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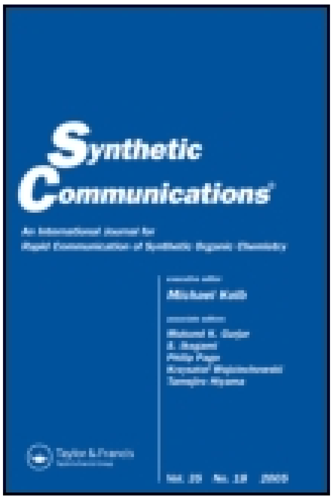

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

MICROWAVE-ASSISTED COUPLING REACTION BY COPPER(I)-CATALYZED OF TERMINAL ALKYNES WITH AROYL CHLORIDES

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Published online: 22 Aug 2006.

To cite this article: Jin-Xian Wang , Bangguo Wei , Yulai Hu , Zhanxiang Liu & Ying Fu (2001) MICROWAVE-ASSISTED COUPLING REACTION BY COPPER(I)-CATALYZED OF TERMINAL ALKYNES WITH AROYL CHLORIDES, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:22, 3527-3532, DOI: 10.1081/SCC-100106214

To link to this article: http://dx.doi.org/10.1081/SCC-100106214

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SYNTHETIC COMMUNICATIONS, 31(22), 3527–3532 (2001)

MICROWAVE-ASSISTED COUPLING REACTION BY COPPER(I)-CATALYZED OF TERMINAL ALKYNES WITH AROYL CHLORIDES

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ABSTRACT

A rapid and efficient method for synthesis of α,β-conjugated acetylenic ketones involves reaction of phenylacetylene with aroyl chlorides in the presence of catalytic amount CuI under microwave irradiation to give the corresponding α,β-conjugated acetylenic ketones 3 a–i in 76–93% yields.

α,β-Conjugated acetylenic ketones compounds are highly valuable precursors or intermediates in synthetic organic chemistry,[1] and many of them are of biological interest.[2] One of the most efficient methods for the synthesis of α,β-conjugated acetylenic ketones involves the reaction of a metal acetylide with an acyl chlorides or another carboxylic acid derivative.[3]

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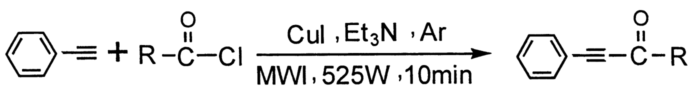
Recently, the direct coupling reaction between an acyl chloride and terminal alkynes catalyzed by CuI[4] or $Pd(PPh_3)_2Cl_2$-CuI[5] have been described. However, many of these reactions suffer from lack of generality, poor yield, long reaction time and even require low temperature (−78°C).[3h] This communication describes a very convenient method for the synthesis of α,β-conjugated acetylenic ketones by the reaction of 1-alkynes with aroyl chlorides in the presence of catalystic amount CuI under microwave irradiation conditions.

In recent years, interest has been shown in the study of microwave assisted organic reactions in polar solvents or in absent of solvent and some important reviews have been published.[6] Microwave irradiation has also been applied to several organic reactions. Recently, we have also reported the synthesis of dibenzyl diselenide,[7] diaroyl diselenides[8] under microwave irradiation conditions. We now wish to report the synthesis of α,β-conjugated acetylenic ketones from phenylacetylene with aroyl chloride using CuI as catalyst under microwave irradiation. This method is simple, fast and affords good yields. The reactions are shown in Scheme 1 and results are summarized in Table 1.



1 2a-i 3a-i

3a. R=C_6H_5; 3b. R=4-Cl-C_6H_4; 3c. R=2-Cl-C_6H_4; 3d. R=4-Br-C_6H_4; 3e. R=2-Br-C_6H_4;

3f. R=$C_6H_5CH{=}CH$; 3g. R=4-CH_3-C_6H_4; 3h. R=4-CH_3O-C_6H_4; 3i. R= α -Np

Scheme 1.

Using the reaction of phenylacetylene with benzoyl chloride as an example, we investigated the effects of various catalysts on the formation of 3a, and results are summarized in Table 2. The results show that CuI is the best catalyst for the reactions, because Pd(II) reagent is very expensive and CuCN is a poisonous reagent.

