

## 191. Synthesis of a Tetracyclo[4.4.0.0<sup>2,4</sup>.0<sup>3,8</sup>]decanone *via* Intramolecular Reductive Coupling

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### Summary

The reduction of *cis*-4 *a*-methyl-1, 2, 4 *a*, 7, 8, 8 *a*-hexahydronaphthalene-2, 7-dione (**1**) was studied by cyclic voltammetry and product analysis. On a preparative scale, 6-hydroxy-3-methyltetracyclo[4.4.0.0<sup>2,4</sup>.0<sup>3,8</sup>]decan-10-one (**2**) was obtained in 22% yield *via* an intramolecular hydrodimerization/aldol reaction sequence. The CV. results (Hg, DMF) suggest that the cyclopropane ring is formed after the *first* electron transfer by coupling of the anion radical with the second C, C-double bond.

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We recently presented results of cyclovoltammetric studies [1] and of product analysis [2] on the electrohydrodimerization (EHD.) of several alkyl-substituted 2-cyclohexenones. CV.-Analysis suggests that in the absence of water the reaction occurs *via* addition of an anion radical to a substrate molecule in a 'radical-substrate coupling' reaction<sup>1)</sup>.

Intramolecular EHD. reactions of bis( $\alpha, \beta$ -unsaturated ketones) have been utilized to generate perhydrophenanthrenes [6] or substituted barbaralanes [7]. In this latter publication it was stated that the intramolecular coupling does *not* take place after the first electron transfer. This reasoning is in disagreement with results on the electrohydrocyclization of bis ( $\alpha, \beta$ -unsaturated esters), where it was shown [8] that cyclization occurs through initial attack of the anion radical on the unreduced C, C-double bond.

We have investigated the reduction of bis (enone) *cis*-4 *a*-methyl-1, 2, 4 *a*, 7, 8, 8 *a*-hexahydronaphthalene-2, 7-dione (**1**) [9], expecting it to represent a suitable model compound for such studies. In fact, the *cis*-fusion of the two rings allows an easy approach of the two C, C-double bonds, as observed in the intramolecular [2+2]-photocycloaddition to a tetracyclic diketone containing a bicyclo[2.1.0]pentane unit [10].

Preliminary CV.-runs in CH<sub>3</sub>CN showed the occurrence of an inverted peak in the oxidation sweep at scan rates up to 100 mV/s [11] [12]. No such phenomenon

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<sup>1)</sup> For detailed discussions concerning the question of radical-substrate *vs.* radical-radical coupling in the EHD. of  $\alpha, \beta$ -unsaturated carbonyl compounds *cf.* also [3-5].

was observed in DMF and therefore the complete CV. analysis was performed in this solvent. Typical voltammograms at low and high sweep rates are shown in the *Figure*. The results are summarized in *Table 1*.

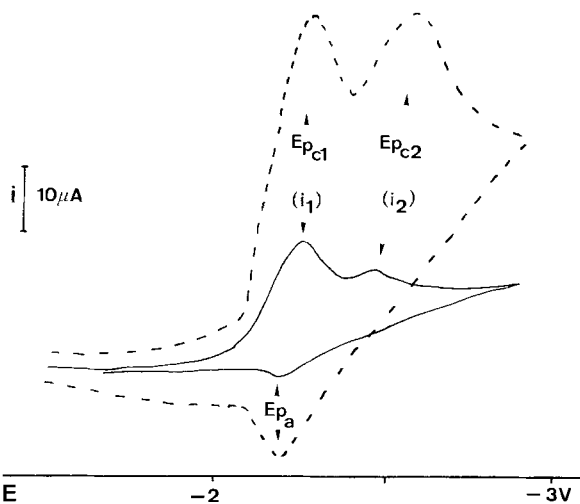


Figure. Cyclic voltammograms of **1** ( $10^{-3}$  M in DMF) on a HMDE with  $\text{Bu}_4\text{NBF}_4$  (0.5 M). Reference electrode:  $\text{Ag}/\text{Ag}^+$   $10^{-2}$  M. (—): 500 mV/s; (---): 50000 mV/s

