ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 4, pp. 619–621. © Pleiades Publishing, Ltd., 2011.
Original Russian Text © D.S. Ryabukhin, A.V. Vasil'ev, E.V. Grinenko, 2011, published in Zhurnal Organicheskoi Khimii, 2011, Vol. 47, No. 4, pp. 612–614.

SHORT COMMUNICATIONS

Intramolecular Cyclization of *S*-Phenyl 3-Arylpropynethioates by the Action of Brønsted and Lewis Acids

D. S. Ryabukhin, A. V. Vasil'ev, and E. V. Grinenko

St. Petersburg State Academy of Forestry Engineering, Institutskii per. 5, St. Petersburg, 194021 Russia
e-mail: aleksvasil@mail.ru

Received December 22, 2010

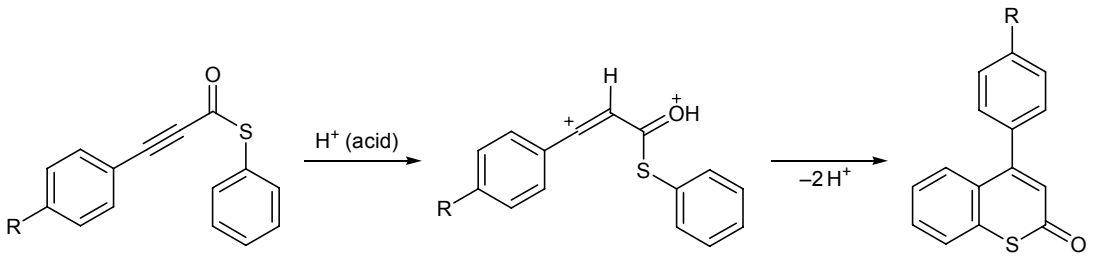
DOI: 10.1134/S1070428011040282

Intramolecular cyclization of *N*,3-diarylpropynamides or phenyl 3-arylpropynoates in various acidic systems is used for the synthesis of quinoline [1] or coumarin derivatives [2]. The present communication reports on the transformations of *S*-phenyl 3-arylpropynethioates **Ia** and **Ib** by the action of Brønsted (H_2SO_4, HSO_3F, CF_3SO_3H) or Lewis acids ($AlCl_3$, $AlBr_3$), leading to the corresponding 4-aryl-2*H*-thiochromen-2-ones **IIa** and **IIb** through electrophilic intermediates **A** (Scheme 1). The reaction conditions and yields are given in table. *S*-Phenyl 3-phenylpropynethioate (**Ia**) in sulfuric acid at 20°C was converted in 5 h into 4-phenyl-2*H*-thiochromen-2-one (**IIa**) in 96% yield (run no. 1). The transformations of compounds **Ia** and **Ib** in stronger acids (HSO_3F, CF_3SO_3H) required a shorter time (1 h at 0–20°C), the yield being fairly high (84–90%; run nos. 3, 4, 8). In HSO_3F at –75°C (reaction time 0.25 h) thiocoumarins **IIa** and **IIb** were formed in poor yield, and the conversion of initial compounds **Ia** and **Ib** was not complete (run nos. 2, 7), in contrast to analogous transformations of phenyl 3-arylpropynoates [2]. Such Lewis acid as $AlBr_3$ also promoted intramolecular cyclization of **Ia** to thiocoumarin **IIa** (run no. 5), but the yield of **IIa** was lower (60%) than in the reactions catalyzed by Brønsted acids.

The transformation of propynethioate **Ia** in the presence of $AlCl_3$ gave not only cyclization product **IIa** but also isomeric *S*-phenyl 3-chloro-3-phenylprop-2-enethioates *E*-**III** and *Z*-**III** (run no. 6). The latter are formed via abstraction of chloride ion from associated $AlCl_3$ species by strong electrophile **A** (Scheme 2). It should be noted that no analogous bromine-containing products were detected in the reaction with $AlBr_3$ (run no. 5).

The product mixture obtained in run no. 6 could not be separated by preparative chromatography on silica gel, and it was analyzed by gas chromatography–mass spectrometry and ^{1}H NMR. Theoretical calculation (ChemDraw Ultra 10.0) of the chemical shifts of vinyl protons in isomers *E*-**III** and *Z*-**III** gave a larger value for the *Z* isomer (δ_{calc} 6.80 ppm against 6.42 ppm for the *E* isomer). Therefore, the isomer characterized by larger experimental chemical shift of the vinyl proton (δ_{exp} 6.88 ppm) was assigned *Z* configuration, and that with δ_{exp} 6.68 ppm, *E* configuration.

