The Stereoselectivity of the Anodic Acetoxylation of Double Bonds. The Reactivity of 2,3-Diphenylindenone

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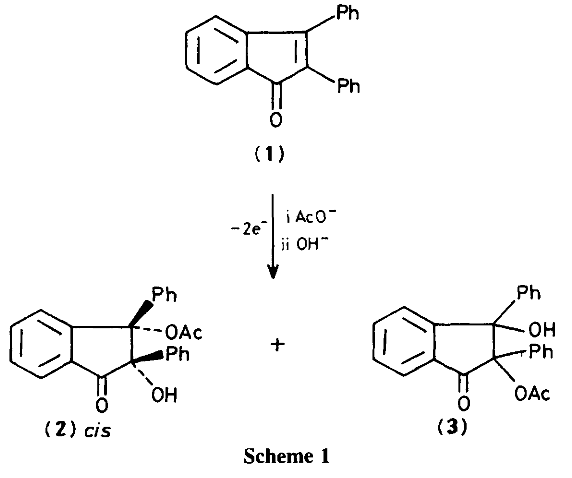
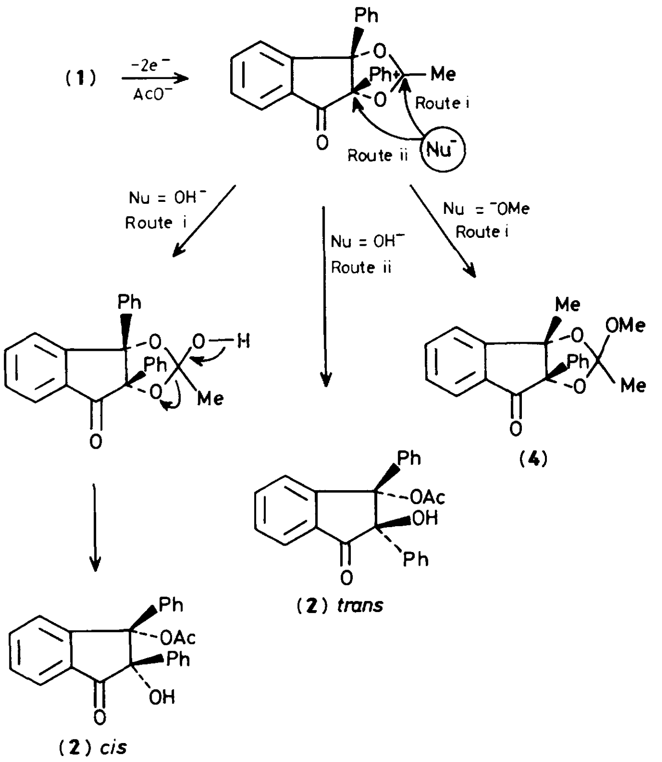
When the anodic addition of 2,3-diphenylindenone is conducted in acetic acid, the predominance of the *cis*-isomer may be explained by the formation of an acetoxonium ion intermediate; this assumption is verified by isolation in high yield of the methoxylated form of this intermediate under particular conditions, and its structure has been determined by *X*-ray crystallography.

In most cases, anodic addition to double bonds is treated as a question of interfacial reactivity (specific adsorption of the substrate, of key intermediate and/or controlled zone of reaction near the interface with a directional flux of nucleophilic reagents from the bulk). So, for example, the *erythro/threo* ratio (for stilbene)[1] or *cis/trans* ratio (for hindered indenes)[2] during oxidation in methanol–sodium methoxide could be interpreted in terms of interfacial reactivity. On the other hand, the acetoxylation selectivity could also be discussed by taking into account the possible formation of a transient acetoxonium ion ($-$e, AcO$^-$, $-$e sequence) decomposed by the action of a nucleophile either in the anolyte or during the work-up. A significant yield of hydroxyacetate would then be expected. Under such conditions its configuration would obviously depend not on the interfacial reactivity but on the stereochemistry of the attack in solution of the acetoxonium cation by a nucleophile. The example which is here discussed is that of 2,3-diphenylindenone (1) oxidized in



