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SHORT COMMUNICATIONS

Synthesis of Substituted Indenes from 3-Phenyl-2-propyn-1-ol Derivatives

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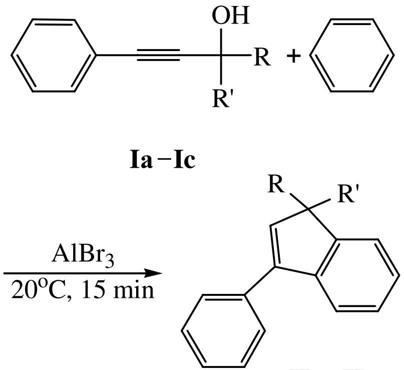
Indene series compounds attract deep interest due to the opportunities of their practical application [1].

Nowadays indenes preparation procedures are extensively developed with the use of expensive catalysts based on transition metals; palladium, platinum, ruthenium, and niobium [2]. We recently reported on a method of substituted indenes synthesis by reaction of acetylene carbonyl compounds with benzene in the presence of aluminum bromide [3].

We present here a new preparation method for indene compounds from 3-phenyl-2-propyn-1-ol derivatives **Ia–Id**. Stirring for 15 min at room temperature benzene solutions of compounds **Ia–Id** in the presence of aluminum bromide (at a molar ratio substrate **I** : $AlBr_3$: benzene = 1:5:50) followed with the treatment of the reaction mixture with water, the extraction of the reaction products into chloroform, and their isolation by column chromatography on silica gel (eluent hexane–ethyl acetate) led to the formation of substituted indenes **IIa–IIc** in 9–53% yield.

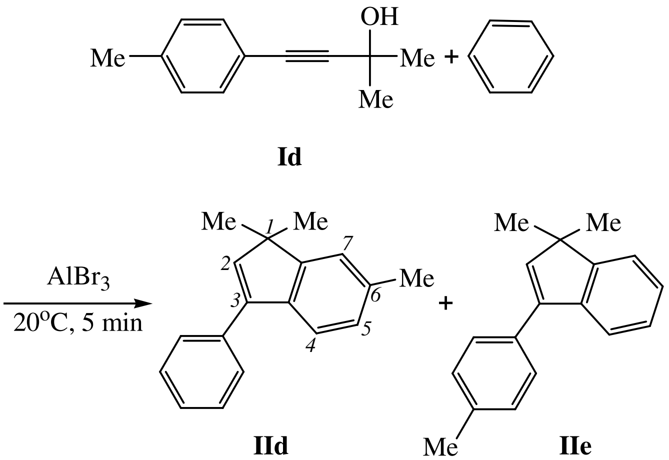


Ia–Ic

IIa–IIc

R = R' = Me (**a**), R = Ph, R' = Me (**b**), R = R' = Ph (**c**).

A similar reaction of 2-methyl-4-(4-methylphenyl)-3-butyn-2-ol (**Id**) provided a mixture of products **IId** and **IIe** in a ratio 3:1 with an overall yield 30%. Therewith after the addition of the benzene molecule to acetylene alcohol **Id** the indene system of compounds **IId** and **IIe** was formed by the cyclization at the tolyl and the phenyl rings respectively.



Id

IId

IIe

The structure of compounds **IId** and **IIe** in the mixture inseparable by the common column chromatography on silica gel was established by ^1H NMR and GC-MS spectroscopy. According to the GC-MS analysis both compounds have identical molecular ions $[M]^+$ 234 and similar mass spectra of fragment ions. A careful analysis of ^1H NMR spectrum of the mixture of compounds **IId** and **IIe** revealed that the spectrum of the principal component of the mixture contained proton signals characteristic of 1,2,4-trisubstituted benzene ring. This group of signals consisted of two doublets at δ 7.08 and

7.38 ppm with coupling constants *J* 7.8 Hz and a singlet at δ 7.20 ppm. This combination of signals corresponds to the indene system of compound **IId**. The mentioned doublets belong to protons H^4 and H^5, and the singlet, to proton H^7 of the indene ring. In the ^{1}H NMR spectrum of isomer **IId** appeared also multiplets characteristic of the phenyl ring attached to the position *3* of the indene structure: a doublet at δ 7.59 ppm (*ortho*-protons), a triplet at 7.42 ppm (*meta*-protons), and a triplet at δ 7.34 ppm (*para*-proton), *J* 7.5 Hz. Similar chemical shifts of these protons were observed in the spectra of other 3-phenyl-substituted indenes (see ^{1}H NMR spectra in [3]).

