ISSN 1070-4280, Russian Journal of Organic Chemistry, 2013, Vol. 49, No. 9, pp. 1264–1269. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © A.A. Golovanov, D.R. Latypova, V.V. Bekin, V.S. Pisareva, A.V. Vologzhanina, V.A. Dokichev, 2013, published in Zhurnal Organicheskoi Khimii, 2013, Vol. 49, No. 9, pp. 1282–1286.

Synthesis of 1,5-Disubstituted (*E*)-Pent-2-en-4-yn-1-ones

A. A. Golovanov[a], D. R. Latypova[b], V. V. Bekin[a], V. S. Pisareva[a], A. V. Vologzhanina[c], and V. A. Dokichev[b]

[a] *Togliatti State University, Belorusskaya ul. 14, Togliatti, 445667 Russia*

[b] *Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences, pr. Oktyabrya 71, Ufa, 450054 Bashkortostan, Russia*
e-mail: dokichev@anrb.ru

[c] *Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, ul. Vavilova 28, Moscow, 119991 Russia*

Received March 27, 2013

Abstract—The condensation of 3-arylpropynals with aryl methyl ketones in the presence of sodium hydroxide in 50% aqueous ethanol at 0°C (Claisen–Schmidt reaction) afforded up to 89% of the corresponding (*E*)-1,5-diarylpent-2-en-4-yn-1-ones. The *E* configuration of the double C=C bond and *cis* conformation of the enone fragment in the products in crystal and $CDCl_3$ solution were determined by X-ray analysis and ^1H NMR spectroscopy.

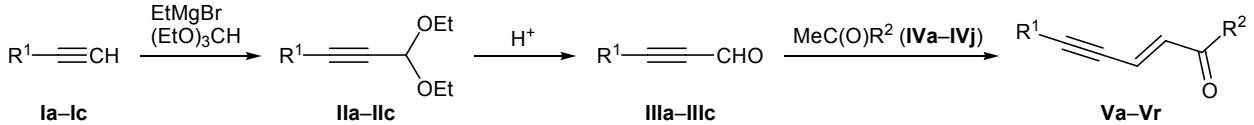
DOI: 10.1134/S1070428013090030

In recent years pentenynones, conjugated vinylacetylenic ketones, have attracted appreciable interest as promising biologically active compounds and building blocks ensuring selective modification of C=C, C≡C, or C=O bonds to pyrazole [1, 2], furan [3–5], pyran [6–8], dihydrothiopyranone [7–9], and other pharmacophoric fragments [10]. 1,5-Disubstitued pent-2-en-4-yn-1-ones are also interesting as initial compounds for the synthesis of new PI3K inhibitors which possess a huge potential for the treatment of cardiovascular, inflammatory, and autoimmune diseases, as well as of cancer and AIDS [5]. New compounds of this series are extensively synthesized; they are generally prepared by the Claisen–Schmidt condensation [11, 12], catalytic vinylation of iodoacetylenes [13], or base-catalyzed isomerization of 1,5-disubstituted penta-2,4-diynyl silyl ethers [14].

The present work was aimed at synthesizing a wider series of 1,5-disubstituted pent-2-en-4-yn-1-ones and studying how the structure of initial acetylenic aldehydes **IIIa**–**IIIc** and methyl ketones **IVa**–**IVj** affects the yield and structure of products of their base-catalyzed condensation. Initial phenyl-, 4-methylphenyl-, and 4-bromophenylprop-2-ynals **IIIa**–**IIIc** were prepared by hydrolysis of propynal diethyl acetals **IIa**–**IIc**, which were synthesized in turn by successive reactions of arylacetylenes **Ia**–**Ic** with ethylmagnesium bromide and triethyl orthoformate in diethyl ether.

The condensation of aldehydes **III** with methyl ketones **IV** was carried out at 0°C in aqueous ethanol, the molar ratio **III**–**IV**–NaOH being 1:1:0.5. In all cases, the reaction did not stop at the aldolization step and resulted in selective formation of *E* isomers **Va**–

Scheme 1.



