This article was downloaded by: [University of Waterloo] On: 11 October 2014, At: 11:56 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Cathodic Reduction of Enediol Diesters Obtained by Electrochemical Methods

Carmen Polo^a, Ma Gloria Quintanilla^a & Fructuoso Barba^a

^a Department of Organic Chemistry , University of Alcalá de Henares , Madrid, Spain Published online: 23 Sep 2006.

To cite this article: Carmen Polo , Ma Gloria Quintanilla & Fructuoso Barba (1994) Cathodic Reduction of Enediol Diesters Obtained by Electrochemical Methods, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 24:7, 907-915, DOI: <u>10.1080/00397919408020764</u>

To link to this article: http://dx.doi.org/10.1080/00397919408020764

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any

losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

CATHODIC REDUCTION OF ENEDIOL DIESTERS OBTAINED BY ELECTROCHEMICAL METHODS

Carmen Polo, Mª Gloria Quintanilla and Fructuoso Barba*.

Department of Organic Chemistry. University of Alcalá de Henares. Madrid. Spain.

ABSTRACT: The electrochemical reduction of 1,2-di-alkylphenyl-1,2-ethenediol dialkylbenzoates, on a Hg cathode in DMF/LiClO₄, yields 1,2-di-alkylphenylacetylenes. The enediol diesters were obtained from alkylbenzoyl chlorides, by the same method, using dry acetone / LiClO₄.

The cathodic reduction of aroyl chlorides in dry acetone-LiClO₄ has proved to be an ideal method for the synthesis of enediol diesters^{1,2}.

These compounds can undergo further reduction at a more negative potential, as demonstrated by voltametric methods³. However the synthetic value of this reaction is still unexplored.

The aim of this paper is to study the cathodic reduction of enediol diesters 2 in aprotic medium on a mercury cathode. To this purpose, we have prepared 2, starting from alkylbenzoyl chlorides 1 which were electrochemically reduced in dry acetone-LiClO₄, as was described in a previous paper¹. (Figure 1).

^{*} To whom correspondence should be addressed.

Copyright © 1994 by Marcel Dekker, Inc.

$$4R - C_6H_4 - COCI + 4e^{-} \begin{pmatrix} Mercury \\ cathode \end{pmatrix} \xrightarrow{Dry acetone / LiClO_4}{Inert atmosphere}$$

$$R - C_{6}H_{4} - CO - O_{C_{6}H_{4}} - R$$

$$C = C_{6}^{r}$$

$$R - C_{6}H_{4}^{r} - C_{6}^{r} - C_{6}^{r}$$

$$O - CO - C_{6}H_{4} - R$$
2.a-f

Starting	Ep (V)*	Obtained	R	
Compound		Compound		
1.a	-1.32	2.a	Н	
1.b	-1.34	2.b	p-CH ₃	
1.c	-1.43	2.c	p-Pr	
1.d	-1.40	2.d	p-Bu ^t	
1.e	-1.32	2.e	m-CH ₃	
1.f	-1.30	2.f	m-CH2Cl	

(*): All potentials were quoted with respect to a Ag / AgCl reference electrode.

FIG. 1

Further reduction of **2** in dry acetone-LiClO₄ was not possible since the discharge of this SSE takes place at a lower negative potential (aprox. -1.8 V vs. SCE) than that of the corresponding enediol diesters (see Figure 2).



$$R - C_6H_4 - C \equiv C - C_6H_4 - R$$

3.a,d,	e
--------	---

Starting	Ep (V)*	Obtained	R
Compound		Compound	
2.a	-1.90	3.a	Н
2.d	-2.03	3.d	p-Bu ^t
2.e	-1.85	3.e	m-CH ₃
2.f	-1.74	3.e	m-CH3

(*): All potentials were quoted with respect to a Ag / AgCI reference electrode.

FIG. 2

However when DMF-LiClO₄ under argon atmosphere was employed, no problems were found in the process. By this procedure, the following acetylenes **3** were synthetized (Figure 2).

The benzilic carbon-chlorine bond in **2.f** was reduced at a less negative potential than the carbon-oxygen one, yielding exclusively the acetylene **3.e**. Ten electrons were involved in the process. Compounds **2.b** and **2.c** were nearly insoluble in DMF, therefore the flow current was very low. When the potential was increased in order to

obtain a higher current, the small amount of acetylene formed, was reduced to the corresponding ethylene and saturated derivatives, due to the traces of water contained in the comercial DMF.

EXPERIMENTAL SECTION

1,2-DIARYL-1,2-ETHENEDIOL DIAROYLATES.

