crystals: mp 62–65 °C; $[\alpha]^{25}_D$ –104.5° (*c* 1.00, CHCl₃); IR (CHCl₃) 3665, 3032, 3015, 3009, 2925, 2857, 1955, 1880, 1810, 1603, 1556, 1537, 1494, 1453, 1368, 1307, 1281, 1223, 1180, 1151, 1127, 1092, 1051, 1025, 996, 967, 911, 858, 824, 700, 670, 667, 649 cm⁻¹; ¹H NMR (CDCl₃) δ 0.58 (1, q), 0.78–1.10 (2, m), 1.14–1.50 (3, m), 1.60–1.70 (3, m), 2.08–2.20 (3, m), 4.54 (1, d), 4.75 (1, d), and 7.18–7.40 (10, m); ¹³C NMR (CDCl₃) δ 9.7 (CH₂), 14.8 (CH), 24.1 (CH), 24.4 (CH₂), 28.0 (CH₂), 29.5 (CH₂), 41.2 (CH₂), 84.0 (CH), 85.3 (CH), 111.0 (C), 126.6 (CH), 126.7 (CH), 127.0 (CH), 128.0 (CH), 128.1 (CH), 128.2 (CH), 128.3 (CH), 136.7 (C), and 136.8 (C); mass spectrum (70 eV), *m/z* (relative intensity) 252 (3), 251 (16), 215 (15), 214 (89), 180 (31), 179 (39), 178 (16), 168 (11), 167 (52), 165 (19), 108 (14), 107 (17), 105 (36), 104 (13), 93 (72), 91 (41), 82 (13), 81 (15), 80 (98), 79 (100), 98 (14), 77 (41); exact mass calcd for C₁₅H₁₈O (M⁺ – C₆H₅CHO) 214.1358, obsd 214.1354.

2,3,5,6,7,8-Hexahydro-1*H*,4*H*-azulen-1-one (*S*,*S*)-Hydrobenzoin Ketal (7). From 2,3,5,6,7,8-hexahydro-1*H*,4*H*-azulen-1-one (1.148 g, 7.65 mmol), (*S*,*S*)-hydrobenzoin (1.091 g, 5.10 mmol), and pyridinium *p*-toluenesulfonate (100 mg, 0.40 mmol) product **7** was obtained as a very viscous pale yellow oil. Upon standing for 96 h this oil solidified: mp 46–51 °C; $[\alpha]^{25}_D$ –39.7° (*c* 1.74, CHCl₃); yield 850 mg, 2.46 mmol, 48%; IR (CHCl₃) 3065, 3033, 3022, 3015, 3009, 2923, 2335, 1949, 1880, 1806, 1730, 1677, 1650, 1603, 1495, 1453, 1360, 1311, 1282, 1259, 1157, 1120, 1091, 1036, 1024, 988, 938, 914, 866, 824, 700, 669, 650 cm⁻¹; ¹H NMR (CDCl₃) δ 1.5–1.86 (6, m), 2.08–2.26 (2, t), 2.27–2.48 (6, m), 4.66 (1, d), 4.80 (1, d), and 7.18–7.38 (10, m); ¹³C NMR (CDCl₃) δ 25.2 (CH₂), 26.8 (CH₂), 27.7 (CH₂), 31.0 (CH₂), 31.3 (CH₂), 34.0 (CH₂), 36.4 (CH₂), 84.8 (CH), 86.4 (CH), 122.8 (CH), 126.4 (CH), 126.7 (CH), 127.6 (CH), 127.9 (CH), 128.2 (CH), 136.2 (C), 136.7 (C), 137.5 (C), and 146.9 (CH); mass spectrum (70 eV), *m/z* (relative intensity) 241 (5), 240 (29), 180 (11), 179 (9), 178 (5), 167 (21), 165 (11), 150 (18), 149 (100), 148 (17), 122 (11), 107 (14), 105 (14), 91 (33); exact mass calcd for C₁₇H₂₀O (M⁺ – C₆H₅CHO) 240.1515, obsd 240.1517.

