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# Potassium Permanganate Oxidations of Terminal Olefins and Acetylenes to Carboxylic Acids of One Less Carbon[1]

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The potassium permanganate cleavages of terminal olefins and acetylenes to prepare carboxylic acids of one less carbon have been studied under a variety of conditions. Overoxidation is a problem if the reaction is performed in an initially neutral or basic aqueous permanganate solution under heterogeneous liquid–liquid conditions or under heterogeneous liquid–liquid conditions using organic solvents and quaternary ammonium salts as phase-transfer agents. The presence of acetic acid in the two-phase liquid–liquid aqueous permanganate oxidations using organic solvents and quaternary ammonium salts leads to good yields of carboxylic acids with small amounts of overoxidized acids. The results of experiments which attempt to elucidate the overoxidation mechanism are described.

The initial goal of the present research was an exploration of the use of the operationally simple heterogeneous liquid–liquid aqueous permanganate oxidations of the commercially available even-numbered continuous chain $\alpha$-olefins to prepare high purity odd-numbered carboxylic acids of one less carbon.

$$CH_3(CH_2)_nCH{=}CH_2 \rightarrow CH_3(CH_2)_nCOOH$$

It had previously been reported that 1-decene could be oxidized to nonanoic acid (91% yield, 98% purity) in the heterogeneous two-phase water–benzene system by permanganate and the phase-transfer agent Aliquat 336.[4,5] Similarly, the conversion of 1-octene to heptanoic acid (81%) had been reported using tetrabutylammonium bromide as the phase-transfer catalyst.[6]

Oxidation of the 1-decene following the published procedure[4] (a four-times more dilute aqueous permanganate solution was used to permit effective stirring as $MnO_2$ fills the flask) led to an excellent yield of a crude acid mixture which consisted of nonanoic acid (90%) and octanoic acid (10%). Similarly, permanganate oxidations of 1-octene and 1-dodecene led to the desired carboxylic acids which were contaminated by hexanoic acid (8%) and decanoic acid (9%), respectively. Under these reaction conditions, the desired one-carbon cleavage products are contaminated with the overoxidation product resulting from a loss of two carbons.

It seemed reasonable to speculate that the overoxidation of the $\alpha$-olefins was related in some manner to the $OH^-$ formed as a permanganate oxidation proceeds. A study of the oxidation was then undertaken.

Numerous studies have been reported in which the products and rates of product formation from oxidations by permanganate of various substrates depend on the reaction conditions and the pH if an aqueous medium is employed.[7] Mechanistic rationalizations have been advanced to account for the products and rates found during oxidations of olefinic substrates.[7a,b,e–g]

Oxidations by permanganate, although quite effective, are usually plagued by the insolubility of the organic substrate in water. Methods for effecting reaction are rapid stirring to facilitate interfacial contact between the reactants or addition of a cosolvent such as acetic acid to the aqueous phase to enhance solubility. Along with phase-transfer agents,[4,5] crown ethers have found use in solubilizing permanganate in organic solvents.[5e,7l] Acetic anhydride has been used as a solvent in permanganate oxidations.[7h–j] Surfactants in two-phase reactions can also operate as emulsion or micellar catalysts.[8]

The stoichiometry for the cleavage of $\alpha$-olefins is represented by the equation:

$$3RCH{=}CH_2 + 8MnO_4^- \rightarrow 3RCO_2^- + 3HCO_2^- + 8MnO_2 + 2OH^- + 2HOH$$

Manganese(IV) dioxide is the usual product from permanganate oxidations of most organic substrates in alkaline or mildly acidic solutions. In the equation, formate could possibly undergo further oxidation to $CO_2$ (to produce $CO_3^{2-}$ in a basic medium) with a net consumption of permanganate.[7a]

The permanganate oxidation of 1-octene was studied under a variety of conditions and the results are summarized in Table I.

