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Gold Chloride ($AuCl_3$) Catalyzed Expeditious Homocoupling of Terminal Alkynes at Ambient and Solvent Free Conditions: Impact of Sodium Acetate on the Reaction Yield

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Abstract: Homocoupling of terminal alkynes to 1, 3-diynes has been investigated, using $AuCl_3$ as catalyst under mild and operationally simple conditions. Effect of different organic and inorganic bases on the product yield and the reaction time were also studied. The catalyst is efficient, furnishes good to excellent yield of the desired products with organic bases and Sodium acetate was found to be the most effective base under solvent free conditions at room temperature.

Keywords: Gold Trichloride, Homocoupling, Terminal Alkyne, Diyne

1. Introduction

C-C bond formation is the essence of organic synthesis [1], provides the basis for generating more complicated organic molecules from simpler ones. Diyne compounds have received significant attention because of their applications not only in material chemistry but also in the formation of valuable intermediates for natural products [2] and pharmaceuticals such as antitumor [3], anti-inflammatory [4] and antifungal agents [5]. As the emerging importance much interest has been paid for the development of new and efficient methods for the synthesis of diynes [6]. Although several routes are available for the synthesis of conjugated 1, 3- diynes, i.e. the homocoupling of terminal alkynes is favoured due to its simple procedure [7] Common methods used for the synthesis of 1, 3-diynes include Glaser coupling [8], Eglinton coupling [9], Hay coupling [10], mediated by copper-catalyzed oxidative homocoupling reaction of terminal alkynes [11] and Palladium-assisted Glaser type coupling reactions [12].

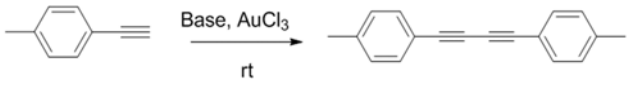
The most striking routes for the homocoupling of terminal alkynes involve palladium (Pd) in combination with copper salts as catalytic systems, but palladium based reagents are toxic and often require ambiguous complex formation with expensive ligands. Several groups have reported homocoupling reactions of terminal alkynes using Pd free catalytic systems, e.g. Jiang *et al.* reported the Cu(II) promoted oxidative homocoupling reaction of terminal alkynes in supercritical carbon dioxide and Jia *et al*. have described the CuI-mediated alkyne homocoupling reaction, employing inorganic base as Na_2CO_3 [13]. These Pd free systems are efficient and economic but require high pressure, high temperature, co-catalysts, excess amines and oxygen atmosphere and long reaction time. Some base free Cu-mediated alkyne homocoupling reaction, have also been reported [14], and even neat processes have also been developed for oxidative homocoupling reaction of terminal alkynes [15]. The use of transition metals mediated homocoupling reactions other than Pd and Cu for the synthesis of 1, 3-diynes are still limited [16].

During the last decade gold salt and its complexes have played an emerging role for activation of C-C multiple bonds toward a variety of nucleophiles [17]. Carbophilic Lewis-acid

based gold salts facilitate the development of novel routes to synthesise complex molecular structures [18]. Recent methods developed for the gold catalyzed reactions involve oxidative dimerization of propargylic acetates and oxidative cross-coupling reactions with arylboronic acids [19], gold-catalyzed diamination of alkenes [18] for the oxidative coupling of non-activated arenes. Previously, Corma and co-workers reported the gold-catalyzed sonogashira reactions via a gold (I)/gold (III) catalytic cycle. In these reactions, 1, 3-diynes were formed as side products in low yields [20]. More recently, *Mei Zhu et al* have developed an efficient protocol for the synthesis of 1, 3-diyne systems catalysed by gold involving homocoupling reaction of terminal alkynes [21]. But the imperfections include requirements of iodosobenzene diacetate [PhI $(OAc)_2$] as additive, longer reaction time and high temperature. There is an assortment of other methods also developed for this successful reaction and every new method tries to rectify the drawbacks of the older one [22]. In continuation to our interest in the alkyne homocoupling [23] and green chemistry protocols [24], We herein report an improved protocol describing homocoupling of terminal alkynes for the synthesis of 1, 3-diyne systems using $AuCl_3$ catalyst under solvent free and milder reaction conditions.

