With vigorous stirring, to a solution of 0.257 g (1 mmole) of $Ni(acac)_2$, 1.048 g (4 mmoles) of Ph_3P, and 25 mmoles of the appropriate allyl compound in 15 ml of THF, cooled to −5°C, was added in an argon stream 30 mmoles of magnesium diacetylide and the mixture was kept at this temperature for 15 min. The solution was transferred to a thermostatted glass reactor and heated for 4 h at 50°C. The catalyzate was decomposed with 50% HCl solution and repeatedly extracted with ether. The ether extracts were washed with water until neutral and dried over $MgSO_4$. After removal of the solvent the residue was vacuum-distilled. The obtained 1,4-enynes has the following constants: 1-nonen-4-yne, bp 52°C (12 mm), n_D^{20} 1.4442, M^+ 122 (bp 58° (22 mm), n_D^{25} 1.4413 [1]); 1-undecen-4-yne, bp 51-52° (2 mm), n_D^{20} 1.4485, M^+ 150 (cf. [6]); 5-phenyl-1-penten-4-yne, bp 85-86° (6 mm), n_D^{20} 1.5586, M^+ 142 (bp 107-108° (22 mm), n_D^{25} 1.5574 [1]).

CONCLUSIONS

A method was developed for the synthesis of 1,4-enynes by the cross-coupling of compounds of type $(RC{\equiv}C)_2Mg$ and $RC{\equiv}CMgBr$ with allyl alcohol derivatives using $Ni(acac)_2$–Ph_3P as the catalyst.

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SYNTHESIS AND TRANSFORMATION OF 2-METHYL-3-ACETYL-1,6-DIOXASPIRO[4.4]-2-NONENE

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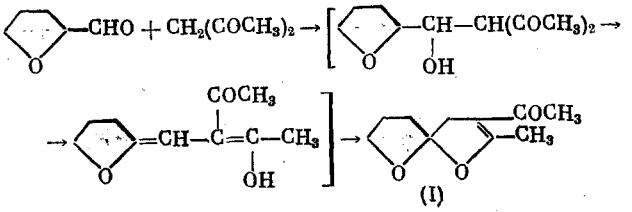
2-Methyl-3-acetyl-1,6-dioxaspiro[4.4]-2-nonene (I) is the first member of a new type of 1,6-dioxaspirononenes, which we obtained by the pyrolysis of 2-(1-acetoxy-2-butynyl)tetrahydrofuran [1]. Continuing the study, we developed a new method for the synthesis of 2,3-disubstituted 1,6-dioxaspirononenes by the condensation of tetrahydrofurfurole with 1,3-dicarbonyl compounds. A similar condensation was accomplished with acetoacetic ester [2]. In the present paper it was shown that the reaction of tetrahydrofurfurole with acetylacetone in the presence of catalytic amounts of β-alanine and AcOH gives a 65% yield of 2-methyl-3-acetyl-1,6-dioxaspiro[4.4]-2-nonene (I), whose physicochemical characteristics coincide completely with those for the thermoisomerization product of 2-(1-acetoxy-2-butynyl)tetrahydrofuran [1].



When the chemical transformation of the obtained spironone were studied we found that the mild alkaline hydrolysis of (I) leads to the formation of 2-(2-hydroxyethyl)-3-methyl-2-cyclopenten-1-one (II) in quantitative yield. 2-Methyl-3-acetyl-5-(3-hydroxypropyl)furan (III) was obtained in good yield when (I) is refluxed in DMSO in an N_2 stream. The reaction

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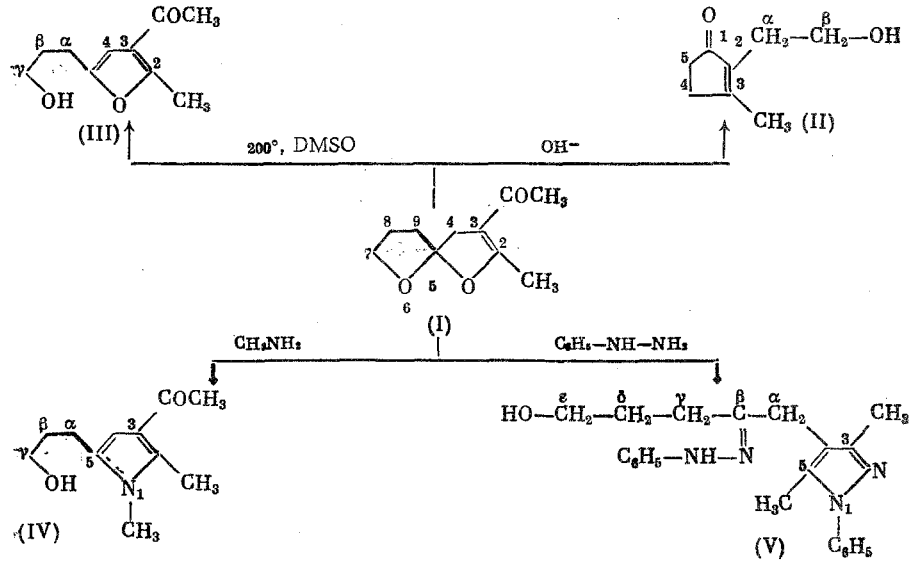
of (I) with methylamine and phenylhydrazine leads to the respective formation of 1,2-dimethyl-3-acetoxy-5-(3-hydroxypropyl)pyrrole (IV) and the phenylhydrazone of 1-phenyl-3,5-dimethyl-4-(5-hydroxy-2-oxopentyl)pyrazole (V).



