Pergamon

Tetrahedron, Vol. 53, No. 47, pp. 16131-16138, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)10052-7

α-Nitrocycloalkanones as a Source of α,ω-Dicarboxylic Acid Dimethyl Esters†

Roberto Ballini,* and Giovanna Bosica.

Dipartimento di Scienze Chimiche dell'Università, Via S. Agostino n. 1, 62032 Camerino - Italy

Abstract: α,ω-Dicarboxylic acid dimethyl esters are easily obtained by ring cleavage of α-nitrocycloalkanones. Thus, reaction of the latter compounds with three equivalents of potassium persulfate, in methanol and in presence of sulfuric acid at 80 °C, provides α,ω-dicarboxylic acid dimethyl esters in high yields. Long-chain, and alkylated α,ω-dicarboxylic acid dimethyl esters can be also efficiently obtained. © 1997 Elsevier Science Ltd.

α,ω-Dicarboxylic acid dimethyl esters are valuable intermediates in organic synthesis due to the many synthetic transformations originated from this class of compounds.[1-3]

Long chain dicarboxylic acid dimethyl esters have been found as components of important natural products,[4] in acid-resistant raw forest humus,[5] or show antifungal properties,[6] moreover, these higher diesters are the key building blocks for the synthesis of dinitriles, diols, ω-haloesters,[7] ω-aminoacids,[8] antivirals,[9] pheromones,[10] propellanes,[11] perfume components,[12] plant growth regulators,[13] inhibitors for skin and mucous membrane diseases,[14] polyurethane foams,[15] viscose rayon fibers,[16] detergents,[17] etc.

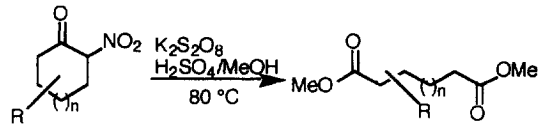
Moreover long chain dionic acid dimethyl esters are employed, without further elaboration, as models for study of polymeric liquid crystals,[18] as perfumes ingredients,[19] as stabilizing compounds for resins,[20] and as preservatives for food and cosmetics.[21]

Several methods have been proposed for their preparation,[22-27] however many of these are patents and/or require electrochemical processes,[22] the extension of skeletons with five or six carbon atoms following tedious procedures,[23] strong oxidating conditions,[24] multistep sequences with low yields,[25] the need of toxic substances and high temperature,[26] and the use of complex catalysts under high pressure.[27]

Many years ago Feuer and Pivawer[28] reported that some α-nitrocycloalkanones can be converted to α,ω-dicarboxylic acid dialkyl esters by reaction with an appropriate alcohol and concentrated sulfuric acid at reflux temperature. Unfortunately, moderate yields and a complex mixture of undesired by-products were

obtained with the associate problems of purification. Moreover, substituted nitro ketones, such as 2-nitro-1-tetralone, were unreactive.

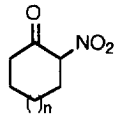
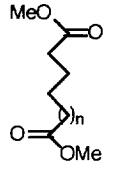
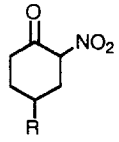
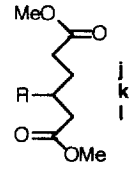
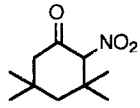
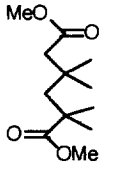
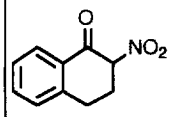
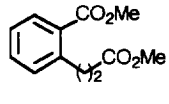
During our studies in the ring cleavage of α-nitrocycloalkanones,[29] we found (Scheme 1) that these compounds can be efficiently cleaved, at 80 °C, by employing three equivalents of potassium persulfate, in methanol, and in presence of sulfuric acid,[30] leading α,ω-dicarboxylic acid dimethyl esters **2**. A variety of 2-nitrocycloalkanones **1** are cleaved in good yields regardless the ring size (Table1).



