21 underwent gradual decomposition. The spectrum also showed that 1 was not formed in a detectable amount.

Rearrangement of 21 to 25 under GLC Conditions. A ca. 3×10^{-2} M solution of 18 in methanol was irradiated through Pyrex to give 21 and the resultant photolysate which was kept at 22–24 °C was intermittently analyzed by HPLC (μ-Porasil, ether/hexane, 1:9) and capillary GLC (columns D and E, 150-170 °C) to monitor the decomposition of 21 at 22–24 °C and its rearrangement to 25 under the GLC conditions. The relative amounts of remaining 21 (1.00 at 0 h) determined by HPLC after 3, 18, and 40 h were 0.77, 0.51, and 0.26, respectively. The amount of 25 observed by the capillary GLC decreased in parallel with that of 21 and was found to be 80%, 45%, and 27% of the initial amount after 3, 18, and 40 h, respectively, despite of its perfect stability in methanol and under the analysis conditions. Moreover, the HPLC analysis showed that 25 was not formed upon standing the solution of 21 at 22–24 °C. When the above experiment was repeated on purified 21, good reproducibility was observed. These observations clearly demonstrate that 21 undergoes rearrangement to 25 under the GLC conditions, but not in a solution at ambient temperature.

Photolysis of 14. A solution of 10 mg of 14 in 7 mL of methanol was deaerated by bubbling nitrogen and irradiated with a high-pressure Hg lamp through Pyrex at 12 °C. GLC analysis showed the formation of a single volatile product, which was identified as 1-indanone (ca. 20% by GLC). The photochemical formation of 1-indanone from 14 was also observed in ether (20% by GLC) and in acetone (50% by GLC).

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Alkynyliodonium Salts as Alkynylating Reagents: Direct Conversion of Alkynylphenyliodonium Tosylates to Dialkyl Alkynylphosphonates with Trialkyl Phosphites

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The treatment of various alkynyl(phenyl)iodonium tosylates 1 (R = *t*-Bu, *s*-Bu, *i*-Pr, cyclopentyl, Ph, and *p*-MeC_6H_4; X^- = OTs^-) with neat trimethyl phosphite gave the dimethyl alkynylphosphonates **4a** and **4d–h** in isolated yields ranging from 34 to 90%. Similar treatment of 1 (R = *t*-Bu, X^- = OTs^-) with neat triethyl and triisopropyl phosphites gave the diethyl and diisopropyl alkynylphosphonates **4b** (81%) and **4c** (58%). The byproducts of these reactions are alkyl tosylates and iodobenzene. The high yields of iodobenzene, determined by GC analysis for the reactions of 1 (R = *s*-Bu, *p*-tolyl; X^- = OTs^-) with trimethyl phosphite, indicate that the cleavage of the alkynyl(phenyl)iodonium ions with trialkyl phosphites proceeds with high regioselectivity at the alkynyl ligand.

The recent development of general methods for the synthesis of alkynylphenyliodonium salts 1[1,2] has stimulated interest in their use as alkynylating reagents. Stang and co-workers have employed 1 (X^- = OTs^-) as precursors to the first examples of alkynyl tosylates,[1d,e] alkynyl carboxylates,[3] and alkynyl phosphates[3a,4] and for the preparation of conjugated enynes by the treatment of 1 with vinylcopper reagents.[5] The photochemical production of alkynylphosphonium salts from 1 (X^- = BF_4^-) with triphenylphosphine has also been described.[6] Not all nucleophilic species are alkynylated with 1. 2-Lithiofuran and 2-lithiothiophenes displace the *tert*-butylethynyl ligand from iodine in various aryl(*tert*-butylethynyl)iodonium tosylates to give aryl(2-furyl)- and aryl(2-thienyl)iodonium salts.[7] Azide ion[8] and β-dicarbonyl anions[9] add to 1 in Michael fashion to give products consistent with intermediate vinylideneiodinanes 2 and vinylidenes 3.

$$\underset{\mathbf{1}}{RC{\equiv}\overset{+}{C}IPh},\ X^- \qquad \underset{\mathbf{2}}{R(Nu)C{=}\overset{+}{C}IPh} \qquad \underset{\mathbf{3}}{R(Nu)C{=}C:}$$

