ISSN 1070-4280, Russian Journal of Organic Chemistry, 2014, Vol. 50, No. 9, pp. 1372–1374. © Pleiades Publishing, Ltd., 2014.
Original Russian Text © M.Yu. Belikov, M.Yu. Ievlev, O.V. Ershov, K.V. Lipin, S.A. Legotin, O.E. Nasakin, 2014, published in Zhurnal Organicheskoi Khimii, 2014, Vol. 50, No. 9, pp. 1387–1388.

SHORT COMMUNICATIONS

Synthesis of Photochromic 5,6-Diaryl-2-chloropyridine-3,4-dicarbonitriles from 3,4-Diaryl-4-oxobutane-1,1,2,2-tetracarbonitriles

M. Yu. Belikov[a], **M. Yu. Ievlev**[a], **O. V. Ershov**[a], **K. V. Lipin**[a], **S. A. Legotin**[b], **and O. E. Nasakin**[a]

[a] *I.N. Ul'yanov Chuvash State University, Moskovskii pr. 15, Cheboksary, 428015 Russia*
e-mail: belikovmil@mail.ru

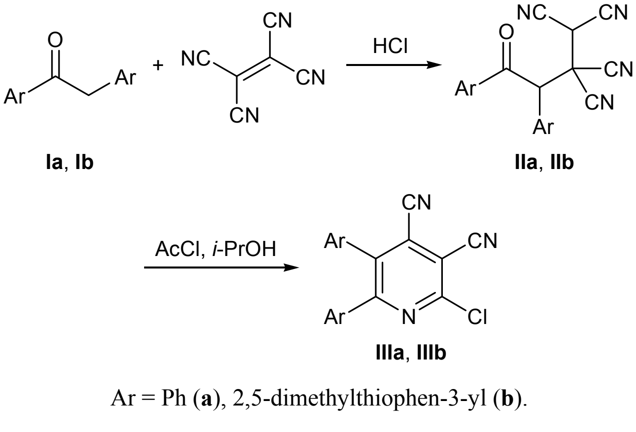
[b] *National University of Science and Technology MISIS, Leninskii pr. 4, Moscow, 119049 Russia*

Received April 24, 2014

DOI: 10.1134/S1070428014090231

1,2-Diarylethenes constitute one of the most promising classes of organic photochromes due to high thermal stability of their photoinduced forms and resistance to photodegradation, and they can be used in data recording and storage systems, as well as in other fields [1–3].

We now propose a new synthetic approach to photochromic diarylethenes, which is based on the reaction of tetracyanoethylene with ketones as key intermediate step. Tetracyanoethylation of ketones has been well documented; however, there are almost no published data on reactions of aryl arylmethyl ketones with tetracyanoethylene. Adducts of tetracyanoethylene with ketones of the general formula $R(CO)CH_2R'$ were used as starting compounds to obtain heterocycles containing an RC=CR′ fragment [4–10]. Analogous reactions with aryl arylmethyl ketones $Ar(CO)CH_2Ar$ could give rise to various 1,2-diarylethenes as new potential photochromes.



Ar = Ph (**a**), 2,5-dimethylthiophen-3-yl (**b**).

We were the first to react tetracyanoethylene with 1,2-diarylethanones **Ia** and **Ib** in the presence of a catalytic amount of hydrochloric acid. As a result, we isolated 3,4-diaryl-4-oxobutane-1,1,2,2-tetracarbonitriles **IIa** and **IIb**. The substrates were deoxybenzoin (**Ia**), the parent compound of the 1,2-diarylethanone series, and 1,2-bis(2,5-dimethylthiophen-3-yl)ethanone (**Ib**). The latter was selected taking into account that diarylethenes containing thienyl substituents are most promising from the viewpoint of the design of practically useful photochromic devices [1]. Ketone **Ib** was synthesized in a number of steps starting from hexane-2,5-dione [11].

Treatment of compounds **IIa** and **IIb** with acetyl chloride in isopropyl alcohol led to the formation of 5,6-diaryl-2-chloropyridine-3,4-dicarbonitriles **IIIa** and **IIIb**. The closest analogs of structures **IIIa** and **IIIb** are diaryl-substituted quinoline derivatives [12].

