

Electrochemical Reduction of Activated Carbon–Carbon Double Bonds. Part 2.¹ Mechanism and Stereochemistry of the Reduction of Self-protonating Indenes

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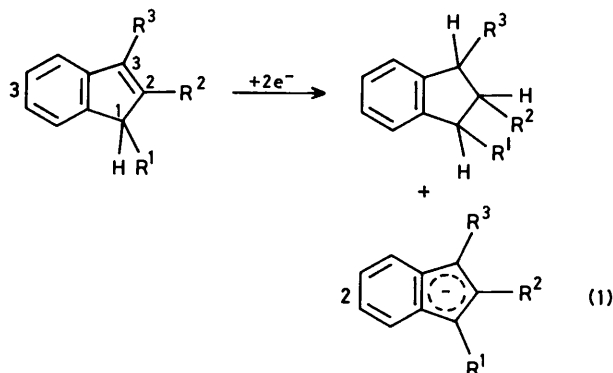
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The reduction at a mercury electrode in dimethylformamide of five variously substituted indenenes bearing at least one (acidic) hydrogen at C(1) was carried out, under self-protonation conditions and in the presence of phenol as a proton donor. Reduction occurred exclusively at the C(2)–C(3) double bond of the five-membered ring and afforded the corresponding indans of various configurations, with a marked predominance of the *cis* isomer, under kinetic control. The stoichiometry was in agreement with a two-electron, two-proton reduction process involving all indene in the case of the presence of phenol or 1/3 indene under self-protonation conditions, the remaining 2/3 acting as a proton donor. Under both conditions direct protonation of the radical anion rather than the dianion formed by disproportionation was observed. Voltammetric and kinetic behaviour of the indenenes was found to be dependent on the structure of the substrates, with differences in rate constants of 3–4 orders of magnitude; the balance between the acidity of the indene and the basicity of the corresponding radical anions was discussed. The stereochemistry observed was rationalised in terms of steric effects on the direction(s) of protonation of the intermediates.

In a recent paper¹ we described the reduction of a series of substituted indenenes at a mercury electrode in dimethylformamide (DMF), and discussed the relationships found between the mechanism and stereochemistry of the process. The reduction involved exclusively the double bond of the five-membered ring and afforded the corresponding indans in practically quantitative yields. Relevant results were obtained for indenenes without a hydrogen in the 1-position, where the different mechanisms and stereochemical courses of the reduction depended, to a first approximation, on the acidity of the added proton donor. In the presence of water the process involved the protonation of a dianion formed by disproportionation of the radical anion generated in the first electron transfer, and led to the exclusive formation of the thermodynamically more stable reduction product [*i.e.* indans with a *trans* configuration around the C(2)–C(3) bond]. In the presence of a stronger proton donor, such as phenol, direct protonation of the radical anion took place; in this case, the thermodynamically less stable reduction product [*i.e.* indans with *cis* configuration around the C(2)–C(3) bond] were preferentially obtained under kinetic control.

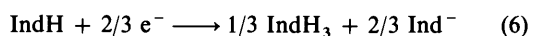
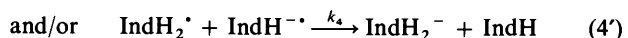
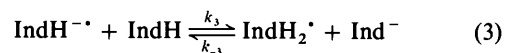
For indenenes bearing at least one (acidic) hydrogen at C(1), the results obtained in the absence of specific proton donors were consistent with a two-electron, two-proton reduction of 1/3 of the starting indene, the remaining 2/3 acting as a proton donor in a self-protonation process [equation (1)]. Under these conditions the predominant formation of the thermodynamically less stable reduction products was observed, corresponding to a formal *syn* addition of hydrogen to the C(2)–C(3) double bond. However, due to the impossibility of carrying out homogeneous kinetics and to the non-completion of the theoretical voltammetric treatment, we were unable to provide definitive evidence on the mechanism of the reaction.

Recently, there has been an upsurge of interest in self-protonation reactions which are probably more frequent than generally recognised and are often overlooked. Self-protonation can be observed with organic molecules bearing not only



relatively strong acidic hydrogens,² but also rather weak ones.^{1,3,4} Several examples of such reactions have been reported,^{2,4} along with a detailed theoretical treatment.⁵

On the basis of this treatment, two alternative mechanisms have been proposed for the reduction of self-protonating indenenes. In the first mechanism direct protonation by indene (IndH) of the radical anion (IndH^{•-}) formed at the electrode

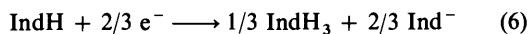
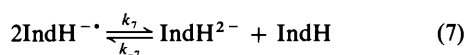


Mechanism 1. Ind⁻ = conjugated base of starting indene

takes place,⁵ followed by one-electron reduction of the neutral radical (IndH_2^{\cdot}) to give the corresponding monoanion (IndH_2^-), which in its turn is protonated by the indene itself to indan(s) (IndH_3) (Mechanism 1).

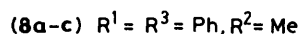
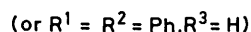
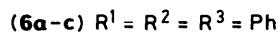
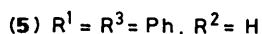
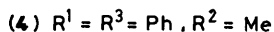
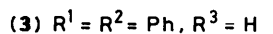
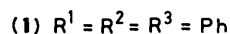
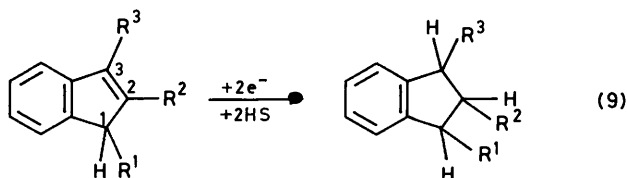
For this mechanism two different limiting regimes can be considered, depending on whether the second electron transfer occurs at the electrode [equation (4), ECE pathway] or in solution with IndH^{\cdot} as the electron source [equation (4'), DISP pathway]. Two ECE subcases are further considered: the ECE_{irr} case, which is observed when the equilibrium constant of the protonation reaction [equation (3)] favours IndH_2^{\cdot} , and the ECE_{rev} case, which is observed for the opposite situation. Two DISP subcases can also be distinguished: DISP1, when the protonation reaction [equation (3)] is the rate-determining step, and DISP2, when the homogeneous electron transfer [equation (4')] is rate determining and reaction (3) is at equilibrium.

