(40%) of **5c** and 13 mg (21%) of **5t**: NMR δ 1.15 (d, 3 H, J = 6.9 Hz, C_2 methyl), 1.41–1.95 (m, 6 H, C_4–C_6 methylenes), 2.30–2.60 (m, 2 H, C_7 methylene), 2.69 (d × q, 1 H, J = 6.9, 6.9 Hz, C_2 methine), 3.22–3.70 (d, 1 H, C_3 methine), 3.29 (s, 3 H, methoxyl). Irradiation at δ 1.15 caused the peak at δ 2.69 to become a doublet, J = 6.9 Hz. Mass spectrum, m/e (rel intensity) 156 (9), 124 (18), 111 (19), 88 (35), 85 (26), 84 (100), 82 (35); high resolution, calcd for $C_9H_{16}O_2$ 156.11502, found 156.11540.

A similar reaction in CH_3OD for 48 h gave 30% recovered **4**, 26% of **5c**-d_3 and 14% of **5t**-d_3. The NMR spectra showed that the deuterium was at C_2 and C_7. For **5c**-d_3: NMR δ 1.15 (br s, 3 H, C_2 methyl), 1.4–1.62 (m, 6 H, C_4–C_6 methylenes), 3.23 (s, 3 H, methoxyl), 3.35 (d, 1 H, J = 5.5 Hz, C_3 methine coupled with a C_4 proton). For **5t**-d_3: NMR δ 1.17 (br s, 3 H, C_2 methyl), 1.21–1.83 (m, 6 H, C_4–C_6 methylenes), 3.20–3.24 (m, 1 H, C_3 methine), 3.31 (s, 3 H, methoxyl).

Base-Catalyzed Exchange of 5. A solution of **5c** (40 mg) in 0.01 M sodium methoxide in CH_3OD (5 mL) was stirred at room temperature for 22 h. Workup, including preparative VPC, of half the solution gave **5c**-d_3 (10 mg, 50%) and **5t**-d_3 (4 mg, 20%); after 44 h, the remainder of the solution gave **5c**-d_3 (9 mg, 45%) and **5t**-d_3 (4 mg, 20%). A similar experiment with 0.1 M sodium methoxide in CH_3OH gave, after 32 h, 21 mg (52%) of **5c** and 11 mg (27%) of **5t**.

Base-Catalyzed Addition of Methanol to 6. A solution of **6** (76 mg, 0.55 mmol) in 15 mL of 0.01 M methanolic sodium methoxide was stirred at room temperature, and the reaction was followed by VPC (5 ft × 0.125 in column, 5% SE30 on Chromosorb G, 170 °C). Only a small amount of product was formed in 24 h. The maximum yield was obtained in 192 h, at which time the mixture contained 45% **6**, 20% **7c** and 35% **7t**. The ratio did not change after 2 weeks. For **7t**: IR (CCl_4) 2940 (s), 1705 (s), 1465 (m), 1100 (s) cm^{-1}; NMR ($CDCl_3$) δ 1.14 (d, 3 H, J = 6 Hz, C_2 methyl), 1.25–2.2 (br m, 8 H, C_4–C_7 methylenes), 2.35 (br m, 2 H), 2.95 (br m, 2 H), 3.28 (s, 3 H, methoxyl); mass spectrum, m/e (rel intensity) 170 (5), 138 (31), 123 (6), 109 (23), 98 (21), 81 (29), 71 (100).

LIS shift date were obtained on **7c** and **7t** using $Eu(fod)_3$. The values of Δ (ppm), the shift of each peak caused by adding 1 mol of shift reagent per mol of substrate, were: for **7c**, 10.4 (C_2 methine), 8.7 (C_2 methyl), 8.2 (C_8 methylene), 7.4 (C_3 methine), 4.4 (methoxyl); for **7t**, 4.9 (C_8 methylene), 4.6 (C_2 and C_3 methine), 3.2 (C_2 methyl), 1.4 (methoxyl).[19]

Base-Catalyzed Exchange of 7. A solution of **7c** (25 mg) in 5 mL of 0.01 N methanolic sodium methoxide was stirred at room temperature, and the reaction was followed by VPC. In 24 h, the composition was 45% **6**, 20% **7c**, and 35% **7t**, after which there was no further change.

