(DICYANO)IODONIUM TRIFLATE - NOVEL IODONIUM SPECIES AND A VERSATILE REAGENT FOR THE PREPARATION OF IODONIUM SALTS VIA AN IODONIUM TRANSFER REACTION WITH ORGANOSTANNANES

Peter J. Stang*, Viktor V. Zhdankin*, Rik Tykwinski Chemistry Department, The University of Utah, Salt Lake City, Utah 84112 USA Nikolai S. Zefirov

Chemistry Department, Moscow State University, Moscow 119899 USSR

Summary. (Dicyano)iodonium triflate $(NC)_2I^+$ ^-OTf can be prepared by the reaction of O=I-OTf with cyanotrimethylsilane and isolated as an air sensitive crystalline solid unstable at room temperature. This compound generated in situ reacts with tributyltin derivatives of various aromatic compounds or acetylenes at - 40 ^{o}C forming the corresponding iodonium salts in good yield.

In recent years a large variety of polyvalent iodine compounds have become available, and their versatility in organic synthesis has been well established¹. Of special synthetic interest are iodine(III) derivatives with one or two cyano ligands covalently attached to the iodine atom². The recently reported phenyl(cyano)iodonium salts²a have been found to be valuable reagents for the preparation of various alkynyl³ and alkenyl⁴ (phenyl)iodonium species via a novel iodonium transfer reaction with the corresponding organotin derivatives.

In this paper we wish to report the preparation of a new cyanated iodinane, (dicyanoiodonium) triflate **3**, and its application as a versatile reagent for a mild in situ synthesis of various iodonium triflate salts.

Compound 3 can be prepared by the reaction of iodosyl triflate 1^5 with trimethylsilyl cyanide in methylene chloride at -20°C. Addition of cold hexane to this solution results in the precipitation of colorless crystals which can be isolated in 40-60% yield by filtration at -78°C under nitrogen. Crystalline 3 completely decomposes at room temperature in 2-5 min with the formation of cyanogen iodine, ICN, as the only isolable stable product. Compound 3 is air-sensitive and if the filtered crystals are exposed to air an explosion may occur. It can however be stored at -20°C under nitrogen for several days.

$$O=I-OTf + 2NCSiMe_3 \xrightarrow{CH_2Cl_2, -78 \text{ to } -20^{\circ}C} (NC)_2I^+ = OTf$$

$$1 \qquad 2 \qquad 3$$

We were able to characterize compound **3** by low temperature IR and NMR spectra⁶. The IR displays an absorption of the cyano group at 2180 cm⁻¹ which is a typical region for related cyano iodinanes². The ¹³C NMR displays signals of the cyano carbon at δ 32 ppm and the quartet of the triflate anion at δ 118 ppm. The fluorine spectrum also supports the presence of the triflate anion in **3**. Chemical reactions of compound **3** in situ give further support to the proposed structure.

Similarly to phenyl(cyano)iodonium triflate^{2a}, compound **3** reacts with various organotin derivatives (**4**, **6**, **8**) under very mild conditions (-40°C, CH_2Cl_2) forming the corresponding iodonium salts in high yield and tributyltincyanide as the by-product. For these reactions reagent **3** can be used in situ, without isolation from the CH₂Cl₂ solution.

$$2ArSnBu_{3} + (NC)_{2}I^{+-}OTf \xrightarrow{C H_{2}CI_{2}, -40 \text{ to } 20^{9}C}_{-Bu_{3}SnCN} Ar_{2}I^{+-}OTf$$

$$4 \qquad 3 \qquad 5$$

$$5a: Ar = C_{6}H_{5}, 5b: Ar = 3-MeOC_{6}H_{4}, 5c: Ar = 4-MeOC_{6}H_{4}$$

$$2 \bigvee_{S} SnBu_{3} + (NC)_{2}I^{+-}OTf \xrightarrow{CH_{2}CI_{2}, -40 \text{ to } 20^{\circ}C}_{-Bu_{3}SnCN} \xrightarrow{S}_{S} I^{+}_{I} \xrightarrow{S}_{OTf}$$

$$2 R - SnBu_3 + (NC)_2 I^+ OTf - \frac{CH_2 CI_2, -40 \text{ to } 20^{\circ}C}{-Bu_3 SnCN} \leftarrow \left(R - \frac{2}{2}I^+ - OTf - \frac$$