I–**III**, R^1 = Ph (**a**), 4-MeC_6H_4 (**b**), 4-BrC_6H_4 (**c**); **IV**, R^2 = Ph (**a**), 4-MeC_6H_4 (**b**), 4-*i*-PrC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 4-$EtOC_6H_4$ (**e**), 4-ClC_6H_4 (**f**), 3-BrC_6H_4 (**g**), 4-BrC_6H_4 (**h**), 3-$H_2NC_6H_4$ (**i**), 2-furyl (**j**); **V**, $R^1 = R^2$ = Ph (**a**); R^1 = Ph, R^2 = 4-MeC_6H_4 (**b**), 4-*i*-PrC_6H_4 (**c**), 4-$MeOC_6H_4$ (**d**), 4-$EtOC_6H_4$ (**e**), 4-ClC_6H_4 (**f**), 3-BrC_6H_4 (**g**), 4-BrC_6H_4 (**h**), 3-$H_2NC_6H_4$ (**i**), 2-furyl (**j**); R^1 = 4-MeC_6H_4, R^2 = Ph (**k**), 4-MeC_6H_4 (**l**), 4-ClC_6H_4 (**m**), Ph (**n**), 4-BrC_6H_4 (**o**), 2-furyl (**p**).

Vp in 10–89% yield (Scheme 1). The products were isolated as light yellow or yellow needles or plates. According to published data, base-catalyzed isomerization of 1,5-disubstituted penta-2,4-diynyl silyl ethers yields mixtures of *E*- and *Z*-isomeric pent-2-en-4-yn-1-ones [14].

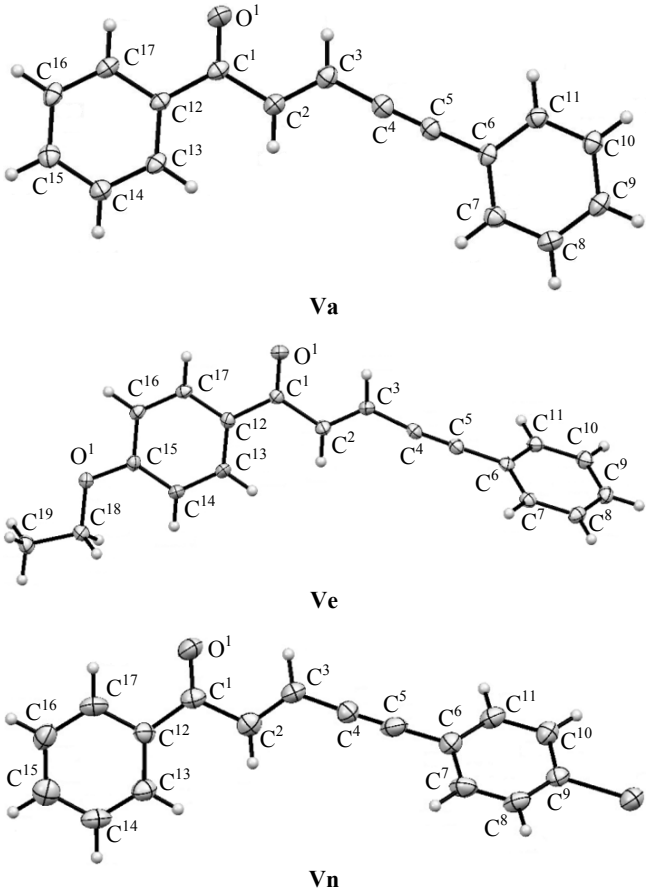
The nature of both aldehyde and acetophenone components exerts a considerable effect on the yield of the condensation products. The reactions of *meta*-substituted acetophenones **IVg** and **IVi** with phenylprop-2-ynal (**IIIa**) were accompanied by tarring, and the yield of pent-2-en-4-yn-1-ones **Vg** and **Vi** was as poor as 30 and 10%, respectively. Introduction of a methyl group or bromine atom into the *para* position of the aromatic ring of phenylprop-2-ynal led to reduction of the yield of **Vk**–**Vp** to 20–68%.

