Preparation, Structure, and Diels–Alder Reaction of Phenyl(trifluoromethanesulfonate)(3,3,3-trifluoropropynyl)-λ^3-iodane

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Phenyl(trifluoromethanesulfonate)(3,3,3-trifluoropropynyl)-λ^3-iodane was prepared from tributyl(3,3,3-trifluoropropynyl)stannane and PhI(CN)OTf. The molecular structure was disclosed by X-ray diffraction analysis to form T-shape geometry with the hypervalent iodine atom as the central point. The iodonium salt underwent smoothly the Diels–Alder reaction with 1,3-dienes, furans, and pyrrole to give trifluoromethyl-substituted cyclohexadienes in good to high yields, respectively, in contrast to the corresponding nonfluorinated counterpart.

Trifluoromethylated compounds have attracted great interest in the fields of pharmaceuticals and materials science because the presence of fluorine atoms in organic molecules often induces superior biological, chemical, and/or physical properties than those of the corresponding non-fluorinated counterparts.[1] Therefore, development of versatile synthetic methods/reagents for CF_3-containing compounds is of great importance for exploration of fluorine-containing biologically active substances and functional organic materials. For example, 3,3,3-trifluoropropynylmetals have emerged as useful nucleophilic reagents for facile incorporation of the CF_3-containing C_3 moiety into organic molecules.[2] In contrast, electrophilic reagents consisting of a 3,3,3-trifluoropropynyl group such as 3,3,3-trifluoro-1-halopropynes remain unexplored probably owing to volatility and instability.[3] From the view that alkynyl(aryl)iodonium salts are generally stable, highly reactive, and widely utilized in various organic reactions,[4] we were interested in the preparation and reactions of 3,3,3-trifluoropropynyliodonium salts as novel synthetic reagents for CF_3-containing compounds. Reported herein are preparation, structure, and the Diels–Alder reaction of phenyl(trifluoromethanesulfonate)(3,3,3-trifluoropropynyl)-λ^3-iodane (**1**). The iodonium salt is stable and easy to handle, and the cycloaddition with dienes smoothly proceeds even at room temperature to give the corresponding CF_3-containing alkenyliodonium salts in good to high yields.

Preparation of **1** was accomplished by slightly modifying the protocol developed by Stang and co-workers.[5] Thus, tributyl(3,3,3-trifluoropropynyl)stannane[6] was added to a solution of PhI(CN)OTf[7] in CH_2Cl_2 at −42 °C and the resulting solution was allowed to warm to 0 °C over a period of 2 h.[8] The addition of hexane to the reaction mixture at −42 °C gave precipitates which were purified by recrystallization from the hexane/CH_2Cl_2 solution at −30 °C, giving rise to colorless microcrystals of **1** (mp 110–111 °C) in 60% yield (eq 1). The structure was characterized by ^{1}H, ^{13}C, and ^{19}F NMR, IR, and elemental analysis, and was unambiguously confirmed by X-ray diffraction analysis of its single crystal (vide infra).[9] The salt **1** was soluble in CH_3CN and CH_2Cl_2, and could be stored without decomposition under argon atmosphere at −30 °C for at least three months.

$$\overset{+}{\mathrm{PhICN}}\bullet{}^{-}\mathrm{OTf}\ \xrightarrow[\substack{\text{2) hexane, }-42\ ^\circ\text{C}\\ 15\text{ min}\\ 60\%}]{\substack{\text{1) } F_3CC{\equiv}CSnBu_3\\ CH_2Cl_2\\ -42\text{ to }0\ ^\circ\text{C, 2 h}}}\ \underset{\mathbf{1}}{F_3C{-}{\equiv}{-}\overset{+}{\mathrm{I}}\mathrm{Ph}\bullet{}^{-}\mathrm{OTf}} \tag{1}$$

