A Simple and Improved Procedure for the Conversion of Alkynes to 1,2-Diketones by Indirect Electrooxidation With Ruthenium Tetroxide as a Mediator

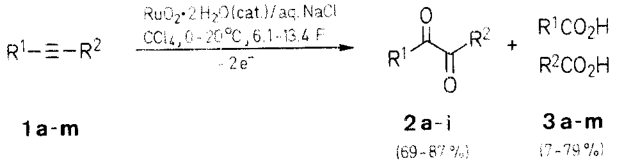
Sigeru Torii,* Tsutomu Inokuchi, Youzou Hirata

Department of Industrial Chemistry, School of Engineering, Okayama University, Okayama 700, Japan

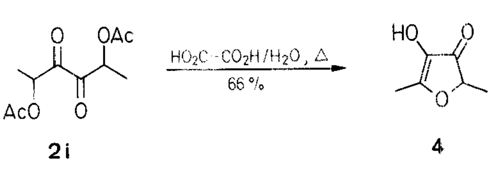
Indirect electrooxidation of alkynes **1** using ruthenium tetroxide as a mediator, leading to 1,2-diones **2** in 72–87%, is described. The electrolysis is carried out in the presence of a catalytic amount of ruthenium dioxide dihydrate in a two phase system of saturated aqueous sodium chloride and carbon tetrachloride. The overoxidation of 1,2-diones to the corresponding carboxylic acid, an unavoidable drawback generally encountered in the metal oxidation of acetylenes, is suppressed greatly by maintaining the pH of the aqueous phase at 4 and conducting the reaction at 0–5 °C. The synthetic utility of this electrochemical oxidation is exemplified by the preparation of **2i** (82%), a key intermediate for the synthesis of furaneol **4**, from the commercially available **1i**.

α-Diketones **2** have attracted considerable interest because of their utility as intermediates in organic syntheses[1] and their widespread occurrance in biologically important compounds.[2,3] Among the reported methods for their preparation,[4–9] the oxidation of acetylenes **1**[10] with oxidants such as thallium(III) trinitrate,[11] potassium permanganate,[12,13] ruthenium tetroxide-sodium hypochlorite,[14] osmium tetroxide-potassium chlorate,[15,16] tris(triphenylphosphine)ruthenium(II) chloride-iodosylbenzene,[17] and others[18–20] is considered to be quite versatile from the standpoint of (a) product selectivity, (b) easy availability of starting acetylenes, and (c) general applicability of the reaction. However, the overoxidation to afford carboxylic acids **3** encountered often in these oxidative transformations is the drawback which makes the product isolation difficult. Thus, a procedure for the selective oxidation of alkynes **1** to α-diketones **2** is needed. In this paper we describe the ruthenium tetroxide mediated electrooxidation of alkynes **1** to 1,2-diones **2** and its application in the synthesis of 4-hydroxy-3(2*H*)-furanone.[3]

In analogy with our reported procedure,[21] the electrooxidation of alkynes **1** was carried out in a two phase system of carbon tetrachloride and aqueous buffered sodium chloride (pH 4) at 0–5 °C. Thus, the electrolysis of **1a** in the presence of a catalytic amount of ruthenium dioxide dihydrate at a constant current density (20 mA/cm²) gave the desired **2a** in 75 % yield along with a small amount of carboxylic acid **3a** (7 %) [when 7.5 F/ mol of electricity (based on **1a**) had been passed.] The pH 4 buffer was found to be essential to supress overoxidation to the corresponding carboxylic acids **3**; the yield of **2a** decreased to 65 % and 58 % upon increasing the pH to 7 (buffered with M/30 potassium dihydrogen phosphate + M/30 disodium hydrogen phosphate, yield of **3a**: 19 %) and pH 9 (buffered with disodium hydrogen phosphate, yield of **3a**: 20 %), respectively. Although the present results were almost identical with respect to the overall yield with that of the ruthenium tetroxide-sodium hypochlorite catalyzed oxidation of **1a**,[14] the relative ratio of **2a** to **3a** was improved from the literature data of 3.6 : 1 to the present data of 10.7 : 1. On the other hand, the chemical oxidation of **2a** with a combination of ruthenium tetroxide and sodium periodate catalytically or stoichiometrically was entirely unsuccessful, possibly because the initially formed **2a** suffered further oxidation with the co-oxidant, sodium periodate, present in the medium.[14]



As noted in Table, disubstituted acetylenes bearing longer alkyl chaines gave the desired **2** in higher yields than the alkynes having shorter alkyl chaines. In accordance with the results reported concerning permanganate[12,13] and ruthenium tetroxide-sodium hypochlorite[14] oxidations, terminal acetylenes **1** lead to a cleavage of carbon-carbon bond to give the corresponding carboxylic acids **3**, exclusively. The oxidation of acetylene **1i** to the corresponding diketone **2i** is of special importance as **2i** is an intermediate in the synthesis of 2,5-dimethyl-4-hydroxy-2*H*-furan-3-one **4**, a key flavor component in a variety of foods.[3] The electrolysis of **1i** at 15–20 °C resulted in the cleavage of a carbon-carbon bond to give predominantly the corresponding carboxylic acid **3i**, while the electrooxidation at 0–5 °C produced the desired **2i** as the major product (82%) along with a small amount of **3i** (7%). According to the method reported,[3] **2i** was converted to **4** in 66 % yields by acidic treatment with aqueous oxalic acid.