The product structure was confirmed by the ^{1}H and ^{13}C NMR spectra. The ^{1}H NMR spectra of pent-2-en-4-yn-1-ones **Va**–**Vp** contained two doublets at δ 6.90–7.14 (2-H) and 7.39–7.45 ppm (3-H) from protons at the double C^2=C^3 bond. The vicinal coupling constant ^{3}J = 15.4–15.6 Hz indicated *E* configuration of that bond. The *E* configuration of the C=C bond and *s-cis* conformation of the enone fragment in molecules **V** in crystal were unambiguously determined by X-ray analysis of 1,5-diphenylpent-2-en-4-yn-1-one (**Va**), 1-(4-ethoxyphenyl)-5-phenylpent-2-en-4-yn-1-one (**Ve**), and 5-(4-bromophenyl)-1-phenylpent-2-en-4-yn-1-one (**Vn**). The structures of molecules **Va**, **Ve**, and **Vn** are shown in figure. The torsion angles $C^1C^2C^3C^4$ (–176.2 to –178.0°) and $OC^1C^2C^3$ (2.6–7.1°) correspond to the *E-s-cis* configuration of the O=C^1–C^2=C^3–C^4 enone fragment. Molecules **Va**, **Ve**, and **Vn** are planar, which implies conjugation of the lone electron pair on the oxygen atom with the unsaturated bond system. It should be noted that the C^3–C^4 bond in **Va**, **Ve**, and **Vn** is appreciably shorter than analogous bond in vinylacetylene (1.45 Å) [15] (Table 1). The other bond lengths and bond angles in molecules **Va**, **Ve**, and **Vn** almost coincide with the corresponding standard values.

Thus the condensation of 3-arylpropynals with acetophenones afforded 1,5-disubstituted (*E*)-pent-2-en-4-yn-1-ones whose yield was largely determined by the nature of the initial compounds.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer at 300.13 and 75.47 MHz, respectively, using tetramethylsilane as internal reference. The IR spectra were measured on an FSM 1201 spectrometer with Fourier transform. The X-ray diffraction data for compounds **Va**, **Ve**, and **Vn** were acquired on a Bruker Smart Apex2 CCD diffractometer. The structures were solved by the direct



Structures of the molecules of 1,5-diphenylpent-2-en-4-yn-1-one (**Va**), 1-(4-ethoxyphenyl)-5-phenylpent-2-en-4-yn-1-one (**Ve**), and 5-(4-bromophenyl)-1-phenylpent-2-en-4-yn-1-one (**Vn**) according to the X-ray diffraction data.

Table 1. Bond lengths in the pent-2-en-4-yn-1-one fragment of compounds **Va**, **Ve**, and **Vn**

Bond	Bond length *d*, Å		
	Va	**Ve**	**Vn**
O^1–C^1	1.224(3)	1.227(2)	1.223(12)
C^1–C^2	1.478(4)	1.490(2)	1.514(15)
C^1–C^{12}	1.484(4)	1.481(2)	1.461(15)
C^2–C^3	1.324(4)	1.317(2)	1.328(16)
C^3–C^4	1.419(4)	1.425(2)	1.414(15)
C^4–C^5	1.204(4)	1.199(2)	1.197(15)
C^5–C^6	1.427(4)	1.442(2)	1.451(15)

Table 2. Principal crystallographic parameters of pent-2-en-4-yn-1-ones **Va**, **Ve**, and **Vn** and details of X-ray diffraction experiments

Parameter	**Va**	**Ve**	**Vn**
CCDC entry no.	922718	925324	925325
Formula	$C_{17}H_{12}O$	$C_{19}H_{16}O_2$	$C_{17}H_{11}BrO$
Molecular weight	232.27	276.36	311.17
Temperature, K	100(2)	100(2)	100(2)
Irradiation wavelength, Å	0.71073	0.71073	1.54178
Crystal system	Rhombic	Rhombic	Monoclinic
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_1$
Unit cell parameters:			
a, Å	5.459(4)	5.3536(7)	4.9937(2)
b, Å	13.641(9)	10.9497(14)	23.1953(10)
c, Å	16.245(11)	24.370(3)	5.7760(2)
β, deg	90	90	98.496(3)
V, Å^3	1209.6(13)	1428.6(3)	661.69(5)
Z	4	4	2
F(000)	488	584	312
Crystal habit, mm	0.36×0.12×0.09	0.42×0.38×0.08	0.16×0.14×0.03
d_{calc}, g/cm^3	1.275	1.285	1.562
μ, mm^{-1}	0.078	0.082	4.123
Number of independent reflections (R_{int})	1695 (0.10)	2216 (0.034)	1946 (0.074)
Number of measured reflections/parameters	1218/163	1931/191	1748/172
R, % [$I > 2\sigma(I)$]	0.045	0.037	0.068
R_w, %	0.097	0.093	0.161
Goodness of fit	1.00	1.01	1.00

