Electrochemical Reduction of Activated Carbon–Carbon Double Bonds. 1. Mechanism and Stereochemistry of the Reduction of Phenyl-Substituted Indenes

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Abstract: The reduction at a Hg electrode in DMF of some phenyl-substituted indenes was carried out, with the aim of finding out possible relationships between stereochemistry and mechanism of the reaction. The two-electron two-proton reduction occurred exclusively at the C_2–C_3 double bond of the pentatomic cycle, affording in all cases the corresponding indans of various configurations. Two different processes were shown to occur, depending on the presence of more or less acidic proton donors: a process via protonation of the radical anion formed in the first electron transfer which afforded preferentially or exclusively indans of cis configuration around the C_2–C_3 bond, under kinetic control, and a process via protonation of the dianion formed by disproportionation of the radical anion which afforded exclusively indans of trans configuration around the C_2–C_3 bond, under thermodynamic control. In the first case the stereochemistry observed was rationalized in terms of a steric effect exerted by the phenyl groups on the direction(s) of protonation of the intermediates; in the second case fast base-catalyzed cis-trans isomerization of the products in the electrolysis conditions prevented the determination of the original stereochemistry of the process. A specific effect by the electrode surface was reasonably excluded on the basis of the electrochemical data.

The interpretation of the stereochemical course of electroorganic processes continues to be an intriguing matter, as pointed out by several exhaustive reviews published on the subject.[2] The knowledge of this field is still quite fragmentary, as all the factors possibly affecting the steric course of these reactions have not been either evidenced or taken into consideration altogether. In fact, from a general point of view one must not only solve the well-known and fundamental problem of ascertaining whether there are heterogeneity effects related to the presence of the electrode (adsorption, orientation, or shielding effects inside the double layer)[2b,c,3] but also take into account factors characteristic of homogeneous electron-transfer reactions, such as the mechanism of the reaction, structure and stereochemical requirements of the intermediates involved, kinetic or thermodynamic control of the products, etc.; moreover, as one becomes more deeply involved in this study other less evident, yet important, factors may come into view, e.g., the recently discussed conformational changes associated with electron-transfer reactions.[4]

The solution of all these problems is undoubtedly a difficult task, particularly if one considers that the intermediates involved in these processes, mostly radical ions or doubly charged ions, are by far less known than more "fashionable" intermediates, like singly charged ions or free radicals. Recently, however, there has been an upsurge of interest in electron-transfer reactions in organic chemistry, with some successful attempts to apply the Marcus theory also to organic reactions; the recent very thorough review by Eberson[5] is a typical example. Hopefully, this interest may also contribute to the understanding of the stereochemical aspects of these processes.

We have been investigating for some years on the possible correlation between stereochemistry and mechanism of electrochemical reduction of phenyl-substituted ethylenes. This field has received minor attention compared with, for example, the reduction of carbonyl groups or halogeno derivatives and still offers, according to an authoritative review,[2b] a "confused and contradictory stereochemical picture"; yet we think that the carbon–carbon double bond, being one of the simplest functional groups, presents general aspects and may be considered as a model for more complex systems. We refer here on the results obtained in the study of the reduction at a Hg cathode in DMF solution of phenyl-substituted indenes **1–3**.

Indenes **1–3** proved to be useful substrates for this kind of study because of the close similarity in structure to triphenylethylene, whose electrochemical behavior was recently reinvestigated;[6] furthermore, the cyclic structure permitted easy establishment of the configuration of the isomeric indan products and their relative thermodynamic stabilities. Indenes have been successfully used in the past in a stereochemical study of anodic oxidation.[7] Besides, the high stability of the radical anions of the not self-protonating indenes in aprotic medium (vide infra) allowed the study of the stereochemical course of the reduction under homogeneous conditions by quenching the radical anions with proton donors and hence a comparison with the reduction at the electrode.[8]

From a stoichiometric point of view, all the results obtained so far, presented in part as preliminary communications,[9] are consistent with a practically quantitative two-electron two-proton reduction of the C_2–C_3 double bond of indenes **1–3** following the

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(3) Eberson, L.; Schäfer, H. *Top. Curr. Chem.* **1971**, *21*, 41–45.

(4) (a) Ahlberg, E.; Hammerich, O.; Parker V. D. *J. Am. Chem. Soc.* **1981**, *103*, 844–849. (b) O'Connell, K. M.; Evans, D. H. *Ibid.* **1983**, *105*, 1473–1481.

(5) Eberson, L. *Adv. Phys. Org. Chem.* **1982**, *18*, 79–185.

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(7) Cedheim, L.; Eberson, L. *Acta Chem. Scand. Ser. B* **1975**, *B29*, 904–908, 969–974.