9a: R = t - Bu, 9b: $R = (i - Pr)_3 Si$

General procedure for the reaction of organostannane derivatives with di(cyano)iodonium triflate in situ. Cyanotrimethylsilane (0.54 ml, 4 mmol) was added to a stirred suspension of O=IOTf (0.58 g, 2 mmol) in CH_2Cl_2 (15 ml) at -78°C under nitrogen. The mixture was allowed to warm to -20°C and stirred for 10-15 min until the formation of a clear solution of reagent **3**. The solution was cooled to -78°C and transferred to a cold, stirred solution of the appropriate tributyltin derivative (**4**, **6**, **8**) (4-4.1 mmoles) in CH_2Cl_2 (15 ml). The mixture was allowed to warm to room temperature and the product crystallized by the addition of dry hexane (20-30 ml). The precipitate of the iodonium triflate salt was filtered under nitrogen, washed with dry hexane (30 ml) and dried in vacuo. Analytically pure materials were obtained by recrystallization from a concentrated solution of the iodonium salt in CH_2Cl_2 by addition of hexane and ether.

The generality of this procedure is indicated by the preparation of iodonium salts of three different types: diaryl **5**, bis-heteroaromatic **7** and bis-alkynyl **9** iodonium triflates. All new compounds are fully characterized by spectral data⁷.

The advantage of the present procedure over the previously reported ones^{1,8,9} is its extremely mild conditions. Due to the non acidic and likely non-oxidizing properties of 3, it is possible to apply it to the synthesis of iodonium salts from easily oxidizable and acid sensitive starting materials such as heterocycles, anisols, etc., cases in which reagent 1 is ineffective⁹.

In conclusion, we have prepared a new type of iodonium salt, (dicyano)iodonium triflate **3** and demonstrated that this compound can be used in situ as a mild and efficient reagent for the preparation of aryl, heteroaryl, and alkynyl iodonium salts via an iodonium transfer reaction with the corresponding tributyltin substituted derivatives.

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References and Notes

 For reviews see: a) R.M. Moriarty, R.K. Vaid, Synthesis, 1990, 431; b) E.B. Merkushev, Russian Chem.Rev. 1987, 56, 826; c) A. Varvoglis, Synthesis, 1984, 7099; d) G.F. Koser in "The Chemistry of Functional Groups, Suppl. D", S. Patai, Z. Rappoport, Eds; Wiley-Interscience, 1983; Chapters 18 and 25, pp 721-811 and 1265-1351; e) A. Varvoglis, Chem.Soc.Rev. 1982 10, 377; f) R.M. Moriarty, R.K. Vaid, G.F. Koser, Synlett 1990, 365; g) T. Urnemoto, Kyokai Yuki Gosie Kagaku Kyeokaishi 1983, 41, 251; h) P.J. Stang, Angew. Chem. Int. Ed. Engl. 1992, 31, 0000, in press.