method. All non-hydrogen atoms were localized by difference syntheses of electron density, and their positions were refined against F^2_{hkl} in anisotropic approximation. All calculations were performed using SHELXTL 5.10 [16]. Selected bond lengths in molecules **Va**, **Ve**, and **Vn** are given in Table 1, and parameters of X-ray diffraction experiments and final divergence factors are collected in Table 2. The sets of crystallographic data for compounds **Va**, **Ve**, and **Vn** (CIF files) were deposited to the Cambridge Crystallographic Data Centre (*http://ccdc.cam.ac.uk/*).

The structure of previously described compounds **IIa** [17], **IIIa** [19], **Va** [22], **Vd**, **Vf**, and **Vj** [14] was confirmed by their ^{1}H and ^{13}C NMR and IR spectra which coincided with those reported in the literature.

3-Arylprop-2-ynal diethyl acetals IIa–IIc (*general procedure*). A solution of 0.085 mol of arylacetylene **Ia**–**Ic** in 15 ml of anhydrous diethyl ether was added dropwise to the Grignard compound prepared from 2.01 g (0.085 mol) of magnesium and 9.30 g (0.085 mol) of ethyl bromide in 100 ml of anhydrous diethyl ether on cooling, and the mixture was heated for 2 h under reflux with stirring and was left to stand for 10 h. A solution of 15 g (0.101 mol) of triethyl orthoformate in 30 ml of diethyl ether was added under vigorous stirring to the resulting precipitate of Iotsitch compound, and the mixture was left to stand for 10 h and was then heated under reflux for 4.5 h. The mixture was treated with a solution of 26 g of ammonium chloride in 74 ml of water on cooling with ice. The organic phase was separated, the aqueous phase was extracted with diethyl ether (3×10 ml), the extracts were combined with the organic phase, dried over $MgSO_4$, and evaporated on a water bath, and the residue was distilled under reduced pressure.

3,3-Diethoxy-1-phenylpropyne (IIa). Yield 79%, bp 121–122°C (1 mm), n_D^{19} = 1.5191 [17].

3,3-Diethoxy-1-(4-methylphenyl)propyne (IIb). Yield 54%, bp 135–136°C (5 mm), d^{20} = 0.985, n_D^{20} = 1.5207. IR spectrum: ν 2238 cm^{-1} (C≡C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.27 t (6H, CH_2CH_3, ^3J = 6.0 Hz), 2.33 s (3H, $C_6H_4CH_3$), 3.60–3.71 m and 3.78–3.87 m (2H each, OCH_2), 5.48 s (1H, CH), 7.05–7.12 m and 7.32–7.40 m (2H each, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.58, 21.01, 62.52, 84.02, 86.01, 92.68, 120.02, 129.02, 130.83, 140.03 [18].

1-(4-Bromophenyl)-3,3-diethoxypropyne (IIc). Yield 54%, bp 161–164°C (7 mm), d^{20} = 1.269, $n_D^{20.2}$ = 1.5503. IR spectrum: ν 2240 cm^{-1} (C≡C). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.16–1.23 m (6H, CH_2CH_3), 3.55–3.61 m and 3.71–3.76 m (2H each, OCH_2), 5.40 br.s (1H, CH), 7.24–7.27 m and 7.34–7.38 m (2H each, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 14.84, 60.67, 83.74, 85.42, 91.44, 120.56, 122.87, 131.28, 133.23. Found, %: C 51.62; H 4.46; Br 31.29. $C_{11}H_{11}O_2Br$. Calculated, %: C 51.79; H 4.35; Br 31.32.

3-Arylprop-2-ynals IIIa–IIIc (*general procedure*). A mixture of 38 mmol of acetal **IIa–IIc**, 10 ml of 5% sulfuric acid, and 10 ml of glacial acetic acid was heated for 1 h on a boiling water bath. Ethanol liberated during the hydrolysis process was distilled off under reduced pressure (water-jet pump). The still residue was cooled, combined with the distillate, and treated with $NaHCO_3$ until neutral reaction. The product was extracted into diethyl ether (3×10 ml), the combined extracts were dried over $MgSO_4$ and evaporated on a water bath, and the residue was distilled under reduced pressure.

