) , Ph (II)

R+R/= -CH_2 CMe_2- CH_2- (III)

R=R/=-OEt (IV)

The structure of synthesized heterocycles (I-IV) is confirmed by NMR spectrums and dates of element analysis.

Experimental Details

The NMR spectrums have been taken on spectrometer «BRUKER-300» (working frequency is 300 and 75 MHz), inner standard TMC); purity of substances was checked by thin-layer chromatography on plates Sulifol «UV-254» in system hexane: izopropyl spirit (3:1)

2,5-dimethyl-3-acetyl-[4-5]-dihydrofuran (I)

The mixture consisting from 10 gram (0.1mole) acetylacetone, 12,1 gram (0.1mole) allyllbromide, 42 gram (0.3mole) K_2CO_3 in 70 ml DMCO have been mixed in 30^0C during 1 hour, then in 70^0C during 12 hours. Further, the reaction mixture have been cooled up to room temperature, distillate water have been added for potassium carbonate dissolution and it have been extracted by benzol. Benzol extracts have been washed by water and dried by anhydrous $CaCl_2$. Then, after benzol removing, the reaction mixture have been distillated under vacuum. It have been received 10,5 gram (75%) substance (I) with b.p. 112-114^{0}C (3mm), d_4^{20} 1,1876; n_D^{20} 1,4523; MR_D31,82. Calcd. 31,70. IR(ν, sm^{-1}): 1108 (C-O-C), 1615(C=C), 1718(C=C), 700, 750, 1420,

1595, 1505, 3090. NMR spectrum H(δ.m.d) 0,95d (3H,CH_3), 1,35d(2H,CH_2), 2,61d (3H,CH_3), 2,2C (3H, 3CH_3). Found., %: C 67,08; H 10,33; $C_8H_{12}O_2$. Calcd., %: C 67,13; H 10,49. (II-IV) compounds have been received similar.

2-phenil-3-benzoil-5methyl-[4,5] dihydrofuran (II)

B.p. 130-132^{0}C (2mm), d_4^{20} 1,2065; n_D^{20} 1,4523; MR_D50,57. Calcd. 50,53. IR(ν, sm^{-1}): 110(C-O-C), 1620(C=C), 1725(C=O), 700, 740, 1485, 1615, 1590, 1504, 3080(C_6H_5). NMR spectrum ^{1}H(δ.m.d) 0,98d (3H,CH_3), 1,38d(2H,CH_2) 7,16C (5H,C_6H_5), 7,25C (5H ,3C_6H_5). Found., %: C 81,78; H 5,98; $C_{18}H_{16}O_2$. Calcd., %: C 81,82, H6,06.

2,6,6-trimethyl-[2,3]-dihydrofuro-[8,9-d]-cyclohexane-4-on (III)

B.p. 168-171^{0}C (3mm), d_4^{20} 1,1693; n_D^{20} 1,4776; MR_D43,54. Calcd. 43,50. IR(ν, sm^{-1}): 1100(C-O-C), 1615(C=C), 1715(C=O). NMR spectrum ^{1}H(δ.m.d) 1,01d (3H,CH_3), 1,12C(6H,$(CH_3)_2$), 2,21m (4H,$(CH_2)_2$), 2,65C (2H,CH_2). Found., %: C 73,26; H 8,64%; $C_{11}H_{16}O_2$. Calcd., %: C 73,31, H 8,88.

2-etoxy-3-etoxycarbonyl-5-metyl-[4,5]- dihydrofuran (IV)

B.p. 127-130^{0}C (2mm), d_4^{20} 1,9762; n_D^{20} 1,4814; MR_D46,60. Calcd. 46,56. IR(ν, sm^{-1}): 1108(C-O-C), 1112(C-O), 1615(C=C), 1710(C=O). NMR spectrum ^{1}H(δ.m.d): 0.98t (3H,CH_3), 1.02t (CH,CH_3), 1.12d(3H,CH_3), 1.21m(1H,CH), 3.45(2H,CH_2O), 3.48(2H,CH_2O), 3.58m (2H,CH_2). Found., %: C 59.82, H 7.84 $C_{10}H_{16}O_4$. Calcd., %: C 60.00, H 8.00.

Conclusions

Equimolar interaction of the symmetric β-diketones and allylbromide in presence of K_2CO_3/DMCO leads to formation of exclusively products of intramolecular heterocyclization of intermediate-forming C-alkenylation products.

C-alkenylation of the β-dicarbonyl compounds by allylbromide in the conditions of interphase catalysis is common method of substituted dihydrofuranes synthesis.

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