ISSN 1070-4280, Russian Journal of Organic Chemistry, 2009, Vol. 45, No. 8, pp. 1252–1254. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © D.S. Ryabukhin, G.K. Fukin, A.V. Cherkasov, A.V. Vasil'eva, 2009, published in Zhurnal Organicheskoi Khimii, 2009, Vol. 45, No. 8, pp. 1260–1262.

SHORT COMMUNICATIONS

Cyclization of Phenyl 3-Arylpropionates under the Action of HSO_3F or $AlBr_3$

D. S. Ryabukhin[a], G. K. Fukin[b], A. V. Cherkasov[b], and A. V. Vasil'eva[a]

[a]*St. Petersburg State Academy of Forestry Engineering, St. Petersburg, 194021 Russia*
e-mail: aleksvasil@mail.ru
[b]*Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Russia*

Received December 11, 2008

DOI: 10.1134/S1070428009080259

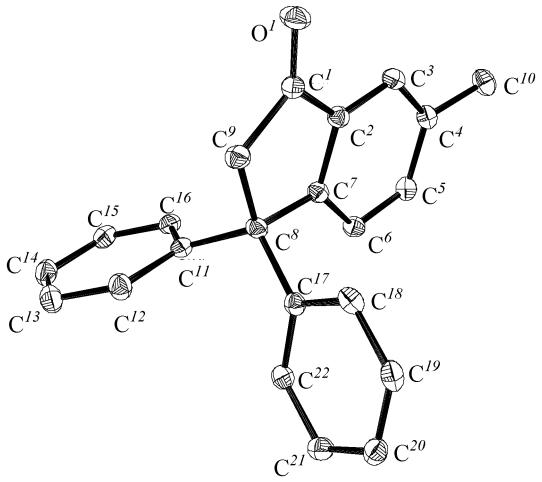
Superacids of Brønsted type (HSO_3F, CF_3SO_3H etc.) and strong Lewis acids (SbF_5, $AlHlg_3$ etc.) are widely used for superelectrophilic activation of organic compounds in generation of reactive polycation intermediates resulting from the protonation or coordination interaction with basic (electron-donor) sites of the molecules of organic substances [1]. These reactions underlie the newly developed methods of synthesis of versatile compounds [1], in particular, the synthesis of cyclic structures of indan [2–7] and quinoline series [8–10] from acetylene derivatives.

We report here on the results of the study of phenyl 3-arylpropionates **Ia** and **Ib** transformation under the action of HSO_3F or $AlBr_3$. The protonation in HSO_3F or the coordination with $AlBr_3$ at the carbonyl oxygen and acetylene bond of substrates **Ia** and **Ib** results in the formation of cationic intermediates **Aa**, **Ab** or **B** respectively reacting further along different paths (see the scheme.

In HSO_3F at –75°C in 0.5 h propionates **Ia** and **Ib** were transformed into the products of intramolecular cyclization, 4-arylcoumarines **IIa** and **IIb**, in 12 and 10% yield respectively at a complete conversion of the initial compounds.

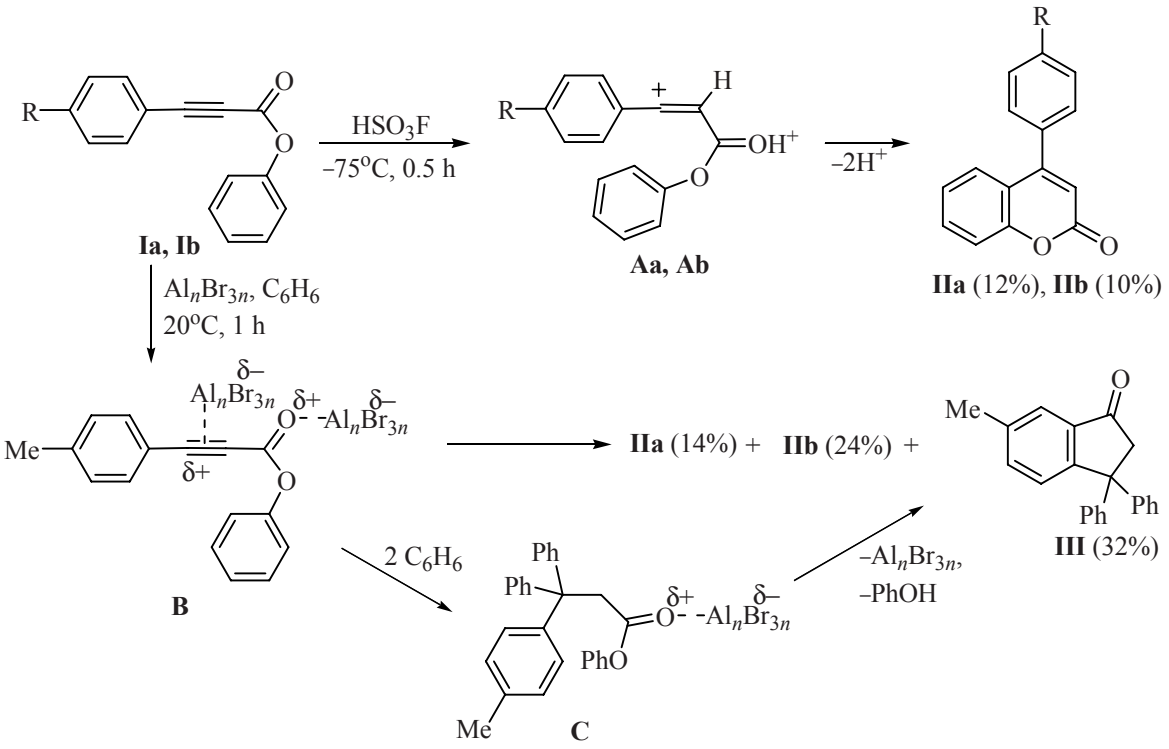
The reaction of ester **Ib** in benzene for 1 h at 20°C gave coumarines **IIa** and **IIb** and indanone **III** whose structure was established by XRD analysis (see the figure). In this case the overall yield of coumarines **IIa** and **IIb** reached 38% and significantly exceeded the yield of these compounds in HSO_3F. 4-Phenylcoumarine (**IIa**) formed under the reaction conditions as a result of the replacement of the *para*-tolyl group by a phenyl in the structure of **IIb** under the action of $AlBr_3$ in benzene analogously to a similar exchange of aryl goups in indene systems [5].