2. Results and Discussion

In Our previous report [23] 1, 3-diyne were prepared from terminal alkynes at high temperature under O_2 atmosphere, but here our aim was to develop a low temperature protocol under atmospheric conditions. During our initial studies, 4-tolylacetylene (1 mmol.) was taken as model substrate using $AuCl_3$ as a catalyst at room temperature (scheme-1). The model reaction was conducted in acetonitrile (as solvent) to study the influence of various bases on the yield as well as on the reaction time (table-1).



Scheme 1. *Reaction of 4-tolylacetylene.*

However lower yields were obtained with inorganic bases (table 1, entries 1-3). Application of organic bases was found to show tremendous improvement. With triethylamine (1.2 eq) the product yield turned up to 67% within 45 min (table 1, entry 4), but DABCO could bring lesser conversion and only 59% product yield was obtained even after 1.5h (table 1, entry 5). Sodium acetate was found to be most effective organic base for conversion the terminal alkynes to 1, 3-diyne products within 30 min and more than 92% product yield was obtained (table 1, entry 10). Other organic bases, like DBU, 4-Dimethylaminopyridine and piperidine were also very effective to promote the desired reaction, among which piperidine enhanced the product yield up to 88% within 1h (table 1, entries 6-8). From the above results, it is evident that organic bases have a promoting effect not only on the yield but also on the reaction time of terminal alkyne homocoupling.

Table 1. *Reaction of 4-tolylacetylene with $AuCl_3$ as the catalyst at room temperatures in presence of different bases using acetonitrile as solvent.*

Entry	Base	Time	Yield (%)[a]
1	NaOH	3h	29
2	K_2CO_3	2.5h	49
3	Na_2CO_3	1h	57
4	Triethylamine	45 min	67
5	DABCO	1.5h	59
6	DBU	45 min	76
7	4-Dimethylaminopyridine	1h	88
8	Piperidine	1h	87
9	Pyrrolidine	30 min	92
10	CH_3COONa	30	93

[a] isolated yields

Further we screened the reaction in different solvent conditions for the model reaction using Sodium acetate as a base (table 2). The product yield was very poor in solvents such as DCM, DMF, methanol, ethanol, ethyl acetate, isopropanol and DMSO (table 2, entries 1-3, 5, 7, 8), but better yields were obtained in acetonitrile, 1, 4-dioxane, and THF, where acetonitrile was found to be the most suitable solvent yielding 92% desired product(table 2, entries 4, 6, 10). When the reaction was put under solvent free conditions, the product yield increased to >95% within 30 min (table 2, entry 1).

Table 2. *Reaction of 4-tolylacetylene in different solvents with Sodium acetate as the base using $AuCl_3$ as catalyst.*

S. No.	Solvents	Yeild (%)[a]
1	Ethylacetate	31
2	DCM	41
3	Methanol	41
4	THF	79
5	DMF	37
6	Dioxane	69
7	Ethanol	5
8	Isopropanol	52
9	DMSO	50
10	Acetonitrile	92
11	No solvent	95

[a]isolated yield

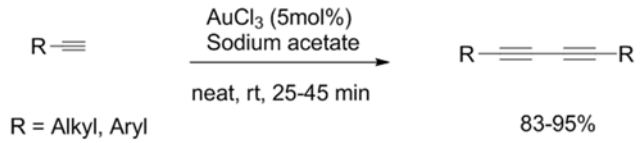
To monitor the influence of catalyst amount on the reaction different a ranges of catalyst concentrations were used for the model reaction. With $AuCl_3$ (0.05 mol %) using Sodium acetate (1.0 eq) as base, the desired product was formed in 58% yield at room temperature (table 3, entry 1). When concentration of the catalyst was increased, the yield was significantly increased and 5 mol % was found to be the optimum amount for getting the desired product in 96% (table 3, entry 7). Further when the concentration of the catalyst was increased, no significant increase was observed in terms of yield (table 3, entry 8).

