Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2011, **21**, 36–37
Mendeleev Communications

The reaction of 2-arylazo-1-vinylpyrroles with trifluoroacetic anhydride: unexpected formation of *N*-aryl-2,2,2-trifluoroacetamides and conjugated polymers

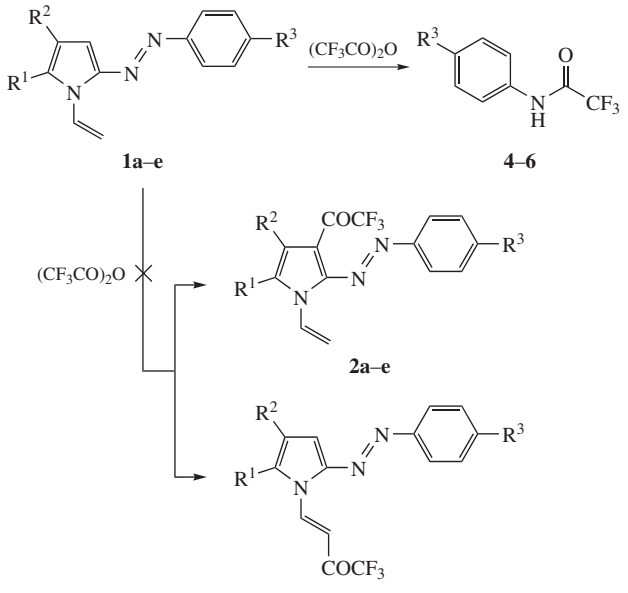
Elena Yu. Schmidt, Igor A. Ushakov, Nadezhda V. Zorina, Albina I. Mikhaleva and Boris A. Trofimov*

A. E. Favorsky Irkutsk Institute of Chemistry, Siberian Branch of the Russian Academy of Sciences, 664033 Irkutsk, Russian Federation. Fax: +7 3952 419 346; e-mail: boris_trofimov@irioch.irk.ru

DOI: 10.1016/j.mencom.2011.01.015

2-Arylazo-1-vinylpyrroles under the action of trifluoroacetic anhydride (CH_2Cl_2 or benzene, –5–0 °C, 1 h) form *N*-aryl-2,2,2-trifluoroacetamides along with conjugated (electroconducting and paramagnetic) polymers.

2-Arylazo-1-vinylpyrroles of the type **1a–e**, a recently synthesized new family of reactive dyes of the pyrrole series,[1] present more challenge for the design of optoelectronic materials and intrinsically coloured polymers. Variation in their structure can be reached by the involving of now available diversely substituted 1-vinylpyrroles (*via* the one-pot Trofimov reaction[2] from ketones and acetylene)[3] into the azo coupling which will bring about new pyrrole azo dyes or their precursors with tailor-made optical and chemical properties. Obviously, this is to be facilitated by the systematic study of principal properties of 2-arylazo-1-vinylpyrroles, which are sometimes unusual. For example, along with the expected CF_3CO_2H-catalyzed addition of alcohols at the *N*-vinyl group of pyrroles **1a–e**, formation of 2-methylquinolines was observed.[4] The latter are also formed on treatment of 2-arylazo-1-vinylpyrroles with only trifluoroacetic acid.[5] In air, these pyrroles undergo unprecedented facile chemo- and regiospecific autooxidation involving alkyl substitutents only (with retaining the pyrrole ring and *N*-vinyl group) to afford formyl- and hydroxyalkyl-substituted *N*-vinylpyrroles.[6] With $PdCl_2$, pyrroles **1a–e** form catalytically active complexes[1] and with BF_3 produce brightly coloured species being new pyrrole dyes.[1]



1a–e	R^1	R^2	R^3	Yields of **4–6** (%)
a	Me	H	H	**4**, 29
b	Me	Me	H	**4**, 32
c	$(CH_2)_5$		H	**4**, 22
d	Me	Me	OEt	**5**, 23
e	Me	Me	NO_2	**6**, 25

Scheme 1

Herein we briefly report on an unexpected pathway of the reaction between 2-arylazo-1-vinylpyrroles **1a–e** and trifluoroacetic anhydride (TFAA). The latter is known to be capable of easy acylating the pyrroles and 1-vinylpyrroles to furnish trifluoroacetyl derivatives.[7] Also known is that the trifluoroacetic cation generated by TFAA is able to electrophilically replace β-hydrogen atom in vinyl ethers,[8] enamines,[9] *N*-vinylamides[10] and *N*-vinylindoles.[11] Therefore, the expected reactions of pyrroles **1a–e** with TFAA can be the formation of trifluoroacetyl derivatives **2a–e** or 1-(2-trifluoroacetylvinyl)pyrroles **3a–e** (Scheme 1).