Acid-Catalyzed Addition of Methanol to 4. A solution of **4** (60 mg) in 3 mL of 0.01 M sulfuric acid in methanol was kept at room temperature. After 29 h, very little **4** remained. The solution was neutralized with sodium bicarbonate, the methanol was removed in vacuo, and the aqueous solution was extracted with ether. NMR (180 MHz) on the crude product showed a 1:1 mixture of **5c** and **5t** (integration of the methyl and methoxyl signals). The ratio was the same after 49 h.

Isomerization Test on 5c with Acid. A solution of **5c** (30 mg) in 0.01 M sulfuric acid in methanol (1.5 mL) was kept at room temperature for 50 h. An NMR spectrum on the crude product, worked up as above, showed only recovered **5c**, no **5t**.

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Registry No. 4, 65371-57-5; **5c**, 70527-90-1; **5c**-d, 70527-91-2; **5c**-d_3, 70527-92-3; **5t**, 70527-93-4; **5t**-d_3, 70527-94-5; **6**, 70527-95-6; **7c**, 70527-96-7; **7t**, 70527-97-8; **8**, 14525-83-8; **9**, 70527-98-9; **10**, 60934-87-4; **11**, 70527-99-0; **12**, 70528-00-6; **12** epoxide, 70528-01-7; cycloheptanone, 502-42-1; *unsym*-dimethylhydrazine, 57-14-7; cycloheptanone *N*,*N*-dimethylhydrazone, 39672-01-0; 2-methylcycloheptanone *N*,*N*-dimethylhydrazone, 70528-02-8; 2-methylcycloheptanone, 932-56-9; 2-bromo-2-methylcycloheptanone, 70528-03-9; cyclooctanone, 502-49-8; cyclooctanone *N*,*N*-dimethylhydrazone, 62461-18-1; 2-methylcyclooctanone *N*,*N*-dimethylhydrazone, 70528-04-0; 2-methylcyclooctanone, 10363-27-6; 2-bromo-2-methylcyclooctanone, 70528-05-1; 1,2-dimethyl-2-cycloocten-1-ol, 70528-06-2.

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[19] Important differences between the two isomers are (a) generally larger Δ's for **7c** than for **7t**, (b) a larger difference between the C_2 and C_3 methine slopes for **7c** than for **7t**, and (c) a greater Δ for the C_2 methine than for the C_8 methylene protons in **7c** but not in **7t**. These data suggest coordination only at the carbonyl in **7t**, in a conformation in which both the C_2 methyl and C_3 methoxyl are pseudoequatorial, but some bidentate coordination[5] in **7c**, with the methoxyl and methyl pseudoaxial and equatorial, respectively.

Oxidation of Hydrocarbons. 9. The Oxidation of Alkynes by Potassium Permanganate

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A study of the oxidation of nonterminal alkynes by potassium permanganate has revealed that the reaction can be directed along any one of three different pathways: (i) In aqueous solutions, cleavage of the carbon–carbon triple bond, with formation of carboxylic acids, is the main reaction. (ii) In anhydrous methylene chloride solutions, the phase transfer assisted reaction leads to formation of α-diketones in good yields. (iii) In methylene chloride solutions in contact with aqueous permanganate, the phase transfer assisted reaction gives α-diketones plus cleavage products. In the last case, the cleavage reaction results in the loss of one carbon atom, indicating that it proceeds by way of an enol (RCOC(OH)=CHR′) to an α-ketocarboxylic acid which subsequently undergoes an oxidative decarboxylation. The assumption that α-diketones are intermediates in the cleavage reactions was substantiated by a study of the oxidation of 8,9-hexadecanedione and 7,8-tetradecanedione under a variety of conditions.

There appears to be little agreement among various authors on the products to be expected from the oxidation of alkynes by potassium permanganate. For example, Freeman[1] states that "Neutral permanganate solution oxidizes carbon–carbon triple bonds to diketones in excellent yield", while Raphael[2] maintains that "the end products [are] two carboxylic acid molecules". This confusion is also reflected in the statements found in

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[1] Freeman, F. *Rev. React. Species Chem. React.* **1973**, 2, 179. This particular statement appears on p 197.