(3a*S*,8a*R*)-2,3,5,6,7,8-Hexahydro-3a,8a-methano-1*H*,4*H*-azulen-1-one (*S*,*S*)-Hydrobenzoin Ketal (8). Cyclopropanation of ene ketal **7** (333 mg, 0.962 mmol) gave **8** as a viscous oil: $[\alpha]^{25}_D$ –46.8° (*c* 0.60, CHCl₃); yield: 214 mg, 0.595 mmol, 62%; IR (CHCl₃) 3064, 3030, 3019, 3011, 2921, 2860, 1945, 1880, 1800, 1494, 1453, 1361, 1331, 1311, 1276, 1236, 1194, 1174, 1153, 1130, 1107, 1091, 1074, 1049, 1024, 977, 951, 915, 868, 699, 670, 668, 650 cm⁻¹; ¹H NMR (CDCl₃) δ 0.76 (2, s), 1.28–1.98 (12, m), 2.35–2.52 (2, t), 4.70 (2, dd), 7.10–7.18 (2, m), and 7.24–7.35 (8, m); ¹³C NMR (CDCl₃) δ 15.5 (CH₂), 26.3 (CH₂), 27.3 (CH₂), 27.6 (CH₂), 30.5 (C), 32.2 (CH₂), 32.5 (CH₂), 33.3 (C), 33.9 (CH₂), 36.0 (CH₂), 85.1 (CH), 85.8 (CH), 121.6 (C), 126.3 (CH), 127.0 (CH), 127.8 (CH), 128.1 (CH), 128.3 (CH), 136.1 (C), and 137.6 (C); mass spectrum (70 eV), *m/z* (relative intensity) 255 (10), 254 (45), 180 (41), 179 (19), 167 (24), 165 (16), 164 (17), 163 (35), 148 (15), 122 (24), 121 (14), 107 (22), 106 (17), 105 (100), 94 (11), 92 (22), 91 (53); exact mass calcd for C₁₈H₂₂O (M⁺ – C₆H₅CHO) 254.1671, obsd 254.1675.

(+)-Norcaranone (9). To a solution of recrystallized bicyclo[4.1.0]heptan-2-one (*S*,*S*)-hydrobenzoin ketal (4) (278 mg, 0.91 mmol) in methanol (10 mL) at room temperature was added 2.7 M aqueous HCl (1.0 mL). Progress of the reaction was monitored by TLC (20% ethyl acetate/hexanes). After 1.5 h the mixture was poured into saturated aqueous sodium bicarbonate (30 mL) and extracted with pentane (3 × 50 mL) and anhydrous diethyl ether (3 × 50 mL). The combined ether/pentane extracts were dried (MgSO₄), filtered, and concentrated by atmospheric distillation. Chromatography on silica gel 60 (75 g) eluted with 20% ether/pentane and removal of the volatiles by atmospheric distillation gave (+)-norcaranone (9) mixed with a small amount of ether/pentane. Yield corrected for solvents (by ¹H NMR): 75.3 mg, 68.5 mmol, 75.3%; $[\alpha]^{25}_D$ +15.6° (*c* 3.7, CHCl₃) [lit.¹³ᵃ $[\alpha]^{25}_D$ +15.3° (*c* 1.28, CHCl₃)]. (*S*,*S*)-Hydrobenzoin was also recovered in 90% yield.

Facile Oxidation of Manganese(II) to Manganese(III) in Long Chain Carboxylic Acids

Leon B. Levy

Hoechst Celanese Corporation, Chemical Group, Technical Center, P.O. Box 9077, Corpus Christi, Texas 78469

Manganese compounds have commonly been used as oxidizing agents and catalysts in organic reactions.¹ Occasionally, it is difficult to find a suitable manganese compound that is also soluble in the appropriate reaction medium. In this connection, during the preparation of manganese(II) nonanoate, we observed an interesting series of reactions that lead to facile formation of Mn(III) from Mn(II) when manganese(II) acetate tetrahydrate is heated with long chain fatty acids.

Manganese(II) acetate tetrahydrate dissolves in nonanoic acid at room temperature after about 30 min of stirring, giving a cloudy mixture that gradually yields a white, gelatinous mass. This gel is evidently the solvated Mn(II) salt of nonanoic acid. If this mixture is then heated to 95 °C in air, the gel dissolves, and the solution gradually turns deep reddish brown. If the solution is purged with nitrogen at 95 °C, the red-brown color is gradually expelled and the mixture becomes water-white. The development and discharge of color by sparging with air or nitrogen at 95 °C is quite reversible over many cycles.

If the mixture in its colorless state (under nitrogen) is cooled to room temperature, a white, gelatinous mass of manganese(II) nonanoate precipitates from the solution as described above. If the mixture is brought to the red-brown state with air and cooled, the material stays clear for several days but then slowly precipitates white gel on further standing.

