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COUPLING OF TERMINAL ALKYNES PROMOTED BY ORGANIC POLYVALENT IODINE COMPOUNDS

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

Since the early 1980s interest in organic polyvalent iodine compounds has experienced a resurgence.¹ A few examples of homo-coupling reactions via these compounds have been reported.² During our research, 1-alkynes were found to couple smoothly in the presence of Phl(OAc)₂ or Phl(OH)OTs, catalytic amount of CuI and base, affording conjugated diynes. The 1,3-diyne structural unit plays an important role in studies of molecular recongnition³ and in synthesis of several natural products⁴. Although the Eglinton reaction⁵, the Cadiot-Chodkiewicz coupling⁵ and the Glaser reaction⁵ have provided convenient methods to prepare conjugated diynes, up to now, new approaches are being developed⁶. Accorcing to

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our knowledge, coupling of terminal alkynes via organic polyvalent iodine compounds has not been reported. Herein we describe our results.





We found that $PhI(OAc)_2$ can effectively promote the coupling of 1-aikynes under mild conditions. Besides NEt₃ and NaHCO₃ work well. PhI(OH)OTs (Koser's reagent) along with CuI and NaHCO₃ was found to promote the above reaction as well, affording 1,3-diynes in slightly lower yields. The outcomes are summarized in Table 1. In order to avoid the possible Glaser Reactior⁵, the reaction in Fig. 1 was performed under an atmosphere of N₂. The possible mechanism is probably similar to that proposed in some other cases of carbonearbon bond formation via organic polyvalent iodine compounds.^{2a}



The possible mechanism of coupling of 1-alkynes via PhI(OAc)2.

We studied the possibility of cross-coupling reaction of two different 1-a kynes via organic polyvalent iodine compounds. The products of cross-coupling were indeed obtained in about 50% yield, however, accompanied by minor homocoupling products (Fig. 3). The results are summarized in Table 2. It is noteworthy that some functional groups in the substrates, such as -OH, can be tolerated in the above reactions.

RC≡CH	Organic polyvalent	Products	Iso]ated
R	iodine reagents		yields(%)
Ph	PhI(OAc) ₂	PhPh	89
n-Bu	PhI(OAc) ₂	BuBu	78
MeOCH ₂	PhI(OAc) ₂	MeOCH ₂ CH ₂ OMe	82
Ph	PhI(OH)OTs	PhPh	73
n-Bu	PhI(OH)OTs	Bu n <u>an</u> B u	67
MeOCH ₂	PhI(OH)OTs	MeOCH2CH2OMe	71

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

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

 $R \xrightarrow{H} (1eq) + R' \xrightarrow{H} (1eq)$

Entry	RC≡CH	R'C≡CH	Major products	Isolated yields(%)
	R	R'		
2d	Ph	HOCH₂	PhCH ₂ OH	45
2e	Ph	MeOCH ₂	PhCH ₂ OMe	51
2f	Ph	n-Bu	PhBu	42

Table 2. Cross-coupling of 1-alkynes via organic polyvalent iodine compounds.

Experimental Section

IR spectra were recorded on a PE-683 spectrometer, and ¹H-NMR spectra were recorded on a JEOL-60S₁ spectrometer in CCl₄ solution using hexamethyld silane as internal standard. MS were obtained on a HP5989B spectrometer. Melting points were not corrected.

Typical procedure for homo-coupling reaction: To a mixture of 0.2 mmol Cul and 1.6 mmol phenylacetylene in 4 ml DMF under a N₂ atmosphere was added dropwise 4 mmol NEt₃ with stirring. 20 Min. later, 1 mmol PhI(OAc)₂ (in 4 ml DMF) was added dropwise. After stirring for 6h, the mixture was quenched with 15ml of water, then extracted with Et₂O (3x15 ml). The organic phase was separated and dried with anhydrous MgSO₄. The solvent was evaporated and the residue was purified by preparative thin layer chromatography on silica gel, affording 2a in 89% yield.

Diphenylbuta-1,3-diyne(2a): white solid, mp 84-86°C (lit.⁷ 83-85°C), ¹H-NMR: $\delta7.70-7.20(m)$. IR: $v_{max}[cm^{-1}]$ 3060, 2150(C=C), 1600, 1480, 1445, 912, 750, 680. MS(m/z): 202(m⁺). **Dodeca-5,7-diyne**(2b):^{6a} colorless oil, ¹H-NMR: $\delta 2.0(t, J=6.0Hz, 2H)$, 1.75-1.20(m, 4H), 0.90(t, J=6.0Hz, 3H). IR: $v_{max}[cm^{-1}]$ 2260(C=C).

1,6-Dimethoxyhexa-2,4-diyne(2c):^{6e} yellow oil, ¹H-NMR: δ 4.10(s, 2H). 3.32(s, 3H). IR: v_{max} [cm⁻¹] 2190, 2170(C=C), 1280, 1190, 1100. MS(m/z): 138(m⁺) Typical procedure for cross-coupling reaction: To a mixture of 0.2 mmol Cal. 0.8

mmol phenylacetylene and 0.8 mmol 1-hexynes in 4 ml DMF under a N_2 atmosphere was added dropwise 4 mmol NEt₃ with stirring. 20 Min. later, 1 mmol PhI(OAc)₂ (in 4 ml DMF) was added dropwise. After stirring for 6h, the mixture was quenched with 15 ml of water, then extracted with Et₂O (3x15 ml). The organic phase was separated and dried with anhydrous MgSO₄. The solvent was evaporated, and the residue was purified by preparative thin layer chromatography on silica gel, affording 2f in 42% yield and minor amount of homo-coupling products.

5-Phenylpenta-2,4-diyn-1-ol(2d): yellowish solid, mp.36-38°C (lit.⁸38-39°C). ¹H-NMR: δ7.60-7.20(m, 5H), 4.30(s, 2H), 2.50(s, 1H). IR: ν_{max}[cm⁻¹] 3300(-OH), 2240(C≡C), 1020(-OH), 750, 680. MS(m/z): 156(m⁺).

5-Methoxy-1,3-pentadiynylbenzene(2e):⁹ yellow oil. ¹H-NMR: δ7.60-7 20(m, 5H), 4.20(s, 2H), 3.40(s, 3H). IR: ν_{max}[cm⁻¹] 3060, 2241(C≡C), 1186, 1100, 750, 682. MS(m/z): 170(m⁺).

1,3-Octadiynylbenzene(2f):^{6d} colorless oil, ¹H-NMR: δ 7.60-7.20(m, 5H), 2.40(t, J=6.6Hz, 2H), 1.75-1.30(m, 4H), 0.96(t, J=6.0Hz, 3H). IR: $v_{max}[cm^{-1}]$ 3060, 2250(C=C),1604, 1492, 750, 682.

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