Compounds **IIIa** and **IIIb** turned out to display photochromic properties in ethanol solution. UV irradiation of their solutions in ethanol at λ 365 nm gave rise to photoinduced form, while the reverse transformation was induced by the action of full-spectrum visible light.

4-Oxo-3,4-diphenylbutane-1,1,2,2-tetracarbonitrile (IIa). Deoxybenzoin (**Ia**), 1.00 g (5.1 mmol), was dissolved in 20 mL of 1,4-dioxane, 0.64 g (5 mmol) of tetracyanoethylene and two drops of concentrated aqueous HCl were added, and the resulting yellow solution was stirred for 2–3 min at 35–40°C until tetracyanoethylene dissolved completely. The mixture was left to stand for 2–3 days in a closed vessel at room temperature, and the presence of tetracyanoethylene was checked by the hydroquinone test (formation of a blue complex). When the reaction was complete, the mixture was diluted with a fivefold volume of water and stirred until a uniform suspension was obtained. The precipitate was filtered off and washed on a filter with water and cold propan-2-ol. Yield 1.12 g (68%), mp 140–141°C (decomp.); published data [13]: mp 141–142°C. IR spectrum, ν, cm^{-1}: 2246 (C≡N), 1696 (C=O). UV spectrum: λ_{max} 242 nm (ε = 12476). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 5.77 s (1H, C**H**Ph), 6.01 s (1H, CHCN), 7.46–7.69 m (8H, H_{arom}), 8.07 d (2H, H_{arom}, J = 7.9 Hz). Found, %: C 74.13; H 3.79; N 17.19. $C_{20}H_{12}N_4O$. Calculated, %: C 74.06; H 3.73; N 17.27.

3,4-Bis(2,5-dimethylthiophen-3-yl)-4-oxobutane-1,1,2,2-tetracarbonitrile (IIb). 1,2-Bis(2,5-dimethylthiophen-3-yl)ethanone (**Ib**), 1.08 g (4.1 mmol), was dissolved in 20 mL of 1,4-dioxane, 0.51 g (4 mmol) of tetracyanoethylene and two drops of concentrated aqueous HCl were added, and the dark brown mixture was stirred for 5–7 min at 35–40°C until tetracyanoethylene dissolved completely. The mixture was then left to stand for 8–9 h in a closed vessel at room temperature, and the presence of tetracyanoethylene was checked by the hydroquinone test (formation of a blue complex). When the reaction was complete, the mixture was treated as described above in the synthesis of **IIa**. Yield 1.32 g (82%), mp 85–86°C (decomp.). IR spectrum, ν, cm^{-1}: 2249 (C≡N), 1699 (C=O). UV spectrum, λ_{max}, nm (ε): 215 (19378), 257 (9782). ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 2.34 s, 2.36 s, 2.69 s, and 2.71 s (3H each, CH_3); 5.50 s (1H, CHCO), 5.77 s (1H, CHCN), 6.65 s and 6.89 s (1H each, 4′-H). Found, %: C 61.28; H 4.19; N 14.18. $C_{20}H_{16}N_4OS_2$. Calculated, %: C 61.20; H 4.11; N 14.27.

2-Chloro-5,6-diphenylpyridine-3,4-dicarbonitrile (IIIa). Acetyl chloride, 0.5 mL, was added dropwise to a solution of 0.162 g (0.5 mmol) of 4-oxo-3,4-diphenylbutane-1,1,2,2-tetracarbonitrile (**IIa**) in 3 mL of anhydrous propan-2-ol. The mixture was stirred for 2 h at 50–60°C, cooled to room temperature, and evaporated to one third of the initial volume. The precipitate was filtered off and washed with cold propan-2-ol. Yield 0.114 g (72%), mp 202–203°C. IR spectrum: ν 2223 cm^{-1} (C≡N). UV spectrum, λ_{max}, nm (ε): 278 (4962), 347 (4862). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.26–7.39 m (8H, H_{arom}), 7.44–7.48 m (2H, H_{arom}). Mass spectrum: m/z 315 $[M]^+$. Found, %: C 72.19; H 3.25; N 13.39. $C_{19}H_{10}ClN_3$. Calculated, %: C 72.27; H 3.19; N 13.31. M 315.06.

