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REACTION OF ALKYNYLTRIMETHYLSILANES WITH A HYPERVALENT ORGANOIODINE COMPOUND: A NEW GENERAL SYNTHESIS OF ALKYNYLIODONIUM SALTS

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Summary: New general methods for the synthesis of alkynyl(phenyl)iodonium tetrafluoroborate **2** from alkynyltrimethylsilanes **1** utilizing the combination of iodosylbenzene and triethyloxonium tetrafluoroborate or boron trifluoride etherate were developed. The medium effect observed in the reaction was also discussed.

In contrast to numerous studies on the chemistry of diaryliodonium salts, little is known about alkynyliodonium salts.[1,2] In 1965, phenyl(β-phenylethynyl)iodonium chloride was synthesized from lithium phenylacetylide by the reaction with (dichloroiodo)benzene in yields ranging from 12 - 20%.[3] The reaction of [hydroxy(tosyloxy)iodo]benzene with phenylacetylene has been found to give phenyl(β-phenylethynyl)iodonium tosylate in 60% yield, but the reaction does not seem to be general: with cyclohexylacetylene, [hydroxy(tosyloxy)iodo]benzene afforded only a 5% yield of phenyl(β-cyclohexylethynyl)iodonium tosylate. Furthermore, 1-heptyne did not give the corresponding alkynyliodonium salt at all.[4] We now report the first, general synthesis of alkynyliodonium salts **2** utilizing alkynyltrimethylsilanes **1** (Scheme 1).

$$\underset{\mathbf{1}}{R-\equiv-SiMe_3} \longrightarrow \underset{\mathbf{2}}{R-\equiv-\overset{+}{I}-C_6H_5\ BF_4^-}$$

Method A : $(C_6H_5IO)_n$, $Et_3O^+BF_4^-$, CH_2Cl_2

Method B : $(C_6H_5IO)_n$, BF_3-Et_2O, CH_2Cl_2, and then aq $NaBF_4$

Scheme 1

Table 1. Synthesis of Alkynyliodonium Salts from Alkynylsilanes

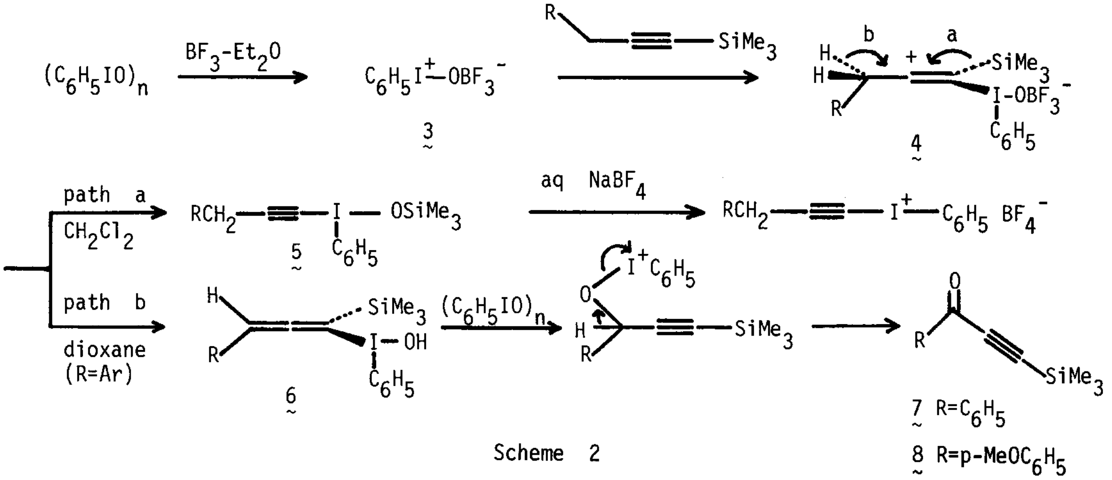
Entry	1	R	Method	Reaction Time (hr)	Product	Yield[a] (%)	mp (°C)	FABMS[b] (*m/z*)
1	1a	n-C_8H_{17}	A	22	2a	70	59.5-65	341
2	1a	n-C_8H_{17}	B	2.5	2a	85		
3	1b	cyclo-C_6H_{11}	A	25	2b	64	137-138	311
4	1c	C_6H_5	A	27	2c	65	oil	305
5	1c	C_6H_5	B	3	2c	79		
6	1d	$C_6H_5CH_2$	A	24	2d	56	oil	319
7	1d	$C_6H_5CH_2$	B	3	2d[c]	53		
8	1e	$C_6H_5CH_2CH_2$	A	18	2e	75	oil	333

a) Isolated yields. b) Peaks corresponding to $(M-BF_4)^+$. c) Acetylenic ketone 7 was also obtained in 11% yield.