The described transformations of (I) open up a path for the synthesis of previously unknown difficultly available furan, cyclopentenone, pyrrole, and pyrazole derivatives.

EXPERIMENTAL

The PMR spectra were recorded on a Tesla BS-467 instrument (60 MHz), the ^{13}C NMR spectrum was recorded on a Bruker WM-250 instrument (in $CDCl_3$ solution and using HMDS as the internal standard), the IR spectra were taken on a UR-20 spectrometer, and the mass spectra were taken on a Varian MAT CH-6 spectrometer (70 eV). The TLC was run on Silufol SiO_2 (Czechoslovakia).

2-Methyl-3-acetyl-1,6-dioxaspiro[4,4]-2-nonene (I). A mixture of 40 g (0.4 mole) of freshly distilled tetrahydrofurfurole, 40 g (0.4 mole) of acetylacetone, 6 g (0.1 mole) of AcOH, and 2.7 g (0.03 mole) of β-alanine in 150 ml of benzene was stirred for 18 h at ~20°C. Then a water separator and reflux condenser were attached and the mixture was heated for 2 h until the water separation ceased. The mixture was cooled, washed with 3 × 10 ml of satd. NaCl solution, and dried over $MgSO_4$. After distilling off the benzene the residue was vacuum-distilled. We obtained 47 g (65%) of (I), bp 116-117° (3 mm), n_D^{20} 1.5109; m/z 182. Infrared spectrum (ν, cm^{-1}): 1600 (C=C), 1625, 1675 (C=O). PMR spectrum (δ, ppm): 1.72-2.25 m (4H, 8,9-CH_2), 2.08 s (3H, O=C-CH_3), 2.12 t (3H, 2-CH_3, $J_{4,2}$ = 1.8 Hz), 2.95 g (2H, 4-CH_2, $J_{2,4}$ = 1.8 Hz), 3.87-4.05 m (2H, 7-CH_2).

2-(2-Hydroxyethyl)-3-methyl-2-cyclopenten-1-one (II). To 50 ml of 15% NaOH solution was added 9.1 g (0.05 mole) of freshly distilled (I) and the mixture was stirred for 2.5 h at 45°C neutralized to pH 4 with 20% H_2SO_4 solution, and then saturated with $NaHCO_3$ and extracted with ether. From the ether layer we isolated (II) in quantitative yield, bp 110-111° (2 mm), n_D^{20} 1.5162, m/z 140. Found: C 68.43; H 8.51%. $C_8H_{12}O_2$. Calculated: C 68.54; H 8.63%. Infrared spectrum (ν, cm^{-1}): 1640 (C=C), 1690 (C=O), 3450 (OH). PMR spectrum (δ, ppm): 2.10 s (3H, 3-CH_3), 2.38 m (2H, 4-CH_2), 2.45 t (2H, α-CH_2, $J_{\beta\alpha}$ = 4.5 Hz), 2.57 m (2H, 5-CH_2), 3.60 t (2H, β-CH_2, $J_{\alpha\beta}$ = 4.5 Hz), 3.75 br. s (1H, OH). ^{13}C NMR spectrum (δ, ppm): 16.2 q (3-CH_3), 25.8 t (C_α), 30.7 t (C_4), 33.1 t (C_5), 59.3 t (C_β), 136.1 s (C_2), 172.4 s (C_3), 209.1 s (C=O).

2-Methyl-3-acetyl-5-(3-hydroxypropyl)furan (III). A solution of 6 g (0.03 mole) of freshly distilled (I) in 25 ml of DMSO was refluxed for 3 h in a nitrogen stream. After fractional distillation of the reaction mixture in vacuo in a nitrogen stream we isolated 3.8 g (63%) of (III), bp 140-141° (1 mm), n_D^{20} 1.5122, m/z 182. Found: C 65.63; H 7.61%. $C_{10}H_{14}O_3$. Calculated: C 65.91; H 7.74%. Infrared spectrum (ν, cm^{-1}): 1570, 1609, 1670 (C=O), 3430 (OH). PMR spectrum (δ, ppm): 1.90 m (2H, β-CH_2), 2.30 s (3H, CH_3-C=O), 2.50 s (3H, 2-CH_3), 2.60 m (2H, α-CH_2), 3.40 s (1H, OH), 3.60 t (2H, γ-CH_2, $J_{\beta\gamma}$ = 6.2 Hz), 6.20 s (1H, 4-CH=C<).

