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A NEW FACILE SYNTHESIS OF α-DICARBONYL COMPOUNDS BY OXIDATION OF ALKYNES WITH Mo(VI) PEROXOCOMPLEX PROMOTED BY MERCURIC ACETATE

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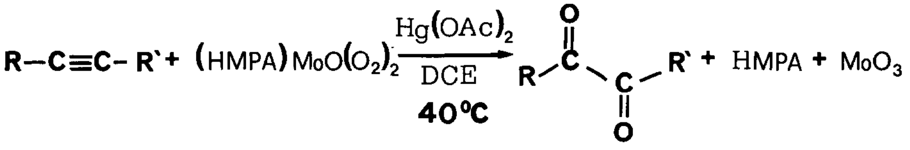
Summary: Mercuric acetate promoted oxidation of diaryl-, dialkyl-, and aralkyl alkynes with (HMPA)MoO$(O_2)_2$ in 1,2-dichloroethane affords the corresponding α-diketones in good yields. Likewise, terminal alkynes can be converted into α-ketoaldehydes in excellent yields by using the same oxidizing system.

The oxidation of alkynes with peroxides offers in principle a clean and very attractive route to the synthesis of 1,2-dicarbonyl compounds[1,2,3]. On the other hand the use of peroxoacids as oxidant agents suffers from the drawbacks to give complex reactions, whose products composition greatly depends upon the nature of both the substrate and the peroxoacid and upon the reaction conditions[3,4,5]. As a rule, products deriving from the complete cleavage of the carbon-carbon triple bond are accompanied by the formation of α,β-unsaturated ketones[3,4,5], which -with certain substrates - can be the main derivatives[5].

Moreover alternative oxidants as osmium[6] or ruthenium tetroxide[7] or potassium permanganate have been extensively used. These systems yield α-diketones with nonterminal alkynes but for terminal alkynes cleavage products of the C≡C bond results as in the case of peroxocarboxylic acids.

In the present work we wish to report a novel one step synthetic method to obtain α-diketones and α-oxo-aldehydes by oxidation of representative nonterminal and terminal alkynes respectively by using the metalperoxide complex hexamethylphosphoramido molybdenum(VI) oxide diperoxide[8] (HMPA)MoO$(O_2)_2$ in the presence of Hg$(OAc)_2$. The reaction occurs readily in 1,2-dichloroethane (DCE) at 40°C, according to the stoichiometry in equation (1).



$$R{-}C{\equiv}C{-}R' + (HMPA)MoO(O_2)_2 \xrightarrow[\substack{DCE \\ 40^{\circ}C}]{Hg(OAc)_2} R{-}\overset{\overset{O}{\|}}{C}{-}\underset{\underset{O}{\|}}{C}{-}R' + HMPA + MoO_3 \qquad (1)$$

A B

1A : R = R' = PH

2A : R = PH; R' = H

3A : R = R' = $CH_3(CH_2)_5$

4A : R = $CH_3(CH_2)_3$; R' = H

5A : R = $CH_3(CH_2)_2$; R' = PH

Representative data are collected in Table 1. According to a typical procedure, in a thermostatic bath at 40°C a DCE-methanol 9:1 (10 mL) metalperoxide solution was added in one portion to a DCE solution (15 mL) containing 0.01-0.1 M of the alkyne and the catalyst Hg$(OAc)_2$. The progress of the reaction was monitored by following the disappearance of the peroxide (iodometric titre)[9] and the appearance of the 1,2-dicarbonyl compound by g.l.c. (after quenching of the peroxide with Ph_3P[8], 2m OV-17 column). The products were isolated by column chromatography (silica-gel, cyclohexane-ethyl acetate 9:1), and identified by comparison with authentic samples and by their MS (Kratos MS 50), ^1H-NMR and ^{13}C-NMR (80 MHz, Bruker FT WP 80) spectra.

The presence of the mercuric salt-catalyst is required to promote the oxidation because the alkynes are totally inert toward oxodiperoxomolybdenum (VI) complex alone, and rather low alkyne to Hg$(OAc)_2$ ratios should be adopted to obtain high alkyne conversions in reasonable reaction times (Table 1). In the absence of the alkyne, one finds Hg$(OAc)_2$ does not enhance the decomposition of the metalperoxide significantly (a side reaction which invariably com-

Table 1. Mercuric acetate-promoted oxidation of representative alkynes with $(HMPA)MoO(O_2)_2$ in DCE at 40°C.

Substrate	Ratios[a]		%Conversion[b]	Reaction time (hrs)	Product[c]	%Yield[d]
	Alkyne to metal peroxide	Metal peroxide to $Hg(OAc)_2$				
(1a)	1.6	1.0	-	20	(1b)	80[e]
(1a)	0.4	2.5	94	20	(1b)	77
(1a)	0.4	2.5	75	3.5	(1b)	77
(2a)[i]	1.1	1.1	-	0.25	(2b)	90[e]
(3a)	1.0	1.0	76	3.5	(3b)	64[f]
(3a)	9.5	9.0	-	3.5	(3b)	55[e,g]
(4a)	1.1	1.0	-	0.25	(4b)	86[e,h]
(5a)	1.1	1.1	65	2.0	(5b)	70

[a] Alkyne initial concentration ranged from 0.01-0.1 M. [b] Based on alkyne reacted as determined by g.l.c. [c] Identified by recording the i.r., ^{1}H-NMR, U.V. and m.s. spectra of isolated samples (column chromatography). [d] As determined by g.l.c. with respect to the alkyne reacted. [e] As determined by g.l.c. with respect to the peroxide reacted. [f] Accompanied by tetradec-5-en-7-one (yield 11%). [g] Accompanied by tetradec-5-en-7-one (yield 25%). [h] Accompanied by 2-hexenal (yield ca. 8%). [i] At t = 0°C.

petes with substrate oxidation).

Furthemore we have observed that addition of 0.3 M $Hg(OAc)_2$ to 0.3 M $Ph-C\equiv C-CH_2CH_2CH_3$ in $CDCl_3$ results in a ca. 55 ppm downfield shift of the ^{13}C resonances for both carbons engaged in the carbon-carbon triple bond; similar observations were made by taking the ^{13}C-NMR spectra of substrates 3a and 4a in the presence of the mercuric salt. Akin to Hg^{2+}-promoted additions to alkynes[10], we believe that the role of mercuric acetate might be that of yielding π-complexes with the alkynes, thus favoring oxidative attack by the metalperoxide.

Inspection of data in Table 1 reveals that diaryl- and monoaryl, dialkyl and monoalkyl-, as well as aralkyl alkynes can all be converted into the corresponding α-dicarbonyl compounds in fair to good yields. These compare well with the yields of α-diketones obtainable by oxidation of alkynes with peroxoacids[3,4,5], osmium[6] or ruthenium[7] tetroxide or potassium permanganate[2]; oxidations with the latter oxidizer, however, should be carried out under carefully controlled conditions to afford α-diketones in good yields[2,11].

At any rate our method offers the advantage that also α-oxoaldehydes can be synthesized in excellent yields. Kinetics and further spectroscopic studies are now in progress to elucidate the oxidation mechanism into details. Meanwhile, we believe the data presented in this study outline that the mercuric acetate promoted oxidation of alkynes by (HMPA)$MoO(O_2)_2$ shows promise of becoming a new and general entry into the synthesis of α-dicarbonyls.

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