[2] Raphael, R. A. "Acetylenic Compounds in Organic Synthesis"; Academic Press: New York, 1955; p 31.

Table I. The Oxidation of Alkynes by Aqueous Potassium Permanganate[a]

substrate	reaction time, h	recovered substrate, %	products (% yield)
8-hexadecyne	18	94	
8-hexadecyne[b]	6	93	
7-tetradecyne	18	91	
1-phenyl-1-pentyne	12	90	benzoic acid (8), 1-phenyl-1,2-pentanedione (trace)
5-decyne	18	56	valeric acid (19), 5,6-decanedione (trace)
4-octyne	17	6	butyric acid (73), propionic acid (6)
4-octyne[c]	2	20	butyric acid (62), propionic acid (trace), 4,5-octanedione (2)

[a] 1.7 mol of potassium permanganate per mol of alkyne. [b] 0.1 M NaOH. [c] 1% H_2SO_4.

textbooks of organic chemistry. Some books show cleavage as the primary reaction,[3] while others suggest that formation of diketones is a general reaction.[4] Almost all assume that diketones are intermediates in the cleavage reactions,[1,4] although the oxidative cleavage of α-diones has not been studied.

The assumption that diketones can be easily prepared from alkynes by permanganate oxidations appears to have originated primarily with the work of Khan and Newman[5] who showed that stearolic acid could be converted to 9,10-diketostearic acid.

$$CH_3(CH_2)_7C{\equiv}C(CH_2)_7CO_2H \xrightarrow[\text{pH 7.5}]{MnO_4^-} CH_3(CH_2)_7C(O)C(O)(CH_2)_7COOH \quad (1)$$

It should be noted, however, that in order to obtain a good yield these authors found it necessary to meet two specific conditions: (i) careful pH control was required to avoid the corresponding cleavage reaction, and (ii) the alkyne contained a substituent that made it soluble in aqueous solutions. When the pH of the solution was increased to about 12, cleavage products (including azelaic acid) were obtained, and at low pH no reaction occurred because of the insolubility of the substrate.

In order to obtain a better understanding of this potentially important reaction, we have made a study of the oxidation of several representative alkynes and diketones, both in aqueous solutions and, with the aid of phase transfer agents,[6] in nonaqueous solvents.

Results

Oxidations were carried out under three different conditions: (i) in aqueous solutions, (ii) in "wet" methylene chloride solutions containing a phase transfer agent and in contact with aqueous permanganate, and (iii) in anhydrous methylene chloride solutions containing a phase transfer agent and in contact with powdered potassium permanganate.[7] The results of these experiments are summarized in Tables I and II. The use of phase transfer agents to solubilize permanganate ion in nonaqueous solvents has previously been discussed by several authors.[8-10]

The oxidation of alkynes requires slightly more vigorous conditions than those which have been used for alkene oxidations;[10] in order for the reaction to proceed at a reasonable rate, it is necessary to work above room temperature. Experimentation showed that the use of refluxing methylene chloride provided a convenient temperature at which to work. Permanganate ion may also be solubilized in benzene[11] by phase transfer agents; however, this solvent reacts with oxidant fairly rapidly at reflux temperatures.

Since it seems quite probable that α-diketones are formed as intermediates during the oxidative cleavage of alkynes, we also studied the oxidation of 8,9-hexadecanedione and 7,8-tetradecanedione under several conditions (Table III).

In all of these reactions, the solvent was acidified (3–12% by volume acetic acid). Previous work has shown that this is necessary to neutralize the hydroxide ions formed (according to eq 2) whenever permanganate ion is reduced.[8,10]

$$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^- \quad (2)$$

Discussion

The results presented in Table I indicate that long chain alkynes such as 8-hexadecyne and 7-tetradecyne are not readily oxidized by aqueous permanganate. The lack of reaction appears to be associated with the insolubility of these compounds in water; shorter chain compounds, such as 4-octyne, which have greater solubility in water, undergo cleavage more easily. In every case where reaction occurred, cleavage products predominated, suggesting that the proposed intermediate diketones undergo oxidative cleavage faster than formation. This may also be a consequence of the solubility properties of the respective compounds; the diketones, being more polar than the parent alkynes, would be more soluble in aqueous solutions and thus experience greater contact with the oxidant.