2-Chloro-5,6-bis(2,5-dimethylthiophen-3-yl)pyridine-3,4-dicarbonitrile (IIIb) was synthesized in a similar way from 0.96 g (0.5 mmol) of compound **IIb**. Yield 0.146 g (76%), mp 142–143°C. IR spectrum: ν 2229 cm^{-1} (C≡N). UV spectrum, λ_{max}, nm (ε): 305 (8362), 377 (6122). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 1.99 s, 2.24 s, 2.28 s, and 2.38 s (3H each, CH_3); 6.15 s and 6.61 s (1H each, 4′-H). Mass spectrum, m/z 383 $[M]^+$. Found, %: C 59.36; H 3.676; N 10.99. $C_{19}H_{14}ClN_3S_2$. Calculated, %: C 59.44; H 3.68; N 10.95. M 383.03.

The progress of reactions and the purity of products were monitored by TLC on Silufol UV-254 plates; spots were visualized under UV light, by treatment with iodine vapor, or by heating. The IR spectra were recorded on an FSM-1202 spectrometer with Fourier transform from samples dispersed in mineral oil. The ^{1}H NMR spectra were measured on a Bruker DRX-500 spectrometer at 500.13 MHz using tetramethylsilane as internal reference. The UV spectra were recorded from solutions in ethanol ($c = 5 \times 10^{-5}$ M) on an SF-2000 spectrophotometer. The elemental compositions were determined on a £aboratorni Přistroje analyzer. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan MAT INCOS-50 spectrometer.

This study was performed under financial support by the President of the Russian Federation (project no. MK-97.2014.3.

REFERENCES

1. Irie, M., *Chem. Rev.*, 2000, vol. 100, p. 1685.
2. Minkin, V.I., *Chem. Rev.*, 2004, vol. 104, p. 2751.
3. Barachevsky, V.A., Strokach, V.P., Puankov, V.A., Kovaleva, O.T., Valova, T.M., Zavchenko, K.S., and Krayushkin, M.M., *Arkivoc*, 2009, part (ix), p. 70.
4. Belikov, M.Yu., Ershov, O.V., Lipovskaya, I.V., Fedoseev, S.V., and Nasakin, O.E., *Russ. J. Org. Chem.*, 2013, vol. 49, p. 864.
5. Ershov, O.V., Nasakin, O.E., and Belikov, M.Yu., Russian Patent no. 2475489, 2013.
6. Belikov, M.Yu., Ershov, O.V., Eremkin, A.V., Kayukov, Ya.S., and Nasakin, O.E., *Russ. J. Org. Chem.*, 2010, vol. 46, p. 615.
7. Belikov, M.Yu., Ershov, O.V., Eremkin, A.V., Kayukov, Ya.S., and Nasakin, O.E., *Russ. J. Gen. Chem.*, 2010, vol. 80, p. 2078.
8. Ershov, O.V., Lipin, K.V., Maksimova, V.N., Eremkin, A.V., Kayukov, Ya.S., and Nasakin, O.E., *Russ. J. Org. Chem.*, 2009, vol. 45, p. 475.

9. Nasakin, O.E., Sheverdov, V.P., Moiseeva, I.V., Lyshchikov, A.N., Ershov, O.V., and Nesterov, V.N., *Tetrahedron Lett*., 1997, vol. 38, p. 4455.
10. Kayukov, Ya.S., Nasakin, O.E., Urman, Ya.G., Khrustalev, V.N., Nesterov, V.N., Antipin, M.Yu., Lyshchikov, A.N., and Lukin, P.M., *Chem. Heterocycl. Compd*., 1996, vol. 32, no. 10, p. 1200.
11. Krayushkin, M.M., Lichitskii, B.V., Mikhalev, A.P., Dudinov, A.A., and Ivanov, S.N., *Russ. J. Org. Chem*., 2005, vol. 41, p. 87.
12. Krayushkin, M.M., Lichitskii, B.V., Pashchenko, D.V., Antonov, I.A., Nabatov, B.V., and Dudinov, A.A., *Russ. J. Org. Chem*., 2007, vol. 43, p. 1357.
13. Dickinson, C.L., *J. Am. Chem. Soc*., 1960, vol. 82, p. 4367.