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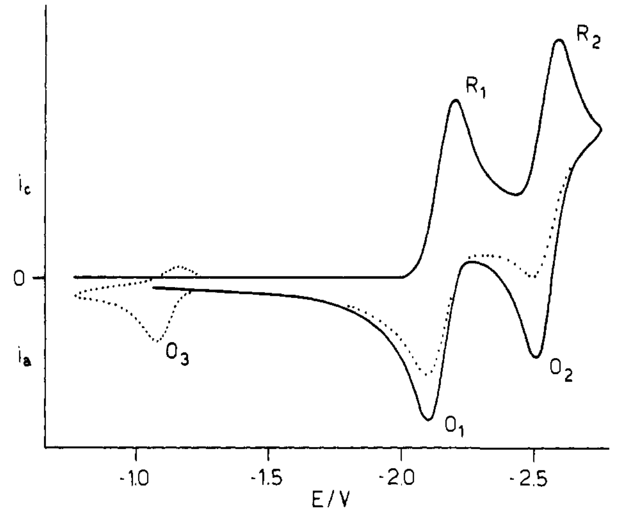


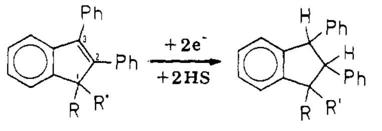
Figure 1. Cyclic voltammograms of indene **3** (1.0 mM) at 20 °C, in dried solution (—) and in the presence of traces of proton donors (....). Voltage sweep rate 0.60 V s^{-1}.

Table I. Standard Potentials[a] and Disproportionation Equilibrium Constants

indene	T, °C	$-E°_1$, V	$-E°_2$, V	K_4[b]
1	-30	2.145	2.422	$1.8 \cdot 10^{-6}$
1	0	2.142	2.427	$5.5 \cdot 10^{-6}$
1	20	2.140	2.435	$8.4 \cdot 10^{-6}$
2	-30	2.185	2.577	$7.5 \cdot 10^{-9}$
2	0	2.176	2.574	$4.5 \cdot 10^{-8}$
2	15	2.171	2.572	$9.7 \cdot 10^{-8}$
2	50	2.161	*c*	$4.1 \cdot 10^{-7}$ [d]
2	60	2.158	*c*	$6.0 \cdot 10^{-7}$ [d]
3	-30	2.303	2.603	$6.0 \cdot 10^{-7}$
3	0	2.294	2.610	$1.5 \cdot 10^{-6}$
3	15	2.291	2.615	$2.2 \cdot 10^{-6}$
3	40	2.286	*c*	$3.4 \cdot 10^{-6}$ [d]
3	50	2.283	*c*	$4.1 \cdot 10^{-6}$ [d]

[a] Referred to a SCE; ±3 mV. [b] ±10% ca. [c] The chemical or electrochemical irreversibility of the second reduction peak at low- or high-voltage sweep rates, respectively, does not allow a good evaluation of $E°_2$. [d] Extrapolated from a large set of values obtained at lower temperatures.

general eq 1, where HS represents the proton donor, such as water, phenol, or the indene **1** itself.



(1)

1, R = H; R' = Ph	**4a–c**, R = H; R' = Ph
2, R = Me; R' = Ph	**5a–d**, R = Me; R' = Ph
3, R = R' = Me	**6a,b**, R = R' = Me

Results

Voltammetric Behavior. In a carefully dried solution[10] indenes **1–3** show, in cyclic voltammetry (CV), two couples of peaks (e.g., see Figure 1) whose differences in potential between cathodic and related anodic peaks are in agreement (in the temperature range investigated) with reversible one-electron-transfer processes. This indicates that the reduction takes place by the following steps:

$$\mathrm{Ind} + e^- \underset{}{\overset{E°_1}{\rightleftharpoons}} \mathrm{Ind}^{-}\cdot \tag{2}$$

$$\mathrm{Ind}^{-}\cdot + e^- \overset{E°_2}{\rightleftharpoons} \mathrm{Ind}^{2-} \tag{3}$$

where $\mathrm{Ind}^{-}\cdot$ and Ind^{2-} represent the radical anion and the dianion of indene (Ind), respectively. The standard potentials $E°_1$ and $E°_2$ obtained from the values of peak potentials are reported in Table I. The difference between the standard potentials, $E°_1 - E°_2$, allows the determination of the disproportionation equilibrium constant of the radical anions, $K_4 = k_4/k_{-4}$,

$$2\mathrm{Ind}^{-}\cdot \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} \mathrm{Ind} + \mathrm{Ind}^{2-} \tag{4}$$

whose values are reported in Table I.