Let us examine some of the salient features of the data recorded in Table I. The oxidation of 1-octene proceeds in aqueous permanganate under liquid–liquid heterogeneous conditions at a rate which depends on the mode of stirring and the stirring speed (entries 1, 2, and 3). The extent of overoxidation appears to be a function of reaction time (entries 1 and 2). In the presence of acetic acid (3.3 M) the oxidation is rapid and overoxidation is suppressed (entry 4). The use of pentane or benzene in the oxidation with Aliquat 336 or benzylhexa-

**Table I. Permanganate Oxidations of 1-Octene**[a]

| | | | Product analysis | | |
|---|---|---|---|---|---|
| Additives | Reaction time, h | Stirring | 1-Octene | Hexanoic acid | Heptanoic acid |
| None[b] | 4 | Mech[c] | 6 | 10 | 84 |
| None[b] | 2 | Mech | 9 | 5 | 86 |
| None[b] | 4 | Mag[d] | 55 | 10 | 35 |
| 15 mL of acetic acid[e] | 2 | Mag | 1 | 3 | 96 |
| 100 mL of pentane,[e] 0.2 g of Aliquat 336 | 10 | Mag | 9 | 7 | 84 |
| 300 mL of benzene,[f] 0.2 g of bzl-PTC | 6 | Mag | | 10 | 90[g] |
| 100 mL of pentane,[e] 30 mL of acetic acid, 0.2 g of Aliquat 336 | 2 | Mag | 3 | 2 | 95 |
| 300 mL of benzene,[f] 60 mL of acetic acid, 0.2 g of bzl-PTC | 3 | Mag | | 3 | 97[g] |
| 300 mL of benzene,[f,h] 35 g of 85% $H_3PO_4$, 0.2 g of bzl-PTC | 5 | Mag | | 6 | 94[g] |
| 100 mL of pentane,[e] 30 mL of acetic acid | 3 | Mech | 20 | 2 | 78 |

[a] Product analysis was done by VPC of the reaction products treated with ethereal diazomethane in most cases; ±2–3% reliability. [b] $KMnO_4$ (0.06 mol) in 75 mL of water treated with 1-octene (0.015 mol) and any listed additives. See Experimental Section for reaction details. [c] Motor-driven shaft and propeller blade (about 400 rpm). [d] One-inch egg-shaped magnet with a Fisher Thermix motor. [e] $KMnO_4$ (0.10 mol) in 150 mL of water to which 1-octene (0.015 mol) containing the acetic acid was added, along with solvent or PTC. [f] $KMnO_4$ (0.20 mol) in 300 mL of water treated with 1-octene (0.06 mol) and any listed additives. [g] Distilled products isolated in 65–75% yields. [h] About 1 M in $H_3PO_4$.

**Table II. Permanganate Oxidations of 1-Decene**

| Additives | Reaction[a] time, h | 1-Decene | Octanoic acid | Nonanoic acid |
|---|---|---|---|---|
| None[b] | 15 | 78 | 4 | 18 |
| None[b] | 14[c] | 15 | 8 | 77 |
| 30 mL of acetic acid[d] | 2 | 2 | 4 | 94 |
| 150 mL of benzene,[d] 0.1 g of bzl-PTC | 19 | 15 | 8 | 77 |
| 150 mL of benzene,[d,e] 30 mL of acetic acid | 7.5 | 78 | 2 | 20 |
| 150 mL of benzene,[d] 30 mL of acetic acid, 0.1 g of bzl-PTC | 5 | 10 | 3 | 87 |
| 150 mL of benzene,[d] 0.1 M KOH, 0.1 g bzl-PTC | 17 | 4 | 14 | 82 |

[a] All done with magnetic stirring, except in the one case where noted. [b] $KMnO_4$ (0.05 mol) in 75 mL of water treated with 1-decene (0.015 mol). [c] Mechanical stirring. [d] $KMnO_4$ (0.095 mol) in 150 mL of water treated with 1-decene (0.03 mol) and any listed additive. [e] Purple permanganate color completely disappeared, indicating that oxidation of acetic acid was also occurring.