Ac = CH_3CO

In this paper, we have demonstrated the utility of the indirect electrochemical oxidation of alkynes to 1,2-diones. The *in situ* generation of ruthenium tetroxide by electrolysis in this two phase system seems to be particulary suitable for the synthesis of 1,2-diones susceptible to further oxidations with metal oxidant to the corresponding carboxylic acids.

Commercially available alkynes were purified by distillation or column chromatography (silica gel, *n*-hexane/ethyl acetate) prior to use. Other acetylenes were prepared by the known procedures.[10]

Ruthenium Tetroxide Mediated Electrooxidation of Alkynes 1 to 1,2-Diketones 2 and/or Carboxylic Acid 3; Typical Procedures:

Decane-5,6-dione (**2a**): To a solution of 5-decyne (**1a**; 138.3 mg, 1.0 mmol) in carbon tetrachloride (5 ml) in a cylindrical vessel (2.5 cm diameter and 10 cm height, 30 ml volume) is added ruthenium dioxide dihydrate (4.6 mg, 0.03 mmol) and saturated aqueous sodium chloride (buffered to pH 4 with 0.2 molar sodium dihydrogen phosphate, 10 ml).

Table 1. Ruthenium Tetroxide Mediated Electrooxidation of Alkynes **1**

Substrate	R^1	R^2	Reaction Conditions		Product(s), Yield (%)[a]	
			Temp. (°C)	Electricity[b] (F/mol)	**2**	**3**[c]
1a	n-C_4H_9	n-C_4H_9	0–5	7.5	75	7
1b	n-C_6H_{13}	n-C_6H_{13}	0–5	8.1	83	7
1c	C_6H_5	C_2H_5	15–20	6.7	73	10
1d	C_6H_5	n-C_4H_9	0–5	7.3	72	17 (13)[c]
1e	C_6H_5	n-C_6H_{13}	0–5	6.6	79	8 (11)[d]
1f	n-C_5H_{11}	CH_2OAc	0–5	6.7	69	29
1g	n-C_6H_{13}	CH_2OAc	15–20	6.7	80	11
1h	n-$C_{10}H_{21}$	CH_2OAc	15–20	7.1	87	7
1i	$CH_3CH(OAc)$	$CH_3CH(OAc)$	0–5	6.1	82	7
1j	$CH_3CH(OAc)CH_2$	CH_2OAc	15–20	7.5	–	77
1k	C_6H_5	H	15–20	11.6	–	59
1l	C_6H_{13}	H	15–20	11.3	–	76
1m	C_8H_{17}	H	15–20	13.4	–	79

[a] Yield of isolated product by column chromatography (silica gel).
[b] Passed electricity based on **1** for complete conversion into **2** and **3**.
[c] Number in parenthesis indicates the yield of pentanoic acid.
[d] Number in parenthesis indicates the yield of heptanoic acid.
[e] Characterized after esterification with diazomethane.

Table 2. Properties of Dialkyl Diketones **2** and the Carboxylic Acid **3** Prepared from Alkynes **1**