In the alternative mechanism of decay of the radical anions (Mechanism 2) protonation occurs on the indenyl dianion IndH^{2-} formed by disproportionation of the radical anion⁵ according to equation (7).



Mechanism 2.

In the light of the above considerations we have studied the electrochemical reduction of a series of indenenes under self-protonation conditions. We have also carried out the reduction of the same substrates in the presence of phenol in order to check, both from kinetic and stereochemical points of view, the effect of different proton donors. We report here the results obtained for the reduction at a Hg cathode in DMF solution of indenenes (1)–(5), according to the general equation (9), where HS represents the indene itself or phenol.



Results

Voltammetric Behaviour.—As previously reported,¹ in a carefully dried solution the electrochemical reduction of indene (1) takes place by the one-electron steps (2) and (10).

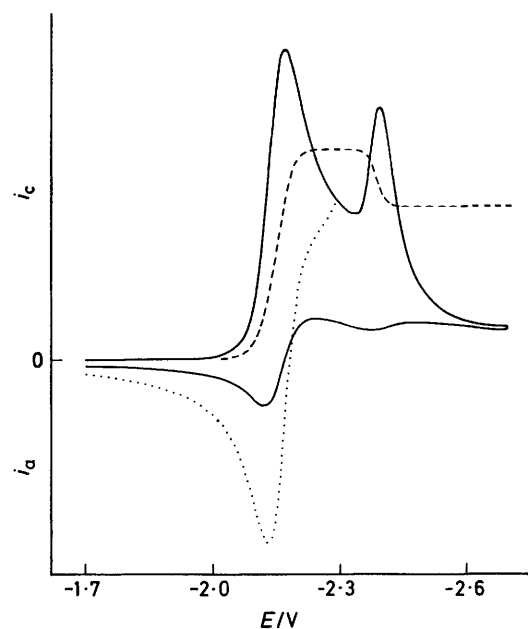
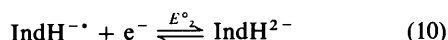


Figure 1. Cyclic voltammograms (— and ···) and polarogram (---) of indene (1) (3.0mm) in dry DMF-0.1M-TBAP at -40°C . Voltammetric sweep rate 0.15 V s^{-1} ; polarographic renewal time 3 s

Table 1. Standard potentials^a

Indene	$T/^\circ\text{C}$	$-E^{\circ}_1/\text{V}$	$-E^{\circ}_2/\text{V}$
(1)	-30	2.145	2.422
(1)	20	2.140	2.435
(2)	-30	2.179	>2.51 ^b
(2)	20	2.175	>2.51 ^b
(3)	-30	2.224	>2.68 ^b
(3)	20	2.220	>2.68 ^b
(4)	20	2.615	^c
(5)	20	>2.6 ^b	^c

^a Referred to s.c.e.; $\pm 3 \text{ mV}$. ^b The chemical irreversibility of the corresponding reduction peak even at low temperatures and high sweep rates does not allow precise determination of E° . ^c Beyond the discharge of the supporting electrolyte (at ca. -3.0 V).

At low temperatures (e.g. -40°C) and high sweep rates ($v > 50 \text{ V s}^{-1}$) the voltammetric pattern shows that a first completely reversible peak is followed by a second quasi-reversible heterogeneous electron-transfer. Both the chemical reversibility of the second reduction step and the ratio between the heights of the second and first reduction peaks decrease on decreasing the sweep rate, the first reduction step remaining completely reversible (Figure 1).

Under these conditions the polarographic pattern shows a first one-electron wave, as indicated by the comparison with the corresponding wave of a non-self-protonating indene with an almost identical structure (1,2,3-triphenyl-1-methylindene).¹ However, at variance with the behaviour of the latter, the first wave of (1) is not followed by a second one-electron wave; actually, a decrease of the limiting current at the potential of the second voltammetric reduction peak is observed (Figure 1). For a polarographic renewal time $> 1 \text{ s}$, the ratio between the second (i_2) and the first (i_1) limiting current is ca. 0.70, in agreement with the theoretical value of 0.67 expected for a fast protonation of the dianion by two molecules of indene with no decay of the radical anion in the timescale of the experiment.

At temperatures $> 20^\circ\text{C}$ and, in particular, at low sweep rates the chemical reversibility of the first reduction step

Table 2. Results of macroscale potentiostatic electrolyses at 20 °C

Indene ^a	Proton donor	Total yield (%)	Isomer yield ^b (%)		
			(Z,Z)-(6a)	(Z,E)-(6b) ^c	(E,E)-(6c)
(1)		31 ^d	70	10	20
(1)	PhOH ^e	100	100		
(2)		33 ^d		(Z)-(7a)	(E)-(7b)
(2)	PhOH ^e	100		62	38
(3) ^f	PhOH ^e	100		71	29
				73	27
(4)		30 ^d	(Z,Z)-(8a)	(Z,E)-(8b) ^c	(E,E)-(8c)
(4)	PhOH ^e	100	46	20	34
			60	20	20
(5)		33 ^d		(Z)-(9a)	(E)-(9b)
(5)	PhOH ^e	100		80	20
				50	50

^a [Indene] 0.1M. ^b Determined by integration of the ¹H n.m.r. spectrum of the reaction mixture. Estimated error ca. 3%. ^c Or (E,Z) (racemic mixture). ^d A corresponding amount of indene was recovered unchanged. ^e [PhOH] 0.5M. ^f Fast isomerisation of (3) to (2) takes place under self-protonation conditions.

decreases, and an irreversible peak can be observed. Under these conditions the second reduction peak disappears, and a single polarographic wave corresponding to 2/3 electron per molecule is detected, indicating relatively fast decay of the radical anion.

Indenes (2) and (3) show voltammetric and polarographic reduction patterns similar to those of (1) but, at variance with the latter, the second voltammetric reduction step is always chemically irreversible even at the highest sweep rates and lowest temperatures investigated.

