

Organic Polyvalent Iodine Reagents-Promoted Coupling Reaction of 1-Alkynes

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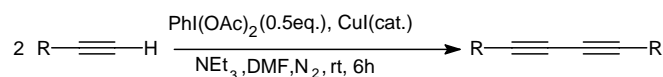
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Abstract: Terminal alkynes couple smoothly in the presence of PhI(OAc)₂ or PhI(OH)OTs, catalytic CuI and base, affording conjugated diynes.

Keywords: Terminal alkynes, coupling, organic polyvalent iodine compounds, conjugated diynes.

Since the early 1980s interest in organic polyvalent iodine compounds has experienced a resurgence¹. A few examples of homo-coupling reactions *via* these compounds have been reported². We found that 1-alkynes were easy to couple in the presence of PhI(OAc)₂ or PhI(OH)OTs, catalytic CuI and base, to afford conjugated diynes. 1,3-Diynes play an important role in studies of molecular recognition³, in natural products⁴, and in synthesis. Although Eglinton reaction⁵, Cadiot-Chalkiewicz coupling⁵ and Glaser reaction⁵ have provided convenient methods to synthesize conjugated diynes, up to now, new approaches have been developing⁶. According to our knowledge, coupling of terminal alkynes *via* organic polyvalent iodine compounds has not been reported. Herein we would like to report our results.

Scheme 1



We found that PhI(OAc)₂ and PhI(OH)OTs (Koser's reagent) can effectively promote the coupling of 1-alkynes under mild conditions to afford 1,3-diynes in the presence of NEt₃ or NaHCO₃, but the later reagent gave a little lower yields. The outcomes were summarized in **Table 1**. In order to get rid of the possible Glaser Reaction⁵, the reaction was proceeded under nitrogen atmosphere. The possible mechanism is probably similar to that proposed in some other cases of carbon-carbon bond formation *via* organic polyvalent iodine compounds^{2a}.

Scheme 2. The possible mechanism of coupling of 1-alkynes promoted by PhI(OAc)₂.

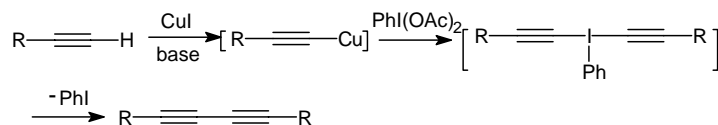


Table 1. Coupling of terminal alkynes promoted by organic polyvalent iodine reagents.

R—C≡C—H	Organic iodine reagents	polyvalent Products ^{a)}	Isolated yields (%)
Ph	PhI(OAc) ₂	Ph—C≡C—C≡C—Ph	89
n-Bu	PhI(OAc) ₂	Bu—C≡C—C≡C—Bu	78
MeOCH ₂	PhI(OAc) ₂	MeOCH ₂ —C≡C—C≡C—CH ₂ OMe	82
Ph	PhI(OH)OTs	Ph—C≡C—C≡C—Ph	73
n-Bu	PhI(OH)OTs	Bu—C≡C—C≡C—Bu	67
MeOCH ₂	PhI(OH)OTs	MeOCH ₂ —C≡C—C≡C—CH ₂ OMe	71

a) All the products were characterized by NMR, MS and IR spectra and the spectroscopic data were identical with those reported previously.

We also studied the possibility of cross-coupling reaction of two different 1-alkynes *via* organic polyvalent iodine compounds. The products of cross-coupling were obtained indeed in about 50% yield, however, accompanied by minor homo-coupling products.

In a sense, the above coupling reactions show the similarities between organic polyvalent iodine compounds and transition metal complexes in ligand exchange, reductive elimination.

Acknowledgments

Project 29772007 is supported by the National Natural Science Foundation of China.

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Received 7 January 1999