1 **2**

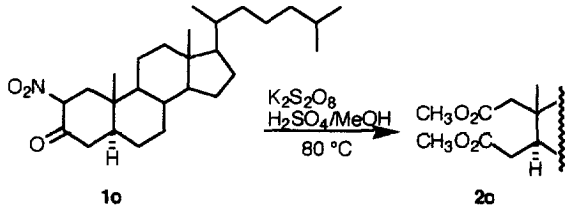
Scheme 1

Table 1. Preparation of α,ω-Dicarboxylic Acid Dimethyl Esters

entry	α-Nitro Ketone (**1**)	Diester (**2**)		Yield (%) of **2**	Reaction time (h)
a-i			**a** n=0 **b** n=1 **c** n=2 **d** n=3 **e** n=4 **f** n=5 **g** n=6 **h** n=7 **i** n=10	92 93 90 86 80 81 85 88 78	2 3 4 3 10 3 2 5 5
j-l			**j** R=Me **k** R=Me$_3$C **l** R=Ph	79 85 88	3 3 2
m				58	15
n				90	16

Alkylated α-nitrocycloalkanones (entry **1j-n**) are also easily converted to **2** affording the opportunity to produce substituted dimethyl esters and, of interest, is the cleavage of 2-nitro-1-tetralone **1n** which produces **2n** in 90% yield. Only 3,3,5,5-tetramethyl-2-nitrocyclohexanone **1m** gave **2m** in moderate yield (58%).

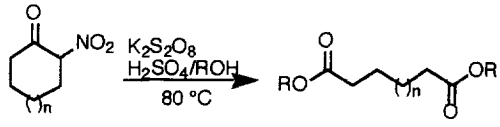
A further, valuable application of this process is the ring cleavage of the steroidal systems and, as a representative example, we choose 2α-nitro-5α-cholestan-3-one **1o** which afforded the corresponding diester **2o** in 68% yield (Scheme 2).



1o **2o**

Scheme 2

Although the dimethyl esters are the most valuable derivatives of dicarboxylic acids, we tried to prepare the corresponding diethyl and diisopropyl esters from some nitrocycloalkanones (**1a,b,i**; Scheme 3), using the right alcohols. Also in this case the method gave good yields (Table 2) of diesters **3**.



1b,c,i **3a-f**

Scheme 3

Table 2. Preparation of α,ω-Dicarboxylic Acid Diethyl and Diisopropyl Esters

entry	n	R	Yield (%) of **3**	Reaction time (h)
3a	1	Et	90	3
3b	1	*i*-Pr	71	3
3c	2	Et	83	3
3d	2	*i*-Pr	73	3
3e	10	Et	82	5
3f	10	*i*-Pr	72	24

Moreover, it is important to point out that this methodology is independent from the ring size and/or the substituents in the ring, and gives high yields with simple and economical chemicals.

In conclusion, since 2-nitrocycloalkanones are commercially available or readily prepared from different sources,[29,30] the present method provides a general and efficient entry to the title compounds.

Experimental

General: All ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 300 and 50 MHz, respectively. Chemical shifts are expressed in ppm downfield from TMS as internal standard. *J* values are given in hertz. Mass spectra were determined on a Hewlett-Packard GC/MS 5970 by means of the EI technique (70 eV). The reactions were monitored by TLC or GC performed on a Carlo Erba Fractovap 4160 using a capillary column of Duran Glass, stationary phase OV1. The α-nitrocycloalkanones are commercially available or prepared by standard methods.[29,31] The compounds **2a-o** and **3a-f** were purified by flash chromatography on Merck silica gel (0.040-0.063 mm).[32]

General Procedure for the Preparation of α,ω-Dicarboxylic Acid Dimethyl Esters (2a-o). A mixture of 96% sulfuric acid (300 mmol), water (5 ml) and methyl alcohol (25 ml) was cooled at 15 °C. Potassium persulfate (16.2 g, 60 mmol) was added gradually with stirring at 10-15 °C. A solution of α-nitrocycloalkanone **1** (20 mmol) in methyl alcohol (7 ml) was added dropwise at 15 °C. After stirring at room temperature for 10 min, the mixture was heated at 80 °C for the appropriate time (see Table 1), then the mixture was diluted with water (120 ml) and extracted with diethyl ether (3 x 50 ml). After drying ($MgSO_4$), evaporation and purification by flash chromatography (hexane/EtOAc, 8:2) of the crude product, the pure α,ω-dicarboxylic acid dimethyl esters **2** were obtained.

