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Phosphomolybdic Heteropolyacid – Catalyst of Allyl β -Iodoethers' Heterocyclization

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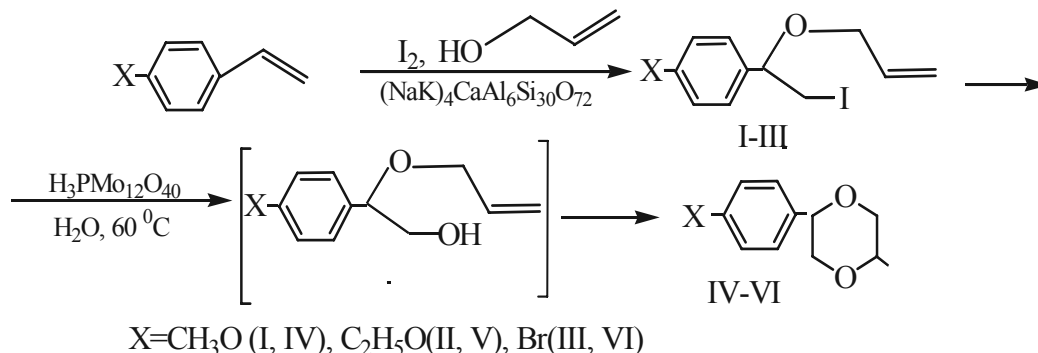
Abstract

Alkoxyiodination of 1-vinyl-4-organilbenzols by the allyl alcohol and crystalline iodine in the presence of $(\text{NaK})_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72}$ clinoptylolite results in receiving of allyl β -iodoethers with high yields. The last ones in the presence of heteropolyacid convert into substituted of 1,4-dioxane.

Introduction

One of the rational ways for allyl β -iodoethers' production is alkoxyiodination of olefins by the propenol and iodine in the presence of HgO [1,2]. It is found by us that replacement of the last one on $(\text{NaK})_4\text{CaAl}_6\text{Si}_{30}\text{O}_{72}$ clinoptylolite promotes carrying out of process with participation of more safe and nonpoisonous catalyst. As substituted olefins the *para*- substituted of styrene were used in result of which alkoxyhalogenation the aromatic series (I-III) allyl β -iodoethers with yield up to 80 % are obtained. Realization of C-I bond hydrolysis in (I-III) compounds promotes their transformation into monoallylic ethers of 1,2-diol which at heating in a water solution of the phosphomolybdic heteropolyacid form the products of the intermolecular cyclization – arylsubstituted 1,4-dioxanes (IV-VI), structural analogues of which are effective inhibitor of acid corrosion of metals in an corrosive medium [3].

Presence of methylene protons' signals of (I-III) compounds at 3.28 d.d (1H, J = 8.3, 5.8, CH_2I) and 3.41 d.d (1H, J = 8.3, 5.8, CH_2I) in the NMR ^1H spectrums of reaction products as well as presence of the absorption band of C-I bond's valence vibrations in the IR spectrums in the field of $545\text{-}560\text{ cm}^{-1}$ testify about regioselective alkoxyiodination of double bond of styrene *para*-substituted. Intermolecular O-H addition to double bond of allyl group in the (I-III) compounds also proceeds regioselectively about what signals of methyl groups connected with 1,4- dioxane ring in the NMR spectrums testify at $\delta=1.09\text{ d}$ (3H, CH_3 , J=6.9 Hz).



The structure of the received substituted heterocycles is confirmed also with the data of the element analysis.

Experimental details

IR spectrums of the compounds in a thin layer and with KBr pellets are taken off on device Specord 75 IR. NMR spectrums of substances in CDCl₃ solution are written down on device Bruker SF-400 (400.134 MHz), the internal standard - HMDS.

2-Iodo-1-(4-methoxyphenyl)-1-prop-2-enyloxyethane (I). 2.6 g of (NaK)₄CaAl₆Si₃₀O₇₂ clinoptylolite was added in cooled (-5±0°C) and intensively mixed mixture from 14 g (0,25 mole) of allyl spirit and 33.2g (0,25 mole) of 4-methoxyphenylstyrene, then 31.5g (0,12 mole) of fine crumbled crystal iodine was added by portions (on 1 g). Mixing continued at room temperature 3-4 hour else, then a mixture has filtered, a filtrate washed out by Na₂S₂O₃ solution and was extracted by ether. An extract was dried by CaCl₂, ether was deleted in the rotary evaporator, and the rest was recrystallized. It is received 54.2g (68 %) of substances (I) with b.p. 137-138°C (1 mm of a mc), d_4^{20} 1.646, n_D^{20} 1.5712, MR_D 63.96, calcd. 63.60. IR (ν, cm⁻¹): 560, 840-850, 1270, 1340-1360, 1515, 1630, 1640, 3010, 3080. NMR ¹H (δ, ppm): 3.24-3.40 m (2H, CH₂), 3.81 s (3H, CH₃), 3.89 d.d (1H, CH, J=12.5, 5.0 Hz), 3.98 d.d (1H, CH, J=12.5, 5.0 Hz), 4.43 d.d (1H, CH, J=8.0, 5.0 Hz), 5.18 d.d (1H, CH, J=10.0, 1.0 Hz), 5.27 d.d (1H, CH, J=17.0, 1.0 Hz), 5.85-5.98 m (1H, CH), 6.89 d (2H, C₆H₂, J=9.0 Hz), 7.24 d (2H, C₆H₂, J=9.0 Hz). NMR ¹³C (δ, ppm): 10.9, 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 134.9, 134.4, 159.6. Found., %: C 45.10, H 4.78, I 39.78. C₁₂H₁₅O₂I. Calcd., %: C 45.30, H 4.75, I 39.89.