We now report that alkynylphenyliodonium tosylates react with trialkyl phosphites in formal Arbusov fashion to give alkynylphosphonates 4, eq 1. For example, when

$$\underset{\mathbf{1}}{RC{\equiv}\overset{+}{C}IPh},\ OTs^- + P(OR')_3 \rightarrow \underset{\mathbf{4}}{R{-}C{\equiv}CP(O)(OR')_2} + R'OTs + PhI \quad (1)$$

an excess of neat trimethyl phosphite was added to solid (*tert*-butylethynyl)phenyliodonium tosylate (1, R = *t*-Bu, X^- = OTs^-) at room temperature, heat was evolved and the iodonium salt rapidly (within 1 min) disappeared. Concentration of the resulting solution and chromatography of the residual oil on silica gel gave methyl tosylate (96%) and a 90% yield of dimethyl (*tert*-butylethynyl)-phosphonate (**4a**, R = *t*-Bu, R′ = Me). Similar treatment of 1 (R = *t*-Bu, X^- = OTs^-) with triethyl phosphite (at 85–7

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Table I. Yields of Alkynylphosphonates 4 and Alkyl Tosylates from Alkynylphenyliodonium Tosylates with Trialkyl Phosphites

		$RC{\equiv}CP(O)(OR')_2$			
phosphonate	solvent	*R*	*R'*	% yield[a]	R'OTs, % yield[a]
4a	none	*t*-Bu	Me	90	96
	MeOH			88	
4b	none	*t*-Bu	Et	81	93
4c	none	*t*-Bu	*i*-Pr	58	86[b]
4d	none	*s*-Bu	Me	63	100
	CH_2Cl_2			55	88
4e	none	*i*-Pr	Me	50	82
4f	none	cyclopentyl	Me	44	91
4g	none	Ph	Me	42	100
	CH_2Cl_2			46	51
4h	none	*p*-tolyl	Me	34	98

[a] Yields of isolated products. [b] Determined for a reaction in which the yield of **4c** was 45%.

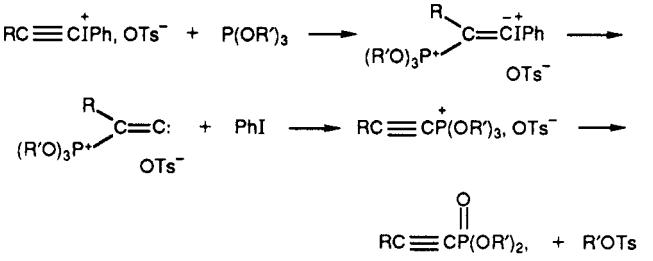
°C) and triisopropyl phosphite (at 95 °C) gave diethyl and diisopropyl (*tert*-butylethynyl)phosphonates (**4b** and **4c**) and high yields of the corresponding alkyl tosylates.

The reactions of **1** (R = *s*-Bu, *i*-Pr, cyclopentyl, Ph, and *p*-tolyl; X^- = OTs^-) with trimethyl phosphite were also investigated and are summarized in Table I. All of the dialkyl alkynylphosphonates thus obtained were characterized by IR, NMR (^1H, ^{13}C, ^{31}P), and elemental analyses. The ^{13}C spectra of **4** are particularly diagnostic of the alkyne–phosphorus linkage. For example, the ^{13}C spectrum of **4a** (R = *t*-Bu, R' = Me) exhibits doublets for the alkynyl carbons at δ 67.0 (C_α, J_{CP} = 305 Hz) and δ 111.1 (C_β, J_{CP} = 51 Hz). In general, the reactions were conducted with an excess of the neat trialkyl phosphite and the solid iodonium salt, and their mediation with a solvent seems to afford no particular advantage. Thus, when **1** (R = *t*-Bu, X^- = OTs^-) was allowed to react with trimethyl phosphite in methanol, the yield of **4a** after isolation was 88%. Similar treatment of **1** (R = *s*-Bu, X^- = OTs^-) with trimethyl phosphite in dichloromethane gave **4d** in 55% yield while the reaction of **1** (R = Ph, X^- = OTs^-) with trimethyl phosphite in dichloromethane gave a 46% yield of **4g** and a 20% yield of a byproduct identified by NMR analysis as phenyl(*β*-phenyl-*β*-(tosyloxy)vinyl)iodonium tosylate, $Ph(TsO)C{=}CHI^+Ph$, OTs^-.