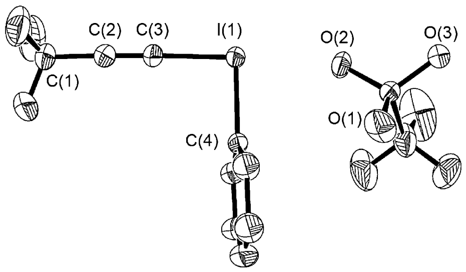


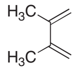
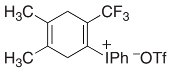
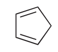
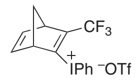
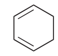
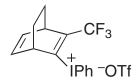
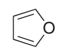
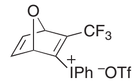
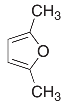
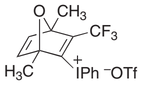
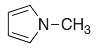
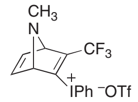
Figure 1. Molecular structure of **1** (hydrogens are omitted for clarity). Selected bond lengths (Å) and angles (°): C(1)–C(2) 1.451(1), C(2)–C(3) 1.176(5), C(3)–I(1) 2.022(3), I(1)–C(4) 2.109(3), I(1)–O(2) 2.596(3); C(1)–C(2)–C(3) 179.2(4), C(2)–C(3)–I(1) 178.3(3), C(3)–I(1)–O(2) 176.99(12), C(3)–I(1)–C(4) 92.67(14), C(4)–I(1)–O(2) 84.33(11).

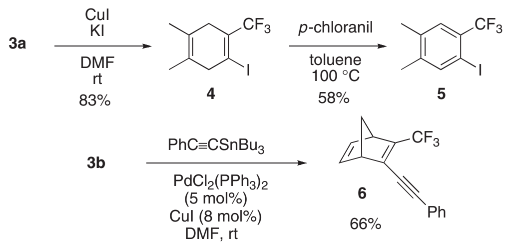
The molecular structure of **1** disclosed by the X-ray analysis is shown in Figure 1. Salt **1** adapted T-shape geometry with bond angles being 92.67(14)° for C(3)–I(1)–C(4) and 84.33(11)° for O(2)–I(1)–C(4). The atomic distance between I(1) and O(2) was 2.596(3) Å longer than the sum of covalent bond radii of iodine and oxygen (2.07 Å), but shorter than sum of the van der Waals radii (3.50 Å).[10] These structural characteristics are clearly consistent with the hypervalent nature of the iodine atom.

To demonstrate the synthetic utility of **1**, we carried out a Diels–Alder reaction (Table 1). Treatment of **1** with 2,3-dimethyl-1,3-butadiene (**2a**) in CH_3CN at room temperature gave the corresponding adduct **3a** in 87% yield (Entry 1). Since phenyl(1-propynyl)(trifluoromethanesulfonate)-λ^3-iodane did not react with **2a** at all under the same conditions, the presence of fluorine atoms apparently enhanced the reactivity of **1**. Cyclic 1,3-dienes such as **2b** and **2c** also underwent the cycloaddition to give alkenyliodonium salts **3b** and **3c** in good yields (Entries 2 and 3). CF_3-substituted 9-oxabicyclo[2.2.1]heptanes **3d** and **3e** were prepared from **1** with furans **2d** and **2e**, respectively (Entries 4 and 5). It is noteworthy that **1** underwent the Diels–Alder reaction even with *N*-methylpyrrole (**2f**) because cycloadditions of **2f** are quite limited (Entry 6).[11]

Versatile reactivity of the alkenyliodonium functionality provides us with various transformations of the Diels–Alder adducts.[12] For example, treatment of **3a** with CuI/KI gave iodocyclohexadiene **4** that was converted into CF_3-containing polysubstituted iodobenzene **5** by dehydrogenation with *p*-chloranil, while CF_3-substituted enyne **6** was synthesized by the Pd/Cu-

Table 1. Diels–Alder reaction of **1**

Entry	Diene		Product		Yield/%
1		**2a**		**3a**	87
2		**2b**		**3b**	78
3		**2c**		**3c**	63
4		**2d**		**3d**	81
5		**2e**		**3e**	81
6		**2f**		**3f**	72



Scheme 1. Synthetic transformation of **3**.

catalyzed coupling reaction of **3b** with phenylethenylstannane (Scheme 1).

In summary, we have described the first preparation and X-ray structure of phenyl(trifluoromethanesulfonate)(3,3,3-trifluoropropynyl)-λ^3-iodane. The Diels–Alder reaction of the iodonium salt provides CF_3-substituted cyclohexadienes hardly accessible via other synthetic methods. Further study on synthetic reactions using the salt is in progress.

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