Although iodosylbenzene has been shown to be a useful oxidizing reagent, the reactivity is rather low.[5] The low reactivity of iodosylbenzene may be attributable in part to the proposed polymeric nature[6] and the very low solubility toward common organic solvents (dichloromethane, dioxane, dimethylsulfoxide, etc.). Thus no reaction was observed between alkynyltrimethylsilane 1 and iodosylbenzene in dichloromethane at room temperature. Triethyloxonium tetrafluoroborate or boron trifluoride etherate was found to be essential for the activation of iodosylbenzene in the synthesis of alkynyliodonium salts 2. When 1-trimethylsilyldec-1-yne (1a) was treated with iodosylbenzene (1.6 equiv.) and triethyloxonium tetrafluoroborate (1.6 equiv.) in dichloromethane at room temperature (Method A), 1-decynyl(phenyl)iodonium tetrafluoroborate (2a)[7] was obtained directly in 70% yield. Reaction of 1a with iodosylbenzene (1.6 equiv.) in the presence of boron trifluoride etherate (1.6 equiv.) in dichloromethane at room temperature followed by the treatment with excess amounts of aqueous sodium tetrafluoroborate (Method B), also gave rise to 2a in 85% yield. Similarly, alkynylsilanes (1b - e) gave the corresponding iodonium salts (2b - e) in good yields. The results are summarized in Table 1. Fast atom bombardment mass spectra (FABMS) of the alkynyliodonium tetrafluoroborates 2 showed relatively abundant fragments corresponding to the cationic portion of the salts. IR spectra of 2 showed a very large broad band at 1100 - 1000 cm^{-1} characteristic of the BF_4^- anion.[8] In the ^{13}C n.m.r. spectra of 2, a characteristic signal corresponding to the acetylenic carbon atom bearing the iodine (III) substituent appeared at near δ 15:[9] for example, 2a : δ 15.6, 2b : δ 16.1, 2e : δ 17.9.

Interesting medium effect was observed in the reaction. In addition to the formation of the iodonium salt 2d (53%), an acetylenic ketone 7[10] was obtained as a minor product in the boron trifluoride etherate-catalyzed reaction (Method B) of trimethylsilylalkyne 1d "in dichloromethane". (Entry 7) The reaction mode, however, was much altered if the reaction was carried out in dioxane: 1d, on treatment with excess amounts of iodosylbenzene and boron trifluoride etherate "in dioxane" at room temperature for 15 hr, afforded the ketone 7 in 69% yield. With 3-(p-methoxyphenyl)-1-trimethylsilylprop-1-yne, a 52% yield of acetylenic ketone 8 was obtained. The oxidation to acetylenic ketones was not observed at all in the reaction of alkynylsilane 1a in dioxane. In view of these observations, the reaction sequence shown in Scheme 2 seems to be plausible.

Transient intermediates of vinyl cations 4, produced by the reaction of alkynylsilanes with BF_3-activated iodosylbenzene 3, may produce the alkynyliodonium tetrafluoroborates *via* the formation of the hypervalent 10-I-3 species 5 by desilylation (path a). When the reaction of 1d is carried out in dioxane, path b may become important and form allenyliodine(III) intermediate 6 ($R=C_6H_5$) by deprotonation. Nucleophilic attack of oxygen of iodosylbenzene to 6 may afford the ketone 7.[11]



Scheme 2

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7. Selected spectral data: **2a**, i.r.($CHCl_3$): 2180, 1120-980, 720, and 660 cm^{-1}; ^1H n.m.r. (400 MHz; $CDCl_3$): δ 0.88(t, 3H, *J* 6.8Hz), 1.20-1.40(m, 10H), 1.59(quint, 2H, *J* 7.3Hz), 2.64(t, 2H, *J* 7.3Hz), 7.52-7.58(m, 2H), 7.64-7.70(m,1H), and 8.05-8.10(m, 2H). ^{13}C n.m.r. ($CDCl_3$): δ 14.3(q), 15.6(s), 20.8, 22.6, 27.5, 28.7, 28.8, 29.0, 31.7(each t), 113.5, 114.1(each s), 132.6, 133.0, and 134.0(each d).
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9. The ^{13}C n.m.r. spectrum of 1-iodohex-1-yne showed the signal of α-acetylenic carbon atom at δ -3.3: D. D. Traficante and G. E. Maciel, *J. Phys. Chem.*, **69**, 1348 (1965).
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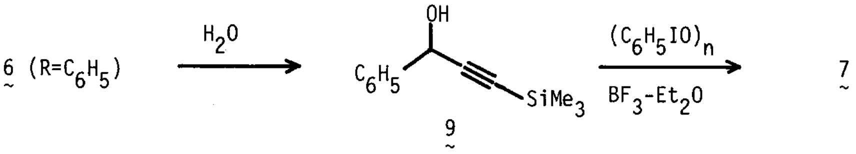
11. As another possible reaction course, nucleophilic substitution of **6** ($R=C_6H_5$) with water produced during the reaction may be considered. Alcohol **9** is oxidized with iodosylbenzene in the presence of boron trifluoride etherate to give the ketone **7**. In fact the alcohol **9** prepared by the reaction of benzaldehyde with 1-lithio-2-trimethylsilylacethylene, on treatment with iodosylbenzene (1.6 equiv.) and boron trifluoride etherate (1.6 equiv.) in dioxane at room temperature for 6 hr, afforded **7** in 77% yield.



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