

## Phase-Transfer Catalytic Oxidation of Terminal Alkynes to Keto Aldehydes by Dilute Hydrogen Peroxide

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A phase-transfer procedure for the oxidation of terminal alkynes under mild conditions is described. The catalytic system involves dilute hydrogen peroxide,  $\text{Na}_2\text{MO}_4$  salts ( $\text{M} = \text{Mo(VI)}, \text{W(VI)}$ ), and  $\text{Hg}(\text{OAc})_2$ . In the absence of mercuric derivative no oxidation takes place. By changing the pH of the aqueous phase and the nature of the phase transfer agent, either cationic or neutral, as well as the metal ( $\text{Mo}$  or  $\text{W}$ ), carboxylic acids or  $\alpha$ -keto aldehydes may be selectively obtained in fairly good yields.

A variety of aromatic and aliphatic hydrocarbons have been oxidized by using hydrogen peroxide or alkyl hydroperoxides in the presence of transition metal derivatives.<sup>1</sup> By contrast, the catalytic oxidation of alkynes appears to be unprecedented.

Moreover, the oxidation of terminal alkynes by customary reagents such as peracids, potassium permanganate, or osmium or ruthenium tetraoxide usually leads to the formation of carboxylic acids.<sup>2</sup> Recently we have found that  $\alpha$ -diketones and  $\alpha$ -keto aldehydes may be obtained by stoichiometric oxidation of internal or terminal alkynes respectively with molybdenum oxodiperoxo complex  $\text{MoO}(\text{O}_2)_2\text{-HMPT}$  in the presence of mercuric acetate.<sup>3</sup>

Molybdenum(VI) or tungsten(VI) peroxy complexes may be catalytically formed in aqueous solutions by addition of hydrogen peroxide to  $\text{H}_2\text{MO}_4$  acids ( $\text{M} = \text{Mo(VI)}, \text{W(VI)}$ ).<sup>4</sup> These peroxy derivatives behave as acids in protic solvents. Consequently they may be present as anionic as well as neutral species,<sup>5</sup> which can be extracted into an organic phase by suitable transfer agents.<sup>6,7</sup>

This technique has been applied to the oxidation of substrates such as organic sulfides,<sup>6</sup> alkenes,<sup>6</sup> or alcohols<sup>8</sup> by using dilute hydrogen peroxide under mild conditions.

In this paper we present results concerning the catalytic oxidation of terminal alkynes by hydrogen peroxide and sodium molybdate or tungstate employing the phase-transfer technique outlined above. The data reported below show that indeed this procedure gives good results also with alkynes.

### Results and Discussion

For comparison purposes we have preliminarily investigated the catalytic oxidation reactions of two model alkynes by dilute  $\text{H}_2\text{O}_2$  in the presence of  $\text{Na}_2\text{MoO}_4$  or  $\text{Na}_2\text{WO}_4$  and  $\text{Hg}(\text{OAc})_2$  under homogeneous conditions in dioxane. However, inconveniently low conversions of the substrates were observed.<sup>9</sup>

The two-phase procedure gave much better results; in our system the aqueous phase contains  $\text{H}_2\text{O}_2$  and  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$  or  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  at a fixed acid pH, whereas the substrate and  $\text{Hg}(\text{OAc})_2$  are dissolved in dichloroethane (DCE). When an appropriate PT agent is used, either a neutral lipophilic agent, e.g., HEPT (hexaethylphosphoric triamide), or a lipophilic quaternary ammonium salt such as Aliquat 336 or Adogen 464, the oxidation reactions proceed smoothly, providing fairly high yields of oxidized products. The pertinent results are reported in Table I.