Those factors which govern the yields of the alkynylphosphonates are not entirely clear, especially since the alkyl tosylates were obtained in high yields and no other major phosphorus-containing products were isolated and identified. It is clear, however, that the trialkyl phosphite induced cleavage of the alkynylphenyliodonium ion is remarkably selective for the alkynyl ligand. Furthermore, it appears that little of the alkynylphosphonate is lost during chromatographic isolation. In one experiment, the yields of iodobenzene and **4d** (R = *s*-Bu, R' = Me) from a reaction of **1** (R = *s*-Bu, X^- = OTs^-) with trimethyl phosphite were determined by GC analysis to be 101% and 69%. With the (*p*-tolylethynyl)phenyliodonium salt, the yield of iodobenzene was found to be 92%.

It seems plausible that ethynylphosphonate formation is initiated by Michael addition of the trialkyl phosphite to the triple bond of **1** followed by vinylidene formation, rearrangement, and Arbusov collapse as shown in Scheme I. Similar mechanisms have been proposed for the alkynylation of the 2-*n*-hexyl-1,3-indandionate ion with **1** (R = Ph, X^- = BF_4^-)[9] and for the conversion of alkynylphenyliodonium phosphates **1** (X^- = $^-O_2P(OR)_2$) to alkynylphosphates in dichloromethane or chloroform.[4] However, the more traditional addition–elimination mechanism for nucleophilic substitution at alkynyl carbon and a mechanism involving the direct nucleophilic addition of the trialkyl phosphite to the iodonium center of the alkynylphenyliodonium ion followed by the reductive elimination of iodobenzene from the iodine(III) adduct seem equally plausible and cannot be ruled out at this time.

Scheme I



The ability of alkynylphenyliodonium tosylates with R = saturated alkyl to give alkynylphosphonates with trialkyl phosphites is noteworthy. The conversion of haloalkynes ($RC{\equiv}CX$) to alkynylphosphonates with trialkyl phosphites is known, but the reactions have been generally limited to haloalkynes in which R = aryl,[10] vinyl,[10a,11] alkynyl,[12] Cl,[10b,13] $PO(OR)_2$,[10b,13] $SiMe_3$,[14] and $SnEt_3$[15] and proceed either poorly or not at all when R = saturated alkyl. Furthermore, the alkynyl(phenyl)iodonium salts are easily prepared and moderately stable. The preparation of dialkyl (*alkyl*ethynyl)phosphonates from **1** with trialkyl phosphites nicely supplements their syntheses by the reactions of sodium diethylphosphonate ($Na^+{}^-PO(OEt)_2$) with bromoalkynes[16] and by the treatment of alkynylmagnesium bromides with dialkyl and diphenyl phosphorochloridates ($ClPO(OR)_2$).[17]

Experimental Section

General. Unless otherwise specified, the NMR spectra reported herein were recorded on a Varian Model VXR-300 spectrometer at resonance frequencies of 300 (^1H), 75 (^{13}C) and 121 MHz (^{31}P), the solvent in all cases being $CDCl_3$. ^1H chemical shifts are expressed relative to chloroform at δ 7.24 and ^{13}C chemical

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shifts relative to $CDCl_3$ at δ 77.0. The ^{31}P spectra are proton-decoupled and referenced to 85% H_3PO_4 (sealed capillary) in $CDCl_3$. Coupling constants are given in hertz. IR spectra were recorded on a Bio-Rad Digilab Model FTS-40 FT-IR spectrophotometer. GC analyses were performed with temperature programming on a Hewlett-Packard Model 5890 gas chromatograph (TC detection) equipped with a Model 3390A integrator and fitted with a 6 ft × $^1/_8$ in. stainless steel column packed with 10% Carbowax 20M on Chromosorb W-HP. Separations by column chromatography were conducted on silica gel (50 g) under nitrogen pressure (ca. 30 mm column diameter) with hexanes–EtOAc (3:1). Elemental analyses were performed by Micro-Tech Laboratories (Skokie, IL) and Midwest Microlab, LTD (Indianapolis, IN). Melting points are uncorrected.

