

SHORT
COMMUNICATIONS

Reaction of Fluoro[trifluoromethanesulfonyloxy- λ^3 -iodanil]-benzene with Nitrogen-containing Heterocycles*

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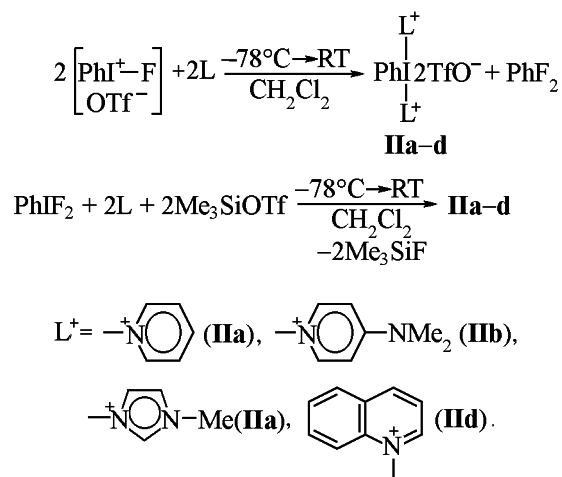
Organic derivatives of trivalent iodine are highly reactive substances that show versatile reactivity with respect to various classes of organic compounds [1]. Among these derivatives the fluoro[trifluoromethanesulfonyloxy- λ^3 -iodanil]benzene (**I**) exhibits pronounced electrophilic qualities due to the presence of the nucleofugic sulfonate group [2-4]. Reagent **I** was applied to transformation of terminal alkynes into alkenyliodonium salts [2-4], nonterminal alkynes into esters of carboxylic acids [5], methyl ketones into 1,4-butanediones [6]. We demonstrated recently that phenyliodosofluorosulfonates react with acyclic and monocyclic olefins to furnish bis-sulfonates and fluorosulfonates [7, 8].

The reaction of iodosobenzene or phenyliodosodiacetate with pyridine in the presence of trimethylsilyl triflate is known to yield bis-onium product **II** [9-12] that cleanly transforms bis-hydrazones into alkynes, and hydrazones into diazo compounds [12, 13]. Therefore this reagent is a valuable product that can be used in organic synthesis. However the above method of compounds **II** preparation is a two-stage procedure and requires preliminary synthesis of iodoso compounds.

We attempted to develop one-step procedure for compound **II** preparation. It was established that fluoro[trifluoromethanesulfonyloxy- λ^3 -iodanil]benzene (**I**) vigorously reacted with various pyridine compounds forming the corresponding bis-onium products **II**. When we carried out this reaction at molar reagents ratio 1:1 we obtained a mixture of bis-onium product **II** and iodosobenzene difluoride.

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The complete consumption of the reagent was attained at the use of trimethylsilyl triflate. In this case the initial compounds react in the molar ratio 1:2. Compounds **IIa-d** protected from moisture are relatively stable and can be stored without visible changes for several days. The structure of compounds **IIa-d** was proved by ¹H and ¹³C NMR spectra and by comparison of their physico-chemical and spectral characteristics with the published data [12].



Thus we demonstrated that reagent **I** can be used for preparation of bis-onium compounds **IIa-d**. The application of phenyliodosofluorotriflate **I** as a new oxidant containing in its structure a triflate group provides a possibility to obtain in high yield bis-onium salts, and it is the first example of one-step preparation of the bis-onium compounds **IIa-d** from aryl iodides and nitrogen-containing heterocycles.

General procedure for reaction of compound I with nitrogen-containing heterocyclic compounds. Into a stirred solution of 4.72 mmol of reagent **I**

[2-5, 7, 8] in 20 ml of CH_2Cl_2 at -78°C was added 9.44 mmol of nitrogen-containing heterocyclic compound in 10 ml of CH_2Cl_2 and 10 mmol of trimethylsilyl triflate. The reaction mixture was stirred for 20 min at -78°C , and then the mixture was gradually warmed to room temperature. Therewith the formation of bis-onium product **II** as colorless precipitate was observed. The precipitate was filtered off, washed with dichloromethane (2×25 ml), and dried in a vacuum.

