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An Onium Transfer Reaction of 1-Alkynyl(phenyl)iodonium Tetrafluoroborates with Triphenylarsine; Synthesis of 1-Alkynyl(triphenyl)arsonium Tetrafluoroborates

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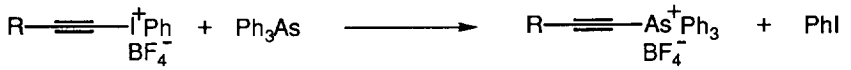
Abstract: An onium transfer reaction between 1-alkynyl(phenyl)iodonium tetrafluoroborates and triphenylarsine provides a useful tool for the synthesis of 1-alkynyl(triphenyl)arsonium tetrafluoroborates in high yields.

1-Alkynyl(triaryl)arsonium salts have not been synthesized nor characterized.[1,2] The two general methods available for the synthesis of tetraorganoarsonium salts are the reaction of tertiary arsines with alkyl or aryl halides and the reaction between tertiary arsine oxides and Grignard reagents,[1,3] neither of which may be applicable for the synthesis of 1-alkynyl(triaryl)arsonium salts. It has been proposed that prop-1-ynyl(triphenyl)arsonium bromide could be generated *in situ* by the base-induced isomerization of prop-2-ynyl(triphenyl)arsonium bromide.[4] We report herein the first general synthesis of 1-alkynyl(triphenyl)arsonium salts **2**, which involves an onium transfer reaction between 1-alkynyl(phenyl)iodonium tetrafluoroborates **1** and triphenylarsine under mild conditions.



1a-i **2a-i**

a; R = H, **b**; R = Me, **c**; R = n-C_8H_{17}, **d**; R = $MeCH_2CH(Me)CH_2$,
e; R = *cyclo*-$C_5H_9CH_2$, **f**; R = *cyclo*-C_6H_{11}, **g**; R = *tert*-Bu, **h**; R = Me_3Si, **i**; R = Ph

Alkynyl(phenyl)iodonium salts are highly electron-deficient species and react with a variety of nucleophiles. Michael addition of nucleophiles to the β-carbon of the alkynyliodonium salts, followed by 1,2-shift of the resulting alkylidenecarbenes, gives a variety of substitution products. Thus, internal and terminal alkynes, alkynyl(triphenyl)phosphonium salts, alkynyl sulfonates, carboxylates, phosphates, sulfides, thiocyanates, sulfones, and halides, and conjugated enynes were synthesized in good yields from alkynyl(phenyl)iodonium salts.[5] These substitutions proceed under mild conditions owing to the superleaving ability of the phenyliodonio group.[6] The attempted nucleophilic substitution of 1-iodo-1-alkynes with triphenylarsine gave poor results and no 1-alkynyl(triphenyl)arsonium salt was obtained; when 1-iodo-1-decyne was treated with triphenylarsine in dichloromethane at room temperature under nitrogen, reductive protodeiodination was observed predominantly, yielding 1-decyne in 84% yield. Use of the more reactive

Table 1. Synthesis of 1-Alkynyl(triphenyl)arsonium Tetrafluoroborates **2**

Run	Substrate	Reaction conditions		Product	Yield[a]/%	FABMS[b] (*m/z*)
		Solvent	Time/h			
1	**1a**	CH_2Cl_2	1	**2a**	91	331
2	**1b**	THF	42	**2b**	63	345
3	**1b**	CH_2Cl_2	1	**2b**	83	
4	**1c**	THF	53	**2c**	94	443
5	**1c**	CH_2Cl_2	1	**2c**	97	
6	**1d**	CH_2Cl_2	4	**2d**	87	401
7	**1e**	CH_2Cl_2	1.5	**2e**	79	413
8	**1f**	CH_2Cl_2	1	**2f**	83	413
9	**1g**	THF	61	**2g**	67	387
10	**1g**	CH_2Cl_2	3	**2g**	92	
11	**1g**	CH_2Cl_2[c]	3	**2g**	95	
12	**1h**	CH_2Cl_2	1.5	**2h**	77	
13	**1i**	CH_2Cl_2	0.5	**2i**	79	407

