SHORT PAPER

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Copper-catalysed oxidative homo-coupling of terminal acetylenes on alumina assisted by microwave irradiation[†]

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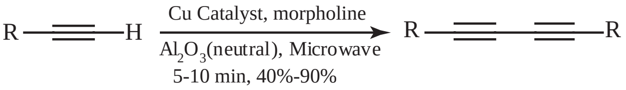
A variety of diacetylenes were prepared in a microwave irradiation promoted reaction on alumina in the presence of catalytic amounts of a copper catalyst with up to 90% yields, in short times and under solvent-free conditions.

Keywords: acetylenes, Glaser reaction, homo-coupling

Diacetylenes are frequently used in the synthesis of natural products, variety polymers and supramolecular materials useful in electronic and optical industries.[1–3] The most useful method for the synthesis of these compounds involves the cupric salt promoted coupling reaction of terminal acetylenes. This reaction has been employed as key step in the preparation of various biological interesting compounds, such as allylamines and alkadienylamines (antimycotics),[4] alkynylindoles,[5] indolocarbazoles (antitumor agents),[6] and pheromones,[7] thus the synthetic challenges associated with these efforts have in turn opened new methods. This reactions was reported for the first time by Glaser.[8] Later, Bayer employed this procedure in the synthesis of indigo.[9] Following this method, many researchers worked on coupling of acetylenic components and developed some other routes such as coupling of alkynyl grignard derivatives,[10] or other organometallic alkenyls[11] using copper and palladium[12] catalysts. Water, methanol, acetone, pyridine cyclohexylamine and toluene can be used as solvents for the Glaser reaction, but amines, most frequently pyridine, are required in almost all $Cu^{(II)}$ promoted Glaser coupling, however, Jiang *et al.* have reported a Glaser coupling reaction in $scCO_2$ using NaOAc instead of amines.[13]

Nowadays, the use of microwave heating in activating a wide variety of organic reactions is growing.[14] Moreover, the importance of surface active catalysts has become more and more significant, because of their enhanced selectivity and milder conditions compared to conventional ones.[15] By the combination of using these catalysts and the activating role of microwave irradiation, it is now possible to perform many kinds of organic reactions in a solvent-free system and with short reaction times (up to some minutes). This is obviously more environmentally friendly than the corresponding reactions in solution and the complicated role of solvents will also be avoided. For example, we have recently reported the solvent-free aminoalkylation of phenols, indoles[16] and terminal alkynes[17] on alumina assisted by microwave irradiation. Kabalka *et al.* have recently reported that terminal aliphatic and aromatic acetylenes couple to yield diacethylenes under a microwave assisted reaction on a KF-alumina base with poor to good yields.[18] Although this method profits of a solvent-free conditions, using about 3.7 mol equiv of a copper catalyst is an obvious disadvantage, although it is not clear why so much copper catalyst should be used, possibly due to using KF-alumina. We now wish to report microwave assisted facile homocoupling reactions of acetylenic components on neutral alumina using catalytic amounts of copper halides (0.05 mol equiv. of CuI, CuCl, or $CuCl_2$). The reaction is shown in Scheme 1 and the results are summarised in Table 1. A variety of terminal acetylenes were successfully coupled. It is evident that this method is also well suitable for homocoupling of aromatic acethylenes (**2a** and **2b**) as well as propargyl amines (**2a**–**2g**), and ethers (**2h**). All the known products have been characterised by comparison of their melting points or NMR spectras with those in the literature. The new products **4f**, and **4g** exhibit satisfactory HRMS results and spectral data.



Scheme 1

The yields of the products are well comparable to the ones reported by similar methods. For example, the yield of **2a** was previously reported as 75% by Kabalka,[18] 40% by Glaser,[19] and 60% by Toda.[20] The yield of 80% for the product **2a** is obviously an advantage, the method needs only catalytic amounts of Cu catalyst (0.05 mol. equiv. instead of 3.7 mol. equiv.[18]), and one should not use organometallic alkenyls as starting materials.[20]

As copper catalyst, we have tested cuprous chloride, cuprous iodide, and cupric chloride. The results in Table 1 indicates that all of these catalysts are effective under the reaction conditions.

In conclusion, we reported herein a facile method for the preparation of diacetylenes in a solvent-free and environmental friendly Glaser reaction. The reaction time is dramatically reduced from several hours to a few minutes using microwave irradiation.

Experimental

Melting points were determined on a hot stage or oil bath apparatus without correction. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 80 MHz in $CDCl_3$ using TMS as internal standard. HRMS were obtained on a Finnigan MAT system MAT 212. Microwave induced reactions were carried out in a domestic microwave oven Moulinex MICRO-CHEF, 900 W at 2450 MHz at moderate power. All of the known products were been characterised with comparison of their melting points or NMR spectra with those in the literature.