General conditions. <u>Reference electrode</u>: Saturated calomel electrode (SCE). <u>Anode</u>: Platinum. <u>Anolyte</u>: Lithium perchlorate (3 mmol) in dry acetone (20 ml, dried at least 24 h. over anhydrous K₂CO₃ and then distilled). <u>Cathode</u>: Mercury pool. <u>Catholyte</u>: Lithium perchlorate (7 mmol) in 40 ml of dry acetone and 5 mmol of the aroyl chloride. <u>Electrolysis cell</u>: Divided, thermostated at 15°C, equipped with a magnetic stirrer, containing a piece of glass tubing with a glass frit of medium porosity at one end (anode compartment). The cell top was fitted with O-ring seals ports for the working electrode, reference electrode and argon connection (bubbling through for twenty minutes before the reaction started and then sweeping smoothly over the solution in the cell during the whole process). Solid potassium carbonate (4.0 g) was added to the anode compartment to neutralize the perchloric acid generated, in order to prevent both possible danger of explosion and benzoin derivatives formation.

In the reduction of **1.a**, **1.b**, **1.c** and **1.e** when the current started to flow, the surface of the mercury cathode became yellow and after a short time the catholyte solution became turbid because the reaction products are only sparingly soluble in acetone. However, during the reduction of **1.d** and **1.f**, the solution remained yellow, but no precipitate was formed.

The electrolyses were performed under controlled cathodic potential with an Amel Model 57 potentiostat. An electronic coulometer (Amel Model 721) coupled to the potentiostat was employed for current integration. In all cases, the electron consumption was 1 Fmol⁻¹.

Products Isolation. 2.a, **2.b**, **2.c**, **2.e** y **2.f**: Crude reaction product was obtained by removing the acetone and adding water in order to dissolve the electrolyte, leaving a white solid, which was collected by vacuum filtration, and washed with methanol **(2.a, 2.b, 2.e)**, hexane **(2.c)** or diethyl ether **(2.f)**.

2.d: After the acetone had been removed, the residue was partitioned between diethyl ether and water. Then the organic extract was dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure. The trituration of the resulting yellow "glass" with petroleum ether gave a white solid which was collected by vacuum filtration, washed with cold petroleum ether and dried in a vacuum heater.

Mass spectra were obtained using a Hewlett-Packard model 5988A spectrometer. IR spectra were obtained using a Perkin-Elmer model 883 spectrometer. ¹H-NMR spectra were obtained using a 300 Mhz Varian apparatus. Melting points were measured using a Reichert-Thermovar apparatus. Microanalyses were performed using a Perkin-Elmer Model 240-B (C, H, N) element analyser. A gas chromatograph (Hewlett-Packard model 5890) or a HPLC instrument (Hewlett-Packard model 1050), both coupled to a Hewlett-Packard model 3394 integrator register, were employed to verify the number of isomers in every case.

2.a: Cis and Trans- α , α '-Stilbenediol dibenzoate. The physical^{4,5} and spectroscopic data¹ are in accordance with those described in the literature.

2.b: Trans-[1,2-Bis(4-methylphenyl)-1,2-ethenediol]-1,2-bis(4methylbenzoate). Only trans isomer was formed (in this case, verified by TLC on silica gel⁶). Yield: 94%. Melting point: 299-300°C (THF, white needles). IR- v_{max} (cm⁻¹)-KBr: 2919, 1736, 1609, 1511, 1240, 1127, 1107, 1035, 1012, 821, 745. MS (70 eV)- m/z (%): 476 (M⁺, 3), 239 (2), 119 (100), 91 (22).¹H-NMR (CDCl₃): δ = 2.26 (s, 6H, CH₃), 2.43 (s, 6H, CH₃), 7.07 (d, 4H, H₃(5), JH₂-H₃= 8.15), 7.27 (d, 4H, H₃'(5'), JH₂-H₃'= 8.06), 7.54 (d, 4H, H₂(6)), 8.00 (d, 4H, H₂'(6')). Calculated for C₃₂H₂₈O₄ (476.59): C, 80.65; H, 5.92. Found: C, 80.72; H, 5.89. **2.c:** Trans-[1,2-Bis(4-propylphenyl)-1,2-ethenediol]-1,2-bis(4-propyl benzoate), (verified by TLC on silica gel). Melting point: 223-224°C (acetone, fine white needles). Yield: 94%. IR- υ_{max} (cm⁻¹)-KBr: 2954, 2927, 2865, 1737, 1609, 1509, 1239, 1111, 1009. MS (70 eV)- m/z (%): 588 (M⁺, 5), 148 (10), 147 (100), 119 (4), 91 (9). ¹H-NMR (CDCl₃): δ = 0.86 (t, 6H, CH₃, J= 7.32), 0.96 (t, 6H, CH_{3'}, J= 7.32), 1.51-1.58 (m, 4H, CH₂), 1.63-1.71 (m, 4H, CH_{2'}), 2.49 (t, 4H, CH₂, J= 7.60), 2.65 (t, 4H, CH_{2'}, J= 7.60), 7.06 (d, 4H, H₃(5), JH₂-H₃= 8.15), 7.26 (d, 4H, H_{3'}(5'), JH_{2'}-H_{3'}= 8.06), 7.55 (d, 4H, H₂(6)), 8.01 (d, 4H, H_{2'}(6')). Calculated for C₄₀H₄₄O₄ (588.79): C, 81.60; H, 7.53. Found: C, 81.87; H, 7.48.