The change of color of manganese nonanoate to red-brown with air and water-white with nitrogen reflects a facile redox cycle, and indeed, a visible spectrum of the colored solution (maxima at 458 and 495 nm) is almost identical with that reported by Kochi² for mixtures of Mn(III) with Mn(II) (maxima at 462 and 494 nm). It can be estimated from quantitative spectrophotometry that in 30 min approximately 37% of the manganese in a 0.059 M solution of manganese(II) acetate tetrahydrate is oxidized to Mn(III) in air-sparged nonanoic acid at 95 °C (corresponding to an estimated rate of 1.2 × 10⁵ mol/L/s). However, Mn(II) is not easily oxidized to Mn(III) by molecular oxygen except under very alkaline conditions,³ which certainly did not prevail in our system.

A likely reaction mechanism for the formation of significant quantities of Mn(III) from Mn(II) in nonanoic acid is as follows. An initial trace of Mn(III) is formed by reaction of Mn(II) salt with small amounts of hydroperoxide⁴ (eq 1) present in the nonanoic acid from aut-

$$ROOH + Mn(II) \rightarrow RO^· + OH^- + Mn(III) \qquad (1)$$
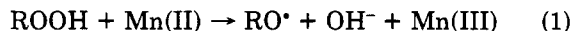
oxidation (the acid was found to contain 9.6 × 10⁻⁴ M active oxygen, a value that rose to 1.8 × 10⁻³ M after heating to 100 °C for 2 h). This initial trace of Mn(III) oxidatively decarboxylates the nonanoic acid according to
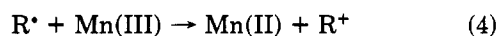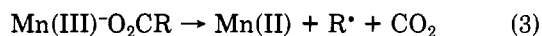
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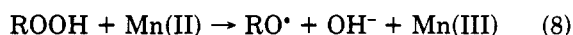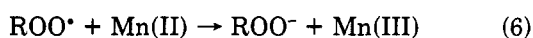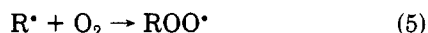
(3) Greenberg, A. E., Ed. *Standard Methods for the Examination of Water and Wastewater*, 15th ed.; American Public Health Association: Washington, D.C., 1981.

(4) Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

a scheme proposed by Kochi[2] (eq 2 and 3).

$$Mn(III) + RCO_2H \rightleftharpoons Mn(III)^-O_2CR + H^+ \qquad (2)$$

$$Mn(III)^-O_2CR \rightarrow Mn(II) + R^{\bullet} + CO_2 \qquad (3)$$

$$R^{\bullet} + Mn(III) \rightarrow Mn(II) + R^+ \qquad (4)$$

In the absence of oxygen, the oxidative decarboxylation results in the reduction of Mn(III) to Mn(II) (eq 3 and 4), as observed by Kochi. In contrast, there was no reduction of the Mn(III) in the presence of air.[2] This was attributed to the rapid formation of peroxy radicals from carbon radicals and molecular oxygen (eq 5) with subsequent electron-transfer reactions between Mn(II) and peroxy radicals (eq 6), as previously reported by de Klein and Kooyman.[5]   In addition, the resulting hydroperoxide would also oxidize Mn(II) (eq 8).

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (5)$$

$$ROO^{\bullet} + Mn(II) \rightarrow ROO^- + Mn(III) \qquad (6)$$

$$ROO^- + H^+ \rightarrow ROOH \qquad (7)$$

$$ROOH + Mn(II) \rightarrow RO^{\bullet} + OH^- + Mn(III) \qquad (8)$$

Another route to the oxidation of Mn(II) may be via the reaction with alkoxy radicals[2] (eq 9). Alkoxy radicals

$$RO^{\bullet} + Mn(II) \rightarrow RO^- + Mn(III) \qquad (9)$$
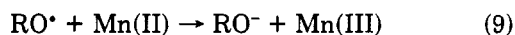
readily abstract hydrogen to form alcohols and new carbon-centered radicals. The latter, in turn, would undergo reactions 5 through 8, thus closing a catalytic cycle.

Thus, in the presence of oxygen, the oxidative decarboxylation of one molecule of acid can potentially result in the oxidation of many Mn(II) ions to Mn(III), which then further induce oxidative decarboxylation. This branching chain mechanism explains why only a trace of peroxide can initiate the oxidation of significant quantities of Mn(II) in nonanoic acid. It also explains why, when air is removed from the system at elevated temperatures, any Mn(III) that had previously formed is reduced back to Mn(II) via the decarboxylation reaction and its resulting carbon radicals (since oxygen-centered radicals are no longer formed). When the mixture is re-exposed to air at 95 °C, autoxidation takes place to provide a trace of fresh peroxide, which reinitiates the chain oxidation of Mn(II) to Mn(III) via the oxidative decarboxylation. The ability of peroxide to initiate the formation of Mn(III) was demonstrated by adding a small amount of tert-butyl hydroperoxide to a sample of nitrogen-sparged, colorless Mn(II) solution in nonanoic acid at 40 °C. The red-brown color of Mn(III) developed within a few minutes.