**Table III. Permanganate Oxidations of Allylbenzene**

| Additives | Reaction time, h | $C_6H_5COOH$ | $C_6H_5CH_2$-$COOH$[a] |
|---|---|---|---|
| None[b] | 5 | 75 | 25 |
| 0.2 g of bzl-PTC[b] | 7 | 50 | 50 |
| 60 mL of acetic acid,[b] 0.2 g of bzl-PTC | 17 | 20 | 80 |
| 1.1 M of KOH, 0.2 g of bzl-PTC[b] | 10 | 95 | 5 |
| 0.2 g of bzl-PTC[c] | 6 | 80 | 20 |
| 0.2 g of bzl-PTC[d] | 1.5 | | |
| 60 mL of acetic acid[b] | 0.5 | 20 | 80 |

[a] Analysis of the crude acid mixture by $^1H$ NMR using the aromatic protons and the phenylacetic acid singlet to extrapolate the aromatic protons constituting the contribution of this acid to the total proton integral. [b] $KMnO_4$ (0.19 mol) in 300 mL of water and the benzene (300 mL) containing allylbenzene (0.06 mol) and any listed additives were added in one portion. All runs were stirred magnetically. Product recovery was in the range of 60–80% in all cases. [c] As in b, except 0.24 mol of $KMnO_4$ was used. [d] As in b, except 0.03 mol of $KMnO_4$ was used. The recovered olefin showed no detectable isomerization to methylstyrene.

decyldimethylammonium chloride (bzl-PTC) as phase-transfer agents, respectively, leads to 7 and 10% overoxidation (entries 5 and 6). The advantageous effect of acetic acid in suppressing overoxidation in the presence of an organic medium and a phase-transfer agent can be seen in entries 7 and 8. Substitution of phosphoric acid for acetic acid under phase-transfer conditions led to more overoxidation (entry 9). The oxidation also proceeds in the two-phase system pentane–water with added acetic acid (entry 10).

Similar studies were also performed using 1-decene as the olefinic substrate and the data are tabulated in Table II.

As can be seen from the data tabulated in Table II, the behavior shown by 1-decene is similar to that seen in Table I for 1-octene. In the heterogeneous benzene–water media the oxidation of 1-decene in the presence of acetic acid proceeds only to the extent of 22% in 7.5 h (entry 5), while the same reaction performed in the presence of the phase-transfer agent affords 90% oxidation in a 5-h period (entry 6). The ability of $OH^-$ in the aqueous medium to increase the amount of overoxidation is shown in entry 7.

The suppression of the amount of overoxidation product when the oxidations are performed in the presence of acetic acid is probably most dramatically illustrated by the oxidation of allylbenzene to produce phenylacetic acid and the overoxidation product benzoic acid. The results of some experiments are summarized in Table III.

The data presented in Table III clearly indicates that in the oxidation of allylbenzene $OH^-$ increases the amount of overoxidation to yield benzoic acid. Acetic acid in all cases suppresses (but does not completely inhibit) the amount of benzoic acid which is produced.

In order to probe into the nature of the reaction pathway which leads to the undesirable overoxidation in allylbenzene, phenylacetic acid (0.015 mol) in benzene (75 mL with 0.1 g of benzyl PTC) was treated with $KMnO_4$ (0.06 mol in 75 mL of water) for 6 h. The isolated acids consisted of phenylacetic acid (35%) and benzoic acid (65%). If the same reaction is performed in the presence of acetic acid (15 mL), the product consisted of about equal amounts of phenylacetic acid and benzoic acid. Thus, phenylacetic acid is quite susceptible to further oxidation and once formed in the allylbenzene oxidation would be further oxidized to benzoic acid.

