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Novel Trifluoroethyliodonium Salts from Cyclic Enaminones and Their Thermal Decomposition

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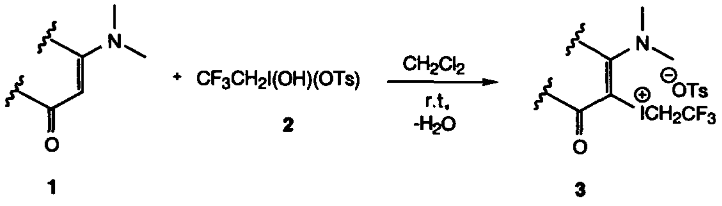
Abstract: Upon reaction of 1-[hydroxy(tosyloxy)iodo]-2,2,2-trifluoroethane with cyclic enaminones, stable iodonium tosylates are obtained. Their mild thermolysis provides iodoenaminones and 2,2,2-trifluoroethyl tosylate.

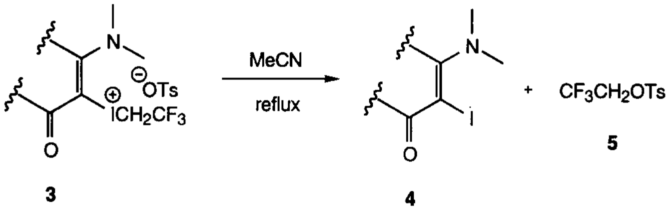
Iodonium salts constitute the largest family among hypervalent iodine compounds, with several hundreds of individual members, most of which are derived from iodoarenes. They usually contain attached to iodine a second aryl or a vinyl or an alkynyl moiety; there are also a few members bearing a perfluoro- or polyfluoroalkyl group. Isolable iodonium salts without an aryl group lack stabilization and are rare.[1]

We report the preparation of a novel type of stable iodonium salts in which the two moieties attached to the iodonium center are a 2,2,2-trifluoroethyl group and a vinyl group derived mostly from cyclic enaminones. These salts, obtained as tosylates, **3**, are formed in good yield from the enaminones **1** and the recently introduced[2] 1-[hydroxy(tosyloxy)iodo]-2,2,2-trifluoroethane, **2**, according to the generalized scheme:



The new iodonium tosylates **3** were formed readily as microcrystalline compounds.[3] All attempts for recrystallization led to decomposition, although in the solid state these salts are fairly stable, with melting (decomposition) points in the region between 88 and 145 °C. Their identification was based mainly on their ^1H NMR spectra; it is noted that the protons of the CF_3CH_2 group in **3** resonate between 3.78 and 4.40 δ, while the corresponding value of **2** is 4.93. Generally, the spectroscopic properties of **3** do not present any unusual feature.[4]

Additional chemical confirmation of the constitution of **3** came from their clean decomposition in boiling acetonitrile; an iodoenaminone, **4**, and 2,2,2-trifluoroethyl tosylate,[5] **5**, were produced according to the equation:



3 **4** **5**

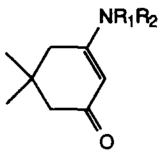
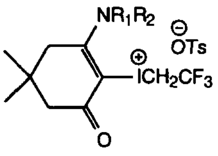
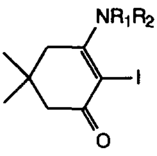
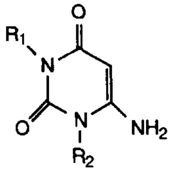
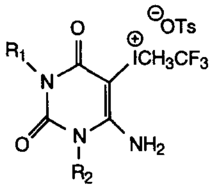
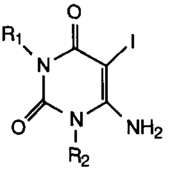
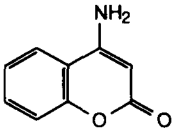
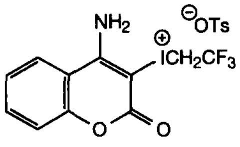
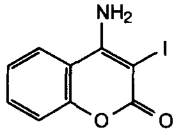
In some cases this decomposition went to completion at room temperature, after stirring in dichloromethane for a few hours. Both products were obtained by column chromatography; all iodo-enaminones are new compounds which were characterized by elemental analysis and their spectroscopic properties.[6] The enaminones, **4**, together with their precursors, **3**, are collected in the Table in the next page.

The reaction of trifluoroethyliodination followed by thermal decomposition of the iodonium tosylate may constitute a new iodination methodology for cyclic enaminones and related substrates, in view of the fact that iodination at sp^2 carbon α- to the carbonyl group of certain enaminones presents some difficulties. Indeed, only *N*-iodosuccinimide with catalytic amounts of PhI(OH)OTs was suitable for the preparation of some iodo derivatives of heterocyclic enaminones.[7] Also, whereas secondary enaminones of the dimedone family were iodinated[8] smoothly at C-2 using $PhCH_2N^+Me_3\ ICl_2^-$, a tertiary analogue underwent by this reagent chlorination rather than iodination; with elemental iodine, it furnished unexpectedly a C-6 iodo-derivative.[9]

Non-cyclic enaminones failed to give either iodonium salts or iodo-derivatives; for example, substrates such as $MeCOCH{=}C(NH_2)Me$ and $Bu^tCOCH{=}CHNMe_2$ reacted with **2** in a complicated way. The only enaminone of this type which reacted cleanly with **2**, although in a different way, was methyl 3-aminocrotonate. The reaction was performed in chloroform with a slight excess of **2** (1.2 mol) and resulted in the formation, after workup, of methyl 2-tosyloxy-3-ketobutanoate and the ammonium salt of *p*-toluenesulfonic acid:

$$MeC(NH_2){=}CHCOOMe \xrightarrow{\mathbf{2}} MeCOCH(OTs)COOMe + Ts\bar{O}\,NH_4^+$$

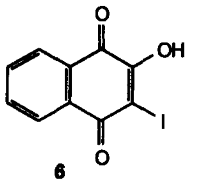
Table. 2,2,2-Trifluoroethyl vinyl iodonium tosylates, **3**, and iodoenaminones, **4**, from enaminones,**1**.