The isolation and purification of the alkynylphosphonates was achieved in much the same way in all cases; a detailed procedure is given for **4a** and serves as an example. Reaction conditions and characterization data are reported for the remaining alkynylphosphonates. Those reactions of alkynylphenyliodonium tosylates with neat trimethyl phosphite which were allowed to proceed at "room temperature" were probably complete as soon as the mixtures became homogeneous (ca. 1–2 min). However, the solutions were allowed to stand for short periods of time prior to workup. The times which are given for reactions of iodonium salts with neat trialkyl phosphites at elevated temperatures refer to periods in which the mixtures were kept in a preheated bath at the specified temperature. Detailed spectral and analytical data for the alkynylphosphonates were *usually* collected on products from preliminary experiments while the reported yields and procedures are for subsequent runs. The identity of the alkyl tosylates (oils in all cases) and alkynylphosphonates for repeat runs was confirmed by 80- and 300-MHz ^1H NMR analysis, respectively. The alkynylphosphonates exhibit weak to moderate hydroxyl absorption in the infrared and are probably a bit hygroscopic.

The alkynylphenyliodonium tosylates employed in this study were prepared by previously reported methods.[1a,b] Two new analogues were synthesized and are described herein.

Dimethyl (*tert*-Butylethynyl)phosphonate (4a). Trimethyl phosphite (3.498 g, 28.2 mmol) was added to solid phenyl (*tert*-butylethynyl)iodonium tosylate (1.004 g, 2.20 mmol) at room temperature. Heat was evolved and, within 1 min, a solution resulted. The solution was concentrated (Kugelrohr, 0.02 mm, room temperature) to remove excess trimethyl phosphite and iodobenzene, and the residual oil was flash chromatographed on silica gel (50 g) with hexanes/EtOAc (3:1), fractions of ca. 30–35 mL in volume being collected. Fractions 3–7 (ca. 165 mL) gave methyl tosylate (oil, 0.395 g, 96%) while fractions 17–34 (ca. 630 mL) gave **4a**: colorless oil; yield 0.378 g (90%); IR (neat, cm^{-1}) 2218 and 2183 (C≡C), 1258 (sh), and 1269 (P=O); ^1H NMR δ 1.25 (s, 9 H), 3.73 (d, 6 H, J_{HP} = 12.3); ^{13}C NMR δ 27.8 (d, J_{CP} = 4.0), 29.7 (d, J_{CP} = 1.8), 52.9 (d, J_{CP} = 5.6), 67.0 (d, J_{CP} = 304.6), 111.1 (d, J_{CP} = 50.8); ^{31}P NMR δ −2.33 (s). Anal. Calcd for $C_8H_{15}O_3P$: C, 50.52; H, 7.95. Found: C, 50.33; H, 8.15.

In another experiment, $(MeO)_3P$ (1.923 g, 15.5 mmol) was added to a solution of the iodonium salt (1.005 g, 2.20 mmol) in MeOH (25 mL) at room temperature (exothermic reaction). After 45 min, the solution was concentrated, and the residual oil was chromatographed to give 0.368 g (88%) of **4a**.