Dimethyl Pentanedioate (2a): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.86-2.05 (m, 2H), 2.39 (t, 4H, *J* = 7.1 Hz), 3.68 (s, 6H); MS *m/z* 129 (M^+ - 31), 128, 101, 100, 87, 59 (100), 55, 42. Anal. Calcd for $C_7H_{12}O_4$: C, 52.49; H, 7.55. Found: C, 52.70; H, 7.48.

Dimethyl Hexanedioate (2b): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.58-1.75 (m, 4H), 2.28-2.42 (m, 4H), 3.68 (s, 6H); MS *m/z* 143 (M^+ - 31), 142, 114, 111, 101, 87, 83, 74, 59 (100), 55, 43, 41. Anal. Calcd for $C_8H_{14}O_4$: C, 55.16; H, 8.10. Found: C, 54.90; H, 8.23.

Dimethyl Heptanedioate (2c): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.31-1.42 (m, 2H), 1.6-1.72 (m, 4H), 2.32 (t, 4H, *J* = 7.3 Hz), 3.67 (s, 6H); MS *m/z* 157 (M^+ - 31), 128, 125, 115 (100), 97, 87, 83, 74, 69, 59, 55, 43, 41. Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.56. Found: C, 57.59; H, 8.68.

Dimethyl Octanedioate (2d): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.3-1.4 (m, 4H), 1.58-1.72 (m, 4H, 2.32 (t, 4H, *J* = 7.4 Hz), 3.68 (s, 6H); MS *m/z* 171 (M^+ - 31), 138, 129 (100), 111, 97, 87, 83, 74, 69, 59, 55, 43, 41. Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.38; H, 8.97. Found: C, 59.15; H, 9.09.

Dimethyl Nonanedioate (2e): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.25-1.4 (m, 6H), 1.55-1.72 (m, 4H), 2.32 (t, 4H, *J* = 7.4 Hz), 3.68 (s, 6H); MS *m/z* 185 (M^+ - 31), 152 (100), 143, 124,

111, 97, 83, 74, 69, 59, 55, 43, 41. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.88; H, 9.44.

Dimethyl Decanedioate (2f): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.24-1.7 (m, 12H), 2.3 (t, 4H, J = 7.4 Hz), 3.68 (s, 6H); MS *m/z* 199 (M^+ - 31), 166, 157, 138, 125, 111, 98, 97, 87, 84, 83, 74 (100), 69, 59, 55, 43, 41. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.72; H, 9.78.

Dimethyl Undecanedioate (2g): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.25-1.35 (m, 10H), 1.53-1.7 (m, 4H), 2.3 (t, 4H, J = 7.4 Hz), 3.68 (s, 6H); MS *m/z* 213 (M^+ - 31), 180, 171, 152, 139, 121, 111, 98 (100), 87, 84, 74, 69, 59, 55, 43, 41. Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.90; H, 9.90. Found: C, 64.02; H, 9.78.

Dimethyl Dodecanedioate (2h): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.21-1.43 (m, 12H), 1.5-1.75 (m, 4H), 2.3 (t, 4H, J = 7.5 Hz), 3.68 (s, SH); MS *m/z* 227 (M^+ - 31), 185, 166, 155, 153, 112, 111, 98 (100), 87, 84, 74, 69, 59, 55, 43, 41. Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.08; H, 10.14. Found: C, 64.91; H, 10.30.

Dimethyl Pentadecanedioate (2i): IR (KBr) 1725 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.22-1.35 (m, 18H), 1.58-1.68 (m, 4H), 2.3 (t, 4H, J = 7.5 Hz), 3.68 (s, 6H); MS *m/z* 269 (M^+ - 31), 227, 195, 177, 154, 112, 111, 98 (100), 87, 74, 69, 59, 55, 43, 41. Anal. Calcd for $C_{17}H_{32}O_4$: C, 67.96; H, 10.73. Found: C, 68.12; H, 10.64.