General procedure for oxidative homo-coupling of terminal acetylenic compound with copper halides on neutral alumina under microwave irradiation: A mixture of 1 mmol acetylenic compound, 2 mmol morpholine and 0.05 mmol copper halide were ground with 2 g neutral alumina in a mortar. The mixture was transferred to a 25 ml beaker and irradiated in a microwave oven for the required time (Table 1) with 30 s interval between any 2 min irradiation. After cooling, the mixture was extracted with ethyl acetate. Evaporation of the

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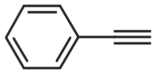
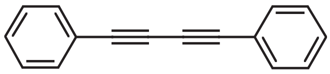
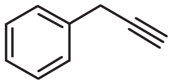
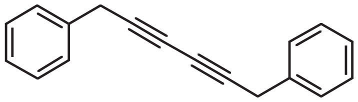
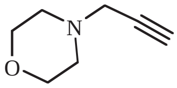
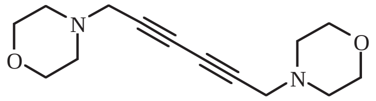
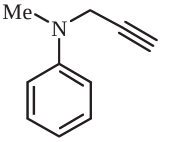
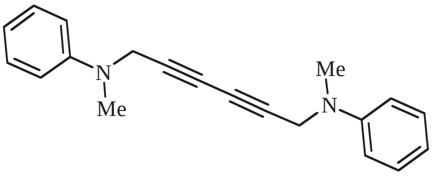
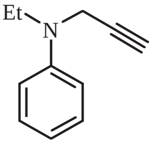
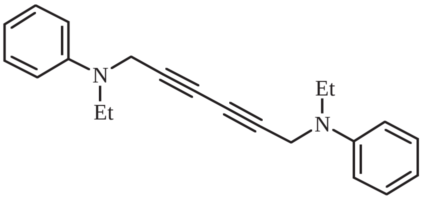
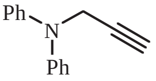
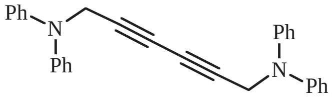
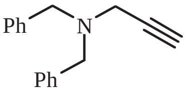
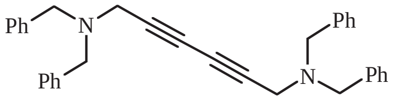
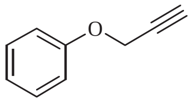
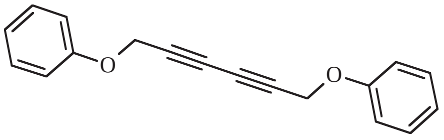
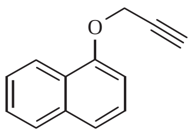
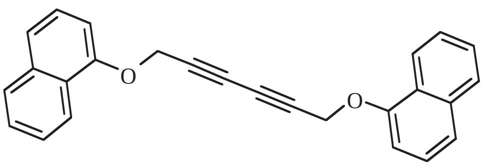
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Oxidative homocoupling of terminal acetylenes with Cupper catalyst on neutral alumina

Alkyne		Diacethylene		Catalyst	Time/min	Yield[a]/%
	**2a**		**4a**[21]	CuI CuCl	10 10	82 80
	**2b**		**4b**[22]	CuI CuCl	10 10	40 50
	**2c**		**4c**[23]	CuI CuCl	10 10	55 50
	**2d**		**4d**[24]	CuI CuCl	10 10	75 72
	**2e**		**4e**[25]	CuI CuCl	10 10	73 78
	**2f**		**4f**	CuI CuCl	10 10	87 90
	**2g**		**4g**	CuI CuCl	10 10	84 86
	**2h**		**4h**[20]	CuI $CuCl_2$	7 7	50 50
	**2i**		**4i**	CuI $CuCl_2$	5 5	40 40

[a] Isolated yields

solvent gave the crude product, which was purified by flash column chromatography (silica gel; eluent: petrol ether).

N,N,N′,N′-Tetraphenyl-2,4-hexadiyne-1,6-diamine (**4f**): m.p. 117°C. ^{1}H NMR: 4.39 (s, $2CH_2$), 6.64–7.32 (m, 20H arom). ^{13}C NMR: 43.0, 75.2, 79.4, 121.0, 122.1, 129.1, 147.5. HRMS (CI) calcd. for $C_{30}H_{24}N_2$ 412.1939, Found 412.1936.

N,N,N′,N′-Tetraphenylmethyl-2,4-hexadiyne-1,6-diamine (**4g**): m.p. 111°C. ^{1}H NMR: δ = 3.28 (s, $2CH_2$), 3.65 (s, $4CH_2$), 7.17–7.36 (m, 20H arom). ^{13}C NMR: δ = 41.8, 57.6, 70.0, 73.5, 127.0, 128.2, 128.8, 138.5. HRMS (CI) calcd. for $C_{34}H_{32}N_2$ 468.2565, Found 468.2575.

1,1′-[2,4-Hexadiyne-1,6-diylbis(oxy)]bisnaphthalene (**4i**): m.p. 119–121°C. ^{1}H NMR: δ = 4.88 (s, $2CH_2$), 6.77-8.24 (m, 14H). ^{13}C NMR: δ = 56.3, 71.2, 75.4, 105.3, 121.2, 121.7, 124.2, 125.2, 125.3, 126.3, 127.2, 134.1, 152.5. HRMS (CI) calcd. for $C_{26}H_{18}O_2$ 362.1307, Found 362.1305

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