Similarly allyl iodoethers (II,III) are obtained.

2-Iodo-1-(4-ethoxyphenyl)-1-prop-2-enyloxyethane (II). Yield 80.2%. B.p. 143-144°C (1 mm of a mc), d_4^{20} 1.5653, n_D^{20} 1.5782, MR_D 70.46, calcd. 69.93. IR (ν, cm⁻¹): 545, 840-850, 1270, 1340-1360, 1515, 1630, 1640, 3010, 3080. NMR ¹H (δ, ppm) : 1.18 t (3H, CH₃, J=7.2 Hz), 3.28 d.d (1H, CH₂I, J=8.3, 5.8 Hz), 3.41 d.d (1H, CH₂I, J=8.3, 5.8 Hz), 3.62 d.k (1H, H₂C, J=14.2, 7.2 Hz), 3.84 d.d (1H, CH, J=12.5, 5.0 Hz), 3.96 d.k (1H, H₂C, J=14.2, 7.2 Hz), 3.98 d.d (1H, CH, J=12.5, 5.0 Hz), 4.43 d.d (1H, CH, J=8.0, 5.0 Hz), 5.18 d.d (1H, CH, J=10.0, 1.0 Hz), 5.24 d.d (1H, CH, J=17.0, 1.0 Hz), 5.83-5.96 m (1H, CH), 6.84 d (2H, C₆H₂, J=9.0 Hz), 7.25 d (2H, C₆H₂, J=9.0 Hz). NMR ¹³C (δ, ppm): 9.9, 25.1, 54.3, 69.4, 80.2, 113.4, 118.6, 126.9, 130.7, 133.6, 133.4, 161.6. Found., %: C 46.96, H 5.20, I 38.12. C₁₃H₁₇O₂I. Calcd., %: C 47.00, H 5.16, I 38.20.

2-Iodo-1-(4-bromophenyl)-1-prop-2-enyloxyethane (III). Yield 67.2%. m.p. 78-79°C (from ethanol). IR (ν, cm⁻¹): 558, 670, 840-850, 1270, 1340-1360, 1515, 1630, 1640, 3010, 3080.

NMR ^1H (δ , ppm): 3.28 d.d (1H, CH_2I , $J=8.3, 5.8$ Hz), 3.41 d.d (1H, CH_2 , $J=8.3, 5.8$ Hz), 3.81 d.d (1H, CH, $J=12.5, 5.0$ Hz), 3.96 d.d (1H, CH, $J=12.5, 5.0$ Hz), 4.48 d.d (1H, CH, $J=8.3, 5.8$ Hz), 5.17 d.d (1H, CH, $J=10.0, 1.0$ Hz), 5.27 d.d (1H, CH, $J=17.0, 1.0$ Hz), 5.84-5.99 m (1H, CH), 6.94 d (2H, C_6H_2 , $J=9.0$ Hz), 7.34 d (2H, C_6H_2 , $J=9.0$ Hz). NMR ^{13}C (δ , ppm): 10.9, 55.3, 69.9, 80.5, 114.0, 117.4, 127.8, 131.9, 134.9, 134.4, 159.6. Found., %: C 35.92, H 3.21, Br 21.45, I 34.57. $\text{C}_{11}\text{H}_{12}\text{BrIO}$. Calcd., %: C 35.97, H 3.27, Br 21.80, I 34.60.

