Registry No.—Boron trifluoride, 7637-07-2; *tert*-butyl nitrite, 540-80-7; nitrosyl fluoride; 7789-25-5.

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Preparation of 1,2-Diketones: Oxidation of Alkynes by Potassium Permanganate in Aqueous Acetone

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Although the oxidation of alkynes to the corresponding 1,2-diones by potassium permanganate is often considered to be a general reaction, the literature describes only two methods for effecting these transformations. One of them is restricted to alkynes such as stearolic acid,[1] which are soluble in aqueous base, and the other necessitates the use of phase-transfer agents.[2] In this note we wish to report a simple, general method for the oxidation of alkynes to the corresponding 1,2-diones in aqueous acetone solutions (Table I).

In order to obtain good yields, it is necessary to maintain an approximately neutral solution. This can be achieved by addition of definite amounts[3] of sodium bicarbonate and magnesium sulfate. The added salts serve as a buffer (pH 7.0–7.5 initially) and neutralize hydroxide ions which are produced during the reduction of permanganate.[4]

Preparation of 8,9-Hexadecanedione. A 2-L Erlenmeyer flask, immersed in a water bath at 25 °C, was charged with reagent grade acetone (1.05 L) and 8-hexadecyne (6 g, 0.027 mol). To this was added a solution of $NaHCO_3$ (1.36 g, 0.0162 mol) and $MgSO_4$ (13.6 g, 0.0552 mol) in water (600 mL). The mixture was stirred with a mechanical stirrer. Powdered potassium permanganate[5] (16.6 g, 0.105 mol) was added in one portion, and the mixture was stirred for 4 h. The unreacted permangante and the precipitated MnO_2 were reduced to soluble Mn^{2+} ions by adding a minimum quantity of $NaNO_2$ (7 g) and 10% H_2SO_4 (70 mL) in small portions. The solution was transferred to a 2-L separating funnel, saturated with NaCl, and extracted with a hexane–ether mixture (1:1, 3 × 200 mL). The organic solvents were removed using a rotary evaporator. The residue was dissolved in ether (50 mL) and extracted with a dilute NaOH solution (5%, 4 × 50 mL) to remove any carboxylic acids present. The ether layer was washed with a saturated solution of NaCl and dried (anhydrous Na_2SO_4), and the solvent was removed in a rotary evaporator. The crude product obtained weighed 6.75 g (98%). The solid, when recrystallized from methanol, gave 8,9-hexadecanedione as yellow plates (5.6 g, 81%): mp 48.5–49.5 °C (lit.[6] 49–50 °C); IR (melt) 2930, 1705, 1475 cm^{-1}; NMR (CCl_4) δ 0.9 (t, 6 H), 1.32 (m, 20 H), 2.67 (t, 4 H).

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(3) It was found that the use of approximately 0.9 g of $NaHCO_3$ and 8.5 g of $MgSO_4$ per liter of solution gave good results. The use of excess $NaHCO_3$ promotes oxidation of the solvent.
(4) The yield of dione decreased if the initial pH was allowed to increase to 7.8 or greater or in the absence of either sodium bicarbonate or magnesium sulfate.
(5) A very finely powdered form of potassium permanganate was used. It is available under the trade name Cairox M from the Carus Chemical Co. Inc., La Salle, Ill.
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Table I. Oxidation of Alkynes by Potassium Permanganate[m] in Aqueous Acetone

alkyne	registry no.	reaction time, h	product (yield, %)[a]	registry no.	mp or bp (lit.), °C
5-decyne[b,c]	1942-46-7	4	5,6-decanedione (40)[d]	5579-73-7	60–61/6 torr (90–91/12 torr)[e]
7-tetradecyne[b,f]	35216-11-6	4	7,8-tetradecanedione (69)[g]	6305-47-1	38–39 (38–39)[h]
8-hexadecyne[b,f]	19781-86-3	4	8,9-hexadecanedione (81)[d]	18229-29-3	48.5–49.5 (49–50)[i]
1-phenyl-1-pentyne[b,c]	4250-81-1	1.75	1-phenyl-1,2-pentanedione (77)[g,j]	20895-66-3	
diphenylacetylene[k,c]	501-65-5	3	1,2-diphenyl-1,2-ethanedione (88)[d]	134-81-6	95–96 (95)[l]

[a] The IR and NMR spectra of the products were consistent with the proposed structures. [b] Obtained from the Chemical Samples Co. [c] Molar ratio of alkyne/$KMnO_4$ = 1.85:1. [d] Isolated yield. [e] Reference 7. [f] Molar ratio of alkyne/$KMnO_4$ = 3.9:1. [g] Based on GLC analysis: 224 × 0.6 cm d., 15% silicone gum rubber SE-30 on Chromosorb W 60–80 column. [h] Reference 2. [i] Reference 6. [j] Isolated by use of preparative GLC. [k] Obtained from the Aldrich Chemical Co. [l] Reference 8. [m] Registry no., 7722-64-7.

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