Indene (4) shows, within the available potential range, only the first reduction peak, where chemical reversibility can be reached only at high sweep rates ($\geq 200 \text{ V s}^{-1}$) and low temperatures, whereas indene (5) shows a chemically irreversible reduction peak even at the highest sweep rates. For these two indenenes a single polarographic wave corresponding to 2/3 electron per molecule is detected.

Values of the standard potentials E°_1 and E°_2 , obtained from the values of peak potentials, are reported in Table 1.

In the presence of excess of phenol, for all substrates (1)–(5) only one irreversible two-electron peak and polarographic wave are observed.

Macroscale Electrolyses.—Under anhydrous conditions, exhaustive controlled-potential electrolyses of indenenes (1)–(5) at the potential of the first or single reduction peak took 2/3 electron per molecule of indene; the recovered products consisted of starting indene (ca. 70%) and of a mixture of the corresponding indan isomers (ca. 30%) (Table 2). These results indicate the occurrence of a two-electron reduction process involving 1/3 of the indene, the other 2/3 acting as a proton source, according to the overall stoichiometry shown in equation (1).

In the reduction of substrate (3) under self-protonation conditions a fast (3) \rightarrow (2) isomerisation takes place starting in the early stage of the electrolysis; this makes meaningless the stereochemical result of the reduction.

In the presence of phenol (0.5M) as a proton donor, exhaustive electrolyses at the potential of the single polarographic wave took 2 electrons per molecule of indene and afforded quantitatively mixtures of the corresponding indan isomers (see Table 2).

Voltammetric Kinetics under Self-protonation Conditions.—From the voltammetric behaviour, coulometric results, and product analyses, the decay of the radical anions under self-protonation conditions could follow Mechanism 1 and/or 2.

As previously reported for indene (4),⁵ on the basis of the evaluated disproportionation rate constant k_7 . Mechanism 2 is too slow to be compatible with the scanty chemical reversibility of the reduction peak. Therefore the E_{pc} and i_{pa}/i_{pc} versus $\log(C^{\circ}/v)$ data (see Experimental) were analysed in the framework of Mechanism 1. The linear portion of the E_{pc} variation has a slope of 29 mV at 20 °C (theoretical 29.1 mV) and, therefore, rules out the possible occurrence of a DISP2 process. The experimental data for E_{pc} and i_{pa}/i_{pc} fit the theoretical curves calculated for DISP1 with $k_{-3}/k_4 \leq 10^{-2}$ (Figure 2). k_3 $3.5 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$ is obtained at 20 °C.

Assuming that k_4 is close to the diffusion limit,^{1,5} values of $k_{-3} \leq 5 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ and $K_3 (= k_3/k_{-3}) \geq 7 \times 10^{-3}$ can be estimated. On the basis of these values the system is unambiguously located in the DISP1 zone,⁵ and the alternative ECE mechanisms can be ruled out.

Indenes (2) and (3) show higher stability of the corresponding radical anions with respect to the radical anions of indene (4), under self-protonation conditions. In these cases, therefore, Mechanisms 1 and 2 could operate together. However, the higher values of the difference $E^{\circ}_1 - E^{\circ}_2$ indicate a very slow disproportionation reaction of the radical anions of (2) and (3), making the occurrence of Mechanism 2 very unlikely as in the case of indene (4). According to this, the i_{pa}/i_{pc} data fit well the same theoretical curve calculated for DISP1 with $k_{-3}/k_4 \leq 10^{-2}$ (see Figure 3).

The values of k_3 thus obtained are reported in Table 3. As in the case of indene (4), the representative points relative to indenenes (2) and (3) unambiguously belong to the DISP1 zone,

* According to Mechanism 2, with the steady-state assumption for the reactive dianion, the decay of the radical anion follows the rate law (i)

$$-d[\text{IndH}^{\cdot-}]/dt = [2k_7k_8/(k_{-7} + k_8)][\text{IndH}^{\cdot-}]^2 \quad (\text{i})$$

corresponding to second-order decay of the radical anion with an apparent rate constant $k_{11} = 2k_7k_8/(k_{-7} + k_8)$.

With the likely hypothesis that the proton transfer between IndH and IndH^{2-} [equation (8)] is slow relative to electron transfer between the same species [reverse of equation (7), with k_{-7} close to the diffusion limit],^{1,5} i.e. $k_8 < k_{-7}$, we obtain $k_{11} \geq 2K_7k_8$, where the value of the disproportionation equilibrium constant $K_7 (= k_7/k_{-7})$ can be determined from the difference between the standard potentials $E^{\circ}_2 - E^{\circ}_1$.¹ Since the value of k_8 is unknown but lower than k_{-7} , we can write $k_{11} < 2k_7$, i.e. the apparent second-order rate constant k_{11} is lower than the rate constant of the disproportionation reaction k_7 , which can be evaluated from K_7 assuming k_{-7} is close to the diffusion limit.

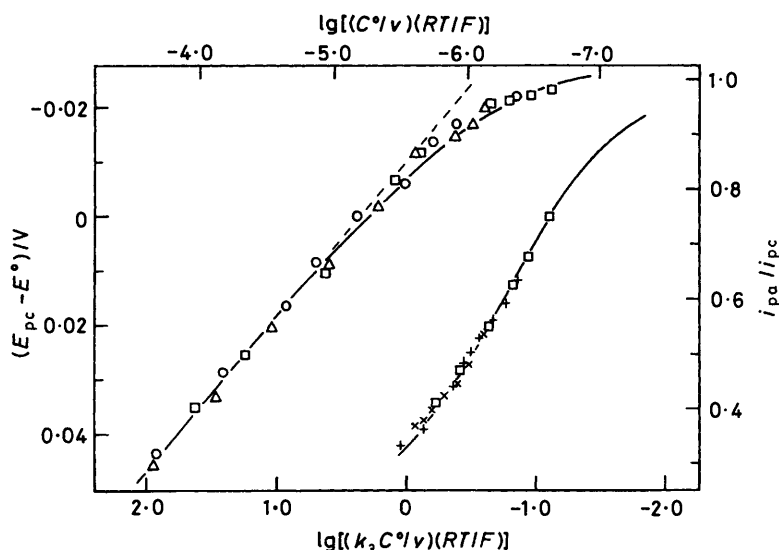


Figure 2. Reduction of indene (4) in dry DMF-0.1M-TBAP at 20 °C. Variation of the cathodic peak potential, E_{pc} (left curve), and of the anodic to cathodic peak current ratio, i_{pa}/i_{pc} (right curve), with the experimental parameters reported on the upper abscissa: C°/mM 1.4 (\square), 2.6 (+), 2.8 (\circ), 6.1 (\times), 9.0 (\triangle). The solid lines (lower abscissa scale) are the working curves obtained for k_{-3}/k_4 10^{-2} and k_3 3.5×10^5 $\text{l mol}^{-1} \text{s}^{-1}$.

