2,3-Dimethylindenone, a New Model Molecule for the Study of the Cathodic Behaviour of Activated Ketones. Electrolyses in the Presence of Primary Organic Halides

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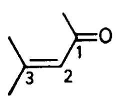
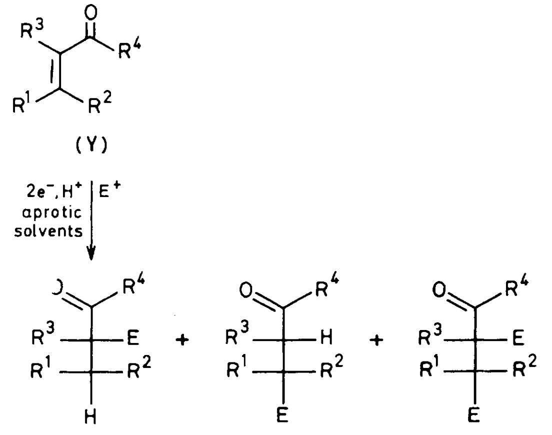
2,3-Dimethylindenone reacts electrochemically with primary organic halides with a low consumption of electricity; the formation of the adducts obtained could imply a chain process induced by the cathode.

There have been many studies of the reactivity of α,β-unsaturated ketones (X),[1] which have demonstrated, in most cases, either the reactivity of C-3, leading to the formation of hydrodimers[2] (*e.g.* in acidic media or in organic solvents), or the saturation[3] of the 2,3-double bond. In aprotic solutions, anion radicals and anions arising from the electrochemical reduction of unsaturated ketones[4-6] may act either as reducing reagents or as nucleophiles (towards primary organic halides, acetic anhydride, or carbon dioxide). Generally speaking, the reaction can be considered as a 'hydroaddition' of the electrophile E with a consumption of electricity of at least 2 Faradays per mole (Scheme 1).

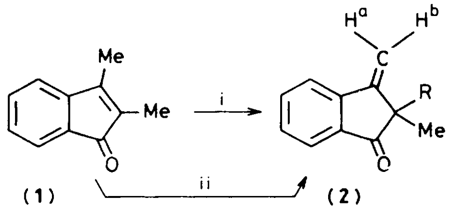


(X)

In most cases, attack at the β-position of the enone is favoured. However, literature reports on the cathodic reactivity of activated double bonds are lacking particularly for compounds (Y) with R^1, R^2, and $R^3 \neq$ H. We have now studied 2,3-dimethylindenone (**1**) as a model compound; its electrolytic reactivity in the presence of primary organic halides RX, including allylic and benzylic halides, is unexpected, a reaction analogous to that carried out chemically with strong bases (occurrence of alkylation–isomerisation) being observed (Scheme 2).



Scheme 1



Scheme 2. i, Electrochemical reaction, Hg or glassy carbon cathode, dimethylformamide (DMF), RX; ii, chemical reaction, BuLi or $NaNH_2$, tetrahydrofuran (THF), RX.

In the case of primary organic halides the yields of (**2**) are high (Table 1) and the electricity consumption is always less than 1 Faraday per mole of the ketone (**1**). The electrochemical reaction also leads partly to the saturated compound (2,3-dimethylindan-1-one) and to a mixture of complex hydrodimers.[7] Several mechanisms may be proposed to account for the formation of (**2**). The abnormally low electricity consumption excludes both the formation of electrogenerated bases (*e.g.* base formation from RX implies the transfer of 2 Faradays in order to create R^-), and H· abstraction from (**1**) to form R· inside a solvent cage, followed by electrochemical reduction of the radical to an intermediate nucleophilic anion. On the other hand, the conjugated *strong* base forms of the saturated compound and of the dimers are present in too small an amount (Table 1) to explain satisfactorily the yield of (**2**).‡ Moreover, the classical scheme of a perturbed redox catalysis process [coupling of $(\mathbf{1})^{\cdot -}$ and R·] cannot explain the formation of (**2**) without the transfer of a hypothetical hydride ion which may have reducing properties towards (**1**).

A chain process induced by electron transfer (from cathode, route i, or from Bu^nLi, here considered as a reducing species, route ii) seems more likely and would be based on the reducing power of the tertiary intermediate radical, as proposed in Scheme 3.