1,2-Dimethyl-3-acetoxy-5-(3-hydroxypropyl)pyrrole (IV). A mixture of 9.1 g (0.05 mole) of freshly distilled (I) and 3.1 g (0.1 mole) of 30% aqueous methylamine solution in 40 ml

of EtOH was stirred for 18 h at ~20°C. After evaporation and recrystallization of the residue from ether we obtained 8.5 g (87%) of (IV), mp 77-78°, m/z 195. Found: C 67.56; H 8.70; N 7.30%. $C_{11}H_{17}NO_2$. Calculated: C 67.66; H 8.73; N 7.17%. Infrared spectrum (ν, cm^{-1}): 1530, 1565, 1635 (C=O), 3340 (OH). PMR spectrum (δ, ppm): 1.94 t.t. (2H, β-CH_2, $J_{\beta\gamma}$ = 6.2 Hz, $J_{\beta\alpha}$ = 7.8 Hz), 2.42 s (3H, 2-CH_3), 2.58 s (3H, CH_3—C(=O)—), 2.70 t (2H, α-CH_2, $J_{\alpha\beta}$ = 7.8 Hz), 2.83 br.s (1H, OH), 3.47 s (3H, >N—CH_3), 3.80 t (2H, γ-CH_2, $J_{\gamma\beta}$ = 6.2 Hz), 6.28 s (1H, 4—CH=C<). ^{13}C NMR spectrum (δ, ppm): 11.3 q ($\underline{CH_3}$—C(=O)—), 2.24 t (C_β), 27.9 q (2-CH_3), 29.5 q (N—CH_3), 31.1 t (C_α), 61.1 t (C_γ), 106.6 d (C_4), 119.5 s (C_3), 131.8 s (C_5), 135.0 s (C_2), 194.7 s (C=O).

1-Phenyl-3,5-dimethyl-4-(5-hydroxy-2-oxopentyl)pyrazole Phenylhydrazone (V). A mixture of 2.7 g (0.015 mole) of freshly distilled (I) and 3.2 g (0.03 mole) of phenylhydrazine in 100 ml of abs. EtOH was stirred for 18 h at ~20°C. After evaporation and recrystallization of the residue from acetone we isolated 2.3 g (42%) of((V), mp 127-128°, m/z 362. Found: C 72.54; H 7.11; N 15.19%. $C_{22}H_{26}N_4O$. Calculated: C 72.90; H 7.23; N 15.46%. Infrared spectrum (ν, cm^{-1}): 1460, 1600, 3315, 3620. PMR spectrum (δ, ppm): 1.75 m (2H, δ-CH_2), 2.16 s (3H, 5-CH_3), 2.15 m (2H, γ-CH_2), 2.24 s (3H, 3-CH_3), 3.30 s (2H, α-CH_2), 3.50 m (2H, ε-CH_2), 7.10 w. m (10H, $-C_6H_5$).

CONCLUSIONS

2-Methyl-3-acetyl-1,6-dioxaspiro[4,4]-2-nonene is formed when tetrahydrofurfurole is reacted with acetylactone, from which some new furan, cyclopentenone, pyrrole and pyrazole derivatives were obtained.

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SYNTHESIS OF ACYL-SUBSTITUTED S-BUTYNE ESTERS OF PROSPHORUS THIOACIDS

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Previously [1, 2] it was shown that the ω-alkylmercaptobutyne esters of phosphorus thioacids exhibit a substantial anticholinesterase and insectoacaricide activity.

It seemed of interest to synthesize and study the S-butyne esters of P thioacids in which the hydrophobic alkylmercapto groups in the ω-position of the thioester radical are replaced by either the less hydrophobic acylmercapto or acyloxy group.

$$RR'P(X)SCH_2C{\equiv}CCH_2YC(O)Me$$

(Ia — k)

where R = Me, R′ = EtO, X = O, Y = S (a); R = Ph, R′ = EtO, X = O, Y = S (b); R = R′ = MeO, X = O, Y = S (c); R = R′ = EtO, X = O, Y = S (d); R = R′ = MeO, X = Y = S (e); R = R′ = EtO, X = Y = S (f); R = R′ = MeO, X = Y = O (g); R = R′ = EtO, X = Y = O (h); R = R′ = MeO, X = S, Y = O (i); R = R′ = EtO, X = S, Y = O (k).

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