

SHORT  
COMMUNICATIONS

# Reaction of Acetylene Carbonyl Compounds with Benzene in the Presence of Aluminum Bromide: a New Preparation Method for Substituted Indenes

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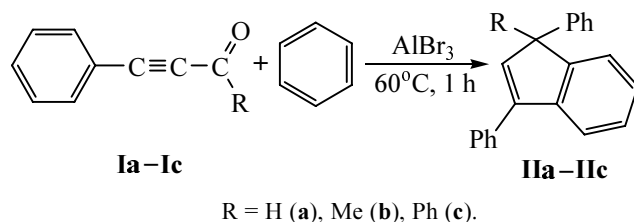
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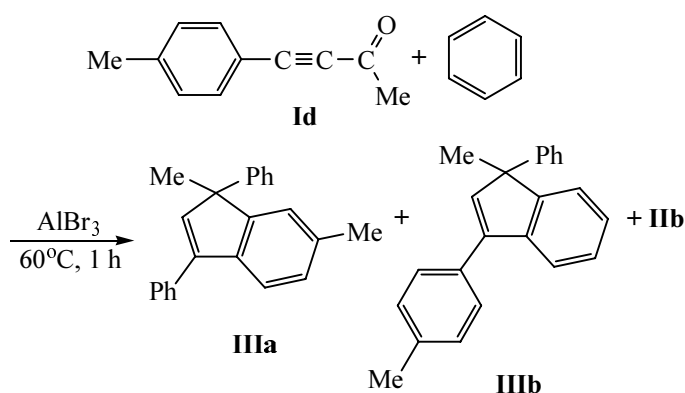
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An opportunity was recently demonstrated for generating from alkynes vinyl type cations using liquid superacids  $\text{HSO}_3\text{F}$  and  $\text{CF}_3\text{SO}_3\text{H}$  permitting the investigation of reactions involving these cations [1–3]. The next step in development of this field is the study of acetylene derivatives transformations in the presence of Lewis acids and solid superacids. Lewis acids like aluminum halides are widely employed in the organic synthesis, in particular, for electrophilic activation of substituted phenols and naphthols, heterocyclic compounds, and enone structures in the reactions of aromatic substitution and ionic hydrogenation [4].

We found that heating at  $60^\circ\text{C}$  for 1 h of acetylene carbonyl compounds **Ia–Ic** in anhydrous benzene in the presence of aluminum bromide at molar ratio substrate **I** :  $\text{AlBr}_3$  : benzene equal to 1:5:80 followed by the quenching of the reaction mixture with water, extraction of the products into chloroform, and chromatographic isolation on a column charged with silica gel (eluent hexane–chloroform) led to the formation of substituted indenenes **IIa–IIc** in 12–38% yields.



Likewise acetylene ketone **Id** gave rise to a mixture of three indene structures **IIIa**, **IIIb**, and **IIb** in an overall yield 70%.



The qualitative and quantitative composition of the mixture of compounds **IIIa**, **IIIb**, and **IIb** inseparable into components by the common column chromatography on silica gel was established with the help of GC-MS procedure and  $^1\text{H}$  NMR spectroscopy. The GC-MS analysis showed that two compounds in this mixture had identical molecular ion peaks  $[M]^+$  296 corresponding to **IIIa** and **IIIb** isomers, but they were distinguished by the fragment ions. The substance containing in its mass spectrum ions of  $m/z$  205  $[M - 91]^+$  and 91  $[\text{MeC}_6\text{H}_4]^+$  indicating the presence of a tolyl fragment possessed **IIIb** structure. The other isomer with a molecular ion  $[M]^+$  296 lacking in its spectrum the characteristic ions of  $m/z$  205 and 91 had **IIIa** structure. The third component of the mixture with a molecular ion ( $[M]^+$  282 according to the GC-MS analysis was substituted indene **IIb** with the  $^1\text{H}$  NMR spectrum identical with that of an authentic sample.