Compound	m.p. (°C) or b.p. (°C)/mbar	Molecular Formula[a] or Lit. m.p. (°C) or b.p. (°C)/mbar	IR (Film) $\nu_{C=O}$ (cm^{-1})	^{1}H-NMR ($CDCl_3$) δ (ppm)
2a	75–77/20	b.p. 60–61/8[13]	1710	0.93 (m, 6H, CH_3); 1.45 (m, 8H, CH_2); 2.71 (t, 4H, $J = 6$ Hz, CH_2CO)
2b	37–38	m.p. 38–39[12]	1710	0.88 (m, 6H, CH_3); 1.32 (m, 16H, CH_2); 2.70 (t, 4H, $J = 6$ Hz, CH_2CO)
2c	107–109/20	b.p. 74–76/0.7[22]	1710, 1670	1.16 (t, 3H, $J = 7$ Hz, CH_3); 2.89 (q, $J = 7$ Hz, 2H, CH_2); 7.30–7.80 (m, 3H_{arom}); 7.88–8.20 (m, 2H_{arom})
2d	76–78/5	b.p. 144–145/27[23]	1705, 1670	0.91 (m, 3H, CH_3); 1.55 (m, 4H, CH_2); 2.84 (t, 2H, $J = 7$ Hz, CH_2CO); 7.20–7.70 (m, 3H_{arom}); 7.77–8.03 (m, 2H_{arom})
2e	125–127/5	$C_{14}H_{18}O_2$ (218.3)	1715, 1680	0.86 (m, 3H, CH_3); 1.30 (m, 8H, CH_2); 2.81 (t, 2H, $J = 7$ Hz, CH_2CO); 7.18–7.55 (m, 3H_{arom}); 7.74–7.98 (m, 2H_{arom})
2f	94–96/37	$C_{10}H_{16}O_4$ (200.2)	1750, 1730, 1705	0.89 (m, 3H, CH_3); 1.38 (m, 6H, CH_2); 2.12 (s, 3H, $COCH_3$); 2.72 (t, 2H, $J = 6$ Hz, CH_2CO); 5.01 (s, 2H, $COCH_2O$)
2g	116–118/24	$C_{11}H_{18}O_4$ (214.3)	1751, 1730, 1707	0.89 (m, 3H, CH_3); 1.35 (m, 8H, CH_2); 2.17 (s, 3H, $COCH_3$); 2.77 (t, 2H, $J = 6$ Hz, CH_2CO); 5.09 (s, 2H, $COCH_2O$)
2h	36–38	$C_{15}H_{26}O_4$ (270.4)	1745, 1735, 1715	0.85 (m, 3H, CH_3); 1.23 (br s, 16H, CH_2); 2.13 (s, 3H, $COCH_3$); 2.72 (t, 2H, $J = 7$ Hz, CH_2CO); 5.03 (s, 2H, $COCH_2O$)
2i	46–48	m.p. 72–73[3]	1735, 1715	1.44 (d, 6H, $J = 7$ Hz, CH_3); 2.07 (s, 6H, $COCH_3$); 5.55, 5.59 (q, 2H, $J = 7$ Hz, COCH)
3j	76–78/31	$C_7H_{12}O_4$ (160.2)	1740	1.32 (d, 3H, $J = 7$ Hz, CH_3); 2.02 (s, 3H, $COCH_3$); 2.59 (d, 2H, CH_2CO); 3.69 (s, 3H, OCH_3); 5.27 (m, 1H, OCH)
3k	120–122	m.p. 122–123[24]	1690	7.19–7.63 (m, 3H_{arom}); 7.96–8.20 (m, 2H_{arom}); 12.40 (br s, 1H, CO_2H)
3l	83–85/23	b.p. 172–173.5/atmos[24]	1741	0.88 (m, 3H, CH_3); 1.26 (m, 8H, CH_2); 2.30 (t, 2H, $J = 6$ Hz, CH_2CO); 3.66 (s, 3H, OCH_3)
3m	109–111/21	b.p. 213–214/atmos[24]	1736	0.85 (m, 3H, CH_3); 1.25 (m, 12H, CH_2); 2.25 (t, 2H, $J = 6$ Hz, CH_2CO); 3.60 (s, 3H, OCH_3)

[a] Satisfactory microanalyses obtained: C ±0.29, H ±0.29.

Two platinum foil electrodes (3 cm^2) are immersed in the upper aqueous layer of this two phase mixture and the entire mixture is electrolyzed under a constant current density of 20 mA/cm^2 with vigorous stirring at 0–5 °C. During the electrolysis, the direction of current is changed every 60 sec. After passing about 7.5 F/mol of electricity through the system (based on **1a**), the mixture is treated with 2-propanol (0.5 ml) to destroy the excess ruthenium tetroxide. The organic layer is separated and the aqueous layer is acidified with 5% hydrochloric acid to pH 2 and extracted with ethyl acetate (5 × 2 ml). The combined extract is dried with sodium sulfate and concentrated *in vacuo*. The crude product is purified by column chromatography (silica gel, *n*-hexane/ethyl acetate) to give a mixture of *decane-5,6-dione* **2a**; yield: 127.7 mg (75%) and *pentanoic acid* **3a**; yield: 14.3 mg (7%) (Tables 1 and 2).

Indirect Electrooxidation of 2,5-Diacetoxy-3-hexyne 1i

A cylindrical vessel (2.5 cm diameter and 10 cm height, 30 ml volume) is charged with a solution of 2,5-diacetoxy-3-hexyne (**1i**; 196.6 mg, 0.99 mmol) in carbon tetrachloride (5 ml). To this solution is added ruthenium dioxide dihydrate (3.9 mg, 0.02 mmol) and then saturated sodium chloride solution (buffered to pH 4 with 0.2 molar sodium dihydrogen phosphate, 10 ml). The platinum foil electrodes (3 cm^2) are immersed in the upper aqueous layer. The mixture is electrolyzed under a constant current density of 20 mA/cm^2 with vigorous stirring at 0–5 °C. After passing about 6.1 F/mol of electricity (based on **1i**), the mixture is treated with 2-propanol (about 0.1 ml). The organic layer is separated and the aqueous layer is extracted with ethyl acetate (2 × 8 ml). The organic layer is dried with sodium sulfate and concentrated. The residue is purified by column chromatography on silica gel (*n*-hexane/ethyl acetate) to afford *2,5-diacetoxyhexane-3,4-dione* **2i**; yield: 186.9 mg (82%)