The potential of the second reduction peak, however, is affected by the sweep rate v when $v > 1$ V s^{-1}, thus indicating a quasi-reversible heterogeneous electron-transfer process. The reversibility of the second reduction step is also chemically affected by the presence of traces of proton donors; this behavior is in agreement with the strong basicity of dianions which are fast protonated to give the corresponding carbanions IndH^-, which can be subsequently protonated to the indan IndH_2.

These protonation steps can be evidenced in less drastic conditions of dryness, when peak O_2 is not completely suppressed. Under these conditions it is possible to detect, at potentials anodic to O_1, an oxidation peak O_3 (see Figure 1) which can be related to the oxidation of the indanyl anion IndH^-, formed by protonation of the dianion Ind^{2-}, to the neutral radical IndH·

$$\mathrm{IndH}^- \rightleftharpoons \mathrm{IndH}\cdot + e^- \tag{5}$$

This process has been found effective for triphenylethylene under similar conditions.[6]

This difference between the peak potentials of O_3 and O_1, which is related to the difference between the standard potentials of the redox couples $\mathrm{Ind}/\mathrm{Ind}^{-}\cdot$ and $\mathrm{IndH}\cdot/\mathrm{IndH}^-$ (ca. 1 V), allows the estimation of the equilibrium constant of the homogeneous electron-transfer process (eq 6)

$$\mathrm{IndH}\cdot + \mathrm{Ind}^{-}\cdot \underset{k_{-6}}{\overset{k_6}{\rightleftharpoons}} \mathrm{IndH}^- + \mathrm{Ind} \tag{6}$$

The value of the equilibrium constant, $K_6 = k_6/k_{-6}$, was found greater than 10^{16} for all substrates **1–3**. This supports the hypothesis that the forward rate constant k_6 must be close to the diffusion limit.[11]

The reversibility of the first reduction peak of **1** decreases even in anhydrous conditions at low-sweep rates ($v < 1$ V s^{-1}) and 20 °C, according to the acidic character of **1** (self-protonation).[9a] For the substrates **2** and **3** the reversibility of the first reduction step in CV is affected by the presence of proton donors such as water or phenol. Addition of water causes an increase of the first reduction peak R_1 in connection with a decrease of peaks O_1 and R_2, the latter showing a completely irreversible behavior. In the presence of phenol, in more than 50:1 excess with respect to the indenyl substrate, only one irreversible two-electron reduction peak is observed for all the substrates considered, at least for $v < 25$ V s^{-1}.

The polarographic pattern of indenes paralleled the one shown in CV. Under anhydrous conditions the reduction of **2** and **3** occurs in two waves of equal height, while **1** shows only one wave. In the presence of added water the first polarographic wave of **2** and **3** increases at the expense of the second one. In the presence of phenol only one two-electron reduction wave is observed for all the indenes considered.

The voltammetric behavior in the presence of proton donors such as water, phenol, or the indene **1** itself is in agreement with the protonation reaction of $\mathrm{Ind}^{-}\cdot$ or of Ind^{2-}, following electron-transfer processes.

In order to elucidate the reduction mechanism, we have determined the stoichiometry of the overall process by coulometric and products analyses and the kinetic behavior of the radical anion intermediates by homogeneous and/or voltammetric measurements.

Macroscale Electrolysis. Under anhydrous conditions, electrolysis at the potential of the first polarographic reduction wave

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(10) Dry conditions were obtained by cycling several times the solution through a column of activated neutral alumina.

(11) Szwarc, M.; Jagur-Grodzinski, J. "Ions and Ion Pairs in Organic Reactions"; Szwarc, M. Ed.; Wiley: New York, 1974; Vol. 2, Chapter 1.

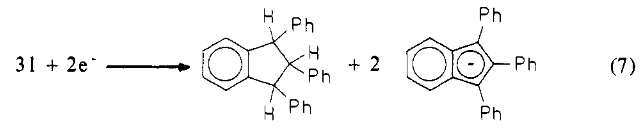
Table II. Results of Macroscale Potentiostatic Electrolyses and Quenching Experiments

indene[a]	proton donor	T, °C	total yield, %	isomers yield, %[b]			
				(*Z*,*Z*)-**4a**	(*Z*,*E*)-**4b**[c]		(*E*,*E*)-**4c**
1		20	31[d]	70	10		20
1	PhOH[e]	20	100	100			
				(*Z*,*Z*)-**5a**	(*E*,*Z*)-**5b**	(*Z*,*E*)-**5c**	(*E*,*E*)-**5d**
2	H_2O[f]	−30 ÷ 20	100			72	28
2	PhOH[e]	20	100	57	12	17	14
2	PhOH[e]	−30	100	59	13	16	12
2	PhOH[g]	−30	50[d]	58	10	19	13
				(*Z*,*Z*)-**7a**	(*E*,*Z*)-**7b**	(*Z*,*E*)-**7c**	(*E*,*E*)-**7d**
2	CD_3COOD[h]	20	100	58	15	14	13
				(*Z*)-**6a**		(*E*)-**6b**	
3	H_2O[f]	−30 ÷ 20	100			100	
3	PhOH[e]	−30	100	75		25	
3	PhOH[e]	20	100	70		30	
3	PhOH[g]	−30	50[d]	60		40	