Isomers **IIIa** and **IIIb** originate from the indene system formation by an intramolecular cyclization involving tolyl

or phenyl ring respectively. Compound **Ib** formed either as a demethylation product of compounds **IIIa** or **IIIb** in the course of the reaction or as a result of aryl groups exchange in the intermediate species on the route of ketone **Id** conversion into the indene structures. The formation of substituted indenenes **II** and **III** involves the condensation of two benzene molecules with the cation intermediates generated from acetylene compounds **I**. In these intermediates the carbonyl group carbon activated by the Lewis acid and the vinyl cation center formed by protonation of the triple carbon-carbon bond constitute the electrophilic centers.

The detailed mechanism and the synthetic potential of this new reaction for preparation of indene derivatives [5, 6] require further special investigation.

**3-Phenylpropynal (Ia)** was a commercial product purchased from Aldrich. The synthesis and characteristics of initial compounds **4-phenylbut-3-yn-2-one (Ib)**, **1,3-diphenylpropynone (Ic)**, and **4-(4-methylphenyl)-but-3-in-2-one (Id)** were published previously [7].

**1,3-Diphenylindene (IIa).** Yield 18%, mp 67–68°C (publ.: mp 66–67°C [6]). IR spectrum,  $\text{cm}^{-1}$ : 1600 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 4.71 d (1H,  $J$  2 Hz), 6.64 d (1H, =CH–,  $J$  2 Hz), 7.18 d (2H<sub>arom</sub>,  $J$  7.5 Hz), 7.21 d (1H<sub>arom</sub>,  $J$  7.5 Hz), 7.23 d (1H<sub>arom</sub>,  $J$  7.5 Hz), 7.26–7.33 m (4H<sub>arom</sub>), 7.39 t (1H<sub>arom</sub>,  $J$  7 Hz), 7.47 t (2H<sub>arom</sub>,  $J$  7 Hz), 7.59 d (1H<sub>arom</sub>,  $J$  7.5 Hz), 7.66 d (2H<sub>arom</sub>,  $J$  7 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 55.38 d.m ( $J$  127.6 Hz), 120.56 d.d ( $J$  159.4, 8.0 Hz), 124.31 d.d ( $J$  159.4, 8.0 Hz), 125.59 d.d ( $J$  161.0, 7.4 Hz), 126.67 d.d ( $J$  158.5, 7.2 Hz), 126.84 d.t ( $J$  160.2, 7.4 Hz), 127.73 d.m, 127.81 d.m, 127.92 d.m, 128.60 d.d ( $J$  158.9, 7.6 Hz), 128.69 d.d ( $J$  159.8, 8.0 Hz), 135.63 m, 136.29 d.d ( $J$  169.1, 7.2 Hz), 139.52 q ( $J$  8.5 Hz), 143.15 q ( $J$  7.6 Hz), 144.61 m, 149.22 q ( $J$  7.0 Hz). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 268 (100) [ $M$ ]<sup>+</sup>, 267 (26), 265 (14), 262 (10), 191 (16), 189 (12), 165 (8), 126 (10).

**1-Methyl-1,3-diphenylindene (IIb).** Yield 38%, mp 56–58°C (publ.: mp 59–59.5°C [8]). IR spectrum,  $\text{cm}^{-1}$ : 1605 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.82 s (3H, Me), 6.60 s (1H, =CH–), 7.21–7.34 m (8H<sub>arom</sub>), 7.39 t (1H<sub>arom</sub>,  $J$  7.2 Hz), 7.47 t (2H<sub>arom</sub>,  $J$  7.2 Hz), 7.57 d (1H<sub>arom</sub>,  $J$  7.4 Hz), 7.66 d (2H<sub>arom</sub>,  $J$  7.2 Hz).  $^{13}\text{C}$  NMR spectrum,  $\delta$ , ppm: 22.98 q ( $J$  122 Hz), 55.58 C, 120.90 d.d ( $J$  158, 7.6 Hz), 123.20 d.d ( $J$  157, 7.6 Hz), 125.85 d.d ( $J$  159, 7.1 Hz), 126.17 d.t ( $J$  156, 6.9 Hz), 126.46 d.t ( $J$  159, 7.1 Hz), 126.62 d.d ( $J$  158, 6.7 Hz), 127.69 d.q ( $J$  160, 6.7 Hz), 127.73 m, 128.41 d.d ( $J$  158, 7.1 Hz), 128.57 d.d ( $J$  158, 7.6 Hz), 135.56 m ( $J$  5.8 Hz),

141.84 m, 142.04 m, 142.88 m, 143.49 d.d ( $J$  166, 3.6 Hz), 154.35 m. Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 282 (100) [ $M$ ]<sup>+</sup>, 268 (21), 267 (86), 265 (28), 252 (17), 203 (20), 191 (22), 165 (16), 131 (13), 126 (20), 77 (15).

