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Articles

Oxidation of Alkynes by Hydrogen Peroxide Catalyzed by Methylrhenium Trioxide

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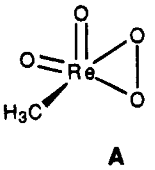
The oxidation of alkynes with hydrogen peroxide is catalyzed by methylrhenium trioxide. The reactions can be rationalized by postulating that an oxirene intermediate is formed between a rhenium peroxide and the alkyne. Internal alkynes yield α-diketones and carboxylic acids, the latter from the complete cleavage of the triple bonds. Rearrangement products were observed only for aliphatic alkynes. Terminal alkynes gave carboxylic acids and their derivatives and α-keto acids as the major products, but their yields varied with the solvent used.

Introduction

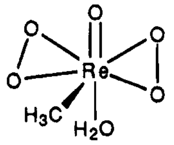
The stoichiometric oxidation of alkynes has been widely studied with reagents such as organic peracids,[1-3] thallium nitrate,[4] ruthenium[5] and osmium[6] tetraoxides, permanganate,[7,8] peroxomonophosphoric acid,[9] peroxomolybdenum complexes,[10] and dioxiranes.[11,12] Examples of catalytic oxidations are fewer.[13-16] The oxidation of terminal and internal alkynes usually yields different products. Terminal alkynes usually give carboxylic acids, coupling products, carboxylic acids with one carbon less, or α-keto carboxylic acids.[17] Internal alkynes, on the other hand, usually form α,β-unsaturated ketones, α-diketones, or cleavage products of the triple bond. The products formed depend on the nature of the oxidizing agent and the reaction conditions.[18-21]

Methylrhenium trioxide (CH_3ReO_3 or MTO) catalyzes the epoxidation of alkenes with hydrogen peroxide.[22-25] In addition, this rhenium compound catalyzes other oxygen-transfer reactions of hydrogen peroxide, such as the conversion of anilines to nitrosobenzenes and *N,N*-dimethylanilines to the amine oxides,[26] phosphines, arsines and stibines to their oxides,[27] organic sulfides to sulfoxides,[28] thiolatocobalt to the sulfenatocobalt complex,[29] and so on.

Two active forms of the catalyst have been identified, with 1:1 and 1:2 ratios of rhenium to peroxide. The formulas are $CH_3Re(O)_2(O_2)$, **A**, and $CH_3ReO(O_2)_2$, **B**, which has been characterized crystallographically.[23]



A



B

We have found that the oxidation of both terminal and internal alkynes by hydrogen peroxide is also catalyzed by MTO. These findings can be rationalized on the basis of an oxirene intermediate.

Results

Internal Alkynes. Three internal alkynes were used: diphenylacetylene, 4-octyne, and 4,4-dimethyl-2-pentyne. The reactions were carried out homogeneously in acetone and in various alcohols, and heterogeneously, in a two-phase system, methylene chloride−water. The products formed depend to some extent on the choice of

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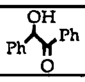
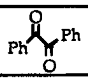
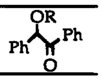
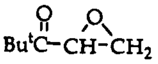
Table 1. Product Yields[a,b] from the Oxidation of Diphenylacetylene by Hydrogen Peroxide Catalyzed by MTO in Different Alcohols

Alcohol	Conv. %	Product			
		PhCOOH			
MeOH	87	7	–	79	4
EtOH	91	8	–	80	6
n-PrOH	90	10	–	74	7
n-BuOH	86	11	–	76	6
n-Amyl-OH	84	14	–	78	–
$PhCH_2OH$	86	16	6	75	–
2-BuOH	90	20	7	69	–
s-Amyl-OH	88	18	8	72	–
Cyclopentanol	89	19	7	71	–
$PhCH(CH_3)OH$	87	17	11	70	–
t-BuOH	86	16	12	72	–
t-Amyl	87	17	10	72	–

[a] Protocol: 1.78 g (10 mmol) diphenylacetylene, 1 mmol MTO, and 30 mmol hydrogen peroxide were used in 15 mL alcohol.

[b] Minor products, <10%, are from GC-MS, others are isolated yields.