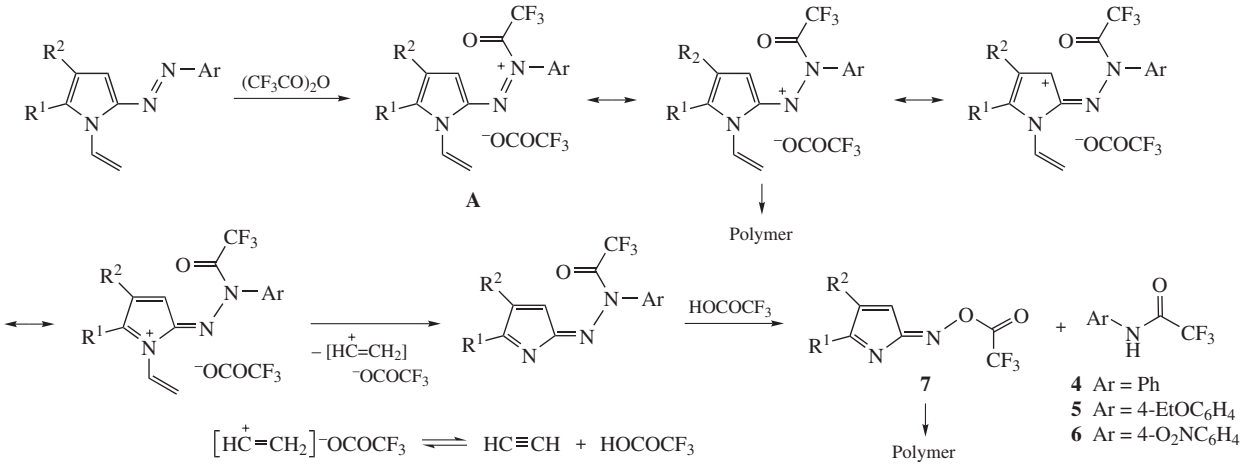
However, when the reaction of pyrroles **1a–e** with TFAA was carried out in CH_2Cl_2 or benzene at –5–0 °C for 1 h, instead of expected compounds **2** and **3**, *N*-aryl-2,2,2-trifluoroacetamides **4–6** were isolated in up to 32% yield (Scheme 1).† Other products are black conjugated paramagnetic (2.5×10^{18} g^{-1}) and electro-

† ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 instrument (400.13 and 101.61 MHz, respectively) equipped with inverse gradient 5 mm probe in $CDCl_3$ with HMDS as internal standard. All 2D NMR spectra were recorded using a standard gradient Bruker pulse programs. IR spectra were obtained on a Bruker Vertex 70 spectrometer.

The reaction of 4,5-dimethyl-2-phenylazo-1-vinylpyrrole **1b** *with TFAA.* To a cooled (–5 °C) solution of pyrrole **1b** (0.225 g, 1 mmol) in CH_2Cl_2 (8 ml), a solution of TFAA (0.210 g, 1 mmol) in CH_2Cl_2 (4 ml) was added dropwise for 20 min. The reaction mixture was stirred at the same temperature for 40 min, and then the solvent was removed *in vacuo*. The black viscous residue (0.420 g) was chromatographed on a column (Al_2O_3, CCl_4) to give 0.060 g (yield 32%) of product **4** and 0.161 g of black polymer. For polymer found (%): C, 34.72; H, 3.50; F, 2.75; N, 13.83; ash, 19.34. Calc. for $C_8H_7F_3N_2O_2$ (%): C, 43.65; H, 3.20; F, 25.89; N, 12.72. The inconsistence of the experimental and theoretical data and the presence of ash in the sample results from hydrolysis of the polymer on $Al_2O_3\cdot H_2O$ and elution of aluminum compounds with the hydrolyzed polymer.

Amides **5** and **6** were isolated analogously.

N-Phenyl-2,2,2-trifluoroacetamide **4**: white crystals, mp 85–88 °C (lit.,[14] 87–89 °C). ^1H NMR ($CDCl_3$) δ: 7.78 (br.s, 1H, NH), 7.56–7.54 (m, 2H, *o*-H), 7.41–7.37 (m, 2H, *m*-H), 7.23–7.21 (m, 1H, *p*-H). ^{13}C NMR ($CDCl_3$) δ: 154.8 (q, C=O, $^2J_{C–F}$ 37.2 Hz), 135.2 (*i*-C), 129.5 (*m*-C), 126.5 (*p*-C), 120.6 (*o*-C), 115.8 (q, CF_3, $^1J_{C–F}$ 288.5 Hz). IR (KBr, ν_{max}/cm^{-1}): 3324, 1715, 1603, 1552, 1491, 1452, 1287, 1244, 1155, 896, 755, 731, 691, 498. Found (%): C, 51.18; H, 3.33; F, 30.37; N, 7.27. Calc. for $C_8H_6F_3NO$ (%): C, 50.80; H, 3.20; F, 30.13; N, 7.41.