**1,1,3-Triphenylindene (IIc).** Yield 12%, mp 136–138°C (publ.: mp 139–140°C [9]). IR spectrum,  $\text{cm}^{-1}$ : 1600 (C=C).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 6.82 s (1H, =CH–), 7.20–7.32 m (14H<sub>arom</sub>), 7.37 t (1H<sub>arom</sub>,  $J$  6.8 Hz), 7.40 d (1H<sub>arom</sub>,  $J$  7.6 Hz), 7.44 t (2H<sub>arom</sub>,  $J$  7.5 Hz), 7.56 d (1H<sub>arom</sub>,  $J$  7.5 Hz), 7.64 d (2H<sub>arom</sub>,  $J$  8.0 Hz). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 344 (100) [ $M$ ]<sup>+</sup>, 267 (32), 265 (27), 165 (6), 134 (5).

**1,6-Dimethyl-1,3-diphenylindene (IIIa) and 1-methyl-3-(4-methylphenyl)-1-phenylindene (IIIb).** The compounds were obtained as an oily mixture with compound **Ib** in an overall yield 70% with a ratio **IIIa** : **IIIb** : **Ib** 4.3:1.3:1.0.  $^1\text{H}$  NMR spectrum of compound **IIIa** (extracted from the spectrum of the mixture),  $\delta$ , ppm: 1.80 s (3H, Me), 2.37 s (3H, Me), 6.53 s (1H, =CH–), 7.09–7.66 m (13H<sub>arom</sub>). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 296 (100) [ $M$ ]<sup>+</sup>, 281 (74), 266 (12), 265 (21), 203 (24), 133 (12), 77 (8).  $^1\text{H}$  NMR spectrum of compound **IIIb** (extracted from the spectrum of the mixture),  $\delta$ , ppm: 1.81 s (3H, Me), 2.43 s (3H, Me), 6.56 s (1H, =CH–), 7.09–7.66 m (13H<sub>arom</sub>). Mass spectrum,  $m/z$  ( $I_{\text{rel}}$ , %): 296 (100) [ $M$ ]<sup>+</sup>, 281 (90), 265 (26), 205 (15), 203 (28), 189 (12), 165 (10), 139 (11), 133 (22), 126 (14), 91 (8), 77 (9).

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were registered on a spectrometer Bruker AM-500 (operating frequencies 500 and 125.76 MHz respectively) in  $\text{CDCl}_3$ . As internal references served the residual signal of  $\text{CHCl}_3$  ( $\delta_{\text{H}}$  7.25 ppm) in the  $^1\text{H}$  NMR spectra and the signal of  $\text{CDCl}_3$  solvent ( $\delta_{\text{C}}$  77.0 ppm) in the  $^{13}\text{C}$  NMR spectra. IR spectra of compounds in chloroform solution were recorded on a spectrophotometer Specord 75IR. Mass spectra were taken on MKh-1321 instrument, ionizing electrons energy 70 eV, direct sample admission at the ion source temperature 100–120°C. GC-MS analysis was carried out on a Hewlett-Packard HP-5995 instrument equipped with a flame-ionization detector, ionizing electrons energy 70 eV, separator temperature 240°C, that of ion source, 250°C, capillary quartz column 25000×0.32 mm, stationary phase Ultra-2 (95% of methylsilicone, 5% of phenylmethylsilicone) 0.53  $\mu\text{m}$  thick, column temperature ramp from 100°C to 240°C at a rate 5–10 deg/min, carrier gas helium, flow rate 1 ml/min, sample volume 2  $\mu\text{l}$  of 3–5% solution.

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