3-Methyl Dimethyl Hexanedioate (2j): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 0.93 (d, 3H, J = 6.6 Hz), 1.4-1.8 (m, 2H), 1.84-2.08 (m, 1H), 2.09-2.4 (m, 4H), 3.67 (s, 6H); MS *m/z* 157 (M^+ - 31), 125, 121, 115 (100), 101, 98, 96, 87, 83, 75, 59, 55, 43, 41.

Anal. Calcd for $C_9H_{16}O_4$: C, 57.43; H, 8.57. Found: C, 57.58; H, 8.70.

3-*terz*-Butyl Dimethyl Hexanedioate (2k): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 0.88 (s, 9H), 1.2-2.54 (m, 7H), 3.66 (s, 6H); MS *m/z* 199 (M^+ - 31), 183, 174, 167, 155, 142, 141, 123, 114, 101 (100), 83, 74, 59, 57, 55, 43, 41. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.70; H, 9.49.

3-Phenyl Dimethyl Hexanedioate (2l): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.8-2.2 (m, 4H), 2.62 (dt, 2H, J = 1.7 and 7.0 Hz), 3.04-3.15 (m, 1H), 3.57 (d, 3H, J = 1.9 Hz), 3.6 (d, 3H, J = 1.9 Hz), 3.6 (d, 3H, J = 1.9 Hz), 7.1-7.33 (m, 5H) ; MS *m/z* 250 M^+), 219, 218, 202, 190 (100), 177, 176, 145, 139, 131, 122, 118, 117, 104, 91, 77, 59, 51. Anal. Calcd for $C_{14}H_{18}O_4$: C, 67.18; H, 7.25. Found: C, 67.02; H, 7.40.

2,2,4,4-Tetramethyl Dimethyl Hexanedioate (2m): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.02 (s, 6H), 1.25 (S, 6H), 1.78 (s, 2H), 2.43 (s, 2H), 3.69 (s, 6H); MS *m/z* 199 (M^+ - 31), 184, 174, 171, 155, 139, 126, 115, 102, 97, 83, 73 (100), 55, 43, 41. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.70; H, 9.49.

Methyl 2-(methylpropionate 3-yl)benzoate (2n): IR (film) 1720, 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 2.68 (t, 2H, J = 7.8 Hz), 3.28 (t, 2H, J = 7.8 Hz), 3.65 (s, 3H), 3.9 (s, 3H), 7.2-7.35 (m, 3H), 7.4-7.5 (m, 2H); MS *m/z* 222 (M^+), 192, 190, 163, 162 (100), 147, 132, 131, 130, 119, 103, 77, 65, 51. Anal. Calcd for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 64.99; H, 6.48.

2o: IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 0.63 (s, 3H), 0.78 (s, 3H), 0.85 (d, 3H, J = 6.7 Hz), 0.86 (d, 3H, J = 6.7 Hz), 0.89 (d, 3H, J = 6.4 Hz), 0.9-1.88 (m, 25H, 1.9-2.03 (m, 2H), 2.25 (d, 1H, J = 14.0 Hz), 2.45 (d, 1H, J = 14.0 Hz), (3.65 (s, 3H), 3.67 (s, 3H); ^{13}C NMR (50 MHz $CDCl_3$) δ 11.953

(CH_3), 15.505 (CH_3), 18.604 (CH_3), 21.320 (CH_2), 22.573 (CH_3), 22.796 (CH_3), 23.731 (CH_2), 24.02 (CH_2), 27.756 (CH_2), 27.991 (CH), 28.226 (CH_2), 31.123 (CH_2), 35.411 (CH), 35.743 (CH), 35.962 (CH_2), 36.091 (CH_2), 39.474 (CH_2), 39.741 (C), 39.789 (CH_2), 40.493 (CH), 41.076 (CH_2), 42.225 (C), 48.391 (CH), 51.166 (CH_3), 51.498 (CH_3), 56.094 (CH), 56.321 (CH), 171.753 (CO), 174.156 (CO); MS *m/z* 431 (M^+ - 31), 389 (100), 373, 357, 315, 275, 248, 235, 207, 175, 133, 105, 95, 55. Anal. Calcd for $C_{29}H_{50}O_4$: C,75.27; H, 10.89. Found: C, 75.38; H, 10.75.