Treatment of heptanoic acid (0.03 mol) with $KMnO_4$ (0.12 mol in a 0.1 M KOH solution) for 6 h led to recovery of an acid which contained about 4% hexanoic acid. Some of the overoxidation seen in the cases of 1-octene and 1-decene under basic conditions may possibly arise from further oxidation of the carboxylic acid which is initially formed ($MnO_2$ is also

**Table IV. Permanganate Oxidations of α-Olefins**

| Registry no. | α-Olefin[a] | Product | Isolated yield, %[b] |
|---|---|---|---|
| 111-66-0 | 1-Octene | Heptanoic acid | 80 |
| 872-05-9 | 1-Decene | Nonanoic acid | 85 |
| 821-95-4 | 1-Undecene | Decanoic acid | 86 |
| 112-41-4 | 1-Dodecene | Undecanoic acid | 90 |
| 1120-36-1 | 1-Tetradecene | Tridecanoic acid | 83 |
| 629-73-2 | 1-Hexadecene | Pentadecanoic acid | 84 |
| 112-88-9 | 1-Octadecene | Heptadecanoic acid | 80 |
| 3452-07-1 | 1-Eicosene | Nonadecanoic acid | 90 |

[a] See Experimental Section for a typical procedure. [b] Purity of at least 97% in all cases. Less than 3% contamination with the overoxidation product. Products were distilled or crystallized.

present and could exert some surface catalytic effect).

The initial intermediates which are formed during oxidations of alkenes by permanganate[7] are the cyclic manganese(V) or manganese(VI) species. These intermediates could then lead to aldehydes,[7l] diols (in cold, dilute alkaline permanganate solutions), or ketols (low hydroxide concentration). Diols would be cleaved to the expected acids but they could also undergo oxidations to ketols, keto aldehydes, or keto acids (sources of overoxidized acids). The aldehydes could be rapidly oxidized to carboxylic acids. Another pathway for the aldehydes is oxidative cleavage via an enol or enolate to yield the carboxylic acid of one less carbon.

In order to probe into the possibility of overoxidation of the aldehyde intermediate, nonanal and valeraldehyde were oxidized under conditions similar to the α-olefins. Treatment of nonanal (0.03 mol) with permanganate (0.03 mol) in a benzene (150 mL)–water (150 mL) medium with Aliquat 336 (0.1 g) led to nonanoic acid which contained less than 3% octanoic acid. If the same reaction is performed with the aqueous phase initially 0.1 M in KOH, a comparable result was seen. Similarly the two-phase oxidation of valeraldehyde under basic conditions led to valeric acid with about 2% butyric acid.

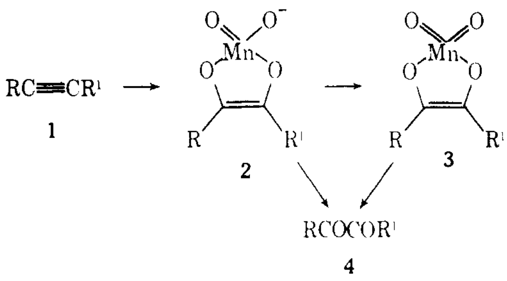
The amount of overoxidation seen in the permanganate oxidations of the α-olefins does not appear to be solely explicable on the premise that the aldehyde initially formed in the cleavage is further oxidatively cleaved.

The function of the acetic acid (soluble in water, benzene, and pentane) in suppressing overoxidation in the reactions conducted under heterogeneous two-phase conditions in the presence of a phase-transfer agent may merely reflect its solubility in the organic phase and rapid destruction of $OH^-$ formed during the disproportionation of manganese(VI) intermediates.[7] Since the acetic acid itself is oxidized at a moderate rate, it might additionally function to destroy any excess permanganate and prevent further oxidation of the initially formed carboxylic acid. In those cases where both the acetic acid and phase-transfer agent are present, it does appear that phase-transfer-type catalysis is occurring.[4]

Since the goal of this research was to produce high-purity carboxylic acids, a series of α-olefins was oxidized using aqueous permanganate and adding solutions of the α-olefins in benzene, acetic acid, and a quaternary ammonium salt. The results of these reactions are tabulated in Table IV. Good yields of reasonably pure carboxylic acids can be obtained in this manner.