3-Phenylprop-2-ynal (IIIa). Yield 94%, bp 105–107°C (13 mm), n_D^{22} = 1.6027 [19].

3-(4-Methylphenyl)prop-2-ynal (IIIb). Yield 75%, bp 126–128°C (12 mm), $n_D^{19.5}$ = 1.6066. IR spectrum, ν, cm^{-1}: 2186 (C≡C), 1657 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.35 s (3H, CH_3), 7.12–7.20 m and 7.42–7.50 m (2H each, H_{arom}), 9.37 br.s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.52, 88.28, 95.65, 116.05, 129.35, 133.10, 141.99, 176.55 [20].

3-(4-Bromophenyl)prop-2-ynal (IIIc). Yield 90%, mp 91–93°C (from EtOH). IR spectrum, ν, cm^{-1}: 2246 (C≡C), 1652 (C=O). ^1H NMR spectrum ($CDCl_3$), δ, ppm: 7.40–7.48 m and 7.51–7.60 m (2H each, H_{arom}), 9.41 s (1H, CHO). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 89.52, 104.28, 118.42, 126.31, 132.26, 134.57, 176.56 [21].

Reaction of 3-arylprop-2-ynals IIIa–IIIc with methyl ketones IVa–IVj (*general procedure*). A solution of 0.01 mol of ketone **IVa–IVj** and 0.01 mol of aldehyde **IIIa–IIIc** in 25 ml of 50% aqueous ethanol was cooled to 0°C, and 0.8 ml of 20% aqueous sodium hydroxide was added. After a solid separated, an additional 0.6-ml portion of 20 aqueous sodium hydroxide was added, and the mixture was left to stand for 10 h at room temperature. The precipitate was filtered off, washed with 10 ml of cold 20% aqueous ethanol, and recrystallized from 70–80% aqueous ethanol.

1,5-Diphenylpent-2-en-4-yn-1-one (Va). Yield 89% [22].

1-(4-Methylphenyl)-5-phenylpent-2-en-4-yn-1-one (Vb). Yield 71%, mp 84–85°C. IR spectrum, ν, cm^{-1}: 2198, 1663, 1573. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 2.43 s (3H, CH_3), 7.13 d (1H, 3-H, ^3J = 15.6 Hz), 7.45 d (1H, 2-H, ^3J = 15.6 Hz), 7.20–8.00 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.53, 87.37, 99.85, 119.12, 125.28, 128.46, 128.61, 129.24, 131.93, 132.56, 133.07, 137.23, 139.78, 188.79. Found, %: C 87.62; H 5.86. $C_{18}H_{14}O$. Calculated, %: C 87.74; H 5.74.

1-(4-Isopropylphenyl)-5-phenylpent-2-en-4-yn-1-one (Vc). Yield 64%, mp 49–50°C. IR spectrum, ν, cm^{-1}: 2198, 1662, 1571. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.29 d (6H, CH_3, ^3J = 7.0 Hz), 2.99 sext (1H, J = 6.9 Hz), 7.12 d (1H, 3-H, ^3J = 15.5 Hz), 7.45 d (1H, 2-H, ^3J = 15.5), 7.20–8.00 m (9H, H_{arom}). Found, %: C 87.38; H 6.77. $C_{20}H_{18}O$. Calculated, %: C 87.54; H 6.63.

1-(4-Methoxyphenyl)-5-phenylpent-2-en-4-yn-1-one (Vd). Yield 50% [14].

1-(4-Ethoxyphenyl)-5-phenylpent-2-en-4-yn-1-one (Ve). Yield 76%, mp 110–111°C. IR spectrum, ν, cm^{-1}: 2198, 1659, 1575. ^1H NMR spectrum ($CDCl_3$), δ, ppm: 1.46 t (3H, CH_3, ^3J = 7.0 Hz), 4.13 q (2H, CH_2, ^3J = 7.0 Hz), 7.11 d (1H, 3-H, ^3J = 15.5 Hz), 7.45 d (1H, 2-H, ^3J = 15.5 Hz), 6.90–8.10 m (9H, H_{arom}). Found, %: C 82.54; H 5.82. $C_{19}H_{16}O_2$. Calculated, %: C 82.57; H 5.85.

1-(4-Chlorophenyl)-5-phenylpent-2-en-4-yn-1-one (Vf). Yield 89% [14].