The results in Table I are in agreement with those reported by Johnson, Schwartz, and Jacobs[12] who found that alkynes such as 3-dodecyne gave propionic and pelargonic acid when treated with aqueous permanganate. Diketones have been reported as products of aqueous permanganate oxidations only when the alkynes contained polar groups that would increase their solubility in water.[5,13] With increased solubility there would be a more even competition between the alkyne and the corre-

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(3) For example see: Solomons, T. W. G. "Organic Chemistry", Wiley: New York, 1976; pp 327 and 328.

(4) For example see: Ternay, A. L., Jr. "Contemporary Organic Chemistry"; W. B. Saunders Company: Philadelphia, Pa., 1976; pp 277 and 278.

(5) Khan, N. A.; Newman, M. S. *J. Org. Chem.* **1952**, *17*, 1063.

(6) Weber, W. P.; Gokel, G. W. "Phase Transfer Catalysis in Organic Synthesis"; Springer-Verlag: New York, 1977. Starks, C. M.; Liotta, C. "Phase Transfer Catalysis"; Academic Press: New York, 1978.

(7) Cairox M, a finely powdered form of potassium permanganate, is available from the Carus Chemical Co.

(8) Krapcho, A. P.; Larson, J. R.; Eldridge, J. M. *J. Org. Chem.* **1977**, *42*, 3749.

(9) Foglia, T. A.; Barr, P. A.; Malloy, A. J. *J. Am. Oil Chem. Soc.* **1977**, *54*, 858A.

(10) Lee, D. G.; Chang, V. S. *J. Org. Chem.* **1978**, *43*, 1532.

(11) Sam, D. J.; Simmons, H. E. *J. Am. Chem. Soc.* **1972**, *94*, 4024. Fieser, L. F.; Williamson, K. I. "Organic Experiments", 3rd ed.; D. C. Health and Co.; Lexington, Mass., 1975; p 386.

(12) Johnson, J. R.; Schwartz, A. M.; Jacobs, T. L. *J. Am. Chem. Soc.* **1938**, *60*, 1882.

(13) Dupont, G.; Dulou, R.; Lefort, D. *Bull. Soc. Chim. Fr.* **1949**, 789. Fiesselmann, H.; Sasse, K. *Chem. Ber.* **1956**, *89*, 1791. Holand, S.; Epsatein, R. *Bull. Soc. Chim. Fr.*, 1971, 1694.

Table II. The Phase Transfer Assisted Oxidation of Alkynes by Permanganate Ion in Methylene Chloride

expt no.	substrate	oxidant[a] ratio	phase transfer agent[b]	oxidant phase	additives	reaction time, h	recovered substrate, %	products (% yield)
1	phenylacelylene	2.7	DMPEG[c]	solid	5% acetic acid	4		benzoic acid (91)
2	1-hexyne	2.7	DCHC[d]	solid	5% acetic acid	4		valeric acid (74)
3	diphenylacetylene	3.0	Adogen 464	aqueous	5% acetic acid	6		benzil (93) benzoic acid (2)
4	1-phenyl-1-pentyne	2.7	Adogen 464[e]	solid	5% acetic acid	4	7	1-phenyl-1,2-pentanedione (81)
5	1-phenyl-1-pentyne	2.7	none	solid	5% acetic acid	4	94	1-phenyl-1,2-pentanedione (trace)
6	1-phenyl-1-pentyne	4.1	Adogen 464	aqueous	5% acetic acid	6	2	1-phenyl-1,2-pentanedione (56), benzoic acid (24), propionic acid (16)
7	1-phenyl-1-hexyne	4.1	Adogen 464[e]	aqueous	5% acetic acid	6	2	1-phenyl-1,2-hexanedione (41), benzoic acid (32), butyric acid (27)
8	7-tetradecyne	2.7	Adogen 464[e]	solid	5% acetic acid	4	39	7,8-tetradecanedione (54)
9	7-tetradecyne	2.0	Adogen 464	aqueous	12% acetic acid	4.7	10	7,8-tetradecanedione (54), heptanoic acid (25), hexanoic acid (17)
10	7-tetradecyne	4.0	Adogen 464	aqueous	3% acetic acid	18		heptanoic acid (78), hexanoic acid (56)
11	8-hexadecyne	1.5	Adogen 464	solid	5% acetic acid	4	5	8,9-hexadecanedione (80), octanoic acid (5), heptanoic acid (trace)
12	8-hexadecyne	2.0	Adogen 464[e]	aqueous	5% acetic acid	4	13	8,9-hexadecanedione (65), octanoic acid (8), heptanoic acid (10)