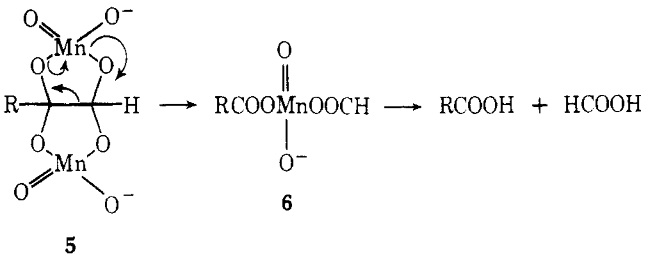
Our attention was next turned to the permanganate oxidations of terminal acetylenes. In Raphael's book[11] several examples of permanganate oxidations of internal alkynes are referenced,[12] and it is stated "As becomes an unsaturated centre the triple bond is very readily attacked by potassium permanganate, the end products being two carboxylic acid molecules". Under controlled conditions α-diketones can be isolated. For example, stearolic acid has been converted into 9,10-diketo stearic acid (92–96%) by performing the oxidation in the pH range 7.0–7.5 ($MnO_4^-$:acid = 2).[13] The diketo acid is oxidatively cleaved at high (>12) or low (<1) pH.

**Scheme I**



In mechanistic studies dealing with permanganate oxidations of acetylenes, a cyclic manganese(V) intermediate has been proposed as the first step in the cleavage process.[14] The formation of diones from internal acetylenes 1 ($R = R^1$ = alkyl) could arise via the pathway depicted in Scheme I.

The α-keto aldehyde 4 ($R^1$ = H, R = alkyl) which would arise from a terminal acetylene by this route would be expected to undergo further oxidation to the α-keto acid 4 ($R^1$ = OH, R = alkyl) and then this acid would be oxidized to RCOOH and $CO_2$.



It is also possible that a bicyclic intermediate such as 5 might be involved in the cleavages of triple bonds [only the manganese(V) state is shown and the manganese(VI) state could also play a role].[14] Breakdown of 5 would lead to 6 which on further reaction would yield the acid fragments.

The stoichiometry for the cleavage of a terminal acetylene (if $MnO_2$ and $CO_2$ are the products) under acid and basic conditions is represented in the following equations:

$$3RC{\equiv}CH + 8MnO_4^- + 8H^+ \rightarrow 3RCO_2H + 3CO_2 + 8MnO_2 + 4H_2O$$

$$3RC{\equiv}CH + 8MnO_4^- + OH^- \rightarrow 3RCO_2^- + 3CO_3^{2-} + 8MnO_2 + 2H_2O$$

In studies similar to the olefin oxidations previously discussed, several alkynes were treated with permanganate under a variety of conditions. The results of experiments on 1-hexyne are summarized in Table V.

It can be seen from the data in Table V that 1-hexyne can be oxidized in good yields without too much problem of overoxidation under a variety of reaction conditions.

Permanganate oxidations of 1-octyne are listed in Table VI.

In the oxidations of 1-octyne the amount of overoxidation increases as the basicity of the aqueous phase increases. The reaction can be performed using aqueous permanganate alone. The oxidation proceeds in the two-phase pentane–water system, and phase-transfer catalysis appears to be occurring to some extent (entries 6 and 7).

A few oxidations were performed using 1-decyne, and the results are tabulated in Table VII.

**Table V. Permanganate Oxidations of 1-Hexyne**

| Additive | Reaction time, h | Valeric acid | Butyric acid |
|---|---|---|---|
| None[a] | 7 | 98 | 2 |
| 0.13 M KOH[b] | 7 | 94 | 6 |
| 150 mL of benzene,[c]<br>0.1 g of bzl-PTC | 4 | 99 | 1 |
| 300 mL of pentane,[d]<br>60 mL of acetic acid<br>0.2 g of Aliquat 336 | 2 | 99 | 1 |

[a] $KMnO_4$ (0.06 mol) in 75 mL of water to which 1-hexyne (0.015 mol) was added. The mixture was stirred magnetically and a 60–70% yield of the crude acid could be isolated. Any 1-hexyne which did not react would have been lost in the concentration process on workup. [b] 0.6 g of KOH (0.01 mol) was added to the aqueous $KMnO_4$ and the reaction was performed as in *a*. [c] $KMnO_4$ (0.10 mol) in 150 mL of water to which 1-hexyne (0.06 mol) and listed PTC were added. A 54% crude yield of acid was obtained. [d] $KMnO_4$ (0.19 mol) in 300 mL of water to which 1-hexyne (0.06 mol) was added containing the listed additives. Isolated crude product in a 60% yield.