Table 1. Cyclovoltammetric data of the reduction of **1** ( $10^{-3}$  M in DMF) on HMDE with  $\text{Bu}_4\text{NBF}_4$  (0.5 M)

Sweep rate	$E_{p_{c1}}^{a)b)}$	$E_{p_{c2}}^{a)b)}$	$E_{p_a}^{a)b)}$	$i_2/i_1^a)$
50 mV/s	-2.20	-2.47	-	0.10
500 mV/s	-2.23	-2.50	-2.18	0.12
5000 mV/s	-2.26	-2.54	-2.18	0.15
50000 mV/s	-2.29	-2.60	-2.18	0.34

a) cf. *Figure*.

b) All potentials vs.  $\text{Ag}/\text{Ag}^+$   $10^{-2}$  M.

Preparative electrolysis at -2.3 V under similar experimental conditions (Hg, DMF,  $\text{Bu}_4\text{NBF}_4$ ) gave a major product **2** as monitored by TLC. Being itself only slightly soluble in ether, **2** could not be separated effectively from the supporting electrolyte. Replacing  $\text{Bu}_4\text{NBF}_4$  by tetramethylammonium - or lithium perchlorate leads to a more complex product mixture, possibly due to partial reduction of the supporting electrolyte itself. Finally **2** was obtained in 22% yield by reduction of **1** with Mg in HMPT, trapping the bis(enolate)  $\text{B}^{2-}$  with  $(\text{CH}_3)_3\text{SiCl}$  and subsequent hydrolysis of the bis(silyl) ether, a sequence described by *Dunoguès et al.* for the preparation of dicarbonyl hydrodimers of 2-cyclohexenones [13]. From the spectroscopic data summarized in *Table 2* it can be safely concluded that **2** is 6-hydroxy-3-methyltetracyclo[4.4.0.0<sup>2,4</sup>.0<sup>3,8</sup>]decan-10-one, formed by an intramolecular aldol reaction after the reductive coupling step (*Scheme*).