Table 2. Product Yields[a] from the Homogeneous Oxidation of Alkynes by Hydrogen Peroxide, Catalyzed by CH_3ReO_3

Alkyne	Acetone	Methanol
PhC≡CPh (% conversion)	(69%)	(87%)
PhC(O)C(O)Ph	57%	79%
PhCH(OMe)C(O)Ph	–	4
$PhCO_2H$	tr.	7
$PhCO_2Me$		9
$Pr^nC≡CPr^n$	(>97%)	(>97%)
$Pr^nC(O)C(O)Pr^n$	43	41
$(Pr^n)_2CH_2CO_2H$	24	–
$Pr^nC(O)CH{=}CHCH_3$	11	17
Pr^nCO_2Me	–	15
$Bu^tC≡CMe$	(>99%)	(>99%)
Bu^tCO_2H	86	58
$Bu^tC(O)C(O)Me$	~3	16
 $Bu^tC(O)-CH(O)CH_2$	~2	~2
$Bu^tC(O)CH{=}CH_2$	~1	~2
Bu^tCO_2Me	–	12
$Bu^tC(O)CH(OMe)CH_3$	–	~4
$CH_3(CH_2)_6C≡CH$	(>96%)	(>96%)
$CH_3(CH_2)_6CO_2H$	95	18
$CH_3(CH_2)_6CO_2Me$	–	81
PhC≡CH	(88%)	(84%)
$PhCH_2CO_2H$	65	~2
$PhCH_2CO_2Me$	–	95
$PhC(O)CO_2H$	11	–

[a] Isolated yields, except minor products, <10%, from the GC-MS.

solvent. None of the alkynes reacted with hydrogen peroxide in 48 h, but all of them were oxidized when the rhenium compound was added.

Diphenylacetylene is resistant to oxidation by common organic peracids,[1,2] which afford complex product mixtures with poor yields and low conversions. With MTO–hydrogen peroxide, however, the reactions can be carried to a satisfactory conversion (>84%) in homogeneous solution. The products formed in twelve alcohol solvents, with excess hydrogen peroxide and 10% MTO, are summarized in Table 1. The product is principally benzil in acetone and methanol. In the biphasic system CH_2Cl_2–water, on the other hand, over-oxidation evidently occurs, and mainly benzoic acid is produced. Rearrangement products were not observed in any of these solvents. In methanol a small amount of the α-methoxy ketone was formed, and a trace of benzoic acid was also observed in acetone and methanol. The product is also principally benzil in the two-phase system. These results are similar to those obtained with trifluoroperacetic acid,[30] with benzil the major product and benzoic acid the minor one. In contrast, with dimethyldioxirane, ketene-derived products predominated.[11] Aromatic alkynes are less reactive under these conditions than aliphatic alkynes, which showed >95% conversion. The aliphatic alkynes led to more complex mixtures of products; however, in acetone and methylene chloride, the α-diketone, the α,β-unsaturated ketone, the α-hydroxy ketone, and the α,β-epoxy ketone were found, along with the carboxylic acid from rearrangement or cleavage of the triple bond. Thus, 4-octyne gave 2–4% of butyric acid in all three solvents. Other products, all minor, were also detected; see Table 2 for homogeneous reactions and Table 3 for the results under heterogeneous conditions.

Terminal Alkynes. Phenylacetylene and 1-nonyne were also included in this study. Compared to the internal alkynes, the products from the terminal alkynes were much simpler. The results are summarized in Tables 3–5. Oxidation of phenylacetylene in alcohols give satisfactory conversions. In primary alcohols, the major products are the esters, but they become minor in secondary alcohols (except cyclopentanol), and are not formed in tertiary alcohols. The major products are the carboxylic acids in acetone, the esters in methanol, and the α-keto carboxylic acid in the biphasic methylene chloride–water system. Not detected were the alkyne dimers, formed by the oxidation of the terminal alkyne, and the carboxylic acid from C–C cleavage.

The ratio of MTO to alkyne did not affect the product distribution, but it did alter the substrate conversion in a given reaction time. Oxidation of 10 mmol diphenylacetylene with 30 mmol hydrogen peroxide in methanol with varying quantities of MTO gave different conversions. MTO at 5% of Ph_2C_2 gave 65% conversion (80%

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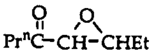
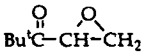
(30) Emmons, W. D.; Pagano, A. S. J. Am. Chem. Soc. 1955, 77, 80.

Table 3. Product Yields[a] from the Oxidation of Alkynes by Hydrogen Peroxide Catalyzed by CH_3ReO_3 in the Biphasic Solvent

Alkyne	Conversion (%)	Yield (%)
PhC≡CPh	73	
$PhC(O)C(O)Ph$		67
$PhCO_2H$		17
$Pr^nC≡CPr^n$	92	
$Pr^nC(O)C(O)Pr^n$		41
$Pr^nC(O)CH(OH)Pr^n$		24
 $Pr^nC(=O)-CH(O)CHEt$		21
$Bu^tC≡CMe$	94	
Bu^tCO_2H		~2
$Bu^tC(O)C(O)Me$		38
 $Bu^tC(=O)-CH(O)CH_2$		~2
$Bu^tC(O)CH=CH_2$		14
$(CH_3)_2C=C(CH_3)C(O)CH_3$		31
$CH_3(CH_2)_6C≡CH$	>95	
$CH_3(CH_2)_7CO_2H$		31
$CH_3(CH_2)_6C(O)CO_2H$		47
PhC≡CH	89	
$PhCH_2CO_2H$		21
$PhC(O)CO_2H$		68

[a] Minor products, <10%, are from the GC-MS, others are isolated yields.

benzil, 17% benzoic acid and ester); at 10% the conversion after 2 days was 87% (79% benzil, 14% benzoic acid and ester).