Scheme 1



Scheme 2

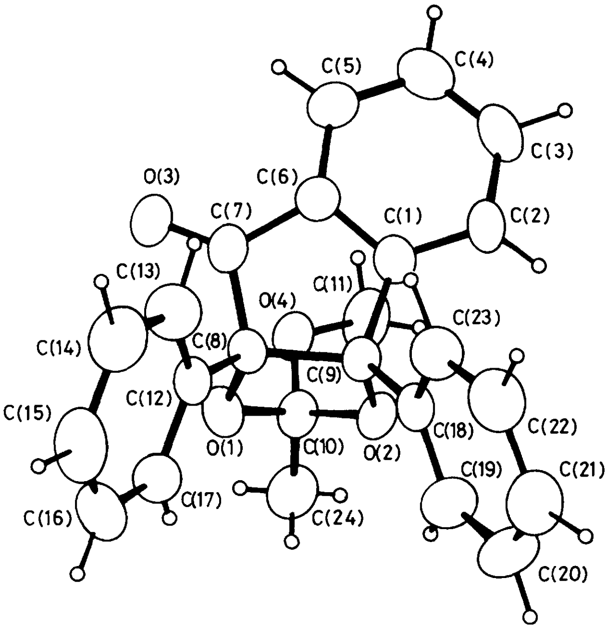


Figure 1. *X*-Ray crystal structure of compound (**4**).

acetic acid–sodium acetate (1 M). Thus, the hydroxyacetoxylation yield is high (96%) with predominant hydroxylation in the 2-position and *cis*-selectivity (>70%) when a glassy carbon anode is used[3] (Scheme 1). Similar results are observed at a platinum anode with, however, a lower hydroacetoxylation yield to give (**2**) + (**3**) (52%) but with a similar stereoselectivity [80% of the *cis*-isomer (**2**) from the mixture including (**2**) and (**3**)]. The structure of compound (**2**) has already been established by *X*-ray analysis.[3]

These results seem to imply a specific decomposition (Nu = OH^-) of the acetoxonium ion postulated as an intermediate in route i (Scheme 2). Attack at C-2 (route ii) would clearly lead to configuration inversion and give *trans*-(**2**) (Scheme 2).

The assumption of the formation of an acetoxy ion for explaining the selectivity without the influence of the interface effect was therefore fully checked by using other experimental conditions. Electrolyses were conducted in dry methanol containing carefully dried sodium acetate (0.5 M) at either a platinum or a glassy carbon anode.† Besides a low yield of *cis*-2,3-dimethoxydiphenylindanone (~10%), compound (**4**) was isolated (85%) and fully characterized by *X*-ray analysis (Figure 1).‡ Compound (**4**) is stable in neutral or basic media, but is converted into the corresponding isocoumarin with acid.

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† Electrolyses were carried out in a H compartment cell, with 2 mmol of indenone (**1**) in 60 ml of methanol containing 0.5 M anhydrous sodium acetate. Oxidations were conducted at + 1.8 V (*vs* Ag/Ag^+, 0.01 M in MeCN, as reference electrode) on a platinum anode (area 16 cm^2), with a current density of 3 mA/cm^2. Electricity consumption was 4 Faradays giving an electrical yield of 50%. Compound (**4**) precipitated during the electrolysis: 85% yield; m.p. 176 °C (from MeOH), *m/z* 372 ($C_{24}H_{20}O_4$); $\nu_{C=O}$ (KBr) 1720 cm^{-1}; n.m.r. ($CDCl_3$) δ 1.94 (s, Me), 2.96 (s, Me), 7.00 (s, 10 H), and 7.20—7.70 (m, 4 H).

‡ *Crystal data:* $C_{24}H_{20}O_4$, M = 372.4, triclinic, space group $P\bar{1}$; a = 8.426(5), b = 8.982(7), c = 14.155(6) Å, α = 76.25(5), β = 89.57(4), γ = 67.23(5)°, Z = 2, μ = 0.82 mm^{-1}. The intensities of independent 3358 reflexions with $I > \sigma(I)$ were measured (Mo-K_α radiation) with an Enraf–Nonius CAD-4 diffractometer of the 'Centre de Diffractométrie' of the University of Rennes. The structure was solved by direct methods[4,5] with the SDP-Enraf–Nonius package.[6] After isotropic and anisotropic refinement, all the hydrogen atoms (isotropic) were located in a difference Fourier (0.44 and 0.27 e A^{-3}); full-matrix least-squares refinement gave a final R value of 0.038. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.