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FRAGMENTATION REACTIONS OF BILINDIONES

Fahimeh Eivazi, W. Michael Lewis, and Kevin M. Smith*
The Robert Robinson Laboratories, University of Liverpool,
P.O. Box 147, Liverpool L69 3BX, England

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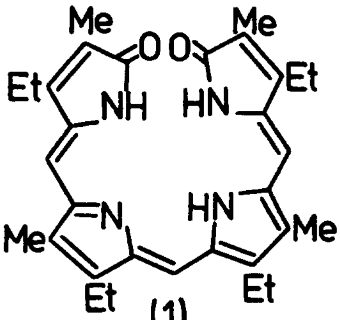
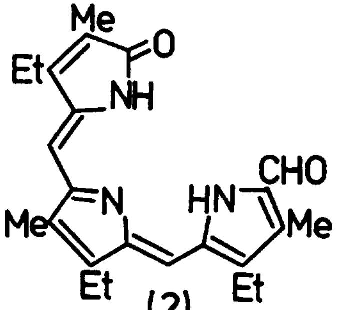
In a recent paper[1] we described the controlled oxidative degradation of a bilindione[2] (**1**) to give a 14-formyltripyrrinone (**2**). A metal complex of the 15,16-dimethoxybilindione (**3**) was shown to be an intermediate in this novel transformation. In this Letter we describe an efficient electrochemical approach to the 15,16-dimethoxybilindione (**3**), and report on some novel chemistry of this particular system; this shows ring cleavage in bilindiones (to afford tripyrrinones) to be a far more general reaction than had heretofore been expected.

15,16-Dimethoxybilindiones have previously been prepared by Siedel[3] and more recently by von Dobeneck,[4] by treatment of bilindiones of type (**1**) with bromine in methanol. In our own work, we visualised[1] the formation of (**3**) as involving one-electron oxidation of (**1**)(or a metal complex) to give the cation-radical which underwent attack by methanol before[5] abstraction of a second electron and attack once more by methanol. In support of this, Figure 1 shows the cyclic voltammogram of compound (**1**); a reversible peak at about 300 mV attests cation radical formation. Thus, preparative electrolysis of a methanol/methylene chloride solution (0.05 M $Bu_4N^+ ClO_4^-$) of the bilindione (**1**) on the plateau (Figure 1) at 0.7 V vs sce (Pt electrodes) in an undivided cell gave a high yield of the 15,16-dimethoxybilindione (**3**). At higher potentials for extended time periods, the 4,5,15,16-tetramethoxybilindione (**4**) was obtained; similar tetramethoxy compounds have been isolated by von Dobeneck,[4] who used oxidation with bromine in methanol.

The NMR spectrum of the thallium(III) complex (**5**)[1] from the



(1)



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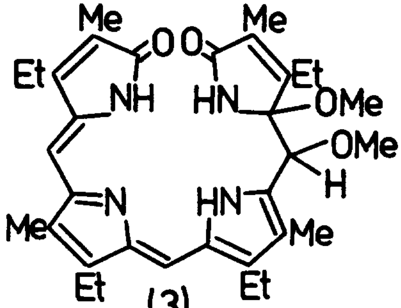

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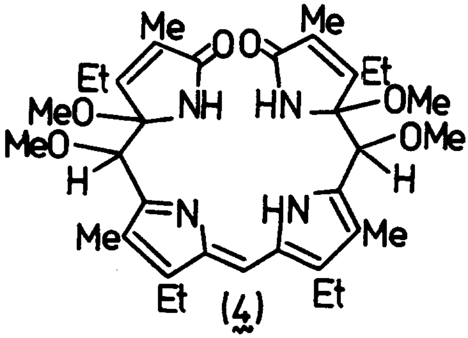

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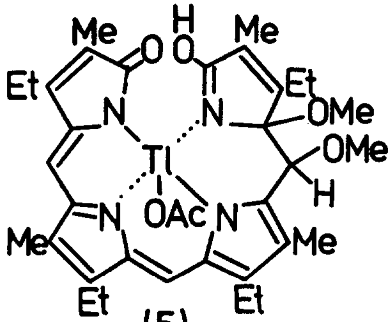
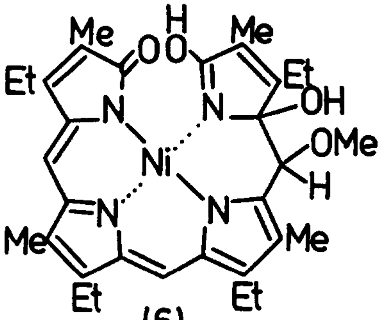
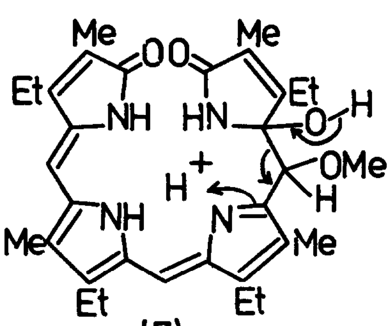