Diethyl (*tert*-Butylethynyl)phosphonate (4b). Obtained from $(EtO)_3P$ (2.986 g, 18.0 mmol) and phenyl(*tert*-butylethynyl)iodonium tosylate (1.004 g, 2.20 mmol) after 1.25 h at 85–7 °C: colorless oil; yield, 0.391 g (81%); IR (neat, cm^{-1}) 2180 and 2214 (C≡C), 1265 (P=O); ^1H NMR δ 1.23 (s, 9 H), 1.31 (t, 6 H, J_{HH} = 6.5–7.2, fine splitting, J_{HP} < 1), 4.07 and 4.10 (overlapping q's, J_{HH} ~ 7, J_{HP} = 8.8); ^{13}C NMR δ 15.8 (d, J_{CP} = 6.9), 27.7 (d, J_{CP} = 4.1), 29.6 (d, J_{CP} = 2.0), 62.6 (d, J_{CP} = 5.5), 68.5 (d, J_{CP} = 301.3), 110.0 (d, J_{CP} = 50.8); ^{31}P NMR δ −5.60 (s). Anal. Calcd for $C_{10}H_{19}O_3P$: C, 55.04; H, 8.78. Found: C, 54.62; H, 9.06. The yield of ethyl tosylate was 0.41 g (93%).

Diisopropyl (*tert*-Butylethynyl)phosphonate (4c). Obtained from $(Me_2CHO)_3P$ (2.16 g, 10.4 mmol) and phenyl(*tert*-butylethynyl)iodonium tosylate (1.004 g, 2.20 mmol) after 1.5 h at 95 °C: pale yellow oil; yield 0.312 g (58%); IR (neat, cm^{-1}) 2180 and 2218 (C≡C), 1258 (P=O); ^1H NMR δ 1.23 (d, 9 H, J_{HP} = 1.1), 1.32 (d, 12 H, J_{HH} = 6.2), 4.67 (m, 2 H); ^{13}C NMR δ 23.3 (d, J_{CP} = 4.8), 23.6 (d, J_{CP} = 4.6), 27.7 (d, J_{CP} = 4.0), 29.7 (d, J_{CP} = 1.9), 70.1 (d, J_{CP} = 299.9), 71.6 (d, J_{CP} = 5.5), 108.9 (d, J_{CP} = 50.5); ^{31}P NMR δ −8.10 (s). Anal. Calcd for $C_{12}H_{23}O_3P$: C, 58.52; H, 9.41. Found: C, 58.16; H, 9.50.

Dimethyl (*sec*-Butylethynyl)phosphonate (4d). Obtained from $(MeO)_3P$ (3.263 g, 26.3 mmol) and phenyl(*sec*-butylethynyl)iodonium tosylate (1.004 g, 2.20 mmol) at room temperature (exothermic reaction): colorless oil; yield 0.265 g (63%); IR (neat, cm^{-1}) 2195 (C≡C), 1277 (P=O); ^1H NMR δ 0.88 (t, 3 H, J_{HH} = 7.4), 1.10 (d, 3 H, J_{HH} = 7.0), 1.41 (m, 2 H), 2.41 (m, 1 H), 3.64 (d, 6 H, J_{HP} = 12.3); ^{13}C NMR δ 11.25 (s), 19.1 (d, J_{CP} = 2.4), 27.7 (d, J_{CP} = 4.2), 28.5 (d, J_{CP} = 2.1), 52.9 (d, J_{CP} = 5.5), 68.8 (d, J_{CP} = 304.0), 107.7 (d, J_{CP} = 51.4); ^{31}P NMR δ −2.68 (s). Anal. Calcd for $C_8H_{15}O_3P$: C, 50.52; H, 7.95. Found: C, 50,56; H, 8.18. The yield of methyl tosylate was 0.41 g (100%).

In another experiment, a solution of $(MeO)_3P$ (1.52 g, 12.3 mmol) and the iodonium tosylate (1.004 g, 2.20 mmol) in CH_2Cl_2 (25 mL) was heated under reflux for 3 h and concentrated. Chromatography of the residual oil in the usual way gave methyl tosylate (0.359 g, 88%) and **4d** (0.232 g, 55%).

Dimethyl (Isopropylethynyl)phosphonate (4e). Obtained from $(MeO)_3P$ (2.398 g, 19.3 mmol) and phenyl(isopropylethynyl)iodonium tosylate (0.36 g, 0.81 mmol) at room temperature (exothermic reaction): pale yellow oil; yield 0.072 g (50%); IR (neat, cm^{-1}) 2195 (C≡C), 1273 (P=O); ^1H NMR δ 1.12 (d, 6 H, J_{HH} = 7.0), 2.59 (m, 1 H), 3.65 (d, 6 H, J_{HP} = 12.3); ^{13}C NMR δ 20.7 (d, J_{CP} = 4.3), 21.45 (d, J_{CP} = 2.1), 52.9 (d, J_{CP} = 5.6), 67.85 (d, J_{CP} = 304.6), 108.5 (d, J_{CP} = 51.9); ^{31}P NMR δ −2.62 (s). Anal. Calcd for $C_7H_{13}O_3P$: C, 47.73; H, 7.44. Found: C, 47.74; H, 7.57. The yield of methyl tosylate was 0.124 g (82%).