2.d: Trans-[1,2-Bis(4-tertbuthylphenyl)-1,2-ethenediol]-1,2-bis (4tertbuthyl benzoate). (verified by HPLC). Melting point: 267-268°C (acetonitrile, white solid powder). Yield: 37%. IR- υ_{max} (cm⁻¹)-KBr: 2963, 1738, 1606, 1267, 1110, 1086. MS (70 eV)- m/z (%): 644 (M⁺, 2), 162 (11), 161 (100), 146 (5), 118 (5). ¹H-NMR (CDCl₃): δ =1.23 (s, 18H, CH₃), 1.36 (s, 18H, CH₃), 7.27 (d, 4H, H₃(5), JH₂-H₃= 8.51), 7.50 (d, 4H, H₃'(5'), JH_{2'}-H_{3'}= 8.42), 7.59 (d, 4H, H₂(6)), 8.07 (d, 4H, H_{2'}(6')). Calculated for C₄₄H₅₂O₄ (644.90): C, 81.95; H, 8.13. Found: C, 81.88; H, 8.16.

2.e: Cis and **Trans-[1,2-Bis(3-methylphenyl)-1,2-ethenediol]-1,2bis(3-methyl benzoate)**. (1: 3, verified by HPLC). Yield: 75%. Crude reaction product was crystallized from acetonitrile to give the trans isomer, melting point: 167-168°C (white solid powder). IR- v_{max} (cm⁻¹)-KBr: 2919, 1733, 1269, 1182, 1106, 742. MS (70 eV)- m/z (%): 476 (M⁺, 5), 237 (1), 120 (8), 119 (100), 91 (17). ¹H-NMR (CDCl₃): δ = 2.23 (s, 6H, CH₃), 2.41 (s, 6H, CH₃), 7.05 (d, 2H, H₄, J_{H4}-H₅= 7.69), 7.17 (t, 2H, H₅), 7.36 (t, 2H, H₅', J_{H4}-H₅= 7.69), 7.45 (d, 2H, H₄'), 7.51 [m, 4H, H₂, H₆ (overlapped)], 7.90-7.92 [m, 4H, H₂', H_{6'} (overlapped)]. Calculated for C₃₂H₂₈O₄ (476.59): C, 80.65; H, 5.92. Found: C, 80.82; H, 5.86.

2.f: Cis and Trans-[1,2-Bis(3-chloromethylphenyl)-1,2-ethenediol]-1,2-bis[3-(chloromethyl)benzoate], (1: 3, verified by HPLC). Yield 63%. Mixture of

REDUCTION OF ENEDIOL DIESTERS

the isomers was crystallized from ethyl acetate to give the trans isomer, melting point: 175°C (white crystals). IR- v_{max} (cm⁻¹)-KBr: 2963, 1737, 1255, 1179, 1124, 705. MS (70 eV)- m/z (%): 614 (M⁺, 1), 271 (3), 155 (30), 154 (8), 153 (100), 125 (22), 89 (15). ¹H-NMR (CDCl₃): δ = 4.48 (s, 4H, CH₂Cl), 4.63 (s, 4H, CH₂·Cl), 7.31-7.34 (d partially overlapped, 2H, H₄, J_{H4}-H₅= 6.47,), 7.31-7.34 (t partially overlapped, 2H, H₅), 7.49 (t, 2H, H₅', J_{H4'}-H_{5'}= 7.63), 7.58 (d, 2H, H₆), 7.66 (d, 2H, H_{4'}), 7.75 (s, 2H, H₂), 8.06 (d, 2H, H_{6'}), 8.11 (s, 2H, H_{2'}). Calculated for C₃₂H₂₄O₄Cl₄ (614.36): C, 62.56; H, 3.94. Found: C, 62.61; H, 3.91.