1-(3-Bromophenyl)-5-phenylpent-2-en-4-yn-1-one (Vg). Yield 30%, mp 58–59°C. IR spectrum, ν,

cm^{-1}: 2198, 1675, 1666, 1568. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, CH_3), 7.14 d (1H, 3-H, ^3J = 15.6 Hz), 7.37 d (1H, 2-H, ^3J = 15.6 Hz), 7.15–8.00 m (8H, H_{arom}). Found, %: C 66.02; H 3.75. $C_{17}H_{11}BrO$. Calculated, %: C 65.61; H 3.57.

1-(4-Bromophenyl)-5-phenylpent-2-en-4-yn-1-one (Vh). Yield 76%, mp 96–97°C. IR spectrum, ν, cm^{-1}: 2198, 1664, 1568. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.14 d (1H, 3-H, ^3J = 15.4 Hz), 7.39 d (1H, 2-H, ^3J = 15.4 Hz), 7.20–8.00 m (9H, H_{arom}). Found, %: C 65.85; H 3.85. $C_{17}H_{11}BrO$. Calculated, %: C 65.61; H 3.57.

1-(3-Aminophenyl)-5-phenylpent-2-en-4-yn-1-one (Vi). Yield 10%, mp 62–63°C. IR spectrum, ν, cm^{-1}: 2196, 1663. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 3.87 s (2H, NH_2), 6.89 d (1H, H_{arom}, ^3J = 6.4 Hz), 7.09 d (1H, 3-H, ^3J = 15.6 Hz), 7.20–7.60 m (9H, H_{arom}, 2-H). Found, %: C 82.28; H 5.58. $C_{17}H_{13}NO$. Calculated, %: C 82.56; H 5.31.

1-(2-Furyl)-5-phenylpent-2-en-4-yn-1-one (Vj). Yield 69% [14].

5-(4-Methylphenyl)-1-phenylpent-2-en-4-yn-1-one (Vk). Yield 50%, mp 70–71°C. IR spectrum, ν, cm^{-1}: 2196, 1664. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, CH_3), 7.14 d (1H, 3-H, ^3J = 15.6 Hz), 7.42 d (1H, 2-H, ^3J = 15.6 Hz), 7.16–8.05 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.61, 87.81, 98.93, 122.26, 124.54, 128.43, 128.63, 129.27, 129.36, 131.94, 133.08, 134.61, 144.08, 188.20. Found, %: C 87.40; H 5.98. $C_{18}H_{14}O$. Calculated, %: C 87.74; H 5.74.

1,5-Bis(4-methylphenyl)pent-2-en-4-yn-1-one (Vl). Yield 40%, mp 92–93°C. IR spectrum, ν, cm^{-1}: 2197, 1662. ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.40, 87.40, 99.40, 119.10, 124.60, 128.50, 129.10, 129.20, 131.80, 132.50, 134.50, 139.60, 143.90, 188.00. Found, %: C 87.89; H 6.16. $C_{19}H_{16}O$. Calculated, %: C 87.65; H 6.21.

1-(4-Chlorophenyl)-5-(4-methylphenyl)pent-2-en-4-yn-1-one (Vm). Yield 68%, mp 112–113°C. IR spectrum, ν, cm^{-1}: 2196, 1663, 1571. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.38 s (3H, CH_3), 7.14 d (1H, 3-H, ^3J = 15.6 Hz), 7.37 d (1H, 2-H, ^3J = 15.6 Hz), 7.15–8.00 m (8H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 21.64, 87.40, 100.46, 119.12, 125.95, 129.07, 129.36, 129.95, 132.06, 132.21, 135.69, 139.65, 140.03, 187.60. Found, %: C 76.85; H 4.62. $C_{18}H_{13}ClO$. Calculated, %: C 76.98; H 4.68.

5-(4-Bromophenyl)-1-phenylpent-2-en-4-yn-1-one (Vn). Yield 54%, mp 86–87°C. IR spectrum, ν, cm^{-1}: 2199, 1667. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.09 d (1H, 3-H, ^3J = 15.4 Hz), 7.27 d (1H, 2-H, ^3J = 15.4 Hz), 7.30–8.10 m (9H, H_{arom}). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 87.68, 99.88, 122.08, 125.64, 128.31, 128.37, 128.49, 129.47, 129.97, 130.13, 131.82, 132.02, 132.14, 132.35, 135.91, 187.65. Found, %: C 65.94; H 3.61. $C_{17}H_{11}BrO$. Calculated, %: C 65.61; H 3.57.