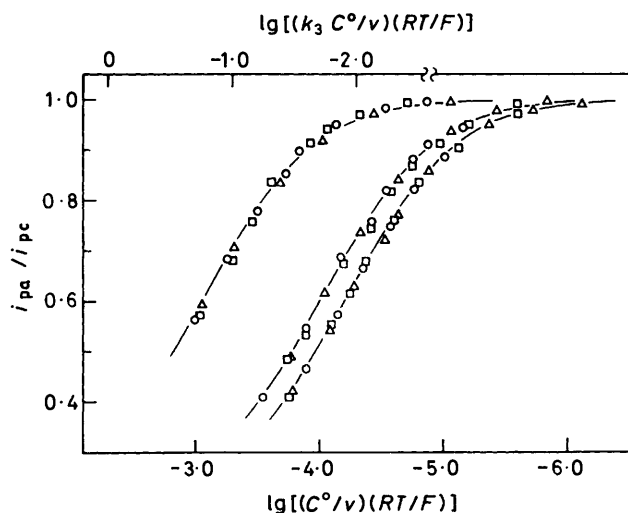


Figure 3. Reduction of indenenes (1)–(3) in dry DMF-0.1M-TBAP. Variation of the anodic to cathodic peak current ratio, i_{pa}/i_{pc} , with the experimental parameters reported on the lower abscissa. Indene (1): C°/mM 1.9 (\triangle), 5.2 (\square), 8.9 (\circ); T 40 °C. Indene (2): C°/mM 1.1 (\triangle), 3.2 (\square), 6.4 (\circ); T 30 °C. Indene (3): C°/mM 1.6 (\triangle), 5.0 (\square), 7.4 (\circ); T 30 °C. The solid lines are the working curves obtained for k_{-3}/k_4 10^{-2} and for the values of k_3 reported in Table 3. The upper abscissa scale refers to the working curve relative to indene (1).

in accord with the fact that a lower value of k_3 favours DISP1 with respect to DISP2 and ECE.⁵

Measurements in different temperature ranges were carried out to verify whether the DISP1 pathway operates under different experimental conditions. The values of k_3 and of the activation energies of reaction (3) are reported in Table 3.

Measurements of variation of E_{pc} versus $\log(C^\circ/v)$ were not carried out for indenenes (2) and (3) due to the fact that as k_3 is relatively small, too low v or too high C° values are necessary to achieve pure kinetic conditions.

In the case of indene (1), which shows high chemical reversibility for the first reduction step, we cannot exclude the possibility that the decay of $\text{IndH}^{\cdot-}$ occurs *via* disproportionation, followed by self-protonation of the dianion (Mechanism

2).^{*} However, i_{pa}/i_{pc} data fit well the curve calculated for the DISP1 situation of Mechanism 1, for a ratio $k_{-3}/k_4 \leq 10^{-2}$ (Figure 3). Measurements have been carried out at $T \geq 30$ °C and the values of k_3 thus obtained are reported in Table 3; of course, due to the possible occurrence of Mechanism 2, these values are overestimated. However, the representative points of indene (1) belong, as in previous cases, to the DISP1 zone of the diagrams.

For indene (5), which has a chemically irreversible reduction peak, kinetic measurements cannot be carried out due to the impossibility of evaluating E°_1 . On the other hand, the absence of the anodic peak at the highest sweep rates investigated indicates $k_3 > 10^7$ $\text{l mol}^{-1} \text{s}^{-1}$.

Voltammetric Kinetics in the Presence of Phenol.—As previously described, in the presence of phenol in excess over indene only one irreversible two-electron reduction peak is observed for all indenenes (1)–(5). The kinetic analysis was carried out by using the criterion of the dependence of the peak potential on the concentration of the reagents and the sweep rate, under pure kinetic conditions.⁶

At 20 °C the potential of the cathodic peak shifts towards more negative values of *ca.* 29 mV per $\log(v/[\text{PhOH}])$ unit, in the range $5 \times 10^{-2} \text{M} \leq [\text{PhOH}] \leq 2 \times 10^{-1} \text{M}$, and is independent of the indene concentration. These results are in agreement with a reversible one-electron transfer process [equation (2)] followed by an irreversible pseudo-first-order protonation of the radical anion $\text{IndH}^{\cdot-}$ by PhOH , as the rate-determining step, to form the neutral radical IndH_2^{\cdot} [equation (11), Mechanism 3]. The latter species, which is also formed in the self-protonation reaction considered in Mechanism 1, can be reduced either at the electrode (ECE pathway) and/or in solution by the anion radical (DISP1 pathway); the monoanion

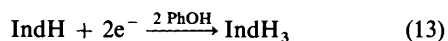
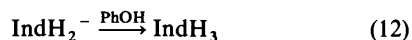
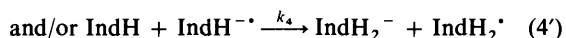
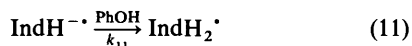
^{*} The observation, at high sweep rates, of a partial reversibility of the second reduction step of indene (1) indicates that $k_8 < 10^8$ $\text{l mol}^{-1} \text{s}^{-1}$. At 30 °C K_7 is *ca.* 10^{-5} ,¹ so that $k_{11} \leq 2 \times 10^3$ $\text{l mol}^{-1} \text{s}^{-1}$ (see footnote †). The value of k_3 obtained for the hypothesis of the occurrence of the DISP1 pathway of Mechanism 1 is 1.2×10^2 $\text{l mol}^{-1} \text{s}^{-1}$ at 30 °C (see text). This indicates that both mechanisms could operate, the relative weights depending on the concentration of the indene and of the corresponding radical anion in the diffusion layer.