General Procedure for the Preparation of α,ω-Dicarboxylic Acid Diethyl and Diisopropyl Esters (3a-f). The compounds **3** were prepared following the above procedure for the preparation of **2**, unless ethyl or isopropyl alcohol was used instead of methanol.

Diethyl Hexanedioate (3a): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.24 (t, 6H, *J* = 7.1 Hz), 1.61-1.7 (m, 4H), 2.29-2.36 (m, 4H), 4.12 (q, 4H, *J* = 7.1 Hz); MS *m/z* 157 (M^+ - 45), 128, 110, 111 (100), 101, 88, 82, 73, 55, 43, 41, 30. Anal. Calcd for $C_{10}H_{18}O_4$: C, 59.39; H, 8.97. Found: C, 59.38; H, 9.06.

Diisopropyl Hexanedioate (3b): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.2 (d, 12H, *J* = 6.4 Hz), 1.45-1.66 (m, 4H), 2.09-2.17 (m, 4H), 4.98 (m, 2H); MS *m/z* 188 (M^+ - 42), 171, 142, 129 (100), 111, 100, 87, 73, 60, 55, 43, 31. Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.58; H, 9.63. Found: C, 62.38; H, 9.56.

Diethyl Heptanedioate (3c): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.24 (t, 6H, *J* = 7.3 Hz), 1.3-1.4 (m, 2H), 1.6-1.7 (m, 4H), 2.28 (t, 4H, *J* = 7.5 Hz), 4.12 (q, 4H, *J* = 7.3 Hz); MS *m/z* 171 (M^+ - 45), 142, 129, 125 (100), 114, 101, 96, 88, 83, 73, 69, 60, 55, 43, 41, 31. Anal. Calcd for $C_{11}H_{20}O_4$: C, 61.09; H, 9.32. Found: C, 60.97; H, 9.46.

Diisopropyl Heptanedioate (3d): IR (film) 1720 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.2 (d, 12H, *J* = 6.4 Hz), 1.25-1.43 (m, 2H), 1.35-1.43 (m, 2H), 1.55-1.67 (m, 4H), 2.25 (t, 4H, *J* = 3.75 Hz), 4.98 (m, 2H, *J* = 6.4 Hz); MS *m/z* 202 (M^+ - 42), 185, 156, 143 (100), 125, 114, 101, 97, 83, 73, 69, 60, 55, 43, 41, 32. Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.91; H, 9.90. Found: C, 64.05; H, 9.96.

Diethyl Pentadecanedioate (3e): IR (film) 1730 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.22-1.35 (m, 28H), 1.58-1.68 (m, 4H), 2.3 (t, 4H, *J* = 7.5 Hz), 4.12 (q, 4H, *J* = 7.1 Hz); MS *m/z* 283 (M^+ - 45), 256, 241, 226, 195, 177, 154, 135, 121, 98 (100), 88, 69, 55, 43, 41, 30. Anal. Calcd for $C_{19}H_{36}O_4$: C, 69.47; H, 11.05. Found: C, 69.60; H, 11.06.

Diisopropyl Pentadecaneioate (3f): IR (film) 1725 cm^{-1}; ^1H NMR (300 MHz $CDCl_3$) δ 1.21 (d, 12H, *J* = 6.1 Hz), 1.23-1.37 (m, 18H), 1.52-1.67 (m, 4H), 2.23 (t, 4H, *J* = 7.5 Hz), 4.98 (m, 2H, *J* = 6.1 Hz); MS *m/z* 297 (M^+ - 59), 255 (100), 236, 213, 195, 177, 154, 129, 98, 73, 43, 41. Anal. Calcd for $C_{21}H_{40}O_4$: C, 70.74; H, 11.31. Found: C, 70.58; H, 11.44.

Acknowledgment: This work was supported by C.N.R.-Italy, MURST-Italy and the University of Camerino-Italy.

References

†Dedicated to Prof. Dieter Seebach in occasion of his 60th birthday.