Limiting Peroxide. The data in the preceding sections pertain to experiments in which the alkyne was the limiting reagent with excess peroxide, the natural emphasis being the conversion of the alkyne. On the other hand, given the side-products observed, it became necessary to learn whether they are an immediate consequence of a complex pattern of reactions, or whether they more simply arise from the overoxidation of the primary and initial product, the α-diketone. Toward this end, we carried out experiments with excess diphenylacetylene (1 mmol), limiting peroxide (0.5 mmol), and 40 mg of MTO (0.16 mmol). Data were obtained for the conversion of the acetylene in the three solvents and for the product yields; the effective conversion relative to peroxide can also be obtained by calculation. These are the results:

Solvent	%Conversion of Ph_2C_2	%Conversion of H_2O_2 (calcd)	PhC(O)C(O)Ph	$PhCO_2H$/ $PhCO_2Me$
Acetone	12	50	87	11
Methanol	24	90	88	10
CH_2Cl_2	24	96	100	-

The reaction produces entirely benzil in methylene chloride and nearly so in the other solvents. The data also illustrate that the reaction is the slowest in acetone, where peroxide remains even after the five days at ambient temperature allowed for these reactions.

Table 4. Products from the Oxidation of Phenylacetylene by Hydrogen Peroxide Catalyzed by MTO in Primary Alcohols

		products (%)	
alcohol	conversion (%)	ester	acid
MeOH	88	96	trace
EtOH	87	96	trace
n-PrOH	85	95	~3
n-BuOH	90	94	~4
n-amyl-OH	87	85	10
$PhCH_2OH$	86	60	33
$PhCH_2CH_2OH$	82	47	50

[a] Protocol: 1.03 g (10 mmol) of phenylacetylene, 1 mmol of MTO, and 30 mmol of hydrogen peroxide were used in 15 mL of alcohol. [b] Minor products, <10%, are from GC-MS; others are isolated yields.

Table 5. Product Yields[a,b] from the Oxidation of Phenylacetylene by Hydrogen Peroxide Catalyzed by MTO in Secondary and Tertiary Alcohols

		product (%)			
alcohol	conversion	$PhCO_2H$	$PhCH_2CO_2H$	$PhCO_2R$	$PhCH_2CO_2R$
2-BuOH	84%	38	17	8	30
sec-Amyl-OH	87	40	15	11	30
cyclopentanol	85	trace	10		84
$PhCH(CH_3)OH$	83	47	41		5
tert-BuOH	79	23	74		
tert-Amyl-OH	84	22	71		

[a] Protocol: 1.03 g (10 mmol) of phenylacetylene, 1 mmol of MTO, and 30 mmol of hydrogen peroxide were used in 15 mL of alcohol. [b] Minor products, <10%, are from GC-MS; others are isolated yields.

The oxidation of benzil itself was also investigated under the same conditions: 0.25 mmol of benzil, 0.5 mmol of peroxide, and 0.26 mmol of MTO in acetone. After five days, only about 8% of the benzil had been converted to benzoic acid, suggesting that the overoxidation of benzil is not the only route to this product.

Discussion

Because the reactions were carried out with excess hydrogen peroxide, **B** was the predominant form of the catalyst given the equilibrium constants for peroxide binding to MTO.[26] From the kinetic data, both **B** and dimethyldioxirane (DMDO)[11] have similar reactivities toward alkenes.[31] This evidently holds as well for alkynes. DMDO gives predominantly ketene-derived products, whereas MTO yields α-diketones as the major products from internal alkynes. In the biphasic solvent mixture, MTO proved more reactive than peroxotungstophosphate, which gave <50% conversion of diphenylacetylene.[32]

The results obtained for alkyne oxidations, along with comparisons with the reactions in which alkenes are converted to epoxides by MTO/H_2O_2, lead us to suggest that the reaction proceeds initially with the formation of an oxirene intermediate. These elusive species have been alluded to previously.[33,34] The initial step may be as shown in eq 1:

The ruthenium tetraoxide-catalyzed reaction[35] serves as a precedent for this reaction. No mechanism was

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[31] Al-Ajlouni, A.; Espenson, J. H. *J. Org. Chem.*, submitted.