[a] [Indene] = 0.1 M. [b] Determined by integration of the ^{1}H NMR spectrum of the reaction mixture. Estimated error ca. 3%. [c] Or (*E*,*Z*)-**4** (racemic mixture). [d] A corresponding amount of indene was recovered unchanged. [e] [PhOH] = 0.5 M. [f] $[H_2O]$ = 0.3–0.5 M. [g] Quenching experiment of indene radical anion with PhOH. [h] $[CD_3COOD]$ = 0.5 M.

of **2** and **3** leads to the formation of the corresponding radical anions as shown by the appearance of the respective polarographic oxidation waves; on the other hand, in the electrolysis of **1** at the potential of the single reduction wave there is no polarographic evidence of the radical anion formation, owing to the relatively fast self-protonation reaction.

Exhaustive controlled-potential electrolysis of **1** takes ca. 0.7 F mol^{-1} and a yellow-green fluorescence attributable to the indenyl anion is observed. After addition of phenol the reduction wave of **1** reappears; the recovered products consist of a mixture of the indan isomers **4a–c** (ca. 30% yield) and of **1** (ca. 70% yield) (see Table II). These results indicate the occurrence of a two-electron reduction process involving one third of the indene **1**, the other two thirds acting as a proton source,[12] according to eq 7.

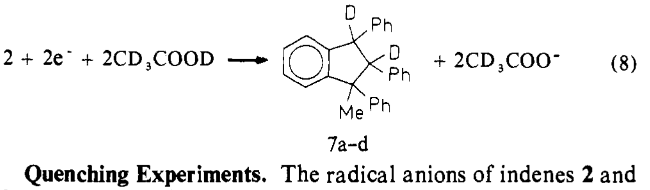


4a-c

In the presence of added water (0.2 M < $[H_2O]$ < 0.5 M) exhaustive controlled-potential electrolyses of **2** and **3** at the potential of the first polarographic reduction wave take 2 F mol^{-1}, with quantitative formation of the corresponding indans **5c**,**d** and **6b** (see Table II). Under similar conditions the behavior of substrate **1** is the same as in anhydrous solution, indicating a greater acidic character of the indene with respect to water.

In the presence of phenol (0.5 M) as proton donor, exhaustive electrolyses at the single polarographic wave of indenes **1–3** take 2 F mol^{-1} and afford quantitatively mixtures of the isomers of the corresponding indans (see Table II).

Electrolysis of **2** in the presence of CD_3COOD (0.5 M) affords quantitatively a mixture of the corresponding indan isomers **7a–d** completely deuterated at C_2 and C_3 (eq 8), in a ratio very close to that obtained in the electrolysis of **2** in the presence of phenol (Table II).



7a-d

Quenching Experiments. The radical anions of indenes **2** and **3** were produced by exhaustive electrolysis at the potential of the first polarographic reduction wave, under dry conditions[10] and at low temperature (−30 °C) with the consumption of 1 F mol^{-1} of indene. The amount of radical anion accumulated was determined on the basis of polarographic measurements and was in both cases quantitative. At the end of the electrolysis the radical anion was quenched by adding, under nitrogen and vigorous stirring, a DMF solution of phenol. In any case, 50% of the radical anion produced was transformed into reduction products (see Table II), whereas the remaining 50% afforded the starting indene, according to the overall stoichiometry

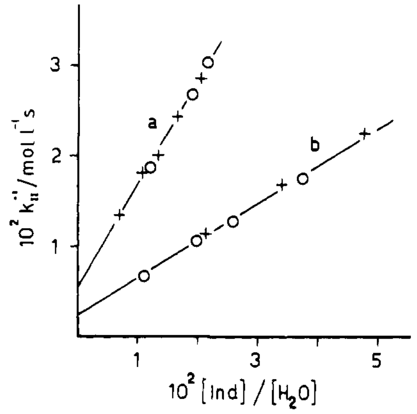


Figure 2. Plot of $1/k_{II}$ vs. [Ind]/$[H_2O]$. (a) Indene **2**, 15.0 °C; $[H_2O]$, 0.27 M (+), 0.38 M (○). (b) Indene **3**, −30.0 °C; $[H_2O]$, 0.070 M (+), 0.16 M (○).

$$2\mathrm{Ind}^{-\cdot} + 2\mathrm{PhOH} \rightarrow \mathrm{Ind} + \mathrm{IndH_2} + 2\mathrm{PhO}^- \qquad (9)$$

The possibility of observing the formation of products deriving from a kinetic control by a quenching experiment of the radical anions with water is prevented by the fast isomerization of the indans under the experimental conditions.