Table 3. Rate constants^a for indenenes (1)–(5) from voltammetric measurements under self-protonation conditions (k_3) and with phenol as proton donor (k_{11})

Indene	T/°C	$10^{-3} k_3 /$ $l \text{ mol}^{-1} \text{ s}^{-1}$	$10^{-5} k_{11} /$ $l \text{ mol}^{-1} \text{ s}^{-1}$	Activation energy of reaction (3) (kcal mol ⁻¹)
(1)	20	0.06 ^{b,c}	0.11	
(1)	30	0.12 ^c		
(1)	40	0.20 ^c		11.6
(1)	50	0.39 ^c		
(1)	58	0.61 ^c		
(2)	20	1.7	0.81	
(2)	30	2.6		
(2)	40	4.9		10.4
(2)	50	7.8		
(3)	-10	0.18		
(3)	0	0.34		
(3)	20	1.2	20 ^d	10.3
(3)	30	1.7		
(4)	20	3.5×10^2	1.3×10^2	
(5)	20	$> 10^{4e}$	$> 10^{3e}$	

^a Values reproducible within $\pm 10\%$. ^b Extrapolated from the set of values obtained at higher temperatures. ^c Limiting values obtained in the hypothesis of the occurrence of Mechanism 1 only (see text). ^d Average between the values obtained in the hypothesis of the occurrence of the limiting ECE and DISP1 pathways of Mechanism 3 (13×10^5 and $26 \times 10^5 \text{ l mol}^{-1} \text{ s}^{-1}$, respectively). ^e Values estimated on the basis of the irreversibility of the voltammetric behaviour.

IndH₂⁻ thus formed is then protonated to give the final product IndH₃.



Mechanism 3.

Both limiting situations, ECE and DISP1, show very similar voltammetric patterns,⁶ so that we cannot discriminate between them under our conditions. On the other hand, the values of k_{11} can be obtained, for both situations, by comparing the standard potential of the first reduction step (E_1^0) with the peak potentials measured, at various sweep rates and phenol concentrations, under pure kinetic conditions.^{6b} The value calculated for the DISP1 situation is twice the value for the ECE pathway. On the basis of these values of k_{11} , the kinetic zone diagram of Savéant *et al.*^{6a} suggests the occurrence of the DISP1 pathway in the case of indenenes (1) and (2), of the ECE pathway in the case of (4), and of both pathways in the case of (3). The rate constant values of the protonation reaction of the radical anion by phenol (k_{11}) are reported in Table 3, with the uncertainty due to the occurrence of both situations in the case of indene (3).

Voltammetric measurements cannot be carried out for indene (5) due to the irreversibility of the peak even in the absence of phenol. However, the peak shift caused by addition of phenol, compared with that of indene (4), indicates a very fast protonation of the radical anion (5⁻), with the occurrence of the ECE pathway.

Identification of the Products.—The indans obtained in the macroscale electrolyses [equation (9)] were identified as follows.

Indans (6a–c) and (8a–c), formed in the macroscale electrolyses of indenenes (1) and (4) respectively, were fully characterised in previous work.^{1,7}

Indans (7a, b), obtained in the macroscale electrolyses of indenenes (2) and (3), were identified on the basis of the ¹H n.m.r. spectra of their mixtures (see Stereochemical Assignments) and characterised by comparison with authentic samples prepared independently and also by comparison with literature data.*

Indans (9a, b), formed in the macroscale electrolyses of indene (5), were identified by comparison with authentic samples prepared independently and also, in the case of the Z-isomer (9a), by comparison with literature data.⁹

Stereochemical Assignments.—The configuration of the isomeric indans (6)–(9) was assigned mainly by analysis of their ¹H n.m.r. spectra.

Characteristic features of the ¹H n.m.r. spectra of phenyl-substituted indan derivatives and related systems¹⁰ are the shielding effect exerted by a phenyl group on β-*cis*-methine protons relative to *trans* protons and, conversely, the deshielding effect of the same phenyl group on the β-*trans*-methine protons. In addition, in these systems the relative values of the vicinal proton coupling constants are, in general, smaller for the *cis* than for the *trans* configuration. These criteria, which allowed us to assign the configuration to indans (6a–c) and (8a–c) in previous work,^{1,7} were applied also to indans (7a, b) and (9a, b).

The ¹H n.m.r. spectra of isomers (7a, b) show the 1-H resonance as a doublet at δ 4.66 and 4.42, respectively, with coupling constants of 8.1 and 9.4 Hz. Isomer (7a) has the 2-H resonance as a quartet at δ 4.03; the same resonance for isomer (7b) is at δ 3.59 (second-order multiplet). Therefore, we attributed the Z configuration to isomer (7a) and E to (7b). This stereochemical assignment was confirmed by independent synthesis of isomer (7a). Catalytic hydrogenation of indenenes (2) and (3) afforded as the only [in the case of (2)] or predominant [in the case of (3)] product, the Z-isomer (7a), in agreement with the commonly observed stereochemistry of catalytic hydrogenation of double bonds.¹¹

The assignment of configuration to indans (9a, b) was more straightforward since the two isomers present rather different ¹H n.m.r. spectra, which can be easily interpreted. The spectrum of isomer (9a) (AMX₂ system) is identical with that reported in the literature^{8b} and attributed to the Z-isomer. The spectrum of isomer (9b) (approximate A₂X₂ system) shows two triplets at δ 4.56 and 2.60 (*J* 7.2 Hz), in agreement with a *trans* (axial-equatorial) arrangement of the protons on the 1- and 3-positions of the cyclopentene ring, indicating an E configuration.