Compound IIa. Yield 79%. ^1H NMR spectrum (CD_3CN), δ , ppm: 7.65 d.d (2H, $\text{H}^{3,5}$ -Ph, 3J 6.6 and 6.0 Hz), 7.80 m (5H, H^4 -Ph, $\text{H}^{3,5}$ -Py), 8.36 t (2H, H^4 -Py, 3J 7.7 Hz), 8.69 d (2H, $\text{H}^{2,6}$ -Ph, 3J 7.7 Hz), 9.00 d (4H, $\text{H}^{2,6}$ -Py, 3J 4.9 Hz). ^{13}C NMR spectrum (CD_3CN), δ , ppm: 121.86 q (CF_3SO_3 , $^1J_{\text{CF}}$ 320 Hz), 124.67 (C^1 -Ph), 129.87 ($\text{C}^{3,5}$ -Py), 134.37 ($\text{C}^{3,5}$ -Ph), 135.95 (C^4 -Ph), 136.73 ($\text{C}^{2,6}$ -Ph), 146.14 (C^4 -Py), 148.58 ($\text{C}^{2,6}$ -Py).

Compound IIb. Yield 71%. ^1H NMR spectrum (CD_3CN), δ , ppm: 3.08 s (12H, 4Me), 7.47 AA'BB' (8H, 3J 7.7 Hz), 7.59 d.d (2H, $\text{H}^{3,5}$ -Ph, 3J 8.2 and 7.7 Hz), 7.72 t (1H, H^4 -Ph, 3J 7.7 Hz), 8.48 d (2H, $\text{H}^{2,6}$ -Ph, 3J 8.2 Hz). ^{13}C NMR spectrum (CD_3CN), δ , ppm: 40.28 (NMe_2), 109.66 ($\text{C}^{3,5}$ -Py), 122.00 q (CF_3SO_3 , $^1J_{\text{CF}}$ 320 Hz), 123.60 (C^1 -Ph), 133.77 ($\text{C}^{3,5}$ -Ph), 134.88 (C^4 -Ph), 135.15 ($\text{C}^{2,6}$ -Ph), 145.94 ($\text{C}^{2,6}$ -Py), 157.14 (C^4 -Py).

Compound IIc. Yield 82%. ^1H NMR spectrum (CD_3CN), δ , ppm: 3.76 s (6H, 2Me), 7.27 d (4H, $\text{H}^{4,5}$ -imidazole, 3J 89.6 Hz), 7.61 d.d (2H, $\text{H}^{3,5}$ -Ph, 3J 8.2 and 7.7 Hz), 7.76 t (1H, H^4 -Ph, 3J 7.7 Hz), 8.42 s (2H, H^2 -imidazole), 8.52 d (2H, $\text{H}^{2,6}$ -Ph, 3J 7.7 Hz). ^{13}C NMR spectrum (CD_3CN), δ , ppm: 36.38 (Me), 122.00 q (CF_3SO_3 , $^1J_{\text{CF}}$ 320 Hz), 124.80 (C^1 -Ph), 126.30 ($\text{C}^{4,5}$ -imidazole), 133.74 ($\text{C}^{3,5}$ -Ph), 134.97 (C^4 -Ph), 135.66 ($\text{C}^{2,6}$ -Ph), 140.11 (C^2 -imidazole).