Similar oxidation of Mn(II) to Mn(III) can be effected in heptanoic and pentanoic acids, but not in propionic or acetic acids. This relates to the relative rates of peroxide formation when these acids are exposed to air at elevated temperatures.

This facile oxidation of Mn(II) in the presence of higher carboxylic acids may represent a convenient method for in situ generation of Mn(III) for use in the oxidation of certain organic compounds. A complete review of the oxidation of organic compounds by manganese(III) compounds appears in ref 1. The reactions that could most likely be run using the Mn(III) generation technique described here are non-ligand-dependent, such as the oxidation of aromatic compounds to quinones (e.g., anthracene to anthraquinone[6]) and the coupling of phenols (e.g.,

2,6-di-tert-butylphenol to 4,4'-dihydroxy-3,3',5,5'-tetra-tert-butylbiphenyl[7]).

Many of the reactions of manganese(III) acetate with organic substrates in acetic acid solvent involve initial attack by radicals derived from the ligands and/or solvent (e.g., 2,5-dimethylbenzyl acetate from p-xylene;[8,9] γ-phenylbutyrolactone from styrene[10]). It is possible that the use of manganese(III) in long chain aliphatic acids would lead to analogous reactions involving α-position carbon radicals derived from the acid used.

Experimental Section

Nonanoic Acid. The nonanoic acid used in this work had been purified 10 months earlier by distillation of commercial Hoechst Celanese nonanoic (pelargonic) acid at 44 to 45 mm (bp 171.8–172.2 °C). This material was found to contain 9.6×10^{-4} M active oxygen by iodimetric analysis. This value increased to 1.8×10^{-3} M active oxygen in a 40-g sample of the acid, which had been heated to 95 °C for 2 h with a 30 mL/min air sparge.

Manganese Acetate and Nonanoic Acid. To 9.85 g (10.87 mL) of nonanoic acid was added 157 mg (0.641 mmol) of manganese(II) acetate tetrahydrate. The mixture was stirred in air for 30 min during which time the crystals dissolved and the liquid became progressively cloudier and more viscous. After a total of 50 min of stirring, a gelatinous mass had precipitated out of the liquid. The mixture was heated with stirring, and the gel redissolved at about 40 °C. The solution developed a light red-brown color while it was slowly heated to 95 °C. As it was held at that temperature, the color darkened. At this point, the hot solution was sparged with nitrogen. The color immediately began to lighten and after about 10 min was completely expelled, leaving a water-white solution. The color was redeveloped and expelled 6 times by sparging the solution for about 10 min with air or nitrogen, respectively.

Manganese(II) in Nonanoic Acid. A 0.059 M Mn(II) solution in nonanoic acid (prepared as described above) was treated with nitrogen at 95 °C until it was colorless. When this solution was cooled, a gel formed as it approached room temperature.

A molar equivalent (to the manganese) of tert-butyl hydroperoxide was added to a colorless, nitrogen-blanketed 0.059 M manganese(II) solution in nonanoic acid at 40 °C. The solution turned to a dark red-brown color over a 5-min period. Heating this solution to 95 °C under the flowing nitrogen blanket resulted in complete discharge of the color in about 5 min.

Manganese(III) in Nonanoic Acid. A sample of the 0.059 M Mn(III) solution (deep red-brown) in nonanoic acid that had been treated for 30 min with air was cooled to room temperature without any solid formation. A visible spectrum of this solution showed maxima at 495 nm (intense) and 458 nm (weaker). The solution was diluted to one-hundredth its concentration with nonanoic acid to eliminate the effect of Mn(II) on the Mn(III) spectrum[2] and the spectrum redetermined. The peak at 495 nm disappeared, leaving a peak with an absorbance of 0.08 at 458 nm. Using the extinction coefficient of 360 reported by Kochi for his 462 nm Mn(III) peak[2] leads to an estimated vlaue of 2.2×10^{-4} M Mn(III), corresponding to 0.022 M Mn(III) in the undiluted solution, or about 37% of the manganese present. On standing for a period of several days, small amounts of gel were observed to have precipitated from the original solution.

Manganese Acetate in Other Acids. Results similar to those described above were obtained when pentanoic or heptanoic acid was used in place of nonanoic acid. However, no visual evidence for the formation of manganese(III) was seen when acetic or propionic acid was used.

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