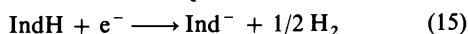
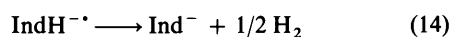
Discussion

The main features of the results may be summarised as follows: (i) the stoichiometry was found in all cases to be in perfect

* The assignment of configuration to indans (7a, b) reported in the literature⁸ is in sharp contrast to the characteristic features of the ¹H n.m.r. spectra of all the phenyl-substituted indans prepared in the present and previous^{1,7} work and, consequently, should be reversed according to the considerations in the text.

agreement with a two-electron, two-proton reduction process involving all the indene in the presence of phenol or 1/3 of indene under self-protonation conditions; (ii) direct protonation of the radical anion rather than of the dianion formed *via* disproportionation was observed either in the presence of phenol and under self-protonation conditions; (iii) the voltammetric and kinetic behaviour of the indenenes was found to be dependent on the structure of the substrates, with difference in rate constants in the range of 3–4 orders of magnitude; (iv) predominant formal *syn* addition of hydrogen to the double bond of the indenenes with formation of the thermodynamically less stable indan isomer(s) took place, with higher stereoselectivity for the reductions carried out in the presence of phenol.

(i) The observed stoichiometry of the process rules out the occurrence of an alternative mechanism involving loss of a hydrogen atom from the radical anion [equations (2) and (14)].



The above monomolecular decay of radical anions was recently discussed.^{5,12} It appears to occur in the case of substrates affording anions stabilised by electron-withdrawing groups or by aromaticity and therefore should be perfectly compatible with phenyl-substituted indenenes.

The absence of secondary products even in small amounts should also be stressed. It rules out the occurrence of alternative pathways involving dimerisations, rearrangements, or fragmentations, which are observed in the reduction of other indenyl substrates under either electrochemical and chemical conditions.¹³

(ii) In principle, indenenes and phenol should be able to protonate both a highly basic dianion and a less basic radical anion. In the case of non-self-protonating indenenes we have previously observed direct protonation of radical anions by a strong proton donor (phenol) and protonation only of dianions by a weaker proton donor (water).¹ The kinetic data obtained in the present work confirm the previous observation and clearly indicate the occurrence of Mechanisms 3 and 1 in the presence of phenol and under self-protonation conditions, respectively. The competing Mechanism 2 does not occur because of the slow disproportionation of the radical anions, with the possible exception of indene (1).

As to the various mechanistic subcases, we can say that under self-protonation conditions the DISP1 pathway of Mechanism 1 operates, whereas in the presence of phenol either DISP1 and/or ECE pathways may occur depending on the values of the rate of protonation of the radical anion.

(iii) The differences in rate observed between the reactions carried out in the presence of phenol and those carried out under self-protonation conditions indicates that under our experimental conditions phenol behaves as a stronger proton donor than indenenes, though the acidities of the latter are rather similar to, or even higher than, that of phenol in terms of pK_a values.* This could be reasonably ascribed to relevant kinetic effects (in particular steric) in the protonation reactions here reported.

From a general point of view, the self-protonation process is affected by the acidic character of the indene and the basic character of the corresponding radical anion, which both depend on thermodynamic and kinetic effects. Therefore, owing to the particular balance between these factors, a generalisation is impossible and the results must be discussed separately. As a first example, the self-protonation process for indene (2) is faster than that for indene (1) (see Table 3), despite the fact that the latter is more acidic than the former owing to better delocalisation of the negative charge in the anion of (2).^{14a} This can be explained by considering that ($2^{\cdot-}$) is more basic than ($1^{\cdot-}$) with respect to phenol (see Table 3) and also, very likely, with respect to the corresponding indene as a proton donor; furthermore, the absence of a phenyl group at C(1) makes this position less hindered and, therefore, proton transfer between (2) and ($2^{\cdot-}$) easier than between (1) and ($1^{\cdot-}$).

Indene (3) should be more acidic than (2), since their conjugated base is the same and (3) is less stable than (2), as demonstrated by the easy (3) \longrightarrow (2) isomerisation in basic medium,^{14a} since the basicity of the radical anion ($3^{\cdot-}$) is higher than that of ($2^{\cdot-}$) toward phenol (see Table 3), in agreement with a lower degree of delocalisation of the negative charge due to the absence of the phenyl group at C(3), a faster self-protonation process should be expected for (3). On the other hand, similar values of k_3 are obtained; evidently, the presence of a phenyl group at C(1) makes more difficult the proton transfer from (3) to ($3^{\cdot-}$) than from (2) to ($2^{\cdot-}$), as observed for (1) with respect to (2). We should also consider that protonation of ($3^{\cdot-}$) can take place either at C(2) and at C(3) (see below), and this fact could affect the comparison made above.

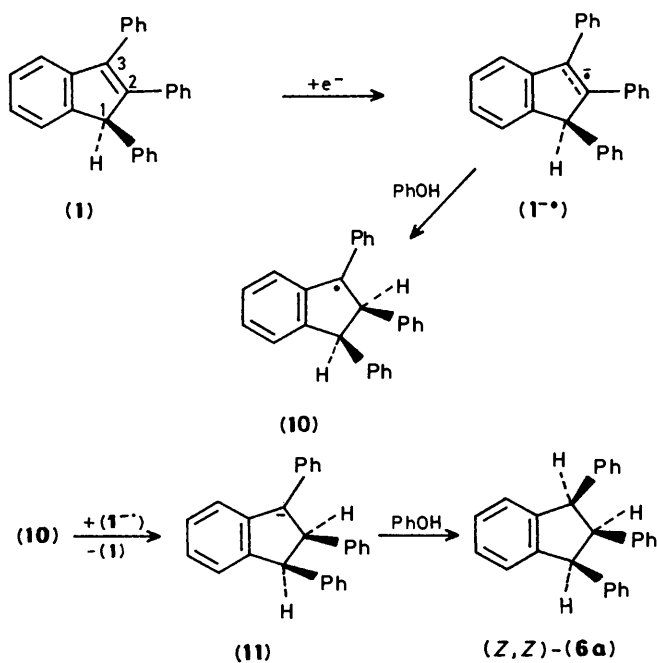
Indenes (4) and (5) show a fast self-protonation reaction, in agreement with their high acidity and the high basicity of the corresponding radical anions.† In fact, (5) is 2.4 and 5.5 pK_a units more acidic than (1) and (2), respectively;^{14a} a similar value of pK_a should be expected for indene (4) owing to the small difference in structure between (4) and (5). The highly basic character of ($4^{\cdot-}$) and ($5^{\cdot-}$) can be explained by the absence of a phenyl group at C(2), which makes protonation at this position easier from both electronic and steric points of view. In addition, the self-protonation reaction for (5) is faster than for (4); this could be ascribed mainly to steric effects exerted by the methyl group at C(2), which make more difficult the protonation of ($4^{\cdot-}$).