Dimethyl (Cyclopentylethynyl)phosphonate (4f). Obtained from $(MeO)_3P$ (3.183 g, 25.7 mmol) and phenyl(cyclopentylethynyl)iodonium tosylate (0.85 g, 1.8 mmol) at room temperature (exothermic reaction): pale yellow oil; yield 0.163 g (44%); IR (neat, cm^{-1}) 2203 (C≡C), 1273 (P=O); ^1H NMR δ ca. 1.35–1.7 (complex m, 5.7 H), ca. 1.77–1.95 (complex m, 2 H), 2.55–2.71 (m, 1 H), 3.64 (d, 6.35 H, J_{HP} = 12.3), weak upfield lines (minor impurity); ^{13}C NMR δ 25.0 (s), 29.85 (d, J_{CP} = 4.4), 32.85 (d, J_{CP} = 2.0), 52.9 (d, J_{CP} = 5.7), 68.0 (d, J_{CP} = 305.8), 108.0 (d, J_{CP} = 52.6); ^{31}P NMR δ −2.45 (s). Anal. Calcd for $C_9H_{15}O_3P$: C, 53.46; H, 7.48. Found: C, 53.62; H, 7.43. The yield of methyl tosylate was 0.309 g (91%).

Dimethyl (Phenylethynyl)phosphonate (4g). Obtained from $(MeO)_3P$ (3.568 g, 28.8 mmol) and phenyl(phenylethynyl)iodonium tosylate (1.048 g, 2.20 mmol) after heating at 80 °C for 1 min; pale yellow oil; yield 0.195 g (42%); IR (neat, cm^{-1}) 2187 (C≡C), 1227 (sh) and 1273 (P=O); ^1H NMR δ 3.83 (d, 6 H, J_{HP} = 12.2), 7.30–7.58 (m, 5 H); ^{13}C NMR δ 53.1 (d, J_{CP} = 6.2), 76.5 (d, J_{CP} = 301.8), 99.6 (d, J_{CP} = 52.7), 118.8 (d, J_{CP} = 5.7), 128.3 (s), 130.6 (s), 132.3 (d, J_{CP} = 2.5); ^{31}P NMR δ −2.59 (s). Anal. Calcd for $C_{10}H_{11}O_3P$: C, 57.15; H, 5.28. Found: C, 56.76; H, 5.38. The yield of methyl tosylate was 0.41 g (100%).

In another experiment, a solution of $(MeO)_3P$ (0.98 g, 7.9 mmol) and the iodonium tosylate (1.048 g, 2.20 mmol) in CH_2Cl_2 (35 mL) was stirred and heated under reflux for 4 h and concentrated to an oil/solid. Treatment of this material with Et_2O (50mL) and filtration gave 0.143 g (20%) of a solid identified as phenyl[β-(tosyloxy)-β-phenylvinyl]iodonium tosylate: mp 161–4 °C; ^1H NMR (80 MHz, $CDCl_3$, TMS) δ 2.30 and 2.37 (singlets, 6 H), ca. 6.75–8.15 (m, 19 H), Et_2O contamination (ca. 20 mol %).

Concentration of the filtrate left an oil, which was chromatographed in the usual way to give methyl tosylate (0.21 g, 51%) and 0.214 g (46%) of **4g**.