The effects of various solvents on the formation of 3a was also investigated, and triethylamine was found to be the best solvent for the reaction. We found the yield was very poor when reaction was carried out in benzene or in DMF and triethylamine (V/V = 5 mL/5 mL). There was no reaction when benzene, CH_2Cl_2, CH_3CN (10 mL) was used as solvent and

Table 1. Preparation of α,β-Conjugated Acetylenic Ketones 3a–i

Entry[a]	Product[b]	Yield[c]/%	MP°C/Lit MP °C
3a	$C_6H_5COC{\equiv}CC_6H_5$	87	47–48/46–48[9]
3b	$4\text{-}Cl\text{-}C_6H_4COC{\equiv}CC_6H_5$	91	103–104/105[10]
3c	$2\text{-}Cl\text{-}C_6H_4COC{\equiv}CC_6H_5$	80	oil
3d	$4\text{-}Br\text{-}C_6H_4COC{\equiv}CC_6H_5$	93	106–107/110[11]
3e	$2\text{-}Br\text{-}C_6H_4COC{\equiv}CC_6H_5$	83	oil/oil[12]
3f	$C_6H_5CH{=}CH\ COC{\equiv}CC_6H_5$	76	72–73/73.5–74[5]
3g	$4\text{-}CH_3\text{-}C_6H_4COC{\equiv}CC_6H_5$	85	67–68/71[13]
3h	$4\text{-}CH_3O\text{-}C_6H_4COC{\equiv}CC_6H_5$	79	98–99/100[10]
3i	α-Np $COC{\equiv}CC_6H_5$	82	93–94/95[13]

[a]Mole ratio: Phenylacetylene: aroyl chloride: CuI = 2.5:3.2:0.25. [b]The reaction were carried out in the presence of Et_3N using CuI as catalyst at 525 W for 10 min under argon atmostphere. [c]Isolated yields.

Table 2. Effect of the Catalyst on the Formation of 3a

Catalyst	$Pd(PPh_3)_2Cl_2$-CuI	CuI	CuCN	CuBr	CuCl	no
Yield/%	91	87	85	57	trace	0

Table 3. Effect of the Power of Microwave Irradiation on the Formation of 3a

Power/W	375	450	525	600	675	750
Yield/%	62	75	87	83	78	56

Table 4. Effect of the Time of Microwave Irradiation on the Formation of 3a

Time/min	6	7	8	9	10	12
Yield/%	57	68	79	83	87	85.5

triethylamine, K_2CO_3, K_3PO_4 as base. So we thought that triethylamine was not only as solvent but also as base and ligand for the reaction.

We also studied the effects of power and time of microwave irradiation for the formation of 3a. The results are summarized in Table 3 and Table 4.

Table 5. Comparison of Times and Yields in Synthesis of Compounds 3a–i Using Microwave and Conventional Heating

	Conventional heating		Microwave heating			
Product	T/h	Yield/%	P/W	T/min	Yield/%	t_c/t_{mw}
3a	30	78	525	10	87	180
3b	30	80	525	10	91	180
3c	30	67	525	10	80	180
3d	30	81	525	10	93	180
3e	30	69	525	10	83	180
3f	36	52	525	10	76	216
3g	30	76	525	10	85	180
3h	30	65	525	10	79	180
3i	30	61	525	10	82	180

The result show that the highest yield compound 3a can be obtained in 525 W for 10 min under microwave irradiation conditions.

The impact of the microwave irradiation and conventional heating for synthesis of compound 3a–i have been compared and results are summarized in Table 5. The result show that compounds 3a–i under microwave irradiation were 180–216 times faster than under conventional heating. The ratio between the reaction time using conventional reaction and microwave irradiation (t_c/t_{mw}) under the same condition, quantifies the microwave heating effect.

EXPERIMENTAL

Infrared spectra were measured as KBr discs (or liquid film) using an Alpha centauri FT-IR spectrometer. ^{1}H NMR spectra (80 MHz) were recorded in $CDCl_3$ using a FT-80 spectrometer. Mass spectra were obtained on a QP-1000A GC-MS spectrometer using the electron impact mode (70 eV or 20 eV). Microwave irradiation was carried out with a commercial microwave oven GlanzWP 750B at 2450 Hz. Melting points were determined with an eletrothermal micromelting point apparatus and are uncorrected.

General Procedure for the Preparation of Compounds 3a–i. A mixture of aroyl chlorides (3.2 mmol), phenylacetylene (2.5 mmol), cuprous iodide (0.125 mmol), triethylamine (10 mL) was irradiated at 525 W for 10 min by microwave under argon atmosphere. The mixture was cooled to room

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temperature then methyl alcohol (5 mL) was added and the mixture was stirred for 5 min. The solvent was removed under reduced pressure, diethyl ether (20 mL) and water (20 mL) was added to residue, the aqueous layer was extracted with diethyl ether (20 mL × 2), the organic extract was washed with water (20 mL × 3), 5% H_2SO_4 (20 mL × 3), saturated $NaHCO_3$ (20 mL × 3), and brine (20 mL × 3) and then dried (magnesium sulfate). The dried diethyl ether solution was concentrated, the product was purified by column chromatography on silica gel (200–300 mesh) using petroleum (bp. 60–90°C)/ethyl acetate (v/v 10 : 1) as the eluent. All products have been previously reported and were characterized by melting point, ^{1}H NMR IR and MS spectroscopy.

ACKNOWLEDGMENTS

We thank the National Natural Science Foundation of China and the Northwest Normal University Science and Technology Development Foundation of China for financial support.

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Received in the Netherlands January 8, 2001

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