In the presence of $AlBr_3$ compound **Ib** was brought into an intermolecular reaction with benzene resulting in indanone **III**. The most likely way of substance **III** formation consists in the primary addition of two benzene molecules to the acetylene bond of **B** species followed by intramolecular acylation of the *para*-tolyl ring in the structure **C**. Analogous mechanism operates in the formation of 3,3-diphenylindanone from 3-phenylpropynic acid and benzene in CF_3SO_3H [2].



Molecular atructure of 6-methyl-3,3-diphenylindan-1-one (**III**) according to XRD data

Scheme.



R = H (**a**), Me (**b**).

XRD study of compound **III** showed that C^{8} atom possessed a tetrahedral coordination, the angle $CC^{8}C$ was in the range 102.5(1)–114.4(2) deg. The distance C^{8}–C was 1.531(2)–1.556(2) Å, a characteristic value of the ordinary C–C bond. The plane of the indan fragment divided the $C^{17}C^{8}C^{11}$ angle materially in halves. In the crystal of compound **III** intermolecular interactions O···H [2.41(2)–2.57(2) Å] existed with the distance considerably shorter that the sum of the van der Waals radii of these atoms (2.7 Å [11]).

Phenyl 3-arylpropionates **Ia** and **Ib** were prepared from phenol and 3-phenylpropynic and 3-(4-methylphenyl)propynic acids respectively in CH_2Cl_2 in the presence of dicyclohexylcarbodiimide and catalytic quantities of pyridine [12].

Phenyl-3-phenylpropionate (Ia). Yield 35%, mp 38–40°C (40°C [13]). IR spectrum, ν, cm^{-1}: 2230 and 2210 (C≡C), 1720 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.19 d ($2H_{arom}$, *J* 7.6 Hz), 7.27 t ($1H_{arom}$, *J* 7.6 Hz), 7.40 t ($2H_{arom}$, *J* 7.4 Hz), 7.42 t ($2H_{arom}$, *J* 7.6 Hz), 7.48 t ($1H_{arom}$, *J* 7.4 Hz), 7.62 d ($2H_{arom}$, *J* 7.4 Hz).

Phenyl-3-(4-methylphenyl)propionate (Ib). Yield 52%, mp 82–84°C. IR spectrum, ν, cm^{-1}: 2230 and 2210 (C≡C), 1720 (C=O). ^{1}H NMR spectrum, δ, ppm: 2.40 s (3H, Me), 7.20 t ($4H_{arom}$, *J* 8.2 Hz), 7.27 t ($1H_{arom}$, *J* 7.2 Hz), 7.41 t ($2H_{arom}$, *J* 7.2 Hz), 7.51 d ($2H_{arom}$, *J* 7.2 Hz). Found, %: C 81.36; H 5.14. $C_{16}H_{12}O_2$. Calculated, %: C 81.34; H 5.12.