Compound II d. Yield 64%. ^1H NMR spectrum (CD_3CN), δ , ppm: 7.45 d.d (2H, H^3 -quinoline 3J 8.2 and 7.7 Hz), 7.58 d.d (2H, $\text{H}^{3,5}$ -Ph, 3J 8.2 and 7.7 Hz), 7.89 m (3H, H^4 -Ph, H^6 -quinoline), 8.17 d (2H, H^5 -quinoline, 3J 7.7 Hz), 8.24 d.d (2H, H^7 -quinoline, 3J 8.8 and 7.1 Hz), 8.72 d (2H, $\text{H}^{2,6}$ -Ph, 3J 7.7 Hz), 8.80 d (2H, H^8 -quinoline, 3J 8.8 Hz), 8.96 d (2H, H^4 -quinoline, 3J 8.2 Hz), 10.00 d (2H, H^2 -quinoline, 3J 5.5 Hz). ^{13}C NMR spectrum

(CD_3CN), δ , ppm: 121.86 q (CF_3SO_3 , $^1J_{\text{CF}}$ 320 Hz), 124.61 (C^3 -quinoline), 125.10 (C^1 -Ph), 125.89 (C^6 -quinoline) 131.13 (C^5 -quinoline), 131.49 (C^{4a} -quinoline), 134.12 ($\text{C}^{3,5}$ -Ph), 135.66 (C^4 -Ph), 135.99 ($\text{C}^{7,8}$ -quinoline), 136.69 ($\text{C}^{2,6}$ -Ph), 141.71 (C^4 -quinoline), 147.93 (C^{8a} -quinoline), 153.94 (C^2 -quinoline).

^1H and ^{13}C NMR spectra were registered on spectrometer Varian-400 at 400 and 100 MHz respectively. Chemical shifts are given in δ ppm measured relatively to the chemical shifts of residual protons of the corresponding solvent.

REFERENCES

1. Varvoglis A., *Synthesis*, 1984, no. 9, pp. 709-726.
2. Kasumov, T.M., Pirkuliyev, N.Sh., Brel, V.K., Grishin, Y.K., Zefirov, N.S., and Stang, P.J., *Tetrahedron*, 1997, vol. 53, no. 38, pp. 13139-13148.
3. Pirkuliyev, N.Sh., Brel, V.K., Kasumov, T.M., Akhmedov, N.G., and Zefirov, N.S., *Zh. Org. Khim.*, 1999, vol. 35, no. 11, pp. 1633-1636.
4. Pirkuliyev, N.Sh., Brel, V.K., Kasumov, T.M., Grishin, Y.K., Zefirov, N.S., and Stang, P.J., *Synthesis*, 1999, no. 8, pp. 1297-1299.
5. Pirkuliyev, N.Sh., Brel, V.K., Zefirov, N.S., and Stang, P.J., *Mendeleev Commun.*, 1999, no. 5, pp. 189-190.
6. Pirkuliyev, H.Sh., Brel, V.K., and Zefirov, N.S., Abstracts of Papers, *Int. Sci. Conf. on Organic Synthesis and Combinatorial Chemistry*, Moscow, 1999, p. 131.
7. Pirkuliyev, H.Sh., Brel, V.K., and Akhmedov, N.G., Magerramov, A.M., Shikhaliev, N.G., and Zefirov, N.S., *Zh. Org. Khim.*, 2001, vol. 37, no. 5, pp. 721-724.
8. Pirkuliyev, H.Sh., Brel, V.K., and Akhmedov, N.G., and Zefirov N.S., *Zh. Org. Khim.*, 2000, vol. 36, no. 9, pp. 1322-1327.
9. Weiss, R., Salomon, N.J., Miess, G.E., and Roth, R., *Angew. Chem.*, 1986, vol. 98, no. 10, pp. 925-926.
10. Weiss, R., Roth, R., Lowack, R.H., and Bremer, M., *Angew. Chem.*, 1990, vol. 102, no. 10, S.1164-1166.
11. Taft, R.W. and Topsom, R.D., *Prog. Phys. Org. Chem.*, 1987, vol. 16, p. 6.
12. Weiss, R. and Seubert, J., *Angew. Chem. Int. Ed.*, 1994, vol. 33, no. 8, pp. 891-893.
13. Weiss, R., Seubert, J., and Hampel, F., *Angew. Chem. Int. Ed.*, 1994, vol. 33, no. 19, pp. 1952-1953.