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## Selective Coupling Reactions of Alkynyl(phenyl)iodonium Tosylates with Alkynylcopper Reagents

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Alkynyl(phenyl)iodonium tosylates react with mixed cuprates coordinated by alkynyl components to give unsymmetrical diacetylenes selectively; the coupling reaction with dialkylcuprates afforded substituted alkynes.

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Of an increasing number of synthetically useful hypervalent iodine reagents,<sup>1</sup> alkynyl(phenyl)iodonium salts are valuable since they contain carbon-carbon triple bonds.<sup>2</sup>

Earlier we described the stereoselective formation of conjugated enynes *via* coupling of alkynyl(phenyl)iodonium tosylates with alkenylcopper(I) reagents.<sup>2h</sup> Since this method gave a conjugated enyne having a trisubstituted olefin

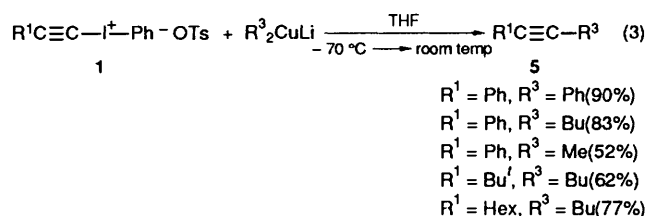
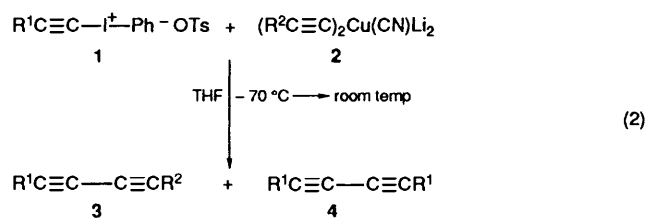
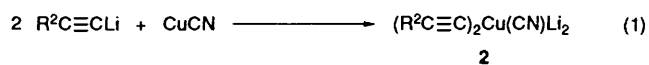
component with complete control of the olefin geometry, we decided to apply it to the selective coupling of alkynyl(phenyl)iodonium tosylates with alkynylcopper(I) reagents. Here we report that the selective coupling reaction provides unsymmetrical diacetylenes.

Alkynyl(phenyl)iodonium tosylates **1** were easily prepared in good yields by reaction of terminal alkynes or 1-trimethylsilyl-

**Table 1** Diacetylenes from the reaction of alkynyl(phenyl)iodonium tosylates with dialkynylcuprates

Iodonium tosylate 1 R <sup>1</sup>	Cuprate 2 R <sup>2</sup>	Diacetylene, yield (%) <sup>a</sup>	
		3	4
Bu	Ph	71 (48) <sup>b</sup>	8 (29) <sup>b</sup>
Bu	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	68	6
Ph	Ph	112 <sup>c</sup>	
Ph	<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	65	10
<i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>	Ph	75	4
Hex	Pr	60	17
Bu'	Bu	65	23

<sup>a</sup> Based on the iodonium tosylate 1. <sup>b</sup> Values in parentheses are yields from the reaction with copper phenylacetylide. <sup>c</sup> Diphenylbuta-1,3-diene is, in part, formed from the cuprate.



1-alkynes with Koser's reagent,<sup>2,j,3</sup> PhI(OH)OTs, or BF<sub>3</sub>-activated iodosylbenzene (PhIO) followed by treatment with NaOTs.<sup>4</sup> In a preliminary experiment, easily available and stable copper acetylides, which have been widely used for coupling reaction with organic halides,<sup>5</sup> were employed. Although the coupling reaction of the alkynylidonium tosylates 1 with the copper acetylides proceeded smoothly by adding the iodonium tosylates 1 to a suspension of the copper acetylides in THF, it induced a homocoupling reaction to produce the desired unsymmetrical diacetylenes 3 together with the symmetrical diacetylenes 4. This may be attributed to the insolubility of the copper acetylides. A mixed cuprate 2 prepared from a lithium acetylide and CuCN was then used for the coupling reaction. Addition of the solid alkynyl(phenyl)iodonium tosylates 1 to the dialkynylcuprate reagent 2 in THF gave the desired heterocoupling products 3 selectively. The yield and selectivity of the unsymmetrical diacetylenes 3 were much improved (see Table 1).

Similar treatment of alkynyl(phenyl)iodonium tosylates 1 with dialkylcuprate reagents,<sup>6</sup> prepared from alkylolithium and copper(I) iodide or bromide, gave good yields of disubstituted alkynes 5.

Together with the coupling reaction with alkenylcopper reagents,<sup>2,b</sup> alkynyl(phenyl)iodonium tosylates react with various organocopper reagents under mild conditions to give selective formation of the corresponding alkyne products. This simple procedure using alkynylidonium tosylates provides a general alkylation procedure for organocopper reagents.

## Experimental

**Typical Procedure.**—To a solution of phenylacetylene (0.31 g, 3.0 mmol) in THF (20 ml) was added dropwise BuLi (1.5 mol dm<sup>-3</sup> hexane solution; 3.0 mmol) at -70 °C under a nitrogen atmosphere. CuCN (0.13 g, 1.5 mmol) was then added and the mixture was stirred at -40 °C for 2 h; it was then cooled to -70 °C. Solid hex-1-ynyl(phenyl)iodonium tosylate (0.46 g, 1.0 mmol) was added to the cooled mixture which was then allowed to warm to room temperature. The whole was poured into saturated aqueous ammonium chloride and the resulting precipitate was filtered off. The filtrate was extracted with ether and the extract was washed, dried, and concentrated. The products were analysed by GC (column, OV-17) and separated by column chromatography on silica gel with hexane-dichloromethane eluent.

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