[a] The mole ratio of $KMnO_4$ to alkyne. [b] Phase transfer agent: Adogen 464, a methyltrialkyl(C_8–C_{10})ammonium chloride, was obtained from Ashland Chemicals;[10] DMPEG is dimethylpoly(ethylene glycol);[10] and DCHC is dicyclohexano-18-crown-6.[10] [c] Similar yields were obtained with DCHC and Adogen 464. [d] Somewhat lower yields were obtained with DMPEG and Adogen 464. [e] Somewhat lower yields were obtained with DCHC and DMPEG.

sponding diketone for reaction with the oxidant.

Table II indicates that the oxidation of alkynes in anhydrous methylene chloride (experiments 4, 8, and 11) leads to formation of the diketone with little or no cleavage. However, when aqueous permanganate was used as the source of oxidant, greater amounts of cleavage occurred (experiments 3, 6, 7, 9, 10, and 12). Interestingly, it was found that under these conditions cleavage took place with the loss of one carbon atom; e.g., the oxidative cleavage of 7-tetradecyne did not produce 2 mol of heptanoic acid, *but* substantial quantities of both heptanoic and hexanoic acid were produced (experiment 10). Similarly, the oxidation of 8-hexadecyne gave octanoic and heptanoic acids in addition to 8,9-hexadecanedione (experiment 12). Such an unsymmetrical cleavage is exactly what would be expected if the intermediate diketone was reacting in its enol form. (See Scheme I, path a.)

Cleavage of the enol of 7,8-tetradecanedione would result in the formation of hexanal (which would undergo subsequent oxidation to hexanoic acid) and α-ketooctanoic acid (which would rapidly undergo oxidative decarboxylation, giving heptanoic acid). Independent experiments showed that both aldehydes and α-ketocarboxylic acids are rapidly oxidized under the experimental conditions employed.

Apparently this cleavage reaction occurs much more rapidly when the organic solvent is "wet" from being in contact with an aqueous solution of potassium permanganate. As previously noted, oxidation of these same compounds under dry conditions does not result in extensive cleavage. Presumably the presence of some water promotes the enolization reactions.

Why then do the oxidative cleavages by aqueous permanganate not also proceed with the loss of a carbon atom? It is possible that enol formation is suppressed in aqueous as compared to organic solvents.[14] Alternatively, the change in products may be a reflection of the possibility that symmetrical cleavage proceeds by way of a more polar transition state (path b, Scheme I) which would be stabilized by solvation in aqueous solvents.

In an attempt to further investigate the reaction, we have examined the oxidation of two diketones in both aqueous and organic solvents (Table III). The results indicate that the oxidative cleavage of these compounds by permanganate in water is almost entirely symmetrical; however, in wet organic solvents (both methylene chloride and acetone) the cleavage of the diketone proceeds with loss of a carbon atom. Since these results are the same as those observed for the oxidative cleavage of the corresponding alkynes, they strongly substantiate the assumption that diones are likely intermediates in the cleavage reactions.

It should be noted that in almost every case where cleavage occurred more of the longer chain acid was obtained. This suggests that there is a competition between the two cleavage reactions under all conditions with unsymmetrical cleavage predominating in organic solvents and the converse in aqueous solvents. Note that small amounts of propionic acid were obtained from the oxidation of 4-octyne by aqueous permanganate (Table I). It is also possible that some products of unsymmetrical cleavage may have been present but were lost during the purification process, for those reactions previously reported in the literature.[12]

The observation that 7,8-tetradecanedione is oxidized more slowly in anhydrous methylene chloride than it is