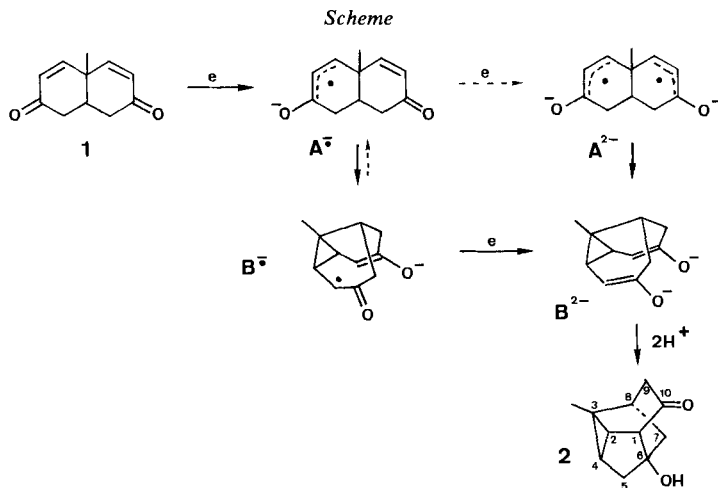


Table 2. Spectroscopic data for compound 2

MS.	<sup>1</sup> H-NMR. (CDCl <sub>3</sub> )	<sup>13</sup> C-NMR. (CDCl <sub>3</sub> )
178 ( <i>M</i> <sup>+</sup> , 55%)	2.47 ( <i>d</i> , <i>J</i> = 4.0 Hz, H-C(1))	216 ( <i>s</i> , C(10))
109 ( <i>M</i> <sup>+</sup> - C <sub>4</sub> H <sub>5</sub> O)	2.37 ( <i>d</i> × <i>t</i> , <i>J</i> = 17.5, 3.0, 3.0 Hz, H <sub>a</sub> -C(9))	79.2 ( <i>s</i> , C(6))
IR. (CH <sub>2</sub> Cl <sub>2</sub> )	2.34 ( <i>d</i> × <i>d</i> × <i>d</i> , <i>J</i> = 6.0, 3.0, 3.0 Hz, H-C(8))	57.9 ( <i>d</i> , <i>J</i> = 143 Hz, C(1))
3580	2.07 ( <i>d</i> × <i>t</i> , <i>J</i> = 10.6, 3.0, 3.0 Hz, H <sub>a</sub> -C(5))	43.8 ( <i>t</i> , <i>J</i> = 129 Hz, C(9))
3360	1.96 ( <i>d</i> × <i>d</i> × <i>d</i> , <i>J</i> = 17.5, 3.0, 1.2 Hz, H <sub>b</sub> -C(9))	42.1 ( <i>t</i> , <i>J</i> = 129 Hz, C(7))
1700	1.84 ( <i>d</i> × <i>d</i> × <i>d</i> , <i>J</i> = 12.2, 6.0, 3.0 Hz, H <sub>a</sub> -C(7))	42.0 ( <i>t</i> , <i>J</i> = 129 Hz, C(5))
	1.81 ( <i>d</i> , <i>J</i> = 10.6 Hz, H <sub>b</sub> -C(5))	34.8 ( <i>d</i> , <i>J</i> = 139 Hz, C(8))
	1.55 ( <i>s</i> , OH)	28.8 ( <i>d</i> , <i>J</i> = 167 Hz, C(2))
	1.48 ( <i>d</i> × <i>d</i> , <i>J</i> = 6.0, 3.0 Hz, H-C(4))	25.1 ( <i>d</i> , <i>J</i> = 176 Hz, C(4))
	1.19 ( <i>d</i> × <i>d</i> , <i>J</i> = 6.0, 4.0 Hz, H-C(2))	22.3 ( <i>s</i> , C(3))
	1.15 ( <i>d</i> × <i>d</i> , <i>J</i> = 12.2, 3.0 Hz, H <sub>b</sub> -C(7))	20.3 ( <i>qa</i> , <i>J</i> = 125 Hz, CH <sub>3</sub> )
	1.03 ( <i>s</i> , CH <sub>3</sub> )	

The cyclic voltammograms at low sweep rates exhibit an irreversible wave for the reduction of **1** to the anion radical **A**<sup>•-</sup> and a very weak second wave corresponding to the reduction of **A**<sup>•-</sup> to the dianion **A**<sup>2•-</sup>. At high sweep rates the first reduction wave tends towards more reversible behavior while the second reduction wave increases in intensity relative to the first one. This picture is compatible with **A**<sup>•-</sup> undergoing a chemical reaction and thus being withdrawn from the system. Although the equilibrium between a 3-butenyl- and a cyclopropylmethyl radical usually lies in favor of the open-chain species [14], an equilibrium between **A**<sup>•-</sup> and **B**<sup>•-</sup> would be shifted to the cyclic species as **B**<sup>•-</sup> can be further reduced to the bis(enolate) **B**<sup>2•-</sup> either directly or by disproportionation of two anion radicals **B**<sup>•-</sup> [3]. At higher sweep rates the reduction of **A**<sup>•-</sup> to **A**<sup>2•-</sup> and its reoxydation to **1** become competitive. It can therefore be concluded that *the intramolecular coupling step occurs at the anion radical level (A<sup>•-</sup> → B<sup>•-</sup>)*. The final intramolecular aldol reaction is not unprecedented [15].

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## Experimental Part

*General.* Chemical shifts in the 400-MHz-NMR. spectra are given in ppm relative to TMS (= 0 ppm) as internal standard. Absorptions in the IR. spectrum are given in  $\text{cm}^{-1}$ .