Table 3. *Study of different concentration of $AuCl_3$ on time and yield of the reaction product of 4-tolylacetylene.*

Entry	$AuCl_3$ (mol %)	Time (h)	Yield (%)[a]
1	0.05	3	58
2	1	1.5	62
3	1.5	1.5	64
4	2	1.5	68
5	3	1	77
6	4	0.5	84
7	5	0.5	96
8	7	0.5	96

[a]isolated yield, room temperature

With optimized reaction conditions in hand [25], we studied the feasibility of this methodology using different terminal alkynes (Scheme-2). Both aromatic and aliphatic terminal alkynes reacted successfully to produce the corresponding homocoupled 1, 3-diynes smoothly in good to excellent overall yields. Aryl alkynes bearing electron donating groups reacted faster with better yields as compared to those bearing electron withdrawing substituents. The results are summarized in table-4.



Scheme 2. *Reaction of different terminal alkynes.*

Table 4. *Reaction of different terminal alkynes in presence of $AuCl_3$ as catalyst, Sodium acetate as base.*

Entry	Substrate	Time (min.)	Product (Yield%)[a]
1	nC_2H_5	30	91
2	nC_4H_9	30	90
3	nC_5H_{11}	30	90
4	nC_8H_{17}	25	87
5	HO	35	87
6		30	88
7	OH	30	92
8		30	96
9		30	96
10		25	96
11	H_3CO	30	95
12	Ph	45	91
13	F	45	69
14	O_2N	45	50
15	F_3C	35	71

[a] isolated yields, room temperature, solvent free.

The products obtained were isolated in good yields and the products were identified by spectral analysis (^{1}H NMR, ^{13}C NMR, IR, and MS). The spectral data was compared with the reported literature.

3. Conclusions

In conclusion, we have developed a mild and efficient protocol for gold-catalyzed oxidative homocoupling of various terminal alkynes. In the presence of $AuCl_3$, a variety of terminal alkynes underwent oxidative homocoupling afford the corresponding symmetrical 1, 3-diynes in moderate to good yields. This method is an efficient and simple process for the synthesis of 1, 3-butadiynes without requiring palladium, ligand, or additive. The application of this powerful strategy makes this present procedure fast, practical and interesting for the synthesis of alkynes homocoupling.

Appendix

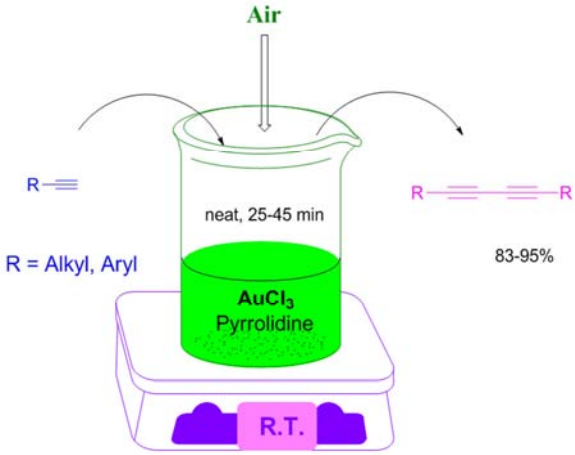


Figure 1. *Graphical representation of general scheme.*

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[25] General Procedure: To 4-tolylacetylene 1(1eq.), Sodium acetate (1.2 equiv) using as base, was added and the contents were stirred for 5 minutes, followed by the addition of $AuCl_3$ (5 mol %) as the catalyst in solvent free conditions afforded the desired product. The reaction mixture was then allowed to stirr at room temperature for 30 minutes. On completion of the reaction (monitored by TLC). The reaction was worked up by dilution with water followed by solvent ethyl acetate. The contents of the reaction mixture were extracted with ethyl acetate (3×50ml), the organic layer washed with water (3×20ml) and dried over anhydrous sodium sulphate and concentrated on rot-vapor to give crude product, which on column chromatography over silica gel (mesh 60–120) using hexane and ethyl acetate (19:1) as eluent to obtain product.