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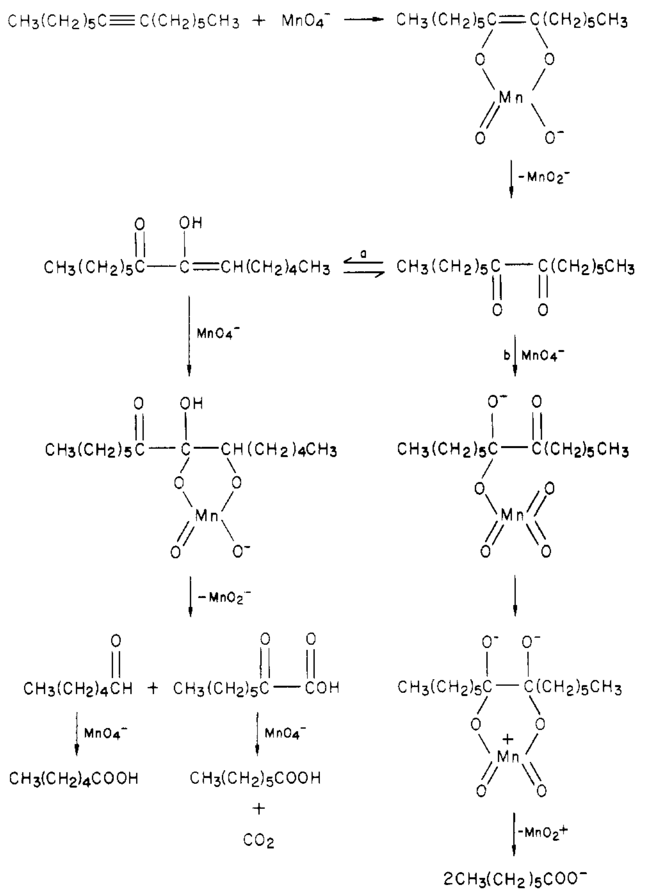
(14) Gould, E. S. "Mechanism and Structure in Organic Chemistry"; Holt-Dryden: New York, 1959; p 380.

Table III. The Oxidation of Diketones by Potassium Permanganate

diketone	solvent	reaction time, h	recovered substrate, %	products (% yield)
7,8-tetradecanedione	methylene chloride[a]	24	70	heptanoic acid (13), hexanoic acid (11)
7,8-tetradecanedione	methylene chloride/water[a,b]	24	26	heptanoic acid (50), hexanoic acid (44)
8,9-hexadecanedione	methylene chloride/water[a,b]	24	6	octanoic acid (83), heptanoic acid (70)
8,9-hexadecanedione	acetone/water[a,c]	24	35	octanoic acid (58), heptanoic acid (38)
8,9-hexadecanedione	water	18	25	octanoic acid (62), heptanoic acid (6)
8,9-hexadecanedione	water/H_2SO_4[d]	18	20	octanoic acid (68), heptanoic acid (3)

[a] 5% acetic acid. [b] The oxidant was added as an aqueous solution. [c] 5% water. [d] 1% H_2SO_4.

Scheme I



when water is present (compare the first two entries in Table III) explains why diketones may be obtained in better yields under anhydrous conditions.

The Reaction Mechanism. The mechanism proposed by Simandi and Jaky[2,15] for the formation of diones appears to be consistent with this work. It involves the formation of an intermediate manganese(V) diester which undergoes an internal electron transfer with the release of manganese(III) as the dione forms (Scheme I). In nonaqueous solvents, the dione would then enolize and be oxidized by a mechanism which would probably be similar to the one which has been proposed to account for the oxidative cleavage of alkenes[16] (path a).

Oxidation of the diketone in aqueous solutions, which results in a symmetric cleavage of the carbon–carbon bond between the two carbonyl groups, may be somewhat reminiscent of the oxidative cleavage of diones by periodate.[17] The reaction is initiated by a nucleophilic attack of the oxidant on a carbonyl carbon followed by cyclization and oxidative decomposition (path b). It should be noted that this reaction involves formation of a highly charged intermediate (and presumably a similar transition state) which would require extensive solvation. Hence we can understand why the reaction does not follow this pathway in organic solvents. The oxidative cleavage of the corresponding enol (path a) does not involve the formation of highly charged intermediates.