(iv) On the whole, the stereochemical results are in agreement with those previously obtained for the reduction of non-self-protonating di- and tri-phenyl-substituted indenenes in the presence of phenol,¹ where the predominant formation of indan isomers derived from a formal *syn* addition of hydrogen to the double bond was discussed in terms of steric hindrance exerted by the phenyl groups against the approach of the protonating species. Therefore, for the reductions carried out in the presence of phenol a rationalisation of a typical example of the stereochemical results [*i.e.*, the exclusive formation of (*Z,Z*)-(6a) in the reduction of (1) occurring *via* Mechanism 3, DISP1 pathway] may be that in the Scheme.

The Scheme may be satisfactorily extended, with appropriate variations, to the reductions of indenenes (2), (4), and (5) in the presence of phenol, for which the same mechanism is operating and the occurrence of the first protonation step at C(2), previously discussed,¹ may be invoked. The lower stereoselectivity observed with respect to (1) may be ascribed to the

* The available pK_a values of indenenes in DMSO^{14a} are the following: (1) 15.2, (2) 17.7, (3) <17.7, (5), 12.8. The reported pK_a value of phenol is 16.4.^{14b} Acidity values for indenenes in DMF are not available; drastic changes in behaviour of the two types of acids in the two solvents can be reasonably excluded.

† A rather high basic character of ($4^{\cdot-}$) is indicated by the high value of k_{11} . Similar behaviour can be expected also for ($5^{\cdot-}$) on the basis of the similar structure of such radical anions; this is supported by the comparison between the voltammetric behaviour of indene (5) in the absence and presence of phenol.



diminished crowding around the positions of the first and/or second protonation step.

The Scheme cannot be directly extended to the reduction of (3) for two reasons: (a) the protonation of the radical anion by phenol may occur, in principle, at either C(2) or C(3) to afford, in either case, a benzyl-type radical; (b) owing to the structure of (3), with a hydrogen at C(3), it is not possible to discriminate between formal *syn* and *anti* addition of hydrogen to the double bond. However, the predominant formation of the indan of *Z* configuration (7a) indicates that the protonation at C(2), which determines the stereochemistry of the reaction, occurs preferentially in this case also on the less hindered side of the five-membered ring of (3).

As for the reductions of (1)–(5) under self-protonation conditions, where Mechanism 1 is operating, the prevalent formation of the indan isomers derived by protonation(s) on the less hindered side indicates that steric effects play a major role in the protonation of the anionic intermediates by the indene itself. Therefore, the Scheme reported above for the reductions carried out in the presence of phenol can be extended to these cases, with the possible exception of the reduction of (1) where the concomitant occurrence of Mechanism 2 cannot be excluded. If so, however, fast protonation of both the dianion and the indanyl anion intermediates¹ would again afford preferentially the (*Z,Z*)-isomer (6a).

Comparison of the stereochemical data obtained in the two different conditions shows a generally lower stereoselectivity for reductions under self-protonation conditions. This may be imputed to the slower protonation of the intermediates by the indenenes with respect to phenol, which could allow the radical anions and/or the indanyl anions to assume more stable conformations, with some staggering of the bulky groups, prior to protonation. The different behaviour of the two protonating species could also be due to the formation, prior to proton transfer, of hydrogen-bonded complexes between the anionic intermediates and an hydroxylic proton donor such as phenol.¹⁵

It should be pointed out that the thermodynamically less stable indan isomers were preferentially formed. As previously discussed,¹ this indicates kinetic control of the reaction, in

agreement with the absence of isomerisation verified under acidic conditions.*

The stereochemical picture presented above does not take into consideration possible effects of the electrode. As a matter of fact, while adsorption phenomena can be reasonably excluded on the basis of electrochemical evidences, heterogeneity effects could play a role in determining the stereochemical course of the reaction; however, this may occur only when an ECE pathway is followed, *i.e.* when the protonation processes are fast and take place close to the electrode.¹ Since macroelectrolysis favours ECE over DISP1 pathways,¹⁶ these effects might be relevant to the stereochemical course of the reduction of indenenes with fast protonation rates, in particular that of (4) and (5) in the presence of phenol. They might be responsible, for example, for the absence of stereoselectivity observed in the reduction of (5) in the presence of phenol. However, the impossibility of performing homogeneous quenching experiments for radical anions of self-protonating indenenes does not allow a comparison between the stereochemical results under homogeneous and 'heterogeneous' conditions, and therefore an assessment of the relevance of such effects.

Experimental

Materials.—The purification of dimethylformamide (DMF) and tetrabutylammonium perchlorate (TBAP) was previously described, as well as the activation of alumina.¹⁷ Phenol (R.P. Carlo Erba) was used as proton donor in some experiments.

M.p.s are uncorrected. ¹H N.m.r. spectra were recorded for solutions in CDCl₃ on a Bruker WP 200 SY spectrometer; chemical shifts are relative to Me₄Si as internal standard. Coupling constants are in Hz and refer to peak separations measured directly from the instrument for spectra not of the first order.

Electrochemical Apparatus and Procedure.—Instruments, cell, and electrodes are as previously reported.¹

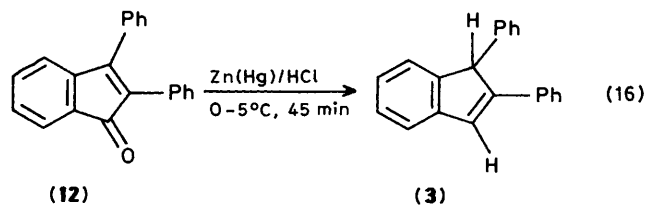
All measurements were carried out in DMF–0.1M-TBAP. Before each experiment the solution was cycled through a column of activated alumina; phenol was then added to the solution when required.

Voltammetric kinetics under self-protonation conditions were carried out by the method previously reported,⁵ measuring the dependence of the anodic to cathodic peak current ratio (*i*_{pa}/*i*_{pc}) and of the cathodic peak potential (*E*_{pc}) of the first step on the voltage sweep rate (*v*) and the indene concentration (*C*^o).