1,5-Bis(4-bromophenyl)pent-2-en-4-yn-1-one (Vo). Yield 30%, mp 130–134°C. IR spectrum, ν, cm^{-1}: 2199, 1679, 1664. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.09 d (1H, 3-H, ^3J = 15.6 Hz), 7.20–8.00 m (9H, H_{arom}, 2-H). Found, %: C 52.52; H 2.71. $C_{17}H_{10}Br_2O$. Calculated, %: C 52.34; H 2.59.

5-(4-Bromophenyl)-1-(2-furyl)pent-2-en-4-yn-1-one (Vp). Yield 20%, mp 129–130°C. IR spectrum, ν, cm^{-1}: 2197, 1661. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 6.50–7.70 m (3H, Fu), 7.11 d (1H, 3-H, ^3J = 15.6 Hz), 7.29 d (1H, 2-H, ^3J = 15.6 Hz), 7.30–7.60 m (4H, H_{arom}). Found, %: C 60.19; H 2.86. $C_{15}H_9BrO_2$. Calculated, %: C 59.85; H 3.02.

This study was performed in the framework of the state problem of the Ministry of Education and Science of the Russian Federation (project no. 3.1168.2011).

REFERENCES

1. Sukhova, L.N., Ostroumov, I.G., Bel'skii, V.K., Galishev, V.A., and Maretina, I.A., *Zh. Org. Khim*., 1994, vol. 30, p. 46.
2. Waldo, J.P., Mehta, S., and Larock, R.C., *J. Org. Chem*., 2008, vol. 73, p. 6666.
3. Miki, K., Nishino, F., Ohe, K., and Uemura, S., *J. Am. Chem. Soc*., 2002, vol. 124, p. 5260.
4. Miki, K., Yokoi, T., Nishino, F., Kato, Y., Washitake, Y., Ohe, K., and Uemura, S., *J. Org. Chem*., 2004, vol. 69, p. 1557.
5. Du, X., Chen, H., Chen, Y., Chen, J., and Liu, Y., *Synlett*, 2011, p. 1010.
6. Iwasawa, N., Shido, M., Maeyama, K., and Kusama, H., *J. Am. Chem. Soc*., 2000, vol. 122, p. 10226.
7. Ohe, K., Miki, K., Yokoi, T., Nishino, F., and Uemura, S., *Organometallics*, 2000, vol. 19, p. 5525.
8. Iwasawa, N., Shido, M., and Kusama, H., *J. Am. Chem. Soc*., 2001, vol. 123, p. 5814.
9. Rosiak, A. and Christoffers, J., *Tetrahedron Lett*., 2006, vol. 47, p. 5095.
10. Oliva, C.G., Silva, A.M.S., Paz, F.A.A., and Cavaleiro, J.A.S., *Synlett*, 2010, p. 1123.

11. Utekhina, N.V., *Cand. Sci. (Chem.) Dissertation*, Khar'kov, 1987.
12. Korshunov, S.P., *Doctoral (Chem.) Dissertation*, Nizhnii Novgorod, 1997.
13. Jeffery, T., *Synthesis*, 1987, p. 70.
14. Chen, J., Fan, G., and Liu, Y., *Org. Biomol. Chem*., 2010, vol. 8, p. 4806.
15. *Spravochnik khimika* (Chemist's Handbook), Nikol'skii, B.P., Ed., Moscow: Khimiya, 1966, vol. 1, p. 367.
16. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2008, vol. 64, p. 112.
17. Zeitler, K., *Org. Lett*., 2006, vol. 8, p. 637.
18. Lemhadhi, M., *Tetrahedron*, 2005, vol. 61, p. 9839.
19. Belot, S., *Adv. Synth. Catal*., 2010, vol. 352, p. 667.
20. Lee, K., *Tetrahedron Lett*., 2004, vol. 45, p. 5043.
21. Belot, S., *Angew. Chem., Int. Ed*., 2009, vol. 48, p. 8923.
22. Stetter, H., *Chem. Ber*., 1960, vol. 93, p. 1253.