Applications to Organic Synthesis. It is apparent that these results have a direct application to organic synthesis. If one wishes to prepare α-diketones uncontaminated by cleavage products, it is best to use anhydrous solvents. On the other hand, if one wishes to cleave the alkyne it can be done symmetrically (in aqueous solutions) or unsymmetrically (in "wet" methylene chloride or acetone).

It has been our experience that the production of a good yield of diketone in anhydrous methylene chloride required the use of excess oxidant, apparently because some of the oxidant gets trapped in the mass of manganese dioxide which precipitates as the reaction proceeds. This problem can be partly avoided by slowly adding finely powdered potassium permanganate[7] as the reaction proceeds; however, the filter cake always contains residual oxidant. It is quite possible that substantial amounts of the residual oxidant are in the form of manganate(VI), which results from the reaction of MnO_2^- (formed in Scheme I) with permanganate ion.

$$MnO_2^- + MnO_4^- \rightarrow MnO_2 + MnO_4^{2-} \quad (3)$$

Since the manganate(VI) ion (being a dianion) would be more difficult to solvate in methylene chloride by use of phase transfer agents,[6] it would likely precipitate with the manganese dioxide.

A possible way to overcome this problem would be to use aqueous permanganate as the source of oxidant. The manganese(VI) would then move into the aqueous phase and disproportionate according to[18]

$$3MnO_4^{2-} + 2H_2O \rightarrow 2MnO_4^- + MnO_2 + 4OH^- \quad (4)$$

Unfortunately, as we have seen previously, the use of aqueous permanganate promotes a cleavage reaction and one is then forced to choose between two alternatives: either to use excess oxidant or to accept decreased yields because of cleavage. Since the oxidant is usually the least expensive component of these reactions, the former alternative is normally to be preferred. These synthetic applications have been briefly discussed in a previous

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(15) Simandi, L. T.; Jaky, M. *J. Chem. Soc., Perkin Trans.* **1973**, 1861.
(16) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1974**, *96*, 5517.
(17) Dryhurst, G. "Periodate Oxidation of Diol and Other Functional Groups"; Pergamon Press: New York, 1970; pp 43 and 44.
(18) Stewart, R. In "Oxidation in Organic Chemistry Part A", Wiberg, K. B., Ed.; Academic Press: New York, 1965; pp 2 and 3.

communication[19] and three typical reactions are described in the following section.

Table II also includes two terminal alkynes, phenylacetylene and 1-hexyne, which were known from previous work[8] to undergo conversion to the corresponding carboxylic acid with the loss of one carbon atom. A possible pathway for these reactions that is consistent with the other work reported here would involve the formation of dicarbonyl intermediates:

$$RC{\equiv}CH \xrightarrow{MnO_4^-} RC(O)C(O)H \xrightarrow{MnO_4^-}$$
$$RC(O)COOH \xrightarrow{MnO_4^-} RCOOH + CO_2$$

Experimental Section

The Oxidation of 4-Octyne by Aqueous Permanganate. 4-Octyne (0.009 mol) was added to a 1% aqueous solution of $KMnO_4$ (250 mL) in a 500-mL flask. The mixture was stirred vigorously for 17 h and then acidified (50% H_2SO_4). The precipitated manganese dioxide was reduced by addition, in small portions, of the required amount of sodium bisulfite. The solution was saturated with sodium chloride and extracted with 3 × 50 mL of ether. The combined organic extracts were dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation. Analysis of the resulting liquid residue by GLC indicated the presence of three compounds in addition to solvent–butyric acid, propionic acid, and 4-octyne. The calculated yields were 73, 6, and 6%, respectively.