Control experiments have shown that in the absence of the mercuric salt no appreciable oxidation of the substrate takes place. The role played by the mercuric derivative is not yet clear, even if some preliminary spectroscopic data indicate that it might form  $\pi$ -complexes with alkynes.<sup>3</sup> The products of the oxidation appear to be a function of the extracting agent, the pH, and the metal. When Aliquat 336 or Adogen 464 is used with molybdenum catalyst (Table I, entries 3-6),  $\alpha$ -keto aldehydes are obtained. A similar behavior, e.g., selective formation of  $\alpha$ -keto aldehydes, had been previously reported for the  $\text{Hg}(\text{OAc})_2$ -catalyzed stoichiometric oxidation of alkynes with  $\text{MoO}_5\text{-HMPT}$  in DCE.<sup>3</sup> As shown in entries 3 and 7-9, the yield of carbonyl compound appears to be related to the pH of the aqueous phase. It should be mentioned that previous studies have revealed a pH dependence of  $\text{Mo(VI)}$  peroxy complex decomposition rate.<sup>10</sup> By contrast, when HEPT is the PT agent, carboxylic acids resulting from the oxidative cleavage of the triple carbon-carbon bond are obtained (Table I, entries 1, 2).

Interestingly, high conversions and high yields of carboxylic acids are obtained by using the  $\text{W(VI)}$  catalyst regardless of the nature of the PT agent (Table I, entries 10-14). As an additional piece of information, it must be mentioned that internal alkynes appear quite unreactive under the conditions adopted in this study.<sup>11</sup>

Although no mechanistic details may be provided at this stage, some preliminary information is worthy of consideration. The two different kinds of products, either  $\alpha$ -keto aldehydes or carboxylic acids, are likely to result from different oxidative pathways. In fact it is known that cationic PT agents such as Aliquat or Adogen extract anionic oxidant species such as  $[\text{MO}_5(\text{OH})(\text{H}_2\text{O})_m]^-$  while neutral ligands such as HMPT or HEPT extract neutral species such as  $\text{MO}_5(\text{H}_2\text{O})_n$ .<sup>6,7</sup> It has been reported that these two peroxy species display different reactivities toward substrates such as olefins or alcohols.<sup>5</sup>

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(9) Phenylacetylene (5 mmol) undergoes 7% of conversion at 20 °C after 16 h to yield only 0.3 mmol of the corresponding  $\alpha$ -keto aldehydes.

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(11) Diphenylacetylene (3.4 mmol) is recovered practically unreacted after 36 h with HEPT as PT agent and  $\text{Na}_2\text{MoO}_4$ ; 1-phenyl-1-pentyne (4.7 mmol) produces low yields of  $\alpha$ -diketone (0.1 mmol) with  $\text{Na}_2\text{WO}_4$  after 17 h.

**Table I. Catalytic Oxidations of Terminal Alkynes by Hydrogen Peroxide in the Presence of Sodium Molybdate or Tungstate in Dichloroethane-Water at 20 °C**

run no.	alkyne (mmol)	Hg(OAc) <sub>2</sub> , mmol	PT agent (mmol)	time, min	$\alpha$ -keto aldehyde, %	acid, <sup>a</sup> %	recovered alkyne, %
Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O (0.15 mmol), H <sub>2</sub> O <sub>2</sub> (20.5 mmol)							
a. pH 1.1							
1	phenylacetylene (6.2)	1.6	HEPT (0.4)	30	13	71	16
2	1-hexyne (4.9)	0.8	HEPT (0.4)	40	29	59	12
3	phenylacetylene (6.2)	1.6	Aliquat (0.6)	60	26	—	74
4	phenylacetylene (6.2)	1.6	Adogen (0.6)	60	32	—	65
5	1-hexyne (4.9)	0.8	Adogen (0.6)	30	20	—	80
6	1-hexyne (4.8)	0.8	Aliquat (0.6)	30	29	—	71
b. pH 2.6							
7	phenylacetylene (6.1)	1.6	Aliquat (0.6)	60	28	—	67
c. pH 3.5							
8	phenylacetylene (6.1)	1.6	Aliquat (0.7)	60	36	—	62
8a	phenylacetylene <sup>b</sup> (6.1)	1.6	Aliquat (0.7)	30	43	—	57
d. pH 4.6							
9	phenylacetylene (6.2)	1.6	Aliquat (0.7)	60	37	—	61
Na <sub>2</sub> WO <sub>4</sub> ·2H <sub>2</sub> O (0.15 mmol), H <sub>2</sub> O <sub>2</sub> (20.5 mmol)							
pH 0.9							
10	phenylacetylene (6.1)	1.6	Aliquat (0.6)	120	8	93	—
11	phenylacetylene (6.0)	1.6	Adogen (0.6)	60	10	63	25
				120	10	92	—
12	1-hexyne (5.0)	0.8	Aliquat (0.6)	120	12	46	40
13	1-hexyne (5.1)	0.8	Adogen (0.6)	120	12	55	29
14	1-hexyne (5.3)	0.8	HEPT (0.5)	120	11	90	—