2-Methyl-4-phenyl-3-butyn-2-ol (**Ia**) and 2-methyl-4-(4-methylphenyl)-3-butyn-2-ol (**Id**) were prepared by procedure [4] reacting in diethylamine 2-methyl-3-butyn-2-ol with iodobenzene and 4-iodotoluene respectively. 2,4-Diphenyl-3-butyn-2-ol (**Ib**) and 1,1,3-triphenyl-2-propyn-1-ol (**Ic**) were obtained by method [5] by a reaction of phenylacetylene lithium derivative with acetophenone and benzophenone respectively.

2-Methyl-4-phenyl-3-butyn-2-ol (Ia). Yield 70%, mp 56–57°C (oily substance [6]). IR spectrum, ν, cm^{-1}: 3600 (OH$_{\text{free}}$), 3500–3200 (OH$_{\text{bound}}$), 2220 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.61 s (6H, 2Me), 2.19 br.s (1H, OH), 7.27–7.30 m (3H$_{\text{arom}}$), 7.39–7.42 m (2H$_{\text{arom}}$).

2,4-Diphenyl-3-butyn-2-ol (Ib). Yield 32%, mp 72–73°C {bp 130–131°C (5×10^{-2} mm Hg) [5]}. IR spectrum, ν, cm^{-1}: 3600 (OH$_{\text{free}}$), 3500–3200 (OH$_{\text{bound}}$), 2250 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.87 s (3H, Me), 2.44 br.s (1H, OH), 7.30–7.33 m (4H$_{\text{arom}}$), 7.39 t (2H$_{\text{arom}}$, *J* 7.7 Hz), 7.46–7.49 m (2H$_{\text{arom}}$), 7.73 d (2H$_{\text{arom}}$, *J* 7.7 Hz).

1,1,3-Triphenyl-2-propyn-1-ol (Ic). Yield 20%, mp 79–81°C (mp 81–82°C [7], oily substance [8]). IR spectrum, ν, cm^{-1}: 3600 (OH$_{\text{free}}$), 3500–3200 (OH$_{\text{bound}}$), 2320 (C≡C). ^{1}H NMR spectrum, δ, ppm: 2.96 br.s (1H, OH), 7.28 t.t (2H$_{\text{arom}}$, *J* 7.3, 1.3 Hz), 7.32–7.37 m (7H$_{\text{arom}}$), 7.51–7.53 m (2H$_{\text{arom}}$), 7.69 d.t (4H$_{\text{arom}}$, *J* 8.4, 1.2 Hz).

2-Methyl-4-(4-methylphenyl)-3-butyn-2-ol (Id). Yield 50%, mp 50–52°C. IR spectrum, ν, cm^{-1}: 3600 (OH$_{\text{free}}$), 3500–3150 (OH$_{\text{bound}}$), 2220 (C≡C). ^{1}H NMR spectrum, δ, ppm: 1.60 s (6H, 2Me), 1.99 br.s (1H, OH), 2.33 s (3H, Me), 7.09 d (2H$_{\text{arom}}$, *J* 8.1 Hz), 7.30 d (2H$_{\text{arom}}$, *J* 8.1 Hz). Found, %: C 82.47; H 8.01. $C_{12}H_{14}O$. Calculated, %: C 82.72; H 8.10.

1,1-Dimethyl-3-phenylindene (IIa). Yield 9%, oily substance. ^{1}H NMR spectrum, δ, ppm: 1.39 s (6H, 2Me), 6.41 s (1H, =CH–), 7.24–7.27 m (2H$_{\text{arom}}$), 7.35 t.t (1H$_{\text{arom}}$, *J* 7.3, 1.3 Hz), 7.37–7.40 m (1H$_{\text{arom}}$), 7.43 t.t (2H$_{\text{arom}}$, *J* 7.3, 1.3 Hz), 7.48–7.51 m (1H$_{\text{arom}}$), 7.59 d.t (2H$_{\text{arom}}$, *J* 7.3, 1.3 Hz). Mass spectrum, *m/z* (I_{rel}, %): 220 (87) [*M*]$^+$, 205 (100), 189 (12), 178 (10), 101 (14). Found, %: C 93.11; H 7.04. $C_{17}H_{16}$. Calculated, %: C 92.68; H 7.32.

1-Methyl-1,3-diphenylindene (IIb). Yield 53%. **1,1,3-Triphenylindene (IIc).** Yield 50%. The characteristics of compounds **IIb** and **IIc** we already published in [3].