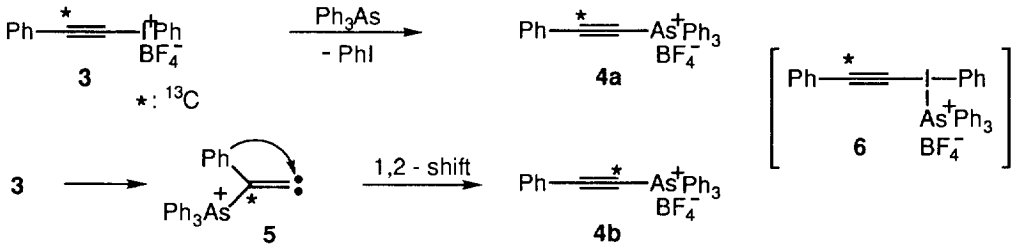
[a] Isolated yield. [b] Peaks corresponding to $(M\text{-}BF_4)^+$. [c] Reactions were carried out in the dark.

alkynyl(phenyl)iodonium tetrafluoroborates **1**,[7] however, dramatically changed the reaction course and led to an onium transfer reaction between the iodonium salts **1** and triphenylarsine affording the 1-alkynyl(triphenyl)arsonium tetrafluoroborates **2** exclusively, along with the reductive elimination of iodobenzene. Dichloromethane is a solvent of choice for the onium transfer reactions. To a solution of 1-decynyl(phenyl)iodonium tetrafluoroborate **1c** (0.2 mmol) in dichloromethane was added a solution of triphenylarsine (0.24 mmol) in dichloromethane dropwise at room temperature under nitrogen and the reaction mixture was stirred for 1 h. After evaporation of the solvent *in vacuo*, decantation with diethyl ether at -78 °C several times gave 1-decynyl(triphenyl)arsonium tetrafluoroborate **2c**[8] in 97% yield. Similarly, the parent, unsubstituted, ethynylarsonium salt **2a** and *tert*-butyl-, trimethylsilyl-, and phenyl-ethynylarsonium salts **2g-i** were prepared in high yields and the results are summarized in Table 1. Fast atom bombardment mass spectra (FABMS) of the alkynylarsonium salts **2** showed relatively abundant fragments corresponding to the cationic portion of the salts. IR spectra of **2** showed sharp bands at 2180 cm^{-1} and large broad bands at 1100-1000 cm^{-1} characteristic of the triple bond and the BF_4^- anion, respectively. In the ^{13}C NMR spectra of **2**, a characteristic signal corresponding to the acetylenic carbon atom attached to arsine(V) appeared at near δ 60.[8,9]

It should be noted that, in contrast to triphenylarsine, the lower homolog of trivalent group 15 compounds, triphenylstibine, undergoes reductive protodeiodination of **1** instead of the onium transfer reaction. For instance, the iodonium salt **1c**, on treatment with triphenylstibine (1.2 equiv.) in dichloromethane at room temperature for 24 h under nitrogen, afforded a mixture of 1-decyne (73%), iodobenzene (94%), and polymeric Ph_3SbO (72%). Neither 1-decynylstibonium salt nor 1-iodo-1-decyne was detected by detailed analysis of the

crude reaction mixture. No deuterium incorporation of the product 1-decyne in the reaction of triphenylstibine in dichloromethane-d_2 shows that the terminal acetylenic hydrogen of the product does not originate from the solvent. When the reaction was carried out in the presence of D_2O (20 equiv.) in dichloromethane, 1-decyne-*1-d* (75% D by GCMS and ^1H NMR) was obtained as a major product, indicating the intermediacy of a reactive species capable of acting as an alkynyl anion in this reductive protodeiodination. Triphenylbismuthine underwent no reaction with the iodonium salt **1c** in dichloromethane at room temperature and was recovered in full. These reactivity differences are probably due to the low nucleophilicity of triphenylbismuthine compared to triphenylarsine and triphenylstibine.[3b,10]