Scheme 2

conducting (5.0×10^{-11} for undoped and 1.1×10^{-7} S cm^{-1} for I_2-doped samples) polymers. Their polyconjugated structure is also confirmed by IR (broad absorptions in the region 1700–1300 cm^{-1} with maxima at 1680, 1500 and 1380 cm^{-1})[12] and UV spectra (broad absorptions in the region 400–500 nm with λ_{max} = 442 nm[13]).‡

Apparently, the site of the primary attack by the trifluoroacetyl cation is neither the pyrrole ring nor *N*-vinyl group, but nitrogen atom of the azo group adjacent to the benzene ring. This is in agreement with data on the protonation of pyrroles **1a**–**e**.[5] The deep charge-transfer from the pyrrole moiety of the molecule onto the azo group has been previously detected by NMR and UV spectroscopy.[1] Thus, one may assume that the cation **A** (chaperoned by the trifluoroacetate anion) is the key intermediate of this reaction (Scheme 2).

In such a cation, the positive charge should be mainly concentrated on the pyrrole nitrogen due to even greater electron density transfer from the pyrrole counterpart of the molecule towards the ionized azo group. One of the anticipated pathways of the intermediate **A** fragmentation is elimination of the vinyl cation with further release of proton. The latter protonates trifluoroacetamide moiety with the N–N bond cleavage. This leads to the formation of *N*-aryl-2,2,2-trifluoroacetamides **4**–**6** and unstable 2,2,2-trifluoro-*N*-(2*H*-pyrrol-2-ylidene)acetamides **7** (Scheme 2), which are finally transformed to polyconjugated polymers.

The reaction found substantially contributes to understanding the reactivity of 2-arylazo-1-vinylpyrroles, especially their behaviour in the presence of strong electrophiles. This result is of significance for the prediction of other electrophilic transformations of 2-arylazo-1-vinylpyrroles.

N-*(4-Ethoxyphenyl)-2,2,2-trifluoroacetamide* **5**: white crystals, mp 140–142 °C. ^{1}H NMR ($CDCl_3$) δ: 7.82 (br. s, 1H, NH), 7.47 (d, 2H, *o*-H, ^3J 8.9 Hz), 6.91 (d, 2H, *m*-H, ^3J 8.9 Hz), 4.05 (q, 2H, CH_2, ^3J 7.0 Hz), 1.43 (t, 3H, Me, ^3J 7.0 Hz). ^{13}C NMR ($CDCl_3$) δ: 157.4 (*p*-C), 154.6 (q, C=O, $^2J_{C–F}$ 37.0 Hz), 127.9 (*i*-C), 122.4 (*o*-C), 115.9 (q, CF_3, $^1J_{C–F}$ 288.0 Hz), 115.2 (*m*-C), 63.9 (CH_2), 14.8 (Me). IR (KBr, ν_{max}/cm^{-1}): 3309, 1702, 1619, 1548, 1516, 1480, 1306, 1255, 1239, 1174, 1156, 1047, 909, 833, 726, 516. Found (%): C, 51.46; H, 4.38; F, 24.32; N, 5.90. Calc. for $C_{10}H_{10}F_3NO_2$ (%): C, 51.51; H, 4.32; F, 24.44; N, 6.01.

N-*(4-Nitrophenyl)-2,2,2-trifluoroacetamide* **6**: black crystals, mp 50–52 °C. ^{1}H NMR ($CDCl_3$) δ: 8.55 (br. s, 1H, NH), 8.26 (d, 2H, *m*-H, ^3J 8.3 Hz), 7.81 (d, 2H, *o*-H, ^3J 8.3 Hz). ^{13}C NMR ($CDCl_3$) δ: 155.3 (q, C=O, $^2J_{C–F}$ 37.3 Hz), 145.2 (*p*-C), 141.1 (*i*-C), 125.2 (*m*-C), 120.5 (*o*-C), 115.5 (q, CF_3, $^1J_{C–F}$ 288.0 Hz). IR (KBr, ν_{max}/cm^{-1}): 3111, 2923, 1741, 1597, 1517, 1504, 1415, 1345, 1254, 1150, 1110, 908, 854, 752, 735, 691, 497. Found (%): C, 41.98; H, 2.08; F, 24.21; N, 11.81. Calc. for $C_8H_5F_3N_2O_3$ (%): C, 41.04; H, 2.15; F, 24.34; N, 11.96.

‡ The detailed study of structure and properties of these polymers will be published elsewhere.

This work was supported by the Russian Foundation for Basic Research (grant no. 09-03-00158).