2-(4-Methoxyphenyl)-5-methyl-1,4-dioxane (IV). To stirring with a magnetic agitator mixture consisting from 1.2g of $\text{H}_3\text{PMo}_{12}\text{O}_{40}$ and 10 ml of water during 30 minutes 15.9g (0.05 mole) of (I) compound are added in 3ml of THF. Temperature of the mixture was gradually raised till 50-60 $^\circ\text{C}$ keeping up within 1 hour. After cooling the mixture was washed by the solution of soda (0.05 mole) and $\text{Na}_2\text{S}_2\text{O}_3$, extracted by ether and dried by MgCO_3 . After vacuum distillation it is extracted 6.64g (69.2 %) of (IV) substance with b.p. 89-90 $^\circ\text{C}$ (1 mm of a mc), d_4^{20} 1.3464, n_D^{20} 1.5595; MR_D 46.15, calcd. 45.75. NMR ^1H (δ , ppm): 1.09 d (3H, CH_3 , $J=6.9$ Hz), 3.45 d.d (1H, CH, $J=8.1, 6.9$ Hz), 3.65 d.d (1H, CH, $J=8.1, 6.9$ Hz), 3.80 c (3H, CH_3), 4.12 d.d (1H, CH, $J=8.1, 6.9$ Hz), 4.20 d.d (1H, CH, $J=8.4, 6.9$ Hz), 4.97 t (1H, CH, $J=6.9$ Hz), 5.13 d.d (1H, CH, $J=8.1, 6.9$ Hz), 6.85-6.89 m (2H, C_6H_2), 7.23-7.29 m (2H, C_6H_2). NMR ^{13}C (δ , ppm): 17.9, 33.3, 42.6, 43.8, 55.2, 75.5, 79.7, 113.5, 126.7, 135.6, 158.5. Found., %: C 79.93, H 8.44. $\text{C}_{12}\text{H}_{16}\text{O}_3$. Calcd., %: C 74.07, H 8.39.

Similarly substituted dioxanes (V,VI) are obtained.

2-(4-Etoxyphenyl)-5-methyl-1,4-dioxane (V). Yield 87.2%. b.p. 94-95 $^\circ\text{C}$ (1 mm of mc), d_4^{20} 1.2860, n_D^{20} 1.5602; MR_D 55.92, calcd. 55.58. NMR ^1H (δ , ppm): 1.09 d (3H, CH_3 , $J=6.9$ Hz), 1.18 t (3H, CH_3 , $J=7.5$ Hz), 2.36-2.50 m (1H, CH), 3.45 d.d (1H, CH, $J=8.1, 6.9$ Hz), 3.75 κ (2H, CH_2 , $J=7.5$ Hz), 4.12 d.d (1H, CH, $J=8.1, 6.9$ Hz), 4.20 d.d (1H, CH, $J=8.4, 6.9$ Hz), 4.97 t (1H, CH, $J=6.9$ Hz), 5.16 d.d (1H, CH, $J=8.1, 6.9$ Hz), 6.85-6.89 m (2H, C_6H_2), 7.23-7.29 m (2H, C_6H_2). NMR ^{13}C (δ , ppm): 16.9, 25.4, 33.3, 42.6, 43.8, 55.2, 75.5, 79.7, 113.5, 126.7, 135.6, 158.5. Found., %: C 70.21, H 8.20. $\text{C}_{13}\text{H}_{18}\text{O}_3$. Calcd., %: C 70.24, H 8.16.

2-(4-Bromophenyl)-5-methyl-1,4-dioxane (VI). Yield 80.2%. b.p. 111-112 $^\circ\text{C}$ (1 mm of mc), d_4^{20} 1.6304, n_D^{20} 1.512; MR_D 52.61, calcd. 52.13. NMR ^1H (δ , ppm): 1.07 d (3H, CH_3 , $J=6.9$ Hz), 2.36-2.50 m (1H, CH), 3.45 d.d (1H, CH, $J=8.1, 6.9$ Hz), 3.63 d.d (1H, CH, $J=8.1, 6.9$ Hz), 4.16 d.d (1H, CH, $J=8.1, 6.9$ Hz), 4.20 d.d (1H, CH, $J=8.4, 6.9$ Hz), 4.97 t (1H, CH, $J=6.9$ Hz), 5.14 d.d (1H, CH, $J=8.1, 6.9$ Hz), 6.85-6.89 m (2H, C_6H_2), 7.23-7.29 m (2H, C_6H_2). NMR ^{13}C (δ , ppm): 16.9, 32.3, 41.6, 54.2, 73.5, 77.7, 112.5, 125.7, 133.6, 157.5. Found., %: C 51.31, H 5.46, Br 31.52. $\text{C}_{11}\text{H}_{14}\text{BrO}_2$. Calcd., %: C 51.36, H 5.06, Br 31.12

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Heteropoliacid fosfomolibdenic – catalizator pentru heterociclizarea alil β - iodoeterilor

Rezumat

Alcoxi iodurarea 1-vinil-4-organilbenzolilor cu alcooli alilici și iod cristalin în prezența de clinoptilolit $(NaK)_4CaAl_6Si_3O_{72}$ conduce la obținerea de alil- β -iodoeteri cu randamente ridicate. Ultimii termeni amintiți, în prezența de heteropoliacizi conduc la 1,4-dioxan substituit.