**Table VI. Permanganate Oxidations of 1-Octyne**

| Additives[a] | Reaction time, h | 1-Octyne | Hexanoic acid | Heptanoic acid |
|---|---|---|---|---|
| None | 5 | 28 | 5 | 66 |
| 0.1 M KOH[b] | 5 | 1 | 14 | 85 |
| 0.5 M KOH[c] | 3 | 2 | 50 | 48 |
| 150 mL of pentane | 5 | 50 | 2 | 48 |
| 150 mL of pentane,<br>30 mL of acetic acid | 7.5 | 21 | 2 | 77 |
| 150 mL of pentane,<br>0.2 g of Aliquat 336 | 5 | 35 | 2 | 64 |
| 150 mL of pentane,<br>0.8 g of Aliquat 336 | 5 | 13 | 3 | 84 |
| 30 mL of acetic acid[d] | 2 | 1 | 4 | 95 |
| 150 mL of pentane,<br>30 mL of acetic acid,<br>0.2 g of Aliquat 336 | 5 | 10 | 2 | 88 |

[a] $KMnO_4$ (0.12 mol) was placed in 200 mL of water in a 1-L flask equipped with a mechanical stirrer and blade. The mixture was immersed in an ice bath and 1-octyne (0.03 mol) was added in one portion with any listed additive. Product recovery in all cases was greater than 80%. [b] 1.5 g of KOH was added to the $KMnO_4$ solution. [c] 5.5 g of KOH was added to the $KMnO_4$ solution. [d] Added to the aqueous layer before octyne addition.

Preparative oxidations of 1-hexyne, 1-octyne, and 1-decyne (pentane, aqueous permanganate, acetic acid, and Aliquat 336) yielded the carboxylic acids in 70–80% yields of greater than 97% overall purity. This is an extremely convenient method to effect oxidations of terminal acetylenes.

Comparative oxidations performed in aqueous permanganate showed that 1-octyne oxidized somewhat more rapidly than 1-octene and less overoxidation occurred in the case of 1-octyne. However, 1-decene and 1-decyne oxidize at comparable rates with more overoxidation in the 1-decene case. Both of these substrates proceed much slower than the oxidations of 1-octene and 1-octyne.

The mechanistic pathway leading to the overoxidation which is seen in the case of 1-octyne as the basicity of the aqueous phase increases is unclear. The question of the importance (in some of the oxidations performed with quaternary ammonium salts) of phase-transfer catalysis also is difficult to assess.

## Experimental Section

**Materials.** All $\alpha$-olefins (99% purity) were obtained from the Humphrey Chemical Co., North Haven, Conn. 06473, and were used as received. 1-Octene (99.9%) and all the acetylenes were obtained from the Chemical Samples Co., Columbus, Ohio. Aliquat 336 (tricaprylylammonium chloride was kindly provided by General Mills Chemical Co., Minneapolis, Minn. 55435) and benzylhexadecyldimethylammonium chloride (J. T. Baker, practical grade) were used as phase-transfer agents. Potassium permanganate (Fisher Certified) was used as received.

**Table VII. Permanganate Oxidations of 1-Decyne**

| Additives | Reaction time, h | 1-Decyne | Octanoic acid | Nonanoic acid |
|---|---|---|---|---|
| None[a] | 15 | 77 | 2 | 21 |
| 15 mL of acetic acid[a] | 3.5 | 2 | 6 | 92 |
| 100 mL of pentane,[b]<br>50 mL of acetic acid<br>0.2 g of Aliquat 336 | 8 | 21 | 3 | 76 |

[a] $KMnO_4$ (0.06 mol) in 75 mL of water and 1-decyne (0.015 mol) were added. [b] $KMnO_4$ (0.15 mol) in 200 mL of water and 1-decyne (0.045 mol) and listed additives were added.