Dimethyl (*p*-Tolylethynyl)phosphonate (4h). Obtained from $(MeO)_3P$ (2.735 g, 22.0 mmol) and phenyl(*p*-tolylethynyl)iodonium tosylate (1.078 g, 2.20 mmol) after heating at 80 °C for 10 min: pale yellow oil; yield 0.17 g (34%); IR (neat, cm^{-1}) 2183 (C≡C), 1231 (sh), 1265 and 1278 (P=O); ^1H NMR δ 2.36(s, 3 H), 3.83 (d, 6 H, J_{HP} = 12.3), 7.12–7.48 (AA′XX′ m, 4 H); ^{13}C NMR δ 21.5 (s), 53.2 (d, J_{CP} = 5.6), 76.15 (d, J_{CP} = 303.4), 100. 4 (d, J_{CP} = 53.6), 116.0 (d, J_{CP} = 5.8), 129.2 (s), 132.5 (d, J_{CP} = 2.5), 141.4 (s); ^{31}P NMR δ −2.31 (s). Anal. Calcd for $C_{11}H_{13}O_3P$: C, 58.93; H, 5.84. Found: C, 58.68; H, 5.69. The yield of methyl tosylate was 0.40 g (98%).

Phenyl(*p*-tolylethynyl)iodonium Tosylate. A mixture of [hydroxy(tosyloxy)iodo]benzene (PhI(OH)OTs, 6.08 g, 15.5 mmol)

and 4-ethynyltoluene (2.03 g, 17.5 mmol) in $CHCl_3$ (60 mL) was allowed to stir for 20 h at room temperature. The resulting solution was diluted with $CHCl_3$ to 90 mL, treated with $MgSO_4$, and concentrated to an oil. Treatment of the oil with CH_2Cl_2 (25 mL) and Et_2O (40 mL) gave phenyl(*p*-tolylethynyl)iodonium tosylate as a white crystalline solid, yield 3.371 g (44%). A portion of the product was recrystallized from CH_2Cl_2/Et_2O for elemental analysis: mp 130–132.5 °C; ^1H NMR δ 2.31 (s, 3 H), 2.37 (s, 3 H), ca. 7.03–8.17 (aromatic m's, 13 H), slight contamination with Et_2O; ^{13}C NMR δ 21.2, 21.6, 37.8, 105.5, 117.05, 118.7, 126.0, 128.6, 129.1, 131.5, 131.6, 132.8, 133.8, 140.0, 141.29, 141.32. Anal. Calcd for $C_{22}H_{19}IO_3S$: C, 53.89; H, 3.91. Found: C, 53.86; H, 3.86.

(Cyclopentylethynyl)phenyliodonium Tosylate. A mixture of [hydroxy(tosyloxy)iodo]benzene (3.922 g, 10.0 mmol) and cyclopentylacetylene (1.12 g, 11.9 mmol) in $CHCl_3$ (80 mL) was allowed to stir for 23 h at room temperature. The resulting solution was washed with H_2O (2 × 25 mL), dried ($MgSO_4$), and concentrated to an oil. Treatment of the oil with a mixture of CH_2Cl_2 (5 mL), Et_2O (25 mL), and pentane (25 mL) followed by filtration gave (cyclopentylethynyl)phenyliodonium tosylate (0.97 g, mp 127–129 °C). A second portion of the iodonium salt (0.308 g, mp 125–128 °C) was isolated from the filtrate: combined yield 1.28 g (27%); ^1H NMR δ 1.45–1.8 (m, 5.1 H), 1.8–2.01 (m, 2.3 H), 2.31 (s, 2.8 H), 2.86 (m, 1 H), ca. 7.05–8.1 (aromatic m's, 9.8 H), relative area of aromatic region ca. 0.8 H high and that of aliphatic region ca. 0.8 H low; ^{13}C NMR δ 21.1, 24.9, 27.1, 31.3, 33.1, 112.5, 118.0, 125.9, 128.5, 131.3, 131.4, 133.5, 139.8, 141.5. Anal. Calcd for $C_{20}H_{21}IO_3S$: C, 51.29; H, 4.52. Found C, 51.11; H, 4.52.