- (a) V.V. Zhdankin, C.M. Crittell, P.J. Stang, N.S. Zefirov, *Tetrahedron Letters* 1990, 31, 4821; (b) V.V. Zhdankin, R. Tykwinski, B.L. Williamson, P.J. Stang, N.S. Zefirov, *Tetrahedron Letters* 1991, 32, 733.
- P.J. Stang, V.V. Zhdankin, J. Am. Chem. Soc. 1990, 112, 6437. P.J. Stang, V.V. Zhdankin, Ibid.
 1991, 113, 4571. P.J. Stang, B.L. Williamson, V.V. Zhdankin, J. Am. Chem. Soc. 1991, 113, 5870.
- 4. P.J. Stang, J. Ullmann, Angew. Chem. Int. Ed. Engl. 1991, 30, 1469.
- 5. J.R. Dalziel, H.A. Carter, F. Aubke, Inorg. Chem. 1976, 15, 1247.
- 6. Compound 3: colorless crystals, mp 25-30 °C (dec); IR (in CCl₄ at 0°C): 2180 (CN), 1447, 1244, 1183, 1030 (OTf) cm⁻¹; ¹³C NMR (at -15°C, CDCl₃, δ): 118.3 (q, J = 318 Hz, CF₃SO₃⁻), 32.1 (CN). ¹⁹F NMR (at -15°C, CDCl₃, δ): -78.2 (CF₃SO₃⁻). Caution: All operations with compound 3 must be conducted under nitrogen, otherwise it may explode when exposed to air.
- 7. For 5a: white crystals (45 %), mp 177-179 °C (dec), lit⁹ 175-177 °C. 5b: white crystals (66 %), mp 109-111 °C (dec); IR (CCL₄): 3076, 2944, 1249, 1163, 1028 cm⁻¹; ¹H NMR (CD₃CN); δ 7.67 (d, J = 1.9 Hz, 2H), 7.64 (d, J = 8.0 Hz, 2H), 7.42 (t, J = 8.1 Hz, 2H), 7.20 (dd, $J_1 = 8.3$ Hz, $J_2 = 2.3$ Hz, 2H), 3.81 (s, 6H); ¹³C NMR (CD₃CN); δ 162.3, 133.8, 128.3, 121.9 (g, J = 320.9 Hz, CF₃SO₃⁻), 121.6, 119.9, 114.2, 56.9: ¹⁹F NMR (CD₃CN): δ -79.71 (CF₃SO₃-); FAB HRMS m/z 341.004776 [M -CF3SO3⁻¹⁺, calcd for C₁₄H₁₄IO₂: 341.003732. 5c: white crystals (71 %), mp 123-125 °C (dec); IR (CCL₄): 3091, 2970, 1570, 1256, 1159, 1025 cm⁻¹; ¹H NMR (CDCl₃): δ 7.88 (d, J = 8.9 Hz, 4H), 6.87 $(d, J = 9.1 Hz, 4H), 3.77 (s, 6H); {}^{13}C NMR (CDCl_3); \delta 162.8, 137.0, 120.3 (q, J = 320.3 Hz, CF_3SO_3),$ 102.4, 55.7; ¹⁹F NMR (CDCl₃): δ -80.17 (CF₃SO₃⁻); FAB HRMS m/z 341.003685 [M - CF₃SO₃⁻]⁺, calcd for C14H14IO2: 341.003732; Anal: Calc. for C15H14ISF3O5; C, 36.74; H, 2.80. Found: C, 36.55; H, 2.85. 7: white microcrystalline solid (74 %), mp 109-112 °C dec; IR (CCl₄): 3105, 3094, 1385, 1222, 1162, 1022 cm⁻¹; ¹H NMR (CD₃CN): δ 7.95 (d, J = 3.9 Hz, 2H), 7.82 (d, J = 5.5 Hz, 2H), 7.12 (dd, J = 5.5, 2H); ¹⁹F NMR (CD₃CN): δ -78.64 (s, CF₃SO₃⁻); ¹³C NMR (CD₃CN): δ 142.24, 139.16, 130.63, 121.61 (q, J = 320.4 Hz, CF₃SO₃⁻), 99.58; FAB HRMS m/z 292.895447 [M - CF₃SO₃⁻]⁺, calcd for C₈H₆IS₂: 292.895157. 9a: white crystals (55 %), mp 100-102 °C (dec), lit⁸ 100-102 °C (dec). 9b: white crystals (63 %), mp 138-139 °C, lit8 137-139 °C.
- 8. P.J. Stang, V.V. Zhdankin, A.M. Arif, J. Am. Chem. Soc. 1991, 113, 8997.
- 9. P.J. Stang, V.V. Zhdankin, R. Tykwinski, N.S. Zefirov, Tetrahedron Letters, in press.

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