The Phase Transfer Assisted Oxidation of 8-Hexadecyne in Dry Methylene Chloride. A 500-mL Erlenmeyer flask, equipped with a reflux condenser, was charged with methylene chloride (100 mL), acetic acid (5 mL), and 8-hexadecyne (2.0 g, 0.009 mol). The solution was heated to reflux temperature before 1.5 g of phase transfer agent (Adogen 464) and powdered potassium permanganate[7] (8.5 g, 0.054 mol) were added. The solution was stirred magnetically and refluxed for 4 h. After cooling, sodium bisulfite (5 g in 100 mL of water) was added to reduce any excess oxidant. After 15 min, the solution was acidified (50% H_2SO_4), and the precipitated manganese dioxide was reduced by addition, in small portions, of the required amount of sodium bisulfite. The aqueous layer was separated, saturated with sodium chloride, and extracted with 3 × 75 mL of methylene chloride. The combined organic extracts were washed with 2 × 50 mL of 10% aqueous NaOH solution, dried over anhydrous $MgSO_4$, and concentrated by rotary evaporation to give a yellow liquid which solidifed on cooling. Recrystallization of this solid from 15 mL of methanol gave 8,9-hexadecanedione (1.82 g, 0.007 mol, 80%), mp 51–52 °C (lit.[20] mp 49–50 °C).

The aqueous solutions were combined, acidified (50% H_2SO_4), and extracted with 3 × 75 mL of ether. The ether solution was dried over anhydrous $MgSO_4$ and concentrated by rotary evaporation, and on analysis (GLC) it was found to contain octanoic acid (5% yield) and a trace of heptanoic acid.

The Phase Transfer Assisted Oxidation of 7-Tetradecyne in "Wet" Methylene Chloride. A 500-mL Erlenmeyer flask was charged with $KMnO_4$ (8.2 g, 0.052 mol in 140 mL of water) and a solution consisting of 7-tetradecyne (5.0 g, 0.026 mol), acetic acid (35 mL), methylene chloride (100 mL), and Adogen 464 (1.8 g). The solution was stirred magnetically and refluxed for 5 h. The workup was performed as described above, and the resulting yellow liquid (obtained by evaporation of the organic solvents) was distilled under vacuum to give unreacted alkyne (10%) and a yellow liquid (bp 108–110 °C (5.5 torr)) which solidified on cooling. The yellow solid was recrystallized from methanol (15 mL) to give 7,8-tetradecanedione (3.2 g, 0.014 mol, 58%), mp 38–39 °C. The aqueous solutions were found to contain heptanoic and hexanoic acids in yields of 25 and 17%, respectively.

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Registry No. 8-Hexadecyne, 19781-86-3; 7-tetradecyne, 35216-11-6; 1-phenyl-1-pentyne, 4250-81-1; 5-decyne, 1942-46-7; 4-octyne, 1942-45-6; benzoic acid, 65-85-0; 1-phenyl-1,2-pentanedione, 20895-66-3; valeric acid, 109-52-4; 5,6-decanedione, 5579-73-7; butyric acid, 107-92-6; propionic acid, 79-09-4; 4,5-octanedione, 5455-24-3; phenylacetylene, 536-74-3; 1-hexyne, 693-02-7; diphenylacetylene, 501-65-5; 1-phenyl-1-hexyne, 1129-65-3; benzil, 134-81-6; 1-phenyl-1,2-hexanedione, 33720-29-5; 7,8-tetradecanedione, 6305-47-1; heptanoic acid, 111-14-8; hexanoic acid, 142-62-1; 8,9-hexadecanedione, 18229-29-3; octanoic acid, 124-07-2; $KMnO_4$, 7722-64-7.

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Comment on the Spectrum of Matrix-Isolated Thiirene and Characterization of New Matrix-Isolated Species

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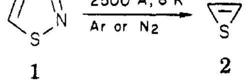
An analysis of the infrared bands of thiirene (**2**), generated from 1,2,3-thiadiazole (**1**), is offered in light of the comments of Torres et al. Some discrepancies and misinterpretations by Torres, as well as criteria for the characterization of matrix-isolated species by infrared spectroscopy, are discussed.

Torres et al.[1] recently described the photolysis of matrix-isolated 1,2,3-thiadiazole (**1**), confirming our report of



1 2

thiirene (**2**),[2] which can be detected by infrared spectroscopy when **1** is photolyzed through narrow-bandpass filters. We observed the following bands[2] for argon matrix-isolated thiirene: 3207, 3169, 3166, 1663, 912, and 563 cm^{-1} (Figure 1). Torres and co-workers have repeated the photolysis of **1** (they did not investigate isotopically labeled thiadiazoles) and list the following bands for **2**: 3208, 3170,

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