Table 1. Electrochemical reactions of compound (**1**) and alkyl halides RX.[a]

RX	Electricity consumption, Faraday/mol	% Isolated yield of (2)	% Isolated yield of saturated product [b]	% Other products[c]
EtBr	0.6	62	6	14
Bu^nBr	0.7	67	17	7
$CH_2{=}CHCH_2Cl$	0.9	63	10	10
$Ph[CH_2]_2Br$	1.0	57	10	4
$PhCH_2Cl$	1.0	72	7	8
Pr^iBr	0.7	45	8	24

[a] Electrolyses were performed in a Metrohm glass divided cell at an applied potential E_{red} of −0.8 V, with a mercury pool cathode (20 cm²). Similar results were obtained with a glassy carbon electrode (16 cm²): for RX = Bu^nBr, (**2**) was obtained in 68% yield with an electricity consumption of 0.78 Faraday/mol. The working electrode potential was measured with respect to the $Ag/AgI/I^-$ (0.1 M) reference electrode. Compound (**1**) (400 mg, 2.5 mmol) and RX (7.5 mmol) were introduced in 50 ml of dimethylformamide (DMF) containing Bu_4NI (0.1 M) and reduced under nitrogen. [b] Mixture of *cis*- and *trans*-2,3-dimethylindan-1-one. [c] Mixture of hydrodimers.[7]

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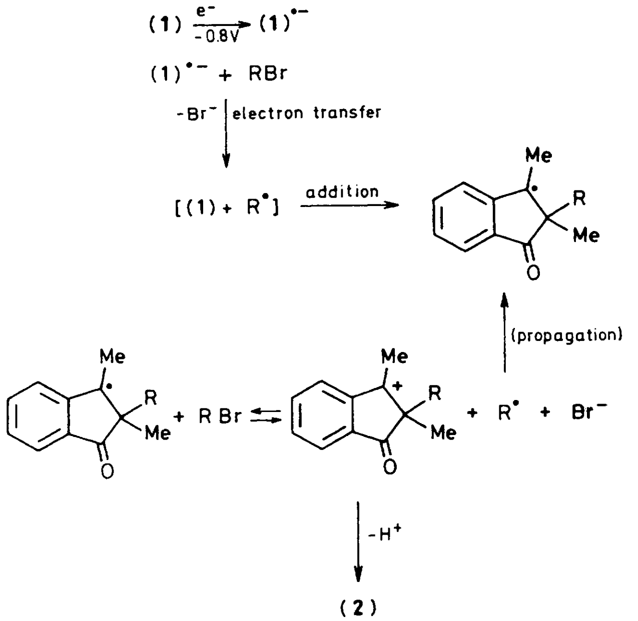
‡ Moreover, sodium amide in excess in dry DMF does not lead to the alkylation of (**1**).



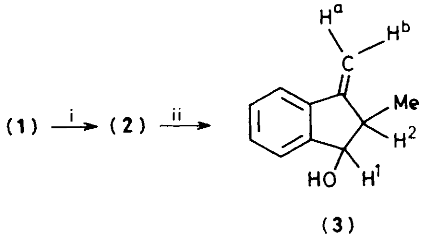
Scheme 3

Termination reactions such as (a) and (b) [the latter after a further electron transfer and side electrochemical reactions

$$(1)^{\cdot -} + R^{\cdot} \rightarrow (1) + R^{-} \xrightarrow{H^{+}} RH \qquad (a)$$

$$(1)^{\cdot -} + H^{+} \rightarrow \text{saturation of } (1) \qquad (b)$$

(*e.g.* $H^+ \rightarrow$ hydrogen evolution)] obviously consume electricity and could explain the values of coulometric measurements. Other types of halide RX have been studied. Secondary halides give similar results with a lower yield of (**2**). However, tertiary halides lead to radically different reactions with exclusive isolation[7] of new types of hydrodimers. It has been checked that (**2**) is electrochemically unreactive (E −1.35 V) at the potential where (**1**) is 'reduced'.



Scheme 4. i, $NaNH_2$, THF, H_2O; ii, $LiAlH_4$, THF, H_3O^+.

The following ^1H n.m.r. spectrum for (**2**; R = Me) is representative of compounds (**2**), produced *via* either route i or route ii: δ ($CDCl_3$): 1.30 (s, 2 × CH_3), 5.25 (s, H^b), 5.80 (s, H^a), and 7.20—7.90 (m, ArH). The structure of compound (**2**; R = H), particularly the location of the methylene group on the β-carbon atom, was confirmed by the n.m.r. spectrum of compound (**3**) obtained as in Scheme 4: the coupling constants involving H^1 and H^2 are as follows: $^3J(H^1\text{-}H^2)$ 5.7 Hz; $^4J(H^2\text{-}H^a)$ 2.8 Hz; $^4J(H^2\text{-}H^b)$ 2.4 Hz.

Received, 15th March 1983; Com. 342

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