All acids which were prepared had $^1H$ NMR spectra in agreement with their structures and these data are not listed here. All boiling and melting points of the acids closely corresponded to the literature values.

**(A) General Procedure for All Oxidations.** The aqueous $KMnO_4$ (0.12 mol) in about 150–200 mL of water was cooled with stirring in an ice bath. The substrate (0.03 mol), and any solvent (100–150 mL), acetic acid (30 mL), or PTC (0.2 g), was added in one portion. The reaction was allowed to proceed for the specified time and recooled. In those runs without solvent, pentane or benzene was added at this point. Sodium sulfite (20 g) was slowly added and then either aqueous HCl (25 mL of concentrated HCl in 50 mL of water) *or* aqueous $H_2SO_4$ (25 g of concentrated $H_2SO_4$ in 100 mL of water) was slowly added. Two clear layers form; the organic layer is washed once with cold water and dried over $Na_2SO_4$. Distillation or concentration on a Buchi rotary evaporator leaves the crude product. The crude product was treated with ethereal $CH_2N_2$ and the methyl esters were analyzed by GLC (DC-200 column).

**(B) $\alpha$-Olefin Oxidations. Preparative Runs. (1) Typical Procedure. Tridecanoic Acid.** A 1-L rb flask is charged with $KMnO_4$ (32 g, 0.20 mol) and 300 mL of water. The flask is immersed in an ice bath and stirred vigorously via an egg-shaped magnet (1 in.). A solution of 1-tetradecene (11.8 g, 0.06 mol), 300 mL of benzene, 60 mL of glacial acetic acid, and benzylhexadecyldimethylammonium chloride (0.2 g, 0.5 mmol) is added in one portion. Stirring is continued without any further addition of ice to the bath for about 4 hr. A total of 35 g of $Na_2SO_3$ is added to the cooled reaction mixture followed by the slow addition of a solution of 35 mL of concentrated HCl in 35 mL of water. Two clear layers result. The layers are separated and the benzene layer is washed once with a 100-mL portion of cold water. The benzene layer is dried over anhydrous sodium sulfate, the drying agent is removed by filtration, and the bulk of the benzene is removed by distillation. The residual benzene is removed on a rotary evaporator to yield 12.7 g (99%) of crude solid. The crude acid is dissolved in pentane (60 mL), filtered to remove traces of insoluble material, and placed in the freezer overnight. Filtration yields 10.6 g (83%) of tridecanoic acid of mp 43–44 °C (lit. mp 44–45 °C).[16] Treatment of a sample of the crude or crystallized acid with $CH_2N_2$ followed by GLC analysis showed about 2% contamination by dodecanoic acid and a trace amount of a short retention time impurity.

(2) **Pentadecanoic acid** was prepared as in the typical procedure, except 1-hexadecene (13.4 g, 0.06 mol) and 1 g of Aliquat 336 were used. The reaction was allowed to proceed overnight (10 h). The crude solid weighed 14.4 g (99%). Crystallization from ligroin (35–60 °C) gave 12.2 g (84%) of mp 52–53 °C (lit. mp 53–54 °C).[16] GLC of the methyl esters showed 2% contamination by tetradecanoic acid.

(3) **Heptadecanoic acid** was prepared as in the typical procedure, except 1-octadecene (15.4 g, 0.06 mol) and 0.1 g of bzl-PTC were used and the reaction was allowed to proceed for 6 h. Workup yielded 13.0 g (80%) of acid after crystallization from ligroin. GLC analysis of the methyl esters showed about 3% contamination by hexadecanoic acid and 0.5% of an unidentified peak of short retention time.