1,1,6-Trimethyl-3-phenylindene (IId) and 1,1-dimethyl-3-(4-methylphenyl)indene (IIe) were obtained in a form of an oily mixture in an overall yield 30% and in a ratio 3:1. ^{1}H NMR spectrum of compound **IId** (extricated from the spectrum of the mixture), δ, ppm: 1.38 c (6H, 2Me), 2.42 c (3H, Me), 6.34 c (1H, =CH–), 7.08 d (1H$_{\text{arom}}$, *J* 7.8 Hz), 7.20 c (1H$_{\text{arom}}$), 7.34 t (1H$_{\text{arom}}$, *J* 7.5 Hz), 7.38 d (1H$_{\text{arom}}$, *J* 7.8 Hz), 7.42 t (2H$_{\text{arom}}$, *J* 7.5 Hz), 7.59 d (2H$_{\text{arom}}$, *J* 7.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 234 (100) [*M*]$^+$, 219 (91), 204 (38), 189 (9), 101 (13). ^{1}H NMR spectrum of compound **IIe** (extricated from the spectrum of the mixture), δ, ppm: 1.38 s (6H, 2Me), 2.40 s (3H, Me), 6.37 s (1H, =CH–), 7.22–7.26 m (5H$_{\text{arom}}$), 7.49 d (2H$_{\text{arom}}$, *J* 7.8 Hz), 7.51 d (1H$_{\text{arom}}$, *J* 7.5 Hz). Mass spectrum, *m/z* (I_{rel}, %): 234 (90) [*M*]$^+$, 219 (100), 204 (31), 189 (9), 101 (14). Found for the mixture of compounds **IId** and **IIe**, %: C 91.98; H 7.48. $C_{18}H_{18}$. Calculated, %: C 92.26; H 7.74.

IR spectra of compounds dissolved in chloroform were recorded on a spectrophotometer Specord 75 IR. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-500 at operating frequencies 500 and 125.76 MHz respectively from solutions in $CDCl_3$. As internal references served the residual signals of $CHCl_3$ (δ 7.25 ppm) in the ^{1}H NMR spectra, and the signals of $CDCl_3$ (δ 77.0 ppm) in the ^{13}C NMR spectra. GC-MS analysis was carried out on G 2570A GC/MSD system of Agilent Technologies equipped with a flame-ionization detector, ionizing electrons energy 70 eV, separator temperature 250°C, ion source temperature 280°C, capillary quartz column 30000 × 0.25 mm, stationary phase Ultra-2 (95% of methylsilicone, 5% of phenylmethylsilicone) 0.25 μm thick, oven temperature ramp from 100°C to 270°C, heating rate 5 deg/min, carrier gas helium, flow rate 1 ml/min, sample volume 1 μl of 3–5% solvent.

REFERENCES

1. Ivchenko, N.B., Ivchenko, P.V., and Nifant'ev, I.E., *Zh. Org. Khim.*, 2000, vol. 36, p. 641.

2. Duan, X.-H., Guo, L.-N., Bi, H.-P., Liu, X.-Y., and Liang, Y.-M., *Org. Lett.*, 2006, vol. *6*, p. 3053; Kuninobu, Y., Nishina, Y., and Takai, K., *Org. Lett.*, 2006, vol. 8, p. 2891; Guo, L.-N., Duan, X.-H., Bi, H.-P., Liu, X.-Y., and Liang, Y.-M., *J. Org. Chem.,* 2006, vol. 71, p. 3325; Bajracharya, G.B., Pahadi, N. K., Gridnev, I.D., and Yamamoto, Y., *J. Org. Chem.,* 2006, vol. 71, p. 6204; Obora, Y., Kimura, M., Tokunaga, M., and Tsuji, Y., *Chem. Commun.,* 2005, p. 901.
3. Vasil'ev, A.V. and Shchukin, A.O., *Zh. Org. Khim.*, 2006, vol. 42, p. 1256.
4. Tretyakov, E.V., Tkachev, A.V., Rybalova, T.V., Gatilov, Y.V., Knight, D.W., and Vasilevsky, S.F., *Tetrahedron,* 2000, vol. 56, p. 10075.
5. Potkin, V.I., Dikusar, E.A., and Kozlov, N.G., *Zh. Org. Khim.*, 2002, vol. 38, p. 1316.
6. Yu, W.-Y. and Alper, H., *J. Org. Chem.,* 1997, vol. 62, p. 5684.
7. Wittig, G. and Harborth, G., *Ber.,* 1944–1946, pp. 77–79, 315.
8. Deagostino, A., Mella, M., Prandi, C., and Venturello, P., *J. Chem. Soc., Perkin Trans. 2*, 1995, vol. 21, p. 2757.