# One-Electron-Transfer Oxidation by Metal Salts. A Convenient Synthesis of γ,δ-Unsaturated Aldehydes

G. I. Nikishin, M. G. Vinogradov, and G. P. Il'ina

N. D. Zelinsky Institute of Organic Chemistry, USSR Academy of Sciences, Moscow, USSR.

In recent publications[1-4], a new initiator of free-radical addition, manganese(III) acetate, has been reported, which allows to greatly expand the synthetic possibilities of this method.

Aliphatic aldehydes (**1**) react with linear α-olefins (**2**) in the presence of manganese(III) acetate to give a mixture of an α-alkyl-substituted aldehyde (**10**), its γ-acetoxy derivative, and a ketone (**9**), the yield of each product depending on the reaction conditions[5].

We now report that the addition of catalytic amounts of copper(II) salts to the reaction mixture alters the course of the reaction entirely. Under these conditions, the reaction affords the unsaturated aldehydes **4**, **5**, and **7** with rather high selectivity (Table 1). Hydrogen abstraction by the intermediate radical **3**, giving aldehyde **10**, is not significant under our reaction conditions. Neither the saturated ketone **9** nor the corresponding unsaturated ketone were detected in the reaction product. This result indicates that addition of acyl radicals to olefinic double bonds does not occur during the copper(II)-catalyzed reaction. In the absence of copper(II) ion, the saturated carbonyl compounds **9** and **10** are the only isolable products.

The results summarized in Table 1 show that the oxidation of aldehydes with manganese(III) acetate in the presence of olefins and of catalytic amounts of copper(II) salts represents a convenient method for the preparation of certain unsaturated aldehydes.

The isolation of $\alpha,\beta$-unsaturated $\gamma$-acetoxyaldehyde **7** as the main product of the independent manganese(III)-acetate oxidation of $\beta,\gamma$-unsaturated aldehyde **4** showed that **4** is the precursor of **7**. The first step of the reaction seems to be the oxidation of **4** to allyl radical **6**; thus, the formation of two isomeric acetoxy derivatives (having the double bond in the $\alpha,\beta$- and $\beta,\gamma$-positions, respectively) would be expected. However, only the $\alpha,\beta$-isomer (**7**) was found in the product mixture. This result can be explained by a polar effect, since the oxidation of 1-substituted radicals, $R-\underset{|}{C}-X$, by electron transfer is known to proceed with difficulty when X is an electron-withdrawing group[6].

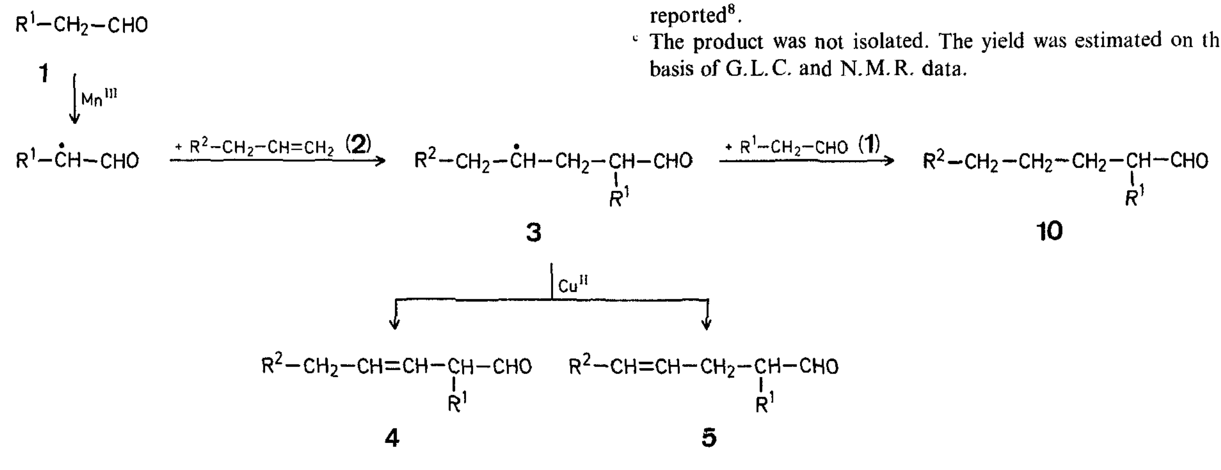
Table 1. Reaction of Aldehydes (**1**) with 1-Alkenes (**2**) in the Presence of Manganese(III) Acetate and Catalytic Amounts of Copper(II) Acetate