(4) **Nonadecanoic acid** was prepared as in the typical procedure, except 1-eicosene (16.8 g, 0.06 mol) and 1 g of Aliquat 336 were used and the reaction was allowed to proceed for 3 h. The crude white solid was placed in cold ethanol and filtered to yield 15.5 g (86%) of acid of mp 65–67 °C (lit. mp 69 °C).[16] Crystallization from $CH_3CN$ raised

the melting point to 67–68 °C. GLC of the methyl esters showed 3% contamination by stearic acid.

**(5) Decanoic acid** was prepared as in the typical procedure, except 1-undecene (9.2 g, 0.06 mol) was used. The reaction was allowed to proceed overnight and on workup the crude acid (10.2 g, 99%) was obtained. Distillation, 105–107 °C/0.5 mm, yielded 8.6 g (84%) of decanoic acid which solidified. GLC of the methyl esters showed about 3% contamination by nonanoic acid.

**(6) Undecanoic acid** was prepared as in the typical procedure, except 1-dodecene (0.06 mol) and a reaction time of 4 h was used. The crude acid, 11.1 g (99%), was distilled at 110–115 °C/0.1 mm to yield 9.9 g (90%) of undecanoic acid. GLC of the methyl esters showed about 3% contamination by decanoic acid and less than 0.5% of a short retention time impurity.

**(7) Nonanoic acid** was prepared as above, except 1-decene (0.06 mol) and 0.1 g of bzl-PTC were used and the reaction was allowed to proceed for 4 h. The crude acid was distilled, bp 89–90 °C/0.1 mm, to yield 8.0 g (85%) of 97% pure nonanoic acid (GLC of esters).

**(8) Heptanoic acid** was prepared as above, except 1-octene (6.7 g, 0.06 mol) was used and the reaction was allowed to proceed for 3 h. Distillation at 83–84 °C/1.5 mm gave 6.2 g (80%) of acid of 98% purity (GLC of methyl esters).

**(C) Acetylene Oxidations. Preparative Runs. (1) Typical Procedure: 1-Octyne → Heptanoic Acid.** In a 1-L rb flask fitted with a 1-in. egg-shaped spinbar is placed $KMnO_4$ (28 g, 0.18 mol) and 200 mL of tap water. The mixture is stirred and immersed in an ice bath. A solution of 1-octyne (5.0 g, 0.045 mol), 120 mL of pentane, 60 mL of acetic acid, and 0.2 g of Aliquat 336 is added in one portion. The mess is stirred for 5 h without replenishing the ice. The black-brown mixture is cooled in an ice bath and $Na_2SO_3$ (30 g) is added in several portions. A solution of 60 mL of concentrated HCl in 60 mL of water is then cautiously added. The top pentane layer is separated and the acidic layer is extracted once with 50 mL of pentane. The combined pentane extracts are washed with 50 mL of cold water, dried over $Na_2SO_4$, decanted from the drying agent, and concentrated on a Buchi rotary evaporator to yield 5.4 g of crude product (90% recovery). Vacuum distillation yields 4.1 g (70%) of heptanoic acid (98% pure by GLC of the methyl esters, trace amounts of short retention time impurities were also present).

**(2) Nonanoic acid** was prepared as above, except 1-decyne (0.045 mol) was used and the reaction was run for 8 h. On distillation, 4.6 g (70%) of acid was obtained of 98% purity (GLC of methyl esters).

**(3) Pentanoic acid** was prepared as above, except $KMnO_4$ (0.24 mol), 300 mL of water, 1-hexyne (0.06 mol), 250 mL of pentane, and 0.3 g of Aliquat 336 were used, and the reaction was run for 3 h to yield 4.0 g (66%) of acid of 98% purity (GLC of methyl esters).

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**Registry No.**—$KMnO_4$, 7722-64-7; decanoic acid, 334-48-5; undecanoic acid, 112-37-8; nonanoic acid, 112-05-0; heptanoic acid, 11-14-8; allylbenzene, 300-57-2; 1-hexyne, 693-02-7; 1-octyne, 629-05-0; 1-decyne, 764-93-2.

## References and Notes

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