GC Determination of the Yield of Iodobenzene from Phenyl(*p*-tolylethynyl)iodonium Tosylate and Trimethyl Phosphite. Trimethyl phosphite (4.73 g, 38.1 mmol) was added to solid phenyl(*p*-tolylethynyl)iodonium tosylate (1.078 g, 2.198 mmol), and the mixture was heated for 10 min at 95 °C. The resulting solution was allowed to cool to room temperature, *p*-xylene (0.1670 g, 1.57 mmol) was added, and the mixture was diluted volumetrically to 50 mL with CH_2Cl_2 (concentration of *p*-xylene, 3.340 $\mu g/\mu L$). After calibration with a standard solution of *p*-xylene (4.534 $\mu g/\mu L$) and PhI (7.734 $\mu g/\mu L$) in CH_2Cl_2, the yield of iodobenzene from the reaction was determined by GC analysis (three 1-μL injections) to be 92.4%, 92.2%, and 90.6% (average yield, 92%).

GC Determination of the Yields of Iodobenzene and 4d from Phenyl(*sec*-butylethynyl)iodonium Tosylate and Trimethyl Phosphite. Trimethyl phosphite (1.741 g, 14.0 mmol) was added to solid phenyl(*sec*-butylethynyl)iodonium tosylate (0.513 g, 1.12 mmol) at room temperature. Heat was evolved, and a solution resulted within 2 min. After the solution had cooled to room temperature, *p*-xylene (0.1057 g, 0.9956 mmol) was introduced, and the mixture was diluted volumetrically to 25 mL with CH_2Cl_2 (concentration of *p*-xylene, 4.228 $\mu g/\mu L$). After calibrations with standard solutions comprised of *p*-xylene (4.534 $\mu g/\mu L$) and PhI (7.734 $\mu g/\mu L$) in CH_2Cl_2 and *p*-xylene (4.240 $\mu g/\mu L$) and authentic **4d** (3.872 $\mu g/\mu L$) in CH_2Cl_2, the yields of iodobenzene and dimethyl (*sec*-butylethynyl)phosphonate from the reaction were determined by GC analysis (three 1-μL injections): iodobenzene (103.8%, 98.4%, 99.5%), average yield, 101%; **4d** (71.4%, 68.3%, 66.7%), average yield, 69%.

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Boron Tris(triflate) Catalyzed Adamantylation of Benzene and Toluene with 1- and 2-Haloadamantanes and Adamantanoyl Chlorides. Isomerization of Phenyl- and Tolyladamantanes[1]

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Boron tris(triflate) catalyzed adamantylation of benzene and toluene was studied with isomeric 1- and 2-haloadamantanes. The alkylations give 1- and 2-phenyl- and isomeric tolyladamantanes in varying ratios. Interconversion of isomeric 2-phenyl(tolyl)adamantanes into the corresponding 1-phenyl(tolyl)adamantanes was observed through intermolecular isomerization involving adamantyl cations and adamantane, which is formed in significant amount in all the reactions. Decarbonylative alkylation of aromatics with adamantanoyl chlorides was also investigated. Adamantanoylated aromatics were formed only in very low amounts, the major product being adamantylated aromatics in accord with extensive decarbonylation of the adamantanoyl cations. The mechanism of the studies adamantylations was further substantiated by studying the boron tris(triflate) catalyzed isomerization of 1- and 2-aryladamantanes under comparable conditions.

Introduction

Friedel–Crafts alkylation of aromatics with diverse alkylating agents[2a] including *tert*-butyl halides[2b] has been extensively investigated.[2] However, the related adamantylation of aromatics remained little explored. Adamantylation of aromatics with 1-adamantyl radical was studied,[3a] and the reactivity of the radical was probed through the effect of substituents on the isomer distribution and relative reactivities. Adamantylation of reactive aromatics using adamantyl nitrate in the presence of H_2SO_4 has also been reported.[3b] $AlCl_3$-catalyzed Friedel–Crafts adamantylation of benzene with 1-bromoadamantane was investigated by Newman.[4] The observation that mixtures of mono, di, and triphenyladamantanes were formed suggested that the $AlCl_3$-catalyzed reaction provides rather harsh conditions for adamantylation. Subsequently adamantylation of benzene and substituted benzenes were carried out in large excess of aromatics using $FeCl_3$ catalyst. In adamantylation of toluene only the para isomer was reported to be formed.[5]

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