4-Phenylcoumarine (IIa). To 2 ml of HSO_3F cooled to –75°C was added 200 mg (0.9 mmol) of propionate **Ia**. The reaction mixture was stirred for 0.5 h at –75°C, then it was poured into 30 ml of concn. HCl cooled to –70°C. The mass obtained was diluted with water (100 ml) and extracted with chloroform (3×50 ml). The combined extracts were washed with water, with saturated water solution of $NaHCO_3$, again with water, dried over Na_2SO_4, the solvent was distilled off in a vacuum of a water-jet pump, the residue was subjected to column chromatography on silica gel (eluent hexane–ethyl acetate). Yield 24 mg (12%), mp 88–90°C (90–91 [14], 101–103°C [15]). IR spectrum, ν, cm^{-1}: 1720 (C=O). ^{1}H NMR spectrum, δ, ppm: 6.38 s (1H, =CH–), 7.23 t ($1H_{arom}$, *J* 7.6 Hz), 7.41 d ($1H_{arom}$, *J* 8.2 Hz), 7.45–7.56 m ($7H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 222 (100) $[M]^+$, 221 (50), 124 (93), 165 (67), 149 (38), 94 (53).

4-(4-Methylphenyl)coumarine (IIb) was similarly obtained from 200 mg (0.8 mmol) of propionate **Ib** in 3 ml HSO_3F at –75°C within 0.5 h. Yield 20 mg (10%),

mp 104–106°C (109–110 [15], 105–106°C [16]). IR spectrum, ν, cm^{-1}: 1720 (C=O). ^1H NMR spectrum, δ, ppm: 2.45 s (3H, Me), 6.36 s (1H, =CH–), 7.20 t ($1H_{arom}$, *J* 8.0 Hz), 7.32–7.36 m ($4H_{arom}$), 7.40 d ($1H_{arom}$, *J* 8.0 Hz), 7.53 d ($2H_{arom}$, *J* 9.0 Hz). Mass spectrum, *m/z* (I_{rel}, %): 236 (100) $[M]^+$, 221 (53), 208 (93), 178 (24), 165 (27), 159 (26), 119 (20), 105 (17), 91 (14).

Conversion of propionate Ib effected by $AlBr_3$. To a solution of 530 mg (2 mmol, 5 equiv) of $AlBr_3$ in 4 ml of benzene at 20°C was added 87 mg (0.4 mmol) of compound **Ib**. The reaction mixture was stirred for 1 h at 20°C, then it was poured into 50 ml of water and extracted with chloroform (3×50 ml). The combined extracts were washed with water, with saturated water solution of $NaHCO_3$, again with water, dried over Na_2SO_4, the solvent was distilled off in a vacuum, the residue was subjected to column chromatography on silica gel (eluent hexane–ethyl acetate). We obtained 12 mg (14%) of compound **IIa**, 21 mg (24%) of compound **IIb**, and also 36 mg (32%) of **6-methyl-3,3-diphenyl-indan-1-one (III)**, mp 133–135°C. ^1H NMR spectrum, δ, ppm: 2.42 s (3H, Me), 3.48 s (2H, CH_2), 7.14–7.31 m ($11H_{arom}$), 7.41 d ($1H_{arom}$, *J* 7.9 Hz), 7.60 s ($1H_{arom}$). Mass spectrum, *m/z* (I_{rel}, %): 298 (100) $[M]^+$, 283 (41), 221 (55), 178 (24), 165 (27), 119 (12), 105 (15), 91 (10). Found, %: C 88.60; H 6.04. $C_{22}H_{18}O$. Calculated, %: C 88.56; H 6.08. *M* 298.14.

XRD of compound III. Crystals of the size 0.10 × 0.08 × 0.05 mm $C_{22}H_{18}O$ at 100(2) K monoclinic, *a* 10.1223(5), *b* 9.0874(5), *c* 17.8697(9) Å, α 90, *b* 104.238(1), γ 90 deg, *V* 1593.3(1) $Å^3$, *Z* 4, space group P2(1)/n, d_{calc} 1.244 g/cm^3, μ 0.074 mm^{-1}, 3.06 ≤ θ ≤ 27.00°, 10032 reflections measured, among them 3470 [R_{int} 0.0312] independent, R_1 0.0474 [$I > 2\sigma(I)$], wR_2 0.1217 (by all data). The structure was solved by the direct method and refined by the least-squares method on F^2_{hkl} in an anisotropis approximation for all nonhydrogen atoms. The hydrogen atoms were revealed from the difference Fourier sybthesis and isotropically refined. All calculations were performed using software SHELXTL v. 6.10 [17].

^1H NMR spectra were registered on a spectrometer Bruker AM-500 (operating frequency 500 MHz) in $CDCl_3$. The residual signal of $CHCl_3$ (δ 7.25 ppm) served as an internal reference. Mass spectra were measured on an instrument MKh-1321 (70 eV). IR spectra were recorded from solutions of compounds in $CHCl_3$ on a spectrophotometer FSM-1201. In performing XRD analysis the experimental sets of intensities were measured on an automatic diffractometer Smart APEX (graphite monochromator, MoK_α radiation, ω-θ scanning).

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