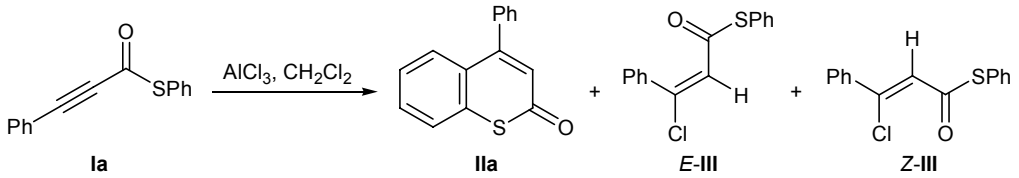
Scheme 1.



Ia, **Ib** **A** **IIa**, **IIb**

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

Scheme 2.



Ia **IIa** ***E*-III** ***Z*-III**

Thiocoumarins constitute a poorly explored class of organic compounds, and their syntheses by other methods were reported in a few publications [3–8].

Initial *S*-phenyl 3-arylpropynethioates **Ia** and **Ib** were prepared according to the procedure described in [9] by reaction of benzenethiol with 3-phenylpropynoic and 3-(4-methylphenyl)propynoic acids, respectively, in methylene chloride in the presence of *N*,*N*′-dicyclohexylcarbodiimide and a catalytic amount of pyridine.

S-Phenyl 3-phenylpropynethioate (**Ia**). Yield 47%, mp 58–60°C [10]. IR spectrum, ν, cm^{-1}: 2185 (C≡C), 1690 (C=O). ^{1}H NMR spectrum, δ, ppm: 7.36 t (2H, H_{arom}, J = 7.6 Hz), 7.44–7.47 m (6H, H_{arom}), 7.52–7.55 m (2H, H_{arom}).

S-Phenyl 3-(4-methylphenyl)propynethioate (**Ib**). Yield 45%, mp 108–110°C. ^{1}H NMR spectrum, δ, ppm: 2.37 s (3H, Me), 7.16 d (2H, H_{arom}, J = 13.9 Hz), 7.34 d (2H, H_{arom}, J = 13.9 Hz), 7.45–7.47 m (3H, H_{arom}), 7.52–7.55 m (2H, H_{arom}). Found, %: C 76.11; H 4.83. $C_{16}H_{12}OS$. Calculated, %: C 76.16; H 4.79.

4-Aryl-2*H*-thiochromen-2-ones IIa and IIb (*general procedure*). *a*. A solution of 0.2 mmol of compound **Ia** or **Ib** in 2 ml of the corresponding Brønsted acid (H_2SO_4, HSO_3F, or CF_3SO_3H) was stirred for 0.25–5 h at –75 to 20°C (see table; run nos. 1–4, 7, 8).

b. A solution of 30 mg (0.13 mmol) of compound **Ia** and 280 mg (0.63 mmol) of $AlBr_3$ in 5 ml of CH_2Cl_2 was stirred for 2 h at 20°C (see table, run no. 5).

The reaction mixture obtained as described above in *a* or *b* was poured into 30 ml of ice water and extracted with chloroform (3 × 50 ml). The extracts were combined, washed with water, a saturated solution of sodium hydrogen carbonate, and water again, and dried over Na_2SO_4, the solvent was distilled off under reduced pressure (water-jet pump), and the residue was subjected to chromatographic separation on silica gel using hexane–ethyl acetate as eluent. The yields are given in table.

4-Phenyl-2*H*-thiochromen-2-one (IIa). Oily substance; published data: mp 100°C [3], 98°C [4]. ^{1}H NMR spectrum, δ, ppm: 6.53 s (1H, 3-CH), 7.24–7.29 m (1H, H_{arom}), 7.37–7.38 m (2H, H_{arom}), 7.45–7.53 m (6H, H_{arom}). ^{13}C NMR spectrum, δ_C, ppm: 124.76, 126.21, 126.27, 126.83, 128.60, 128.89, 129.74, 130.58, 137.84, 138.30, 155.46, 184.52. Mass spectrum, m/z (I_{rel}, %): 238 (19) $[M]^+$, 210 (100), 165 (25).