<sup>a</sup> Carboxylic acids of one less carbon are formed (benzoic and valeric from phenylacetylene and 1-hexyne, respectively). <sup>b</sup> In this run the aqueous layer was saturated with Na<sub>2</sub>SO<sub>4</sub>.

The possibility that carboxylic acids can be formed by a consecutive oxidation of  $\alpha$ -keto aldehydes may be ruled out on the basis of control experiments which indicate that such a process is indeed much slower than the formation of the acids under the same experimental conditions. In conclusion, the results presented here confirm that the oxidation of alkynes by dilute hydrogen peroxide may be accomplished under very mild conditions providing good yields and selectivities. Moreover, simply by changing the nature of the metal or of the PT agent, the reaction may be driven towards the production of  $\alpha$ -keto aldehydes or of carboxylic acids.

### Experimental Section

**Materials.** Phenylacetylene and 1-hexyne are commercially available products (Aldrich), which were purified by distillation. Reagent grade Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were used as catalysts. 1,2-Dichloroethane was purified by standard procedures from highly pure commercial samples. Hexaethylphosphoric triamide (HEPT) was obtained according to literature methods.<sup>6,12</sup> All other chemicals were used as received.

**Procedures.** In a typical run, 1 mL of an aqueous solution of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O or Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O (0.15 mmol) at the desired pH (0.9–4.6) (adjusted by using 96% H<sub>2</sub>SO<sub>4</sub>) was added to a dichloroethane solution (15 mL) containing phenylacetylene (6.1 mmol) or 1-hexyne (5 mmol), Hg(OAc)<sub>2</sub> (1.6 or 0.8 mmol), and the ligand (0.6 mmol) in a glass reactor maintained at 20 °C. Then

1 mL of H<sub>2</sub>O<sub>2</sub>, 70% w/v (20.5 mmol), was added with vigorous stirring. After some hours, the two phases were separated and the products in the organic phase were isolated by column chromatography (silica gel, cyclohexane–ethyl acetate, 9:1, or petroleum ether–diethyl ether, 8:2) and identified by comparison with authentic samples and by their <sup>1</sup>H NMR, IR, and mass spectra.

In an alternative procedure, 5 mL of an aqueous solution of Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O (0.15 mmol) (M = Mo, W) was added to a DCE solution (10 mL) containing the substrate, the ligand, and the mercuric salt. Then 2 mL of H<sub>2</sub>O<sub>2</sub>, 35% w/v (20.6 mmol), was added with vigorous stirring. The presence of a larger amount of water allowed, at the end of the reaction, a faster separation of the two organic and aqueous phases.

When isolation of the products was not carried out, the yields were determined by quantitative GLC analysis (internal standard) using a 3% OV-17 on 80/100 Supelcoport column, with a Carlo Erba 2350 instrument, equipped with a Shimadzu Chromatopac C-E1B integrator for phenylacetylene and an 80/100 Carbopack C/0.1% SP-1000 column with a Hewlett-Packard 5890A instrument equipped with a Perkin-Elmer LCI-100 integrator for 1-hexyne.

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**Registry No.** HEPT, 2622-07-3; Na<sub>2</sub>MoO<sub>4</sub>, 7631-95-0; Na<sub>2</sub>WO<sub>4</sub>, 13472-45-2; phenylacetylene, 536-74-3; 1-hexyne, 693-02-7;  $\alpha$ -oxo-benzeneacetaldehyde, 1074-12-0; benzoic acid, 65-85-0; 2-oxo-hexanal, 2363-84-0; valeric acid, 109-52-4.