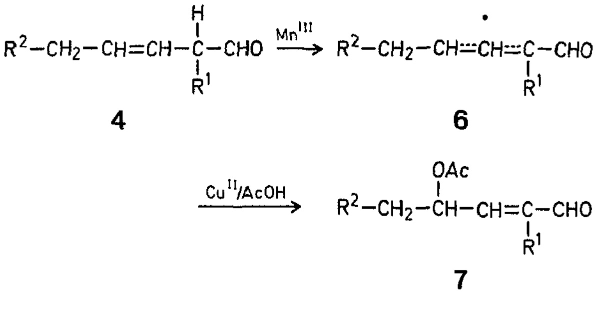
| $R^1$ | $R^2$ | Catalyst | Yield[a] % | | | |
|---|---|---|---|---|---|---|
| | | | 5 | 7 | 9 | 10[b] |
| H | $n$-$C_4H_9$ | – | – | – | 32 | 34 |
| H | $n$-$C_4H_9$ | $Cu^{II}$ | 20 | 10 | – | 1 |
| H | $n$-$C_5H_{11}$ | $Cu^{II}$ | 18 | 10 | – | 1 |
| $CH_3$ | $n$-$C_4H_9$ | $Cu^{II}$ | 25 | 4[c] | – | 2 |
| $CH_3$ | $n$-$C_6H_{13}$ | $Cu^{II}$ | 32 | 4[c] | – | 5 |
| $CH_3$ | $n$-$C_7H_{15}$ | $Cu^{II}$ | 22 | 3[c] | – | 3 |
| $C_2H_5$ | $n$-$C_3H_7$ | $Cu^{II}$ | 40 | – | – | 2 |
| $C_2H_5$ | $n$-$C_5H_{11}$ | $Cu^{II}$ | 25 | – | – | 3 |

[a] Based on oxidant reacted, assuming 1 equiv per **9** or **10**, 2 equiv per **5**, and 4 equiv per **7**.

[b] Identified by G.L.C. The authentic samples were prepared as reported[8].

[c] The product was not isolated. The yield was estimated on the basis of G.L.C. and N.M.R. data.





Under similar conditions, the reaction of aldehydes with branched olefins, such as isobutene or 2-methyl-1-pentene, also leads to unsaturated aldehydes. However, in this case the $\beta,\gamma$-isomer is usually more stable and is not easily oxidized during the course of the reaction.

**Oxidation of Mixtures of Aldehydes and Olefins with Manganese(III) Acetate in the Presence of Copper(II) Salts; General Procedure:**

A mixture of the aldehyde (1 mol), the olefin (0.2 mol), manganese(III) acetate[7] [$Mn(OCOCH_3)_3 \cdot 2H_2O$; 26.8 g, 0.1 mol], copper(II) acetate [$Cu(OCOCH_3)_2 \cdot H_2O$; 2 g, 0.01 mol], and glacial acetic acid (40 ml) is shaken in a closed vessel at 55–60° until the brown color of manganese(III) acetate has disappeared. Ether (200 ml) is then added, the mixture is washed with water (3 x 100 ml), the solvent evaporated, and the products are isolated by distillation.

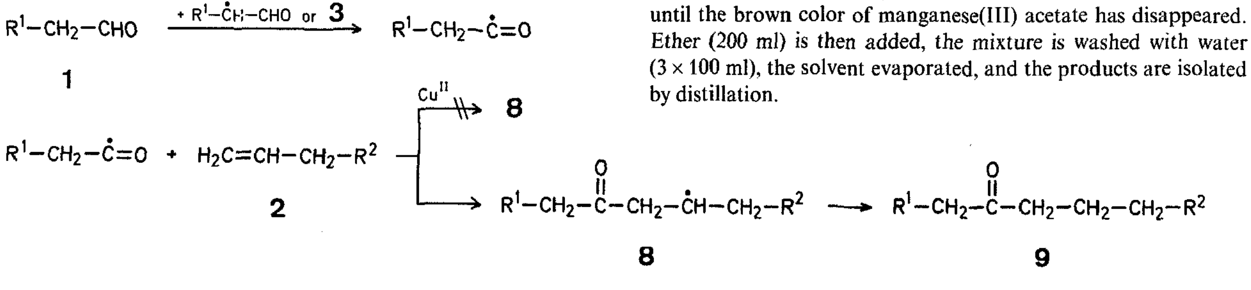


Table 2. $\gamma,\delta$-Unsaturated Aldehydes (**5**) and their 2,4-Dinitrophenylhydrazones