1. Corey, E. J.; Cheng, X-M. *The Logic of Chemical Synthesis;* John Wiley and Sons: New York, 1989.
2. Lindberg, T. *Strategies and Tactics in Organic Synthesis;* Academic Press, Inc.: San Diego, 1994, vol. 1.
3. Ho, T. L. *Tactics of Organic Synthesis;* John Wiley and Sons: New York, 1994.
4. Picher, M. T.; Tortajada, A.; Seoane, E. *An. Quim., Ser. C* **1983**, *79*, 404-406; *C. A.* **1985**, *102*, 21228.
5. Ogener, G. *Acta Chem. Scand.* **1973**, *27*, 1601-1612.
6. Gerson, H.; Shanks, L. *Can. J. Microbiol.* **1976**, *22*, 1198-1201; *C. A.* **1976**, *85*, 117344.
7. Bergstrom, S.; Aulin-Erdtman, G.; Rolander, B.; Stenhagen, E.; Ostling, S. *Acta Chem. Scand.* **1952**, *6*, 1157-1174.
8. Borgdanov, M. N. *J. Gen. Chem. U. S. S. R.* **1956**, *26*, 3103-3105; *C. A.* **1958**, *52*, 8051d.
9. Rubessa, F.; Runti, C.; Uian, F.; Vio, L.; Zonta, F. *Farmaco, Ed. Sci.* **1977**, *32*, 129-140.
10. Deodhar, V. B.; Dalavoy, V. S.; Nayak, U. R. *Indian J. Chem., Sect. B* **1979**, *17B*, 375-378.
11. Ashkenazi, P.; Kattenring, J.; Migdal, S.; Gutman, A. L.; Ginsburg, D. *Helv. Chim. Acta* **1985**, *68*, 2033-2036.
12. Matsushita, K.; Yokota, T.; Watnabe, A. *Jpn Kokai Tokkyo Koho JP* **1988**, 63, 243, 054; *C. A.* **1989**, *110*, 172757.
13. Kamuro, Y.; Kokiuchi, T.; Takahashi, N.; Sakurai, S.; Kamiya, Y.; Takai, M.; Sato, K. *Jpn Kokai Tokkyo Koho JP* **1990**, 02, 169, 554; *C. A.* **1991**, *114*, 121454.
14. Earnshaw, C.; Kirsch, G.; Rach, P.; Thieroff-Ekerdt, R.; Toepert, M. *PCT Int. Appl. WO* **1990**, 90 09, 373; *C. A.* **1991**, *114*, 142685.
15. Haas, P.; Hettel, H. *Ger. Offen. DE.* **1983**, 3, 124, 885; *C. A.* **1983**, *98*, 180393.
16. Kajii, Y. *Japan* **1971**, 71 06, 106; *C. A.* **1972**, *76*, 4816.
17. Von Praun, F.; Amende, J. *Ger. Offen.* **1973**, 2, 143, 010; *C. A.* **1973**, *78*, 126134.
18. Samulski, E. T.; Gauthier, M. M.; Blumstein, R. B.; Blumstein, A. *Macromolecules* **1984**, *17*, 479-483.
19. Sturm, W.; Mansfeld, G.; Reindl, H. *Ger. Offen. DE* **1984**, 3, 229, 300; *C. A.* **1984**, *100*, 161692.
20. Kao-Quater, Co., Ltd *Jpn Kokai Tokkyo Koho JP* **1985**, 60, 121, 036; *C. A.* **1985**, *103*, 219550.
21. Tokunaga, H.; Vejima, T.; Ono, T.; Taoka, E.; Watanabe, A. *Jpn Kokai Tokkyo Koho JP* **1987**, 62, 221603; *C. A.* **1988**, *108*, 54691.
22. (a) *Badische Anilin & Soda-Fabrik Akt.-Ges., Ger.* **1953**, 880, 289; *C. A.* **1958**, *52*, 7914; (b) Vasil'ev, Y. B.; Kanevskii, L. S.; Karapetyan, K. G.; Kovsman, E. P.; Skundin, A. M.; Tarkhanov, G. A.; Freidlin, G. N. *Electrokhimiya* **1978**, *14*, 770-773; *C. A.* **1978**, *89*, 119649;

(c)Yamataka, K.; Ysoya, T. *PCT Int. Appl. WO* **1983**, 8302, 463; *C. A.* **1983**, *99*, 160317; (d) Shul'zhenko, G. I.; Vasil'ev, Y. B. *Electrokhimiya* **1987**, *23*, 1098-1104; *C. A.* **1987**, *107*, 163981.