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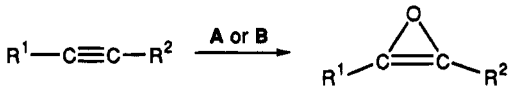
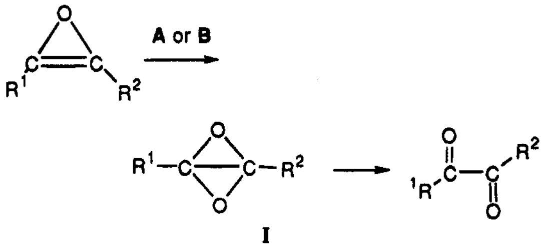


(1)

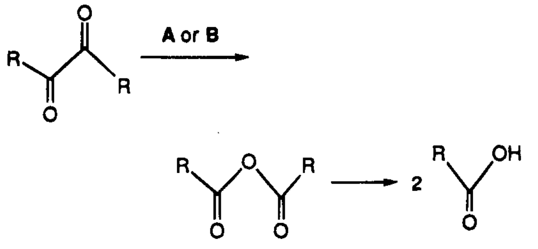
suggested, however, although it seems reasonable that the pathway is analogous to that of osmium tetraoxide.[36] Following that step, it is further reasonable to propose yet another epoxidation step, such that a "double epoxide", intermediate **I**, would intervene on the path to the major product, the diketone:



I (2)

Accepting this proposed pathway provisionally, we ask about the subsequent steps. Either the formation of **I** follows a concerted mechanism, such that an oxirene intermediate does not form, or the rearrangement of the oxirene to form a ketone (or a ketene, as shown subsequently) occurs more slowly than oxygen transfer from **A** or **B** to the oxirene double bond.

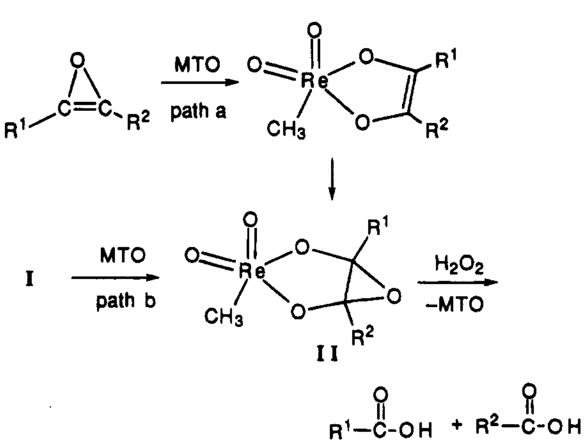
The carboxylic acids are formed by cleavage of the triple bond, for which two pathways can be explored. First, we consider the typical conversion of an α-diketone to two carboxylic acids by a Baeyer–Villiger oxidation, eq 3.[37]



(3)

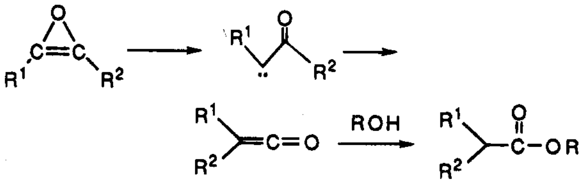
Cleavage of an alkyne triple bond to give two carboxylic acids is well known using metal oxides.[38] The mechanism by which **A** and **B** may act is very likely similar to that proposed for permanganate,[7,8] ruthenium tetroxide,[5] and thallium(III) nitrate.[4]

We would also put forth a mechanism similar to that for the reaction between CH_3ReO_3 and epoxides,[39] This possible pathway involves the reaction of the oxirene with MTO to form a "bisalkoxy" complex whose C=C double bond is then converted to an epoxide with **A** or **B**; we call this path a and note that it will form a second intermediate, **II**. Oxidation of **II** yields the carboxylic acid upon cleavage of the C–C bond. An alternative is presented by path b, which allows **II** to be formed from MTO and **I**, eq 4.



(4)

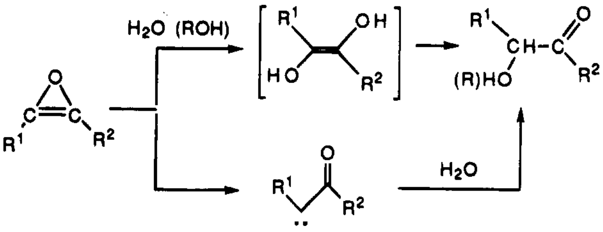
The carboxylic acids, or their methyl esters in methanol, were possibly formed from both terminal and internal alkynes by a ketene rearrangement. The following equations depict the oxidation of the alkyne to an oxirene by **A** or **B**. The oxirene then rearranges to a ketene which adds water (or methanol) to generate the acid (or ester), as in eq 5.