4-(4-Methylphenyl)-2*H*-thiochromen-2-one (IIb). Oily substance. ^{1}H NMR spectrum, δ, ppm: 2.44 s (3H, Me), 6.52 s (1H, 3-H), 7.23-7.30 m (5H, H_{arom}), 7.46 t (1H, H_{arom}, J = 7.6 Hz), 7.51 d (1H, H_{arom}, J = 7.7 Hz), 7.57 d (1H, H_{arom}, J = 8.4 Hz). Mass spectrum, m/z (I_{rel}, %): 252 (12) $[M]^+$, 224 (100), 208 (8). Found, %: C 76.21; H 4.76. $C_{16}H_{12}OS$. Calculated, %: C 76.16; H 4.79. M 252.06.

***S*-Phenyl (*E*/*Z*)-3-chloro-3-phenylprop-2-enethioates (III)** were formed together with compound

Transformations of *S*-phenyl 3-arylpropynethioates **Ia** and **Ib** in various acid systems

Run no.	Initial compound no.	Reaction conditions	Product (yield, %)
1	**Ia**	H_2SO_4, 20°C, 5 h	**IIa** (96)
2	**Ia**	HSO_3F, –75°C, 0.25 h	**Ia** (80), **IIa** (14)
3	**Ia**	HSO_3F, 0°C, 1 h	**IIa** (90)
4	**Ia**	CF_3SO_3H, 20°C, 1 h	**IIa** (84)
5	**Ia**	$AlBr_3$, CH_2Cl_2, 20°C, 2 h	**IIa** (60)
6	**Ia**	$AlCl_3$, CH_2Cl_2, 20°C, 2 h	**IIa** (41), ***E*-III** (20), ***Z*-III** (38)
7	**Ib**	HSO_3F, –75°C, 0.25 h	**Ib** (70), **IIb** (22)
8	**Ib**	CF_3SO_3H, 20°C, 1 h	**IIb** (86)

IIa in the reaction of 50 mg (0.2 mmol) of compound **Ia** with 134 mg (1 mmol) of $AlCl_3$ in 5 ml of methylene chloride in 2 h at 20°C (method *b*, run no. 6). Oily material. ^{1}H NMR spectrum, δ, ppm (isomer mixture): 6.68 s (1H, =CH, *Z*), 6.88 s (1H, =CH, *E*), 7.23–7.71 m (10H, H_{arom}). Mass spectrum, *m*/*z* (I_{rel}, %) (GC–MS data): *E*-**III**: 274 (10) $[M]^+$, 165 (100), 137 (12), 102 (18); *Z*-**III**: 274 (8) $[M]^+$, 165 (100), 137 (10), 102 (15).

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer at 500 and 125 MHz, respectively, using $CDCl_3$ as solvent. The chemical shifts were measured relative to the residual proton and carbon signals of the solvent ($CHCl_3$, δ 7.25 ppm; $CDCl_3$, δ_C 77.0 ppm). The mass spectra were obtained on an MKh-1321 instrument. The IR spectra were recorded from solutions in chloroform on an FSM-1201 spectrometer. GC–MS analysis was performed on an Agilent G 2570A MSD/6850s GC instrument (HP-5MS capillary column, 3 m×0.25 mm, film thickness 0.25 μm). The elemental compositions were determined on an EuroVector EA-300 analyzer.

REFERENCES

1. Ryabukhin, D.S. and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2008, vol. 44, p. 1849.
2. Ryabukhin, D.S., Fukin, G.K., Cherkasov, A.V., and Vasil'ev, A.V., *Russ. J. Org. Chem*., 2009, vol. 45, p. 1252.
3. Ruwet, A. and Renson, M., *Bull. Soc. Chim. Belg*., 1969, vol. 78, p. 449.
4. Tilak, B.D. and Panse, G.T., *Indian J. Chem*., 1969, vol. 7, p. 315.
5. Natarajan, M., Manimaran, T., and Ramakrishnan, V.T., *Indian J. Chem., Sect. B*, 1984, vol. 23, p. 529.
6. Natarajan, M. and Ramakrishnan, V.T., *Indian J. Chem., Sect. B*, 1984, vol. 23, p. 720.
7. Nakazumi, H., Kitaguchi, T., Ueyama, T., and Kitao, T., *Synthesis*, 1984, p. 518.
8. Deprets, S. and Kirsch, G., *Heterocycl. Commun*., 2001, vol. 7, p. 421.
9. Neises, B. and Steglich, W., *Angew. Chem., Int. Ed. Engl*., 1978, vol. 17, p. 522.
10. Yokoyama, T., *Chem. Pharm. Bull*., 1964, vol. 12, p. 683.