Homogeneous Kinetics in the Presence of Water. In the presence of added water ($[H_2O]$ < 0.5 M) the anion radicals of indenes **2** and **3** are stable enough to be accumulated in solution by electrolysis; under these conditions a kinetic study can be carried out by amperometric method. Kinetic measurements were driven in the presence of the parent indene and H_2O, both in excess with respect to $\mathrm{Ind}^{-\cdot}$, thus allowing a pseudo-order treatment. Kinetic runs were carried out for indene **2** at −30 °C and for **3** at +15 °C, owing to the different reactivity of the corresponding radical anions.

For both substrates the disappearance of $\mathrm{Ind}^{-\cdot}$ is second order in its concentration (over at least three half-lives) with a pseudo-second-order rate constant k_{II} depending on H_2O and Ind concentrations, the reaction being sped up by H_2O and retarded

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[12] A similar scheme is operating in the reduction of the carbonyl group of ftalimide. Farnia, G.; Romanin, A. M.; Capobianco, G.; Torzo, F. *J. Electroanal. Chem.* **1971**, *33*, 31–44.

Table III. Rate Constants[a] for Indenes **2** and **3** Obtained from Homogeneous or Voltammetric Measurements with Water as Proton Donor

indene	T, °C	$10^{-3}k_4$, L mol^{-1} s^{-1}	$10^{-9}k_{-4}$,[b] L mol^{-1} s^{-1}	$10^{-6}k_{11}$,[c] L mol^{-1} s^{-1}
2	15	0.10[c]	1.0	4.7
2	50	0.60[d]	1.5	
2	60	1.0[d]	1.7	
3	-30	0.21[c]	0.35	2.1
3	0	1.3[d]	0.87	
3	15	2.3[d]	1.1	
3	40	7.8[d]	2.3	
3	50	11[d]	2.7	

[a] Values reproducible ±10% ca. [b] Calculated from the corresponding values of k_4 and K_4. [c] From homogeneous kinetics. [d] From voltammetric kinetics.

by Ind. The plots of the reciprocal of k_{11} vs. [Ind]/[H_2O] ratio are linear in the concentration range investigated, with a nonzero intercept (see Figure 2) according to the experimental law

$$1/k_{11} = A + B([\mathrm{Ind}]/[\mathrm{H_2O}]) \qquad (10)$$

The kinetic results, combined with the stoichiometry of the overall process and the nature of the reduction products, are in agreement with a mechanism involving protonation of the dianion formed via disproportionation of the radical anion, followed by protonation of the indanyl anion (eq 4, 11, 12).

$$\mathrm{Ind^{2-} + H_2O \xrightarrow{k_{11}} IndH^- + OH^-} \qquad (11)$$

$$\mathrm{IndH^- + H_2O \rightarrow IndH_2 + OH^-} \qquad (12)$$

This leads, in the steady-state assumption for the reactive dianion, to rate law 13

$$-\frac{d[\mathrm{Ind^{-}\cdot}]}{dt} = \frac{2k_4k_{11}[\mathrm{H_2O}]}{k_{-4}[\mathrm{Ind}] + k_{11}[\mathrm{H_2O}]}[\mathrm{Ind^{-}\cdot}]^2 = k_{11}[\mathrm{Ind^{-}\cdot}]^2 \qquad (13)$$

and hence to eq 14

$$1/k_{11} = 1/2k_4 + (1/2K_4k_{11})[\mathrm{Ind}]/[\mathrm{H_2O}] \qquad (14)$$

Comparison of eq 10 and 14 shows that from the experimental values of the intercept A and the slope B, the rate constants k_4, k_{-4}, and k_{11} can be calculated, the value of the disproportionation equilibrium constant K_4 being determined as previously described (see Table I). Rate constant values are listed in Table III.

Voltammetric Kinetics in the Presence of Water. When the dianion protonation step 11 is faster than the comproportionation step (backward of eq 4), i.e.,

$$k_{11}[\mathrm{H_2O}] \gg k_{-4}[\mathrm{Ind}]$$

or

$$[\mathrm{H_2O}]/[\mathrm{Ind}] \gg k_{-4}/k_{11} \qquad (15)$$

eq 13 reduces to eq 16:

$$-d[\mathrm{Ind^{-}\cdot}]/dt = 2k_4[\mathrm{Ind^{-}\cdot}]^2 \qquad (16)$$

which corresponds to the irreversible disproportionation of the radical anion, with a second-order rate constant, $k_{11} = 2k_4$, independent of H_2O and Ind concentrations. As regards indenes **2** and **3** this situation, which may be achieved with an excess of H_2O with respect to Ind, cannot be detected by the amperometric method under homogeneous conditions, owing to the rather high values of k_4.