(5)

The conversion of the carbene to a ketene, the photochemical Wulff rearrangement, finds precedent.[33] Unlike other secondary alcohols, the oxidation of phenylacetylene in cyclopentanol gives a higher yield of the ester. As a result, we suggest the competition between water and alcohols is subject to a steric influence, as the relatively inflexible structure of cyclopentanol offers less steric demand than the other, freely-rotating alcohols.

The α-hydroxy (or methoxy) ketones, we believe, form directly from the oxirene intermediate. Two possible schemes are illustrated by eq 6.



(6)

According to this, the oxirene either undergoes nucleophilic attack by water, giving an intermediate that then rearranges to the α-hydroxy ketone (as suggested by the ring-opening reaction of epoxides with water[40]), or it rearranges to an oxocarbene which then undergoes an insertion reaction with water.[9]

The α,β-unsaturated products were obtained only for the internal alkynes. These products are believed to result from an intermediate that arises from rearrangement of an oxirene. α,β-Epoxy ketones are formed by the direct oxidation of α,β-unsaturated products with **A** or **B**. That is depicted by this equation sequence in which R' is Me for 4,4-dimethyl-2-pentyne and R' is H for all the others:

The final step in this reaction, the conversion of an α,β-unsaturated ketone to an α,β-epoxy ketone, can be carried

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(36) Collin, R. J.; Jones, J.; Griffith, W. P. *J. Chem. Soc. Dalton Trans.* **1974**, 1094.

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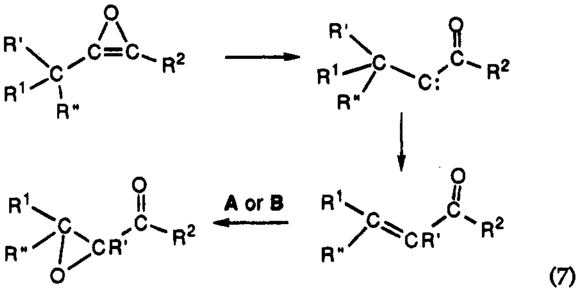
(39) Zhu, Z.; Espenson, J. H. *J. Mol. Catal.* **1995**, in press.



(7)

out by MCPBA[3] and hydrogen peroxide.[41] This conversion requires alkaline conditions and utilized HOO^-. It is possible, based on this precedent, that ring-opened forms of **A** or **B** are responsible for the final step in eq 7.

Experimental Section

Materials. The alkynes were obtained from commercial sources, and the purity of each was verified by GC-MS before use. The solvents were purified by standard methods.[42] Hydrogen peroxide (30%, Fisher) was used without further treatment. Methylrhenium trioxide[43] was prepared from Re_2O_7 and $Sn(CH_3)_4$ according to the literature procedure.[44]

Procedures for the Oxidation of Alkynes. The alkyne (30 mmol) was dissolved in 300 mL of acetone or methylene chloride, and then CH_3ReO_3 (10 mol % of the alkyne) was added. After the solid had dissolved, a moderate excess of hydrogen peroxide (100 mmol) was added. The reaction vessel was closed, and the solution was stirred for two days at room temperature, during which time the reaction was monitored by GC-MS. The excess of peroxide was decomposed by adding a little manganese dioxide. After filtration, most of the solvent was removed under vacuum, and then the solution was extracted with ether three times. The ether was removed, the residue was dried over magnesium sulfate, and the products were separated by fractional distillation under vacuum.

The known products from 4-octyne and 4,4-dimethyl-2-pentyne were identified by comparison to data in the literature.[7,12] Spectroscopic data and the results of elemental analysis are given in the supporting information.

When an alcohol was used as the solvent, only 10 mmol of diphenylacetylene and phenylacetylene, 1 mmol MTO, and 30 of mmol H_2O_2 were used. After decomposition of the excess hydrogen peroxide with MnO_2, the products were separated by distillation under reduced pressure or vacuum. Benzil obtained from the distillation was recrystallized from ethanol. The products were identified by ^{1}H-NMR, ^{13}C-NMR, and by mass spectroscopy in comparison with the results from NMR and MS libraries; see supporting information.[45,46]

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Supporting Information Available: The spectroscopic and analytical data for the materials produced (5 pages). This material is contained in libraries on microfiche, immediately following this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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