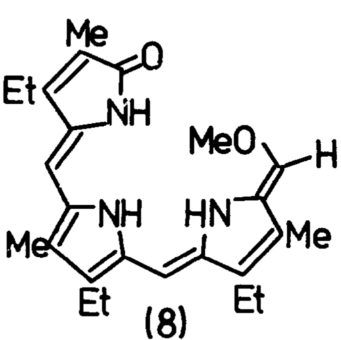
(5)



(6)



(7)



(8)

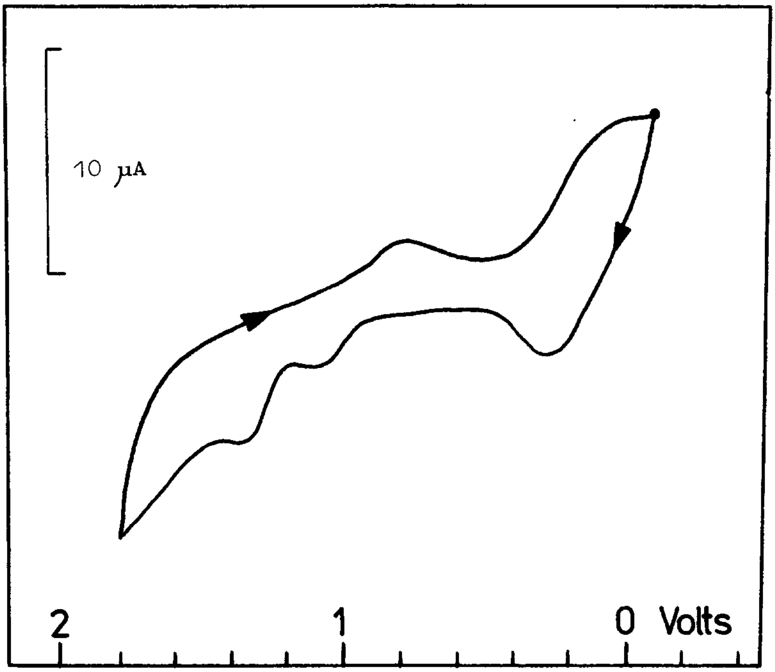


Figure 1: Cyclic voltammogram (Pt button electrode) of bilindione (1)(0.001 M) in methylene chloride (0.1 M Bu_4N^+ ClO_4^-). Scan rate, 0.15 V/sec.

dimethoxybilindione (3) shows[6] the two methoxyl groups to be present. However, treatment of (3) with nickel(II) acetate affords a diamagnetic complex with only one methoxyl group (τ 6.59) in its NMR spectrum, and to which we assign structure (6) on the further evidence of its elemental analysis (Found: C, 63.77; H, 6.64; N, 9.48. $C_{32}H_{40}N_4NiO_4$ requires: C, 63.90; H, 6.70; N, 9.30%). Demetallation of (6) using trifluoroacetic acid, in an attempt to obtain the monomethoxybilindione (7), gave instead the tripyrrolic vinyl ether (8) (m/e 407, 53 %) which showed four methyl groups in its NMR spectrum, and was presumably obtained by a type of retro-aldol reaction as shown in (7). The vinyl ether (8) was very acid labile, and in the presence of air was transformed efficiently into the 14-formyltripyrrinone (2).

On the basis of published chemistry,[4] it might be anticipated that the 16-methoxy group in (3) could be labile under acidic conditions. This is indeed the case; treatment of (3) with aqueous perchloric acid in acetic acid gave a high yield of a mixture of the 14-formyltripyrrinone (**2**) and the parent bilindione (**1**). Formation of (**2**) can be envisaged as proceeding through (**7**), which would be obtained by protonation, elimination of methanol, and then rehydration; transformation of (**7**) into (**2**) would be as described earlier. The formation of (**1**) from (**3**) formally requires elimination of two molecules of methanol, and a reduction step.[9]

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References and Notes

1 F. Eivazi, M.F. Hudson, and K.M. Smith, *Tetrahedron Letters*, 3837 (1976).

2 Prepared as described in: K.M. Smith, *J. Chem. Soc., Perkin I*, 1471 (1972). Nomenclature in this paper follows IUPAC suggestions: IUPAC Commission on the Nomenclature of Tetrapyrroles, 6th Memorandum, 1976.

3 W. Siedel and E. Grams, *Z. Physiol. Chem*., **267**, 49 (1941).

4 H. von Dobeneck, U. Sommer, E. Brunner, E. Lippacher, and F. Schnierle, *Annalen*, 1934 (1973).

5 It is possible that a second electron is abstracted before attack by the nucleophile, or that the cation radical disproportionates to give dication and starting material.

6 F. Eivazi, M.F. Hudson, and K.M. Smith, *Tetrahedron*, in the press.

7 Ethylmethylmaleimide (tlc identification[8]) was also a product from this reaction.

8 W. Rüdiger, *Z. Physiol. Chem*., **350**, 1291 (1969).

9 Note that formation of (**2**) from (**7**) requires an oxidation step in the same reaction mixture.