References

1 B. A. Trofimov, E. Yu. Schmidt, A. I. Mikhaleva, A. M. Vasil'tsov, A. B. Zaitsev, N. S. Smolyanina, E. Yu. Senotrusova, A. V. Afonin, I. A. Ushakov, K. B. Petrushenko, O. N. Kazheva, O. A. Dyachenko, V. V. Smirnov, A. F. Schmidt, M. V. Markova and L. V. Morozova, *Eur. J. Org. Chem.*, 2006, 4021.

2 (*a*) A. I. Mikhaleva and E. Yu. Schmidt, in *Selected Methods for Synthesis and Modification of Heterocycles*, ed. V. G. Kartsev, IBS Press, Moscow, 2002, vol. 1, pp. 334–352; (*b*) R. J. Tedeschi, in *Encyclopedia of Physical Science and Technology*, 3rd edn., ed. R. A. Meyers, Academic Press, San Diego, 2001, vol. 1, pp. 55–89; (*c*) Z. Wang, in *Comprehensive Organic Name Reactions and Reagents*, Wiley, London, 2009, part 3, paragraph 626.

3 (*a*) E. Yu. Schmidt, A. I. Mikhaleva, A. B. Zaitsev, A. M. Vasil'tsov and N. V. Zorina, *ARKIVOC*, 2005, **vii**, 11; (*b*) A. I. Mikhaleva, E. Yu. Schmidt, A. V. Ivanov, A. M. Vasil'tsov, E. Yu. Senotrusova and N. I. Protsuk, *Zh. Org. Khim.*, 2007, **43**, 236 (*Russ. J. Org. Chem.*, 2007, **43**, 228).

4 E. Yu. Schmidt, E. Yu. Senotrusova, I. A. Ushakov, N. I. Protsuk, A. I. Mikhaleva and B. A. Trofimov, *Zh. Org. Khim.*, 2007, **43**, 1502 (*Russ. J. Org. Chem.*, 2007, **43**, 1495).

5 E. Yu. Schmidt, E. Yu. Senotrusova, I. A. Ushakov, A. I. Mikhaleva and B. A. Trofimov, *Tetrahedron*, 2009, **65**, 4855.

6 (*a*) B. A. Trofimov, E. Yu. Schmidt, E. Yu. Senotrusova, I. A. Ushakov and A. I. Mikhaleva, *Zh. Org. Khim.*, 2009, **45**, 1579 (*Russ. J. Org. Chem.*, 2009, **45**, 1567); (*b*) E. Yu. Schmidt, E. Yu. Senotrusova, I. A. Ushakov, O. N. Kazheva, O. A. Dyachenko, G. G. Alexandrov, A. V. Ivanov, A. I. Mikhaleva and B. A. Trofimov, *ARKIVOC*, 2010, **ii**, 352.

7 B. A. Trofimov, A. I. Mikhaleva, S. E. Korostova, L. N. Sobenina, A. N. Vasil'ev and L. V. Balashenko, *Zh. Org. Khim.*, 1979, **15**, 2042 (in Russian).

8 (*a*) M. Hojo, R. Masuda and E. Okada, *Synthesis*, 1990, 347; (*b*) B. A. Trofimov, E. Yu. Schmidt, A. I. Mikhaleva, A. M. Vasil'tsov, L. I. Larina and L. V. Klyba, *Mendeleev Commun.*, 1999, 238; (*c*) A. M. Vasil'tsov, E. Yu. Schmidt, A. I. Mikhaleva, A. B. Zaitsev, O. A. Tarasova, A. V. Afonin, D.-S. D. Toryashinova, L. N. Il'icheva and B. A. Trofimov, *Zh. Org. Khim.*, 2001, **37**, 362 (*Russ. J. Org. Chem.*, 2001, **37**, 334).

9 J. Szmuszkovicz, *Advances in Organic Chemistry*, Interscience, New York, 1963, pp. 25–58.

10 M. Hojo, R. Masuda, Y. Kokuryo, H. Shioda and S. Matsuo, *Chem. Lett.*, 1976, 499.

11 M. F. Shostakovsky, G. G. Skvortsova and E. S. Domnina, *Usp. Khim.*, 1969, **38**, 892 (*Russ. Chem. Rev.*, 1969, **38**, 407).

12 G. Socrates, *Infrared and Raman Characteristic Group Frequencies: Tables and Charts*, 3rd edn., Wiley, Chichester, 2001, p. 272.

13 *Handbook of Conducting Polymers: Conjugated Polymers: Theory, Synthesis, Properties, and Characterisation*, 3rd edn., eds. T. A. Skotheim and J. R. Reynolds, CRC Press, Boca Raton, London, New York, 2007.

14 K. G. Rutherford, S. Y.-S. Ing (Yu) and R. J. Thibert, *Can. J. Chem.*, 1965, **43**, 541.

Received: 24th June 2010; Com. 10/3546