On the other hand, this situation can be easily analyzed by cyclic voltammetry. In fact, under experimental conditions which render the ratio i_a/i_c of the anodic to cathodic peak currents of the first step independent of H_2O concentration, the mechanism corresponds to an irreversible disproportionation of the radical anion following the first electron-transfer process (eq 2), thus allowing the determination of the corresponding kinetics parameters.[13]

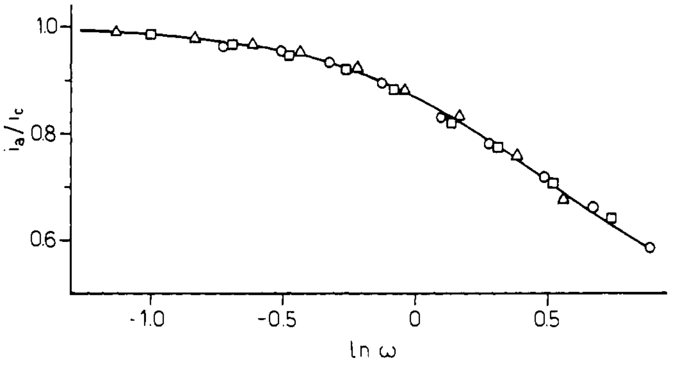

Figure 3. Plot of the ratio i_a/i_c vs. the kinetic parameter log ω at 15.0 °C, for indene **3**. The theoretical working curve (solid line) and log ω for the irreversible disproportionation mechanism are defined in ref 13. The best fitting is obtained for $k_4 = 2.3 \cdot 10^3$ L mol^{-1} s^{-1}. [Ind], $6.22 \cdot 10^{-4}$ M (△), $1.40 \cdot 10^{-3}$ M (□), $3.21 \cdot 10^{-3}$ M (○); [H_2O] = 0.25 M.

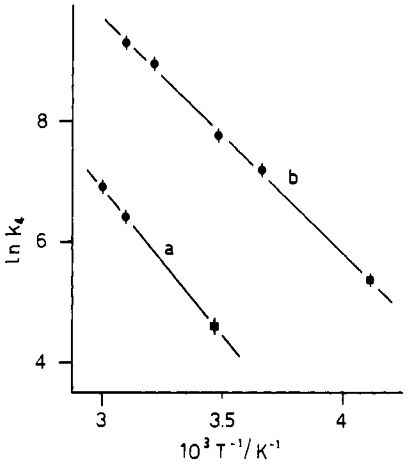

Figure 4. Arrhenius plots of the disproportionation rate constant of radical anions of indenes **2** (a) and **3** (b). Homogeneous data (■), voltammetric data (●). Activation energy: 9.7 ± 0.8 kcal mol^{-1} for **2**; 7.7 ± 0.5 kcal mol^{-1} for **3**.

In order to obtain the values of k_4, voltammetric measurements of the ratio i_a/i_c were carried out at several scan rates (v), at various temperatures, and at different concentrations of substrate and water. The experimental values fit fairly well the theoretical working curve calculated for the irreversible disproportionation mechanism,[13] as it can be seen in Figure 3. The values of k_4 and of the corresponding k_{-4} are listed in Table III. The k_4 values obtained by both homogeneous and voltammetric kinetic measurements are reported in an Arrhenius plot in Figure 4.

It can be pointed out that the behavior reported above for indenes **2** and **3** in the presence of water parallels what has already been observed for triphenylethylene under similar conditions.[6] In particular we can observe that the values of the comproportionation rate constant k_{-4}, calculated from the ratio k_4/K_4, are significantly close to but not higher than the diffusion limit, thus supporting the proposed mechanism also from a thermodynamic point of view.

Voltammetric Kinetics in the Presence of Phenol. As previously described, in the presence of phenol in excess with respect to indene, only one irreversible two-electron reduction peak is observed for all the indenes examined. Under these conditions the fast decay of the radical anions does not allow the use of the i_a/i_c ratio method. Therefore 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 scan rate, under pure kinetic conditions.[14]

At 20 °C the potential of the cathodic peak shifts toward more negative values of ca. 29 mV per log (v/[PhOH]) unit, in the range 5×10^{-2} M < [PhOH] < 2×10^{-1} M explored, and is independent

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(13) Olmstead, M. L.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 862–864.

