

New Cathodic Cyclodimerisations of 4-Pyrones

Gilles Mason,^a Georges Le Guillanton,^a and Jacques Simonet^{*b}

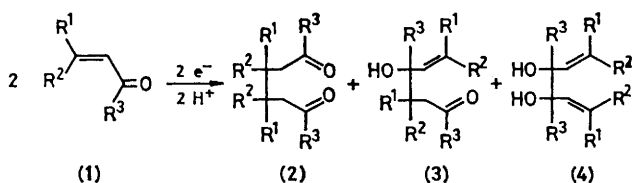
Laboratoire d'Electrochimie organique, ERA CNRS n° 896

^a U.C.O., B.P. 808, 49005 Angers Cedex, France

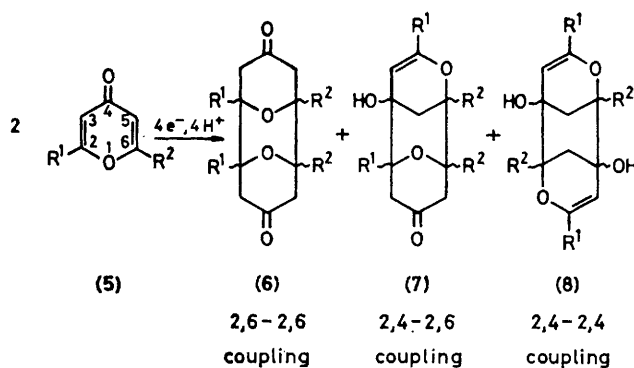
^b Faculté des Sciences, Campus de Beaulieu, 35042 Rennes Cedex, France

Under certain conditions, the electrolysis of pyrones leads to complex 'double dimers' with a degree of selectivity.

Electrochemical methods are known to be useful in the building of carbon-carbon bonds, especially by cathodic means. The formation of the carbon-carbon linkage may be achieved easily through the coupling of activated¹ or non-activated² olefins. In the electrochemical coupling of α,β -unsaturated ketones (1),³ the distribution of the different hydrodimers after reaction depends on several parameters (nature of the double layer, electrolyte, potential, *etc.*)⁴ and it rarely appears to be selective.



Scheme 1



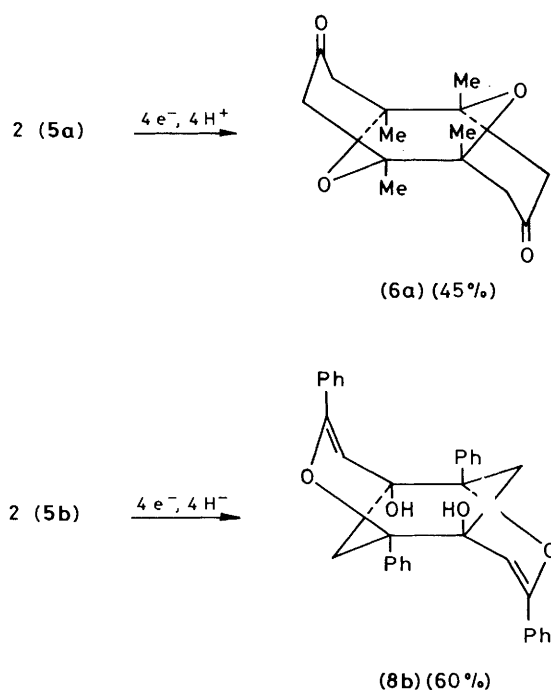
Scheme 2

a; R¹ = R² = Me
b; R¹ = R² = Ph
c; R¹ = Me, R² = Ph

Table 1. Controlled-potential electrolysis of the 4-pyrones (**5a–c**).^a

Substrate	Cathode potential/V ^b	Amount of electricity/(F mol ⁻¹) ^c	% Yield			Total % yield of dimers
			(6)	(7)	(8)	
(5a)	-2.20	2.20	45 ^d	<5	Trace	50
(5b)	-1.80	1.90	—	25 ^e	60 ^g	85
(5c)	-1.90	1.75	6	14 ^f	40 ^h	60

^a Working electrode, mercury pool (area 19 cm²); catholyte 1 g of substrate in MeCN-H₂O (60 ml; 80:20) with Et₄NClO₄ (0.2 M) as supporting electrolyte. ^b vs. saturated calomel electrode. ^c 1 F = 9.6485 × 10⁴C. ^d (**6a**), m.p. 268 °C. ^e (**7b**), m.p. 251 °C. ^f (**7c**), m.p. 132 °C. ^g (**8b**), m.p. 232 °C. ^h (**8c**), m.p. 194 °C.

**Scheme 3**

When R³ (Scheme 1) has another double bond, also in an activated position, new coupling reactions could be expected [for example from reactions of (2)]. However, a more reduc-

tive potential than that for the (1) → (2) transformation would then be required. Moreover, such a one-step electrochemical 'double coupling' reaction (2 F mol⁻¹) is hitherto unknown.

Nevertheless, attempts at electrochemical reduction of 4-pyrones substituted in the 2- and 6-positions (Scheme 2) under certain conditions (in acetonitrile-water, 80:20) may lead to complex 'double dimers' (6)–(8) with a degree of stereoselectivity (Table 1).

In the case of (5a) and (5b), the major products isolated are (6a) and (8b) respectively. These structures are centrosymmetric⁵ (Scheme 3), as established by single-crystal Weissenberg and precession X-ray diffraction studies.

The structural assignments for the other new compounds (7) and (8) are based on analysis of their spectra (i.r., ¹H and ¹³C n.m.r., and mass). However, a defined configuration is for the moment difficult to establish for these dimers.

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References

- 1 M. M. Baizer, in 'Organic Electrochemistry' ed. M. M. Baizer, M. Dekker, New York, 1973, ch. 19, p. 679, and references cited therein.
- 2 G. Mabon, C. Moinet, and J. Simonet, *J. Chem. Soc., Chem. Commun.*, 1981, 1040.
- 3 E. Touboul, F. Weisbüch, and J. Wiemann, *C.R. Acad. Sci., Ser. C*, 1969, **268**, 1170; J. Simonet, *Bull. Soc. Chim. Fr.*, 1970, 1533; J. Grimshaw and R. J. Haslett, *J. Chem. Soc., Perkin Trans. 1*, 1979, 395.
- 4 P. Margaretha and P. Tissot, *Nouv. J. Chim.*, 1979, **3**(4), 13; P. Tissot, J. P. Surbeck, F. O. Gulasar, and P. Margaretha, *Helv. Chim. Acta*, 1981, **64**(5), 1570.
- 5 P. Batail and V. Bleher, personal communication.