23. (a) Plesek, J. *Chem. listy* **1957**, *51*, 533-535; *C. A.* **1957**, *51*, 10380h; (b) Plesek, J. *Collection Czechoslov. Chem. Comm.* **1957**, *22*, 1661-1664; *C. A.* **1958**, *52*, 8051d; (c) Tsutsumi, S.; Kida, Y. *Jpn Kokai Tokkyo Koho JP* **1975**, 75 95, 215; *C. A.* **1976**, *84*, 4506; (d) Kida, Y. *Jpn Kokai Tokkyo Koho JP* **1976**, 76 34, 110; *C. A.* **1976**, *85*, 32455.
24. (a) Hochberg, S. *U. S.* **1976**, 3, 991, 100; *C. A.* 1977, *86*, 43208; (b) *Okamura Oil Mill, Ltd Jpn Kokai Tokkyo Koho JP* **1980**, 80, 139, 336 and 80, 139, 337; *C. A.* **1981**, *94*, 120894 and 120895; (c) Griesbaum, K.; Neumeister, J.; Saxens, M. P. *Erdoel Kohle Erdgas, Petrochem* **1983**, *36*, 252-257; *C. A.* **1983**, *99*, 157796; (d) Cardinale, G.; Laan, J. A. M.; Van der Steen, D.; Ward, J. P. *Tetrahedron* **1985**, *41*, 6051-6054.
25. (a) Yonetani, H.; Kubo, M. *Koryo* **1958**, *48*, 22-25; *C. A.* **1959**, *53*, 2171d; (b) Cardianle, G.; Grimmelikhuysen, J. C.; Van der Steen, D. *Ger. Offen.* **1968**, 1, 928, 705; *C. A.* **1970**, *72*, 100070.
26. Umemura, S.; Matsui, K.; Ikeda, Y.; Masunaga, K.; Kadota, T.; Fujii, K.; Nishihira, K.; Matsuda, M. *Brit. UK Pat. Appl.* **1980**, 2. 024, 821; *C. A.* **1980**, *93*, 113977.
27. Mrowca, J. S. *U. S.* **1981**, 4, 257, 973; *C. A.* **1981**, 95, 97089.
28. Feuer, H.; Pivawer, P. M. *J. Org. Chem.* **1969**, *34*, 2917-2919.
29. (a) Ballini, R.; Petrini, M.; Rosini, G. *Tetrahedron* **1990**, *46*, 7531-7538; (b) Ballini, R.; Petrini, M.; Polzonetti, V. *Synthesis* **1992**, 355-357; (c) Ballini, R.; Bartoli, G.; Giovannini, R.; Marcantoni, E. *Tetrahedron Lett.* **1993**, *34*, 3301-3304; (d) Ballini, R.; Petrini, M.; Polimanti, O. *J. Org. Chem.* **1996**, *61*, 5652-5655.
30. It has been reported that the oxidative potential of potassium persulfate is accelerated by the presence of sulfuric acid: Reissenweber, G.; Mangold, D. *Angew. Chem., Int. Ed., Engl.* **1980**, *19*, 222-223.
31. (a) Rathore, R.; Lin, Z.; Kochi, J. K. *Tetrahedron Lett.* **1993**, *34*, 1859-1862; (b) Rank, W. *Tetrahedron Lett.* **1991**, *32*, 5353-5356. (c) Griswold, A. A.; Starcher, P. S. *J. Org. Chem.* **1966**, *31*, 357-361.
32. Still, W. C.; Kahan, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923-2926.

(*Received in UK* 11 *August* 1997; *revised* 9 *September* 1997; *accepted* 11 *September* 1997)