(14) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1977**, *85*, 27–46.

Table IV. ^{1}H NMR Data for Indans **5a–d** and **6a–b**[a]

indan	H-2[b]	H-3[b]	$J_{2,3}$, Hz	CH$_3$[c]	aromatics[d]
(*Z*,*Z*)-**5a**	3.97	5.02	8.6	1.84	6.10–7.50
(*E*,*Z*)-**5b**	3.94	4.68	7.3	1.51	6.50–7.50
(*Z*,*E*)-**5c**	3.57	4.54	11.5	1.87	6.30–7.40
(*E*,*E*)-**5d**	3.87	4.88	11.4	1.28	6.30–7.40
(*Z*)-**6a**	3.55	4.97	7.9	1.39 and 1.15	6.50–7.50
(*E*)-**6b**	3.35	4.75	11.7	1.40 and 0.90	6.70–7.50

[a] δ in ppm from Me$_4$Si as internal standard. [b] Doublet. [c] Singlet. [d] Complex multiplet.

of the indene concentration. These results are in agreement with a reversible one-electron transfer (eq 2) followed by an irreversible pseudo-first-order protonation of the radical anion Ind$^{-\cdot}$ by PhOH, as the rate-determining step, to form the neutral radical IndH·[15] (eq 17).

$$\mathrm{Ind}^{-\cdot} \xrightarrow[k_{17}]{\mathrm{PhOH}} \mathrm{IndH}\cdot \qquad (17)$$

As pointed out above, the latter has a higher electron affinity than the parent substrate[16] and therefore is reduced to IndH$^-$ either directly at the electrode (backward of eq 5) and/or in solution by the anion radical (eq 6). The anion IndH$^-$, thus formed, is then protonated to give the final product IndH$_2$ (eq 18).

$$\mathrm{IndH}^- \xrightarrow{\mathrm{PhOH}} \mathrm{IndH}_2 \qquad (18)$$

The mechanisms involving the sequences of eq 2–17–5–18 and 2–17–6–18 are generally indicated as ecec and disp 1 processes, respectively. Both mechanisms show very similar voltammetric patterns[17] so that we cannot discriminate between them under our conditions. On the other hand, the values of k_{17} can be obtained, for both mechanisms, by comparing the standard potential of the first reduction step ($E°_1$) with the peak potentials measured, at various scan rates and phenol concentrations, under pure kinetic conditions.[15] The value calculated for the disp 1 mechanism is twice the value for the ecec mechanism. On the basis of these values of k_{17} and under the likely assumption that k_6 is near the diffusion limit (see voltammetric section) the kinetic zone diagram of Savêant et al.[14] shows that disp 1 is the only mechanism operating under our experimental conditions. The rate constant values of the protonation reaction of the radical anion by phenol (k_{17}) at 20 °C are $(1.1 \pm 0.1) \times 10^4$ M^{-1} s^{-1} for **1**, $(1.0 \pm 0.1) \times 10^4$ M^{-1} s^{-1} for **2** and $(2.0 \pm 0.2) \times 10^5$ M^{-1} s^{-1} for **3**.

Identification of the Products. The indan products obtained in the macroscale electrolyses according to eq 1 and 7 (Table II) were all identified on the basis of spectroscopic (mostly ^{1}H NMR) and analytical data and in several cases by comparison with authentic samples prepared independently.

In the case of the reduction of **1**, the independent synthesis and characterization of the three isomeric 1,2,3-triphenylindans **4a–c** were reported in a previous work.[18]

In the case of the reduction of **2**, (*Z*,*E*)- and (*E*,*Z*)-1-methyl-1,2,3-triphenylindans (**5c** and **5b**) were isolated in pure state by fractional crystallization of the reaction mixtures obtained, respectively, from macroscale electrolysis in the presence of water and from catalytic hydrogenation of **2**. The (*Z*,*Z*) and (*E*,*E*) isomers **5a** and **5d** were characterized on the basis of the ^{1}H NMR spectrum of the reaction mixtures.

In the case of the reduction of **3**, (*E*)-1,1-dimethyl-2,3-diphenylindan (**6b**) was obtained as the only product in the macroscale electrolysis of **3** in the presence of water. The *Z* isomer **6a** was characterized on the basis of the ^{1}H NMR spectrum of the reaction mixture obtained by macroscale electrolysis in the presence of phenol.