Voltammetric kinetics in the presence of phenol, exhaustive controlled-potential electrolyses, and work-up of electrolysed solutions were carried out as previously described.¹

Reagents and Products.—1,2,3-Triphenyl-1*H*-indene (1),¹⁸ 1,3-diphenyl-2-methyl-1*H*-indene (4),¹⁹ and 1,3-diphenyl-1*H*-indene (5)¹⁹ were synthesised following literature methods.

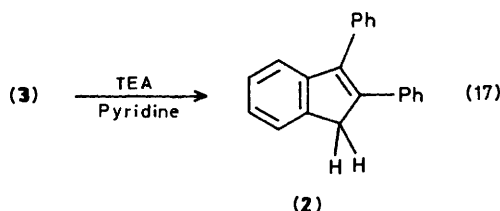
1,2-Diphenyl-1*H*-indene (3) was prepared by the method described by Shriner and Knox²⁰ with minor modifications [equation (16)]. Indene (3) was isolated in 30% yield from the



* The absence of isomerisation under electrolysis conditions both in the presence of phenol and under self-protonation conditions was verified for indans (6)–(9) following the procedure previously reported.¹

complex reaction mixture after low-pressure chromatography on silica gel (eluant light petroleum-dichloromethane) and recrystallisation from 95% ethanol, m.p. 177–178 °C (lit.,²⁰ 177–178 °C) (Found: C, 94.0; H, 6.0. Calc. for C₂₁H₁₆: C, 94.0; H, 6.0%); δ_{H} 4.97 (1 H, s, CH), 7.02–7.56 (15 H, m, 14 Ph and 1 vinylic H).

2,3-Diphenyl-1H-indene (2) was prepared by isomerisation of (3) in the presence of triethylamine (TEA) in pyridine²¹ [equation (17)]. Triethylamine (1 ml) was added to a solution of



(3) (0.560 g, 2.0 mmol) in pyridine (10 ml). The mixture was stirred for 24 h at room temperature. Benzene (50 ml) was added, the organic layer was washed with sufficient volume of dilute hydrochloric acid to remove the base, then with water, and dried (MgSO₄). Distillation of benzene under reduced pressure gave (2) in quantitative yield, m.p. 108–109 °C (from 95% EtOH) (lit.,²⁰ 108 °C) (Found: C, 93.9; H, 5.9. Calc. for C₂₁H₁₆: C, 94.0; H, 6.0%); δ_{H} 4.0 (2 H, s, CH₂) and 7.3–7.8 (14 H, m, Ph).

The synthesis and characterisation of indans (6a–c) and (8a–c) have been previously reported.^{1,7}

(Z)-1,2-Diphenylindan (7a). Catalytic hydrogenations of (2) (0.200 g, 0.75 mmol) in light petroleum (30 ml) in the presence of 10% Pd on charcoal (0.040 g), at 50 atm and 25 °C for 120 h, and in glacial acetic acid (40 ml), in the presence of the same catalyst (0.025 g), at 2 atm and 25 °C for 70 h, afforded quantitatively indan (Z)-(7a) which was purified by low-pressure chromatography and recrystallisation from light petroleum, m.p. 122 °C (Found: C, 93.1; H, 6.6. C₂₁H₁₈ requires C, 93.3; H, 6.7%); δ_{H} 3.26 and 3.39 (2 H, split AB system, J_{AB} 15.6, $J_{2,3}$ 8.1, CH₂), 4.03 (1 H, q, $J_{1,2} = J_{2,3} = 8.1$, 2-H), 4.66 (1 H, d, $J_{1,2}$ 8.1, 1-H), and 6.5–7.5 (14 H, m, Ph).

(E)-1,2-Diphenylindan (7b) was not isolated in pure form; it was obtained, in mixture with isomer (7a), in the catalytic hydrogenation of (3) (0.050 g, 0.18 mmol) in ethanol (25 ml) in the presence of 10% Pd on charcoal (0.030 g), at 25 °C and 3.5 atm for ca. 40 min [(7a)–(7b) 87:13], and as a by-product of the Clemmensen reduction of (12)²⁰ [(7a)–(7b) 55:45].

Low-pressure chromatography and repeated fractional recrystallisations of these reaction mixtures afforded eventually (7a + b) enriched in (7b), δ_{H} ca. 3.30 (2 H, m, CH₂), 3.59 (1 H, second-order m, 2-H), 4.42 (1 H, d, $J_{1,2}$ 9.4, 1-H), and 6.8–7.4 (14 H, m, Ph).

(Z)-(9a) and (E)-1,3-Diphenylindan (9b) were synthesised by reduction of (5) with hydriodic acid and red phosphorus as follows. Indene (5) (1.46 g, 5.4 mmol) was refluxed for 46 h, under nitrogen, with 57% hydriodic acid (4.8 ml) and red phosphorus (0.47 g). After cooling, the mixture was diluted with water and extracted with ether. The organic layer was washed with sodium thiosulphate and dried (CaCl₂). Evaporation of the solvent under reduced pressure gave a residue (0.73 g) which, after repeated fractional recrystallisations from ethanol, afforded pure (9a) (0.34 g, 23%), m.p. 156 °C (lit.,⁹ 156–157 °C) (Found: C, 93.2; H, 6.67. Calc. for C₂₁H₁₈: C, 93.3; H, 6.7%) and pure (9b) (0.15 g, 10%), m.p. 106 °C (Found: C, 93.1; H, 6.6%), δ_{H} (AMX₂ system)^{9b} 2.21 (1 H, dt, J_{AM} 12.5, J_{AX} 11.4, 2-H *cis* to the phenyl groups), 3.05 (1 H, dt, J_{AM}

12.5, J_{MX} 7.2, 2-H *trans* to the phenyl groups), 4.44 (2 H, dd, J_{AX} 11.4, J_{MX} 7.2, 1-H and 3-H), and 6.7–7.3 (14 H, m, Ph), δ_{H} (9b) (approximate A₂X₂ system) 2.60 (2 H, t, J_{AX} 7.2, CH₂), 4.56 (2 H, t, J_{AX} 7.2, 1-H and 3-H), and 6.8–7.2 (14 H, m, Ph).

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