Electrochemical Synthesis of Substituted Barbaralanes by Reduction of Bicyclo[3.3.1]nonadienediones in the Second Wave†

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Summary In contrast to the first wave reduction of 4,8-dimethylbicyclo[3.3.1]nona-3,7-diene-2,6-dione (**1**) or 4,6-dimethylbicyclo[3.3.1]nona-3,6-diene-2,8-dione (**2**) which give dimeric products, reduction in the second voltammetric wave gives substituted barbaralanes.

PREPARATIVE experiments in which anodic oxidations in the second voltammetric wave give products different from the first wave products[1] have been described. Few preparative reductions in the second cathodic wave[2] have been described. Here we show the synthetic utility of such a process in the preparation of substituted barbaralanes by the second wave reduction of the bicyclo[3.3.1]nonadienediones (**1**) and (**2**).

Cyclic voltammetry of the diones (**1**)[3] and (**2**)[3] showed two cathodic waves at $-1{\cdot}67$ and $-2{\cdot}76$ V for (**1**) and $-1{\cdot}71$ and $-2{\cdot}71$ V for (**2**). For both (**1**) and (**2**) the reversibility of the first wave was apparent at sweep rates of $0{\cdot}5\ \mathrm{V\ s^{-1}}$, and chronoamperometry using phenazine[4] as a standard established that transfer of a single electron was associated with the first wave. Preparative reductions of the dione (**1**) were effected in dry acetonitrile at a platinum gauze electrode using tetra-n-butylammonium tetrafluoroborate as electrolyte, in the absence and in the presence of added acetic anhydride. Controlled potential reduction of the dione (**1**) at $-2{\cdot}0$ V with passage of 1 Faraday per mole led in the absence of added acetic anhydride to the isolation by preparative t.l.c. of three fractions in addition

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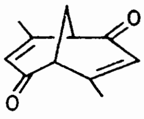
† No reprints available.

to recovered (**1**) (21·5%). The dimeric nature of the three oily fractions was established by mass spectroscopy and the site of coupling by i.r. and ^{1}H n.m.r. spectroscopy. In order of increasing polarity fraction (**3**) associated with coupling at the β-position of the $\alpha\beta$-unsaturated ketone, (**4**) associated with mixed coupling, and (**5**) associated with coupling at the carbonyl centres were isolated in 11·7, 7·3, and 13·2% yields respectively. Each fraction probably represents a mixture of diastereoisomers, and *exo–exo* coupling is assumed by analogy with the known preference[5] for *exo* attack in bicyclo[3.3.1]nonadienediones. A similar reduction of the dione (**2**) was unsatisfactory as the greater polarity of the products precluded efficient separation from the electrolyte. The reduction of the dione (**1**) closely parallels the recently reported[6] reduction of cyclohex-2-enone where again mixtures of diastereoisomers corresponding to the possible couplings were isolated. Reduction of the dione (**1**) at −2·0 V in the presence of acetic anhydride similarly gave dimeric products: preparative t.l.c. afforded after hydrolysis (**4**) (12·1% yield) and (**5**) (63·5% yield).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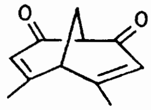
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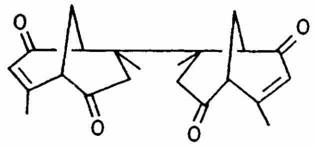
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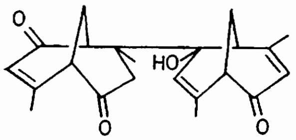
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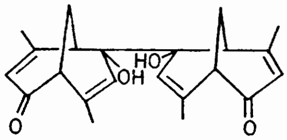
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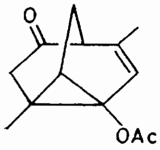
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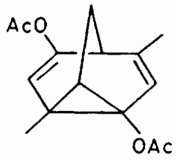
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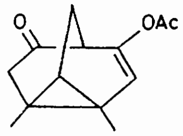
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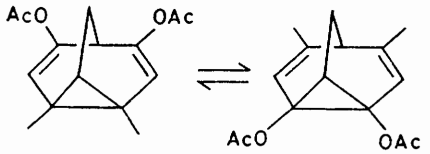
(9a) (9b)

In contrast to these results, electrolysis of the dione (**1**) at −2·75 V in the presence of acetic anhydride afforded the rather unstable ketoacetate (**6**), $\nu_{\max}$ 1730 and 1710 cm^{-1}, τ 4·06 (1H,m), 7·20 (1H,m), 7·45 (2H, dd, *J* 20 Hz), 7·86 (3H,s), 8·05 (2H,m), 8·25 (3H,d), 8·50 (1H,m), and 8·81 (3H,s), isolated by preparative t.l.c. on silica gel in 17% yield. A different work-up procedure requiring direct removal of solvent from the catholyte by evaporation followed by distillation of products (at 130 °C and 0·1 mmHg) from residual electrolyte gave a colourless distillate in which a new product was the major component. Preparative g.l.c. afforded the pure product (**7**), τ 4·82 (2H,m), 7·95 (6H,s), 8·00 (2H, t, *J* 3 Hz), 8·41 (6H,s), and 8·65 (2H, t, *J* 3 Hz). By thermal (220 °C) or hydrolytic cleavage (**7**) readily gave (**6**).

The dione (**2**) was similarly reduced at −2·75 V in the presence of acetic anhydride. Work up by preparative t.l.c. afforded the ketoacetate (**8**), τ 4·33 (1H,m), 7·26 (1H,m), 7·37 (2H,m), 7·90 (3H,s) 8·08 (2H,m), 8·65 (3H,s), 8·80 (3H,s), and 8·95 (1H,m), in 19% yield, and distillation at 130 °C and 0·1 mmHg followed by preparative g.l.c. afforded the barbaralane (**9**), τ 4·94 (2H,m), 8·06 (1H,t), 8·12 (6H,s), 8·83 (2H,t), 8·90 (6H,s), and 9·07 (1H,t).

In the case of the diacetate (**9**) but not (**7**) divinylcyclopropane rearrangement typical of a barbaralane interconverts two different diacetates. The equilibrium in the case of (**9**) lies heavily in favour of (**9a**) where as predicted[7] greater stability is derived from interactions of acetoxy-substituents and double bonds than in (**9b**).

These results establish the possibility of intramolecular coupling by formation of a carbon–carbon bond in reductions conducted in a second cathodic wave, and contrast with intermolecular coupling by reduction in the first wave. This successful extension of the use of acetic anhydride to trap electrogenerated intermediates from diones suggests further synthetic possibilities for this useful technique.

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