4-Hydroxy-2,5-dimethyl-3(2*H*)-furanone (4)

A suspension of the diketone **2i** (195.5 mg, 0.85 mmol) and oxalic acid (153.2 mg, 1.70 mmol) in water (1.5 ml) is heated at reflux under argon for 3.2 h. The mixture is poured into saturated brine (10 ml) and extracted with ethyl acetate (5 × 8 ml). The extract is washed with saturated brine (2 × 10 ml), dried with sodium sulfate and concentrated *in vacuo*. The crude product is purified by HPLC [SEP-PAK (PART No. 51900, Silica Cartrige), Water Associates, Inc.] to give the furanone; yield: 71.9 mg (66%). The product is identified with an authentic sample by comparison of its spectral data.[3]

Received: 26 August 1986

(1) Trost, B.M., Keinan, E. *J. Org. Chem.* **1980**, *45*, 2741.
Mattay, J., Runsink, J. *J. Org. Chem.* **1985**, *50*, 2815.

(2) Recent examples:
Hillis, L.R., Ronald, R.C. *J. Org. Chem.* **1985**, *50*, 470.
Rozwadowska, M.D., Chrzanowska, M. *Tetrahedron* **1985**, *41*, 2885.

(3) Re, L., Maurer, B., Ohloff, G. *Helv. Chim. Acta* **1973**, *56*, 1882.

(4) Hendrickson, J.B., Schwartzman, S.M. *Tetrahedron Lett.* **1975**, 273.

(5) Sharpless, K.B., Lauer, R.F., Repič, O., Teranishi, A.Y., Williams, D.R. *J. Am. Chem. Soc.* **1971**, *93*, 3303.

(6) Bauer, D.P., Macomber, R.S. *J. Org. Chem.* **1975**, *40*, 1990.

(7) Regen, S.L., Whitesides, G.M. *J. Org. Chem.* **1972**, *37*, 1832.

(8) Kimpe, N.D., Verhé, R., Buyck, L.D., Schamp, N. *J. Org. Chem.* **1978**, *43*, 2933.

(9) Leyendecker, J., Niewöhner, U., Steglich, W. *Tetrahedron Lett.* **1983**, *24*, 2375.

(10) Rutledge, T.F. in: *Acetylenes and Allenes*, Reinhold Book Co., New York, Amsterdam, London, 1969.

(11) McKillop, A., Oldenziel, O.H., Swann, B.P., Taylor, E.C., Robey, R.L. *J. Am. Chem. Soc.* **1973**, *95*, 1296.

(12) Lee, D.G., Chang, V.S. *Synthesis* **1978**, 462.

(13) Srinivasan, N.S., Lee, D.G. *J. Org. Chem.* **1979**, *44*, 1574.

(14) Gopal, H., Gordon, A.J. *Tetrahedron Lett.* **1971**, 2941.

(15) Bassignani, L., Brandt, A., Caciagli, V., Re, L. *J. Org. Chem.* **1978**, *43*, 4245.

(16) Schröder, M., Griffith, W.P. *J. Chem. Soc. Dalton Trans.* **1978**, 1599.

(17) Müller, P., Godoy, J. *Tetrahedron Lett.* **1982**, *23*, 3661.

(18) Sheats, W.B., Olli, L.K., Stout, R., Lundeen, J.T., Justus, R., Nigh, W.G. *J. Org. Chem.* **1979**, *44*, 4075.

(19) Sonoda, N., Yamamoto, Y., Murai, S., Tsutsumi, S. *Chem. Lett.* **1972**, 229.

(20) Wolfe, S., Pilgrim, W.R., Garrard, T.F., Chamberlain, P. *Can. J. Chem.* **1971**, *49*, 1099.

(21) Torii, S., Inokuchi, T., Yukawa, T. *Chem. Lett.* **1984**, 1063.
Torii, S. *Electroorganic Syntheses, Methods and Applications. Part 1: Oxidations*, Verlag Chemie, Weinheim, 1985, pp. 288–293.

(22) Emmons, W.D., Freeman, J.P. *J. Am. Chem. Soc.* **1955**, *77*, 4415.

(23) Vinot, N. *Bull. Soc. Chim. Fr.* **1972**, 2708.

(24) Aldrich Chemical Catalog, 1984–1985, Milwaukee, Wisconsin, U.S.A.