For the reaction of 1-alkynyl(phenyl)iodonium salts **1** with nucleophiles, the Michael-carbene mechanism, which was proposed in 1986[5a] and found to be general,[5] should be considered. This Michael-carbene mechanism involves conjugate addition of triphenylarsine to the β-carbon of alkynyliodonium salts **1** followed by 1,2-shift of the resulting alkylidenecarbenes, yielding the alkynyl(triphenyl)arsonium salts **2**, and has been proposed for the reaction of alkynyl(phenyl)iodonium triflates with triphenylphosphine.[11] To gain some insight into the mode of this onium transfer reaction, phenyl(phenylethynyl-*2-*^{13}C)iodonium tetrafluoroborate **3** (99% enriched)[5a] was synthesized and subjected to the onium transfer reaction. The ^{13}C enrichment at the β-acetylenic carbon of the resulting phenylethynylarsonium salt **4a** was found to be more than 95% from the ^{13}C NMR spectrum. Based on the well-known high migratory aptitude of α-aryl groups of alkylidenecarbenes,[5a] the Michael-alkylidenecarbene mechanism involving the generation of a reactive intermediate **5** may lead to expect the predominant formation of the (phenylethynyl-*1-*^{13}C)arsonium salt **4b** via a facile 1,2-phenyl migration. Although there is no experimental evidence, it seems reasonable to assume that the migratory aptitude of a positively charged triphenylarsonio group to the electron deficient carbenic center would be lower than that of a phenyl group. An alternative ligand coupling mechanism on iodine(III) of the arsonium salt **6**, generated by nucleophilic attack of triphenylarsine to the positively charged iodine of **3**, would account for the formation of the arsonium salt **4a**. The latter mechanism has been proposed for copper-catalyzed and uncatalyzed nucleophilic substitutions of vinyl(phenyl)iodonium salts.[6,12] While we cannot exclude the Michael-carbene pathway in this onium transfer reaction, the ligand coupling pathway seems to be more important.



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8. All new compounds were fully characterized by spectroscopic means and/or elemental analyses. Selected spectral data are the following.; **2a**, mp. 154-158 °C; IR (Nujol) 2060, 1220, 1100-1000, 760 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 4.37 (s, 1 H), 7.68-7.96 (15 H). Anal. Calcd for $C_{20}H_{16}AsBF_4 \cdot 1/2H_2O$: C, 56.25; H, 4.01. Found: C, 55.98; H, 3.83. **2b**, mp. 142-144 °C; IR (Nujol) 2800, 2175, 1160-900 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 2.43 (s, 3 H), 7.68-7.92 (15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 5.8 (q), 58.3 (s), 118.0 (s), 121.4 (s), 131.3 (d), 131.8 (d), 134.9 (d). **2c**, IR (Nujol) 2180, 1435, 1100-1000 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 0.87 (t, J = 6.6 Hz, 3 H), 1.16-1.54 (10 H), 1.55-1.84 (2 H), 2.74 (t, J = 7.2 Hz, 2 H), 7.68-7.92 (15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9 (q), 20.2 (t), 22.4 (t), 27.1 (t), 28.6 (t), 28.7 (t), 28.8 (t), 31.5 (t), 58.9 (s), 121.3 (s), 121.7 (s), 131.2 (d), 131.6 (d), 134.8 (d). **2g**, mp. 161-162 °C; IR (Nujol) 2180, 2155, 1250, 1100-1000, 740 cm^{-1}; ^1H NMR (200 MHz, $CDCl_3$) δ 1.48 (s, 9 H), 7.68-7.95 (15 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.6 (s), 29.7 (q), 58.0 (s), 121.4 (s), 128.2 (s), 131.4 (d), 131.6 (d), 135.0 (d). Anal. Calcd for $C_{24}H_{24}AsBF_4$: C, 60.79; H, 5.10. Found: C, 61.09; H, 5.06.
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