| $R^1$ | $R^2$ | b.p. | I.R. (film) $\nu_{max}$ [cm$^{-1}$] | 60-MHz N.M.R. ($CCl_4$) $\delta$ [ppm] | m.p. of 2,4-DNPH[a] |
|---|---|---|---|---|---|
| H | $n$-$C_4H_9$ | 70°/5 mm | 977, 1730 2725 | 5.35 (m, 2H)<br>9.58 (t, 1H) | 76–78° |
| H | $n$-$C_5H_{11}$ | 90°/5 mm | 980, 1730, 2725 | 5.32 (m, 2H),<br>9.58 (t, 1H) | 101–101,5° |
| $CH_3$ | $n$-$C_4H_9$ | 58–60°/3 mm | 975, 1728, 2715 | 5.32 (m, 2H),<br>9.50 (d, 1H) | 76–78° |
| $CH_3$ | $n$-$C_6H_{13}$ | 73°/2 mm | 972, 1730, 2720 | 5.32 (m, 2H),<br>9.57 (d, 1H) | 76–77.5° |
| $CH_3$ | $n$-$C_7H_{15}$ | 125–127°/3 mm | 977, 1732, 2717 | 5.35 (m, 2H),<br>9.59 (d, 1H) | 88–89° |
| $C_2H_5$ | $n$-$C_3H_7$ | 48–50°/2 mm | 975, 1728, 2710 | – | 72–73° |
| $C_2H_5$ | $n$-$C_5H_{11}$ | 72–74°/2 mm | 975, 1728, 2715 | – | 57–58° |

[a] The elemental analyses (N) were in good accordance with the calculated values.

Table 3. Spectral Characteristics of 4-Acetoxy-2-alkyl-*trans*-2-alkenals (**7**)

| $R^1$ | $R^2$ | b.p. | I.R. (film) [cm$^{-1}$] | U.V. (heptane) [nm] | 60-MHz N.M.R. ($CCl_4$) $\delta$ [ppm] |
|---|---|---|---|---|---|
| H | $n$-$C_4H_9$ | 98–100°/5 mm | 980, 1238, 1642, 1692, 1720, 1740, 2730 | 215 ($\varepsilon = 13500$) | 1.99 (s, 3H), 5.42 (m, 1H),<br>6.03 (d/d/d, $J = 16/7/1.5$ Hz, 1H)<br>6.72 (d/d, $J = 16/5$ Hz, 1H).<br>9.36 (d, $J = 7$ Hz, 1 H) |
| H | $n$-$C_5H_{11}$ | 128–130°/5 mm | 980, 1236, 1642, 1692 1720, 1740, 2728 | 215 ($\varepsilon = 16000$) | 2.07 (s, 3H), 5.41 (m, 1H),<br>6.10 (d/d/d, $J = 16/7.5/1.2$ Hz, 1 H)<br>6.71 (d/d, $J = 16/4.5$ Hz, 1 H),<br>9.45 (d, $J = 7.5$ Hz, 1 H) |
| $CH_3$ | $n$-$C_4H_9$ | 125–130°/3 mm | 980, 1240, 1640, 1688, 1723, 2715 | 227 ($\varepsilon = 19000$) | 1.72 (s, 3H), 1.97 (s, 3H),<br>9.28 (s, 1H) |

Received: February 10, 1972

---

[1] E. I. Heiba, R. M. Dessau, W. J. Koehl, J. Amer. Chem. Soc., **90**, 5905 (1968).

[2] G. I. Nikishin, M. G. Vinogradov, S. P. Verenchikov, Izv. Akad. Nauk SSSR, Ser. Chim. **1969**, 1835.

[3] M. G. Vinogradov, S. P. Verenchikov, G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Chim. **1971**, 200.

[4] E. I. Heiba, R. M. Dessau, J. Amer. Chem. Soc. **93**, 524 (1971).

[5] G. I. Nikishin, M. G. Vinogradov, S. P. Verenchikov, I.N. Kostyukov, R.V. Kereselidze, Zh. Org. Khim. **8**, 539 (1972).

[6] J. K. Kochi, F. F. Rust, J. Amer. Chem. Soc. **84**, 3946 (1962).

[7] O. T. Christensen, Z. anorg. Chem. **27**, 325 (1901).

[8] M. G. Vinogradov, R. V. Kereselidze, G. G. Gachechiladze, G. I. Nikishin, Izv. Akad. Nauk SSSR, Ser. Chim. **1969**, 322.