Enaminones	Iodonium salts [a]	Iodoenaminones [a]
 **1** a. $R_1 = R_2 = H$ b. $R_1 = H$, $R_2 = Bu$ c. $R_1 = Me$, $R_2 = Bu$	 **3** (95) (-)[b] (98)	 **4** (72) (55) (40)
 d. $R_1 = Me$, $R_2 = H$ e. $R_1 = R_2 = Me$	 (95) (83)	 (89) (48)
 f	 (80)	 (78)

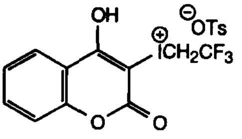
a: (% Yield)

b: Yield above 90%, not accurately determinable, because of the hygroscopic character of **3b**.

The reactivity of **1** was extended using some other substrates related to cyclic enaminones. Two hydroxy analogs of **1**, i.e. 2-hydroxy-1,4-naphthoquinone and 4-hydroxycoumarin, reacted cleanly with **2**. The former gave directly 3-iodo-2-hydroxy-1,4-naphthoquinone, **6**, in high yield (previously obtained from 3-phenyliodonio-1,2,3,4-tetrahydronaphthalenide and hydroiodic acid in 70% yield[10]) and trifluoroethyl tosylate, quantitatively. The latter formed initially the corresponding iodonium salt, **7**, in 90% yield which in refluxing acetonitrile was converted to 3-iodo-4-hydroxycoumarin,[11] **8**, in similarly high yield.



6



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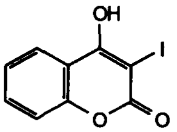

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References and Notes

1. Varvoglis, A. *The Organic Chemistry of Polycoordinated Iodine*, VCH, New York, 1992.
2. a. Zhdankin, V.V. ; Kuehl, C.J. ; Simonsen, A.J. *Tetrahedron Lett.* **1995**, *36*, 2203-2206. b. Zhdankin, V.V. ; Kuehl, C.J. ; Simonsen, A.J. *J. Org. Chem.* **1996**, *61*, 8272-8276.
3. Typically, to a suspension of the enaminone (or 2-hydroxy-1,4-naphthoquinone or 4-hydroxycoumarin) (2 mmol) in CH_2Cl_2 (20 ml) was added with stirring, at room temperature, the iodane **2** (2.1 mmol). After 1-2 h, the iodonium salts **3** were separated, collected by filtration without special precautions, and washed with CH_2Cl_2 and then ether. In *N*-substituted enaminones of dimedone, the iodonium salts were obtained after evaporation of CH_2Cl_2 and trituration with ether.
4. Spectroscopic data of **3a** (mp 112-113 °C) are given: IR (Nujol): 3300, 3140, 1655, 1610, 1540, 1250, 1160, 1110, 1025 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6): δ 1.01 (s, 6H), 2.32 (s, 3H), 2.37 (s, 2H), 2.51 (s, 2H), 3.79 (q, J_{H-F} = 10 Hz, 2H), 5.48-6.26 (br s, 2H), 7.40 (d, J = 8 Hz, 2H), 7.68 (d, J = 8 Hz, 2H); MS m/z 265 (75), 254 (79), 210 (77, CF_3CH_2I), 91 (100).
5. Trifluoroethyl tosylate, **5**, has been described having a mp of 30 °C (Tiers, G.V.D.; Brown, H.A.; Reid, T.S. *J. Am. Chem. Soc.* **1953**, *75*, 5978-5979). The commercial product (Aldrich) has a mp of 36-38 °C. In our hands, it melted around 60 °C. Presumably our product is a polymorph, since all its spectroscopic data are identical with those reported in Aldrich Library (IR, ^1H NMR) and NIST Chemistry Web Book system (MS) developed by P.J. Linstrom; General Editor W.G. Mallard; available on Internet: http:// webbook.nist gor/ chemistry.
6. Experimental procedure for **4**: The iodonium salt **3** (1 mmol) was refluxed in MeCN (20 ml) for 6-8 h. The residue, after evaporation of the solvent, was chromatographed (SiO_2 column, eluant hexanes-ethyl acetate) to give first trifluoroethyl tosylate, **5**, and then **4**. Spectroscopic data of **4a** (mp 186-187 °C): IR (Nujol): 3300, 3090, 1640, 1585, 1160 cm^{-1}; ^1H NMR ($CDCl_3$/DMSO-d_6): δ 1.07 (s, 6H), 2.37 (s, 2H), 2.89 (s, 2H), 5.63 (br s, 2H); MS m/z 265 (M^+,100), 209 (91).
7. Comins, D.L.; Joseph, S.P.; Chen, X.H. *Tetrahedron Lett.* **1995**, *36*, 9141-9143.
8. Matsuo, K.; Ishida, S.; Takuno, Y. *Chem. Pharm. Bull.* **1994**, *42*, 1149-1152.
9. Cordik, C.P.; Reitz, A.B. *J. Org. Chem.* **1996**, *61*, 5644-5645.
10. Hatzigrigoriou, E. ; Spyroudis, S. ; Varvoglis, A. *Liebigs Ann. Chem.* **1989**, 167-170.
11. Covello, M.; Abignente, E.; Dini, A. *Ann. Chim. (Rome)* **1965**, *55*, 239-243.

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