*Materials.* Bis(enone) **1** was synthesized according to [9]. DMF was purified as in [16].  $\text{Bu}_4\text{NBF}_4$  was purchased from Fluka AG and recrystallized from AcOEt/pentane.

*Cyclic Voltammetry.* A Wenking PCA 72L potentiostat and a Amel 565 waveform generator were used with a HMDE, a Pt-wire as counter electrode and  $\text{Ag}/\text{Ag}^+$   $10^{-2}\text{M}$  as reference electrode. The voltammograms were recorded on a Hewlett Packard 141B oscilloscope.

*Preparation of 6-hydroxy-3-methyltetracyclo[4.4.0.0<sup>2,4</sup>.0<sup>3,8</sup>]decan-10-one (2).* A solution of 352 mg **1** ( $2 \cdot 10^{-3}$  mol) in 3 ml HMPT was added under  $\text{N}_2$  at  $40^\circ$  to a mixture of 170 mg Mg, 1.3 g  $\text{Ml}_3\text{SiCl}$  and one drop of  $\text{TiCl}_4$  in 2 ml HMPT. After stirring at  $80^\circ$  for 6 h, cold water was added and the mixture extracted three times with ether. The ether was evaporated and the residue refluxed for 1 h in 4 ml EtOH, 2 ml  $\text{H}_2\text{O}$  and one drop of HCl-solution. Enough  $\text{NaHCO}_3$  was then added to neutralize the acid, the EtOH evaporated and the aqueous phase extracted with  $\text{CH}_2\text{Cl}_2$ . The residue from this organic phase was chromatographed ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2/\text{AcOEt}$  4:1) and the fraction with a Rf-value=0.25 sublimed at  $90^\circ/0.01$  Torr to afford 78.3 mg **2** (22%), m.p.  $125\text{--}127^\circ$ .

## REFERENCES

- [1] P. Margaretha & P. Tissot, *Nouv. J. Chim.* **3**, 13 (1979).
- [2] P. Tissot, J. P. Surbeck, F. Gülaçar & P. Margaretha, *Helv. Chim. Acta* **64**, 1570 (1981).
- [3] P. Margaretha & V. D. Parker, *Acta Chim. Scand.* **B36**, 260 (1982).
- [4] J. M. Savéant, Sandbjerg Meeting on Organic Electrochemistry 1982, Book of Abstracts, p. 7.
- [5] V. D. Parker, *ibidem*, p. 13.
- [6] L. Mandell, R. F. Daley & R. F. Day, *J. Org. Chem.* **41**, 4087 (1976).
- [7] J. M. Mellor, B. S. Pons & J. H. A. Stibbard, *J. Chem. Soc., Perkin I*, 1981, 3092.
- [8] C. P. Andrieux, D. J. Brown & J. M. Savéant, *Nouv. J. Chim.* **1**, 157 (1977).
- [9] E. Wenkert, F. Haviv & A. Zeitlin, *J. Am. Chem. Soc.* **91**, 2229 (1969).
- [10] P. Margaretha & K. Grohmann, *Helv. Chim. Acta* **65**, 556 (1982).
- [11] P. Margaretha & P. Tissot, Sandbjerg Meeting on Organic Electrochemistry 1981, Book of Abstracts, p. 93.
- [12] P. Tissot & P. Margaretha, *Helv. Chim. Acta* **64**, 180 (1981).
- [13] J. Dunoguès, R. Calas, M. Bolourchian, C. Biran & N. Duffaut, *J. Organomet. Chem.* **57**, 55 (1973).
- [14] A. L. J. Beckwith & K. U. Ingold, in: 'Rearrangements in Ground and Excited States', Vol. 1 (P. de Mayo, ed.), Academic Press 1980, p. 161.
- [15] A. T. Nielsen & W. J. Houlihan, *Org. React.* **16**, 1 (1968).
- [16] B. C. Willett & D. G. Peters, *J. Electroanal. Chem.* **123**, 291 (1981).