1,2-DIARYLACETYLENES.

General conditions. The same experimental conditions as above were employed except comercial DMF was used as the solvent instead of dry acetone. 2.0 g of solid potassium carbonate were added to the anode compartment in order to avoid danger of explosion. In all cases, when current started to flow the solution of the catholyte became red and this colour intensified during the reaction. The consumed charge was 2.0 Fmol⁻¹ except in **2.f** in which 10 Fmol⁻¹ were consumed.

Products isolation. The cathodic solution was poured over ice water and extracted with diethyl ether. The extract was washed with water, dried over Na₂SO₄ and evaporated to dryness under reduced pressure. The crude product was a white solid which was collected by vacuum filtration, and washed with ethanol.

3.a: 1,2-Diphenylacetylene. Yield: 82%. The physical⁷ and spectroscopic data⁸ are in accordance with that described in the literature.

3.d: Bis(4-tertbuthylphenyl)acetylene⁹. Melting point: 177°C (ethanol, white needles). Yield: 75%. IR- υ_{max}(cm⁻¹)-KBr: 2956, 2904, 2867, 1664, 1516, 1362, 1265, 1108, 1017, 832. MS (70 eV)- m/z (%): 290 (M⁺, 57), 276 (29), 275 (100), 247 (5), 217 (5), 202 (6), 161 (21), 115 (5), 102 (9), 57 (10). ¹H-NMR (CDCl₃): δ= 1.33 (s, 18H,

CH₃), 7.37 (d, 4H, H₃₍₅₎, J_{H₂-H₃= 8.55), 7.47 (d, 4H, H₂₍₆₎). Calculated for C₂₂H₂₆ (290.45): C, 90.98; H, 9.02. Found: C, 90.83; H, 9.10.}

3.e: Bis(3-methylphenyl)acetylene¹⁰ Melting point: 74°C (lit.¹¹ mp. 73.5-74°C), (ethanol, white crystals). Yield: 90%. IR- v_{max} (cm⁻¹)-KBr: 3048, 2915, 1599, 1486, 911, 784, 686. MS (70 eV)- *m/z* (%): 206 (M⁺, 100), 205 (12), 191 (14), 190 (14), 189 (21), 165 (8), 139 (5), 115 (5), 101 (4), 89 (7). ¹H-NMR (CDCl₃): δ = 2.36 (s, 6H, CH₃), 7.14 (d, 2H, H₄, J_{H4}-H₅= 7.57), 7.23 (t, 2H, H₅), 7.34 (d partially overlapped, 2H, H₆), 7.35-7.36 (b. s partially overlapped, 2H, H₂). Calculated for C₁₆H₁₄ (206.39): C, 93.16: H, 6.84. Found: C, 93.22; H, 6.89.

ACKNOWLEDGEMENT

This study was financed by the DGICYT. PB91-0158.

REFERENCES

 Guirado, A.; Barba, F.; Manzanera, C. and Velasco, M.D., J. Org. Chem., 1982, <u>47</u>, 142.

2. Guirado, A.; Barba, F. and Martín, J., Synth. Commun., 1983, 13, 327.

3. Cheek, G.T. and Horine, P.A., J. Electrochem. Soc., 1984, 131, 1796.

4. Klinger, H. and Standke, O., Ber. Dtsch. Chem. Ges., 1891, 24, 1264.

5. Trisler, J.C. and Erye, J.L., J. Org. Chem., 1965, <u>30</u>, 306.

6. Horner, L. and Dickerhof, K., Chem. Ber., 1983, <u>116</u>, 1603.

 Weast, R.C., "Handbook of Chemistry and Physics", 52ND Edition; The Chemical Rubber Co.: Cleveland., 1971-1972; p.C-297.

8. Horner, L. and Dickerhof, K., Chem. Ber., 1983, <u>116</u>, 1615.

REDUCTION OF ENEDIOL DIESTERS

- 9. Han, G.Y.; Han, P. F.; Perkins, J. and McBay, H.C., J. Org. Chem., 1981, 46, 4695.
- 10. Newkome, G.R.; Roper, J.M. and Robinson, J.M., J. Org. Chem., 1980, 45, 4380.
- 11. Coleman, G.H.; Holst, W.H. and Maxwell, R.D., J. Am. Chem. Soc., 1936, 58, 2310.

(Received in the UK 19 August 1993)