

The Preparation of *alpha*-Diones. Phase-Transfer Assisted Oxidation of Alkynes by Potassium Permanganate

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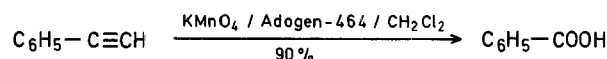
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Although the conversion of alkynes to the corresponding diones through oxidation by potassium permanganate is widely reported as a general reaction¹, the only examples described in the literature are concerned with the oxidation of substrates such as stearolic acid² which are soluble in aqueous base. This limitation, which was imposed historically by the low solubility of potassium permanganate in non-polar solvents, may be overcome through use of phase-transfer reagents³. Either tetraalkylammonium salts⁴ or polyethers (cyclic⁵ and non-cyclic⁶) may be used and in this paper we wish to report on reaction conditions and products that pertain to the oxidation of several typical alkynes.

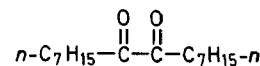
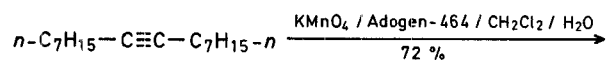
The solvents most commonly used for phase-transfer assisted permanganate oxidations are benzene and dichloromethane.

Since alkynes are relatively resistant to oxidation, elevated temperatures are required to produce convenient reaction rates and this precluded the use of benzene which was found to undergo oxidative decomposition at the required temperatures. However, dichloromethane is more stable toward oxidants and it was found convenient to work at the reflux temperature of this solvent.

As the results presented in the Table indicate terminal alkynes may be converted, by oxidative cleavage of the carbon-carbon triple bond, to the corresponding carboxylic acids (Scheme A). Non-terminal alkynes, on the other hand, do not as readily undergo cleavage and good yields of the intermediate α -diones can consequently be achieved (Scheme B).



Scheme A



Scheme B

The oxidant may be used either in the form of a solid powder (method A below) or as an aqueous solution (method B). It is often necessary to use an excess of oxidant because some of it becomes trapped in the mass of manganese dioxide which precipitates as the reaction proceeds. This problem is less severe when an aqueous solution is used (as in method B). However, in the presence of water cleavage reactions are more likely, particularly if the vigor of the reaction conditions are increased by use of excess oxidant or acetic acid. (The latter is added to neutralize hydroxide ion which is always produced during the reduction of permanganate).

Preparation of 1-Phenyl-1,2-pentanedione; Method A:

A 200 ml Erlenmeyer flask, equipped with a reflux condenser, is charged with dichloromethane (100 ml), acetic acid (5 ml) and 1-phenyl-1-pentyne (2.0 g, 0.014 mol). The solution is stirred magnetically and heated to reflux temperature before powdered potassium permanganate⁷ (5.85 g, 0.037 mol) and the phase-transfer agent (Adogen-464; 1.6 g)⁸ are added. After being stirred vigorously for 4 h the precipitated manganese dioxide is collected and washed with dichloromethane (2 x 50 ml). Residual manganese dioxide is reduced by addition (to the combined filtrates) of 20% hydrochloric acid (40 ml) followed by small portions of sodium hydrogen sulfite until all of the brown color has disappeared. The organic phase is separated, washed with water, and dried with anhydrous magnesium sulfate. Most of the solvent is removed using a rotary evaporator and the remaining yellow oil distilled under vacuum to give unreacted starting material (0.14 g) and 1-phenyl-1,2-pentanedione; yield: 1.98 g (81%); b.p. 108–110°/5.5 torr; Lit.⁹ b.p. 82–84°/3 torr.

I.R. (neat): $\nu_{\text{max}} = 2990, 2950, 2965, 1710, 1680 \text{ cm}^{-1}$.

¹H-N.M.R. (CCl₄): $\delta = 0.99$ (t, 3H); 1.67 (m, 2H); 2.81 (t, 2H); 7.57 ppm (m, 5H_{arom}).

Preparation of 8,9-Hexadecanedione; Method B:

Potassium permanganate (5.85 g, 0.037 mol) is dissolved in water (100 ml) in a 500 ml Erlenmeyer flask and a solution consisting of 8-hexadecyne (2.0 g, 0.009 mol), dichloromethane (100 ml), acetic acid (5 ml), and phase-transfer agent (Adogen-464; 1.5 g)⁸ is added. The solution is stirred magnetically and heated under reflux for 6 h. After cooling sodium hydrogen sulfite (2 g) is added to reduce any unreacted permanganate. After 15 min the solution is acidified (conc. hydrochloric acid) and the precipitated man-

Table. Oxidation of Alkynes

R ¹	Method	Oxidant ratio ^a	Yield [%]	m.p. or b.p./torr	Lit. m.p. or b.p./torr
C ₆ H ₅	A	2.7	90	121–122°	122° ¹¹
n-C ₄ H ₉	A	2.7	61	80–83°/10	96°/23 ¹¹



R ¹	R ²	Method	Oxidant ratio ^a	Yield [%]	m.p. or b.p./torr	Lit. m.p. or b.p./torr
C ₆ H ₅	C ₆ H ₅	B	3.0	93	94–95°	95° ¹¹
C ₆ H ₅	n-C ₃ H ₇	A	2.7	81	108–110°/5.5	82–84°/3 ⁹
C ₆ H ₅	n-C ₃ H ₇	B	4.1	56	—	—
C ₆ H ₅	n-C ₄ H ₉	B	4.1	41	98–102°/1.2	144–145°/20 ¹²
n-C ₆ H ₁₃	n-C ₆ H ₁₃	A	2.7	54	38–39°	—
n-C ₆ H ₁₃	n-C ₆ H ₁₃	B	2.2	57	—	—
n-C ₇ H ₁₅	n-C ₇ H ₁₅	A	4.0	68	51–52°	49–50° ¹⁰
n-C ₇ H ₁₅	n-C ₇ H ₁₅	A	6.0	80	—	—
n-C ₇ H ₁₅	n-C ₇ H ₁₅	B	4.1	68	—	—

^a Molar ratio of KMnO₄ to alkyne.

ganese dioxide reduced by addition, in small portions, of the required amount of sodium hydrogen sulfite. The aqueous phase is separated, saturated with sodium chloride, and extracted with dichloromethane (3 × 75 ml). The organic layers are combined and extracted with 5% aqueous sodium hydroxide (3 × 75 ml), dried over anhydrous magnesium sulfate, and concentrated by rotary evaporation to give a yellow liquid which solidifies on cooling. This yellow solid is recrystallized from methanol (15 ml) to give 8,9-hexadecanedione; yield: 1.55 g (68%); m.p. 51–52°; Lit. ¹⁰ m.p. 49–50°.

I.R. (melt): $\nu_{\max} = 2950, 2910, 2850, 1705 \text{ cm}^{-1}$.

¹H-N.M.R. (CCl₄): $\delta = 0.90$ (t, 6H), 1.32 (m, 20H), 2.68 ppm (t, 4H).

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⁷ A very finely powdered form of potassium permanganate is available from the Carus Chemical Company under the trade name "Cairox M".

⁸ Adogen-464, a methyltrialkyl(C₈–C₁₀)ammonium chloride, was obtained from Ashland Chemicals.

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