Stereochemical Assignments. The assignment of configuration to all isomeric indans obtained by electroreduction of indenes **1–3** was mainly made by ^{1}H NMR spectroscopy (see Table IV). In the case of 1,2,3-triphenylindans (**4a–c**) the assignment was reported in a previous work[18] and was based on the relative values of the vicinal coupling constants ($J_{1,2}$ and $J_{2,3}$) for the methine protons, which are smaller for cis than for trans configuration(s).[19b] Also characteristic of cyclopentene and indene derivatives is the shielding effect of a phenyl group on β-cis-methine protons relative to trans protons and, conversely, the deshielding effect of the same phenyl group on trans protons.[19]

The assignment of configuration to the four isomeric 1-methyl-1,2,3-triphenylindans (**5a–d**) was less straightforward, owing to the lack of symmetry of the latter in respect to the 1,2,3-triphenyl-substituted analogues, and was based on the following points: (i) The relative values of the coupling constant between the methine protons ($J_{2,3}$) indicate a cis configuration around the C$_2$–C$_3$ bond of the isomers **5a** and **5b**, which have the lowest values (8.6 and 7.3 Hz, respectively), and correspondingly, a trans configuration around the same bond of the isomers **5c** and **5d**, which have the highest values (11.5 and 11.4 Hz, respectively). (ii) The well-known shielding effect of a *cis*-phenyl group on a vicinal methyl[18] permitted to assign the *E* configuration around the C$_1$–C$_2$ bond to isomers **5b** and **5d**, which have the signals of the methyl group at highest field (1.51 and 1.28 δ, respectively), and, correspondingly, the *Z* configuration to isomers **5a** and **5c**, which have the same signals at lowest field (1.84 and 1.87 δ, respectively). (iii) In accordance with the deshielding effect of a phenyl group on β-*trans*-methine protons[19] the (*Z*,*Z*) configuration was assigned to the isomer **5a**, having the highest δ values for H-2 and H-3.

From a chemical point of view the assignment was in agreement with the results of isomerization tests and deuterium exchange experiments, which showed the exclusive transformation of the isomer (*Z*,*Z*)-**5a** into (*Z*,*E*)-**5c** and of the isomer (*Z*,*E*)-**5b** into (*E*,*E*)-**5d** (vide infra), in accordance with a higher thermodynamic stability given by a trans arrangement of two phenyl groups. Furthermore, the assignment of the (*Z*,*Z*) and (*E*,*Z*) configuration to isomers **5a** and **5b**, respectively, was in agreement with the commonly observed stereochemistry of catalytic hydrogenation of multiple bonds.[20]

The assignment of configuration to the two isomeric 1,1-dimethyl-2,3-diphenylindans (**6a,b**) was based on the relative values of the coupling constants for the methine protons ($J_{2,3}$) and also on the relative values of chemical shifts of the same protons, both shielded by two *cis*-phenyl groups in the case of (*E*)-**6b** and deshielded by two *trans*-phenyl groups in the case of (*Z*)-**6a**. From a chemical point of view this assignment was confirmed by the isomerization test, which showed that the (*Z*)-**6a** isomer was transformed into the more thermodynamically stable (*E*)-**6b** isomer (vide infra).

For two of the isomers isolated as pure compounds, namely (*E*,*Z*)-**5b** and (*Z*,*E*)-**5c**, the above assigned configurations were confirmed also by NOE experiments. Irradiation of the methyl resonance at δ 1.87 of (*Z*,*E*)-**5c** causes a 16.1% positive enhancement of the methine resonance at δ 3.57 and a 1.5% negative enhancement of the methine resonance at δ 4.54. On the other hand no enhancement of either methine resonance is observed upon irradiation of the other methine proton. It is clear that the proton

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(16) Hoytink, G. J. *Adv. Electrochem. Electrochem. Eng.* **1970**, *7*, 233.

(17) For a detailed discussion about the discrimination between ecec and disp 1 mechanisms see ref 15 and references cited therein.

(18) Marcuzzi, F.; Melloni, G. *J. Chem. Res. Synop.* **1979**, 184–185.

(19) (a) McMillan, J.; Martin, I. L.; Morris, D. J. *Tetrahedron* **1969**, *25*, 905–914. (b) Hiscock, M.; Porter, G. B. *J. Chem. Soc., Perkin Trans. 2* **1972**, 79–83 and references therein.

(20) House, H. O. "Modern Synthetic Reactions", 2nd ed.; Benjamin: New York, 1972; pp 1–28.

Table V. Isomerizations of Indans **4**–**7**

expt	starting mixture (%)	final mixture (%)
1[a]	(*Z*,*Z*)-**4a** (70)	(*Z*,*Z*)-**4a**
	(*Z*,*E*)-**4b** (10)	(*Z*,*E*)-**4b** (80)
	(*E*,*E*)-**4c** (20)	(*E*,*E*)-**4c** (20)
2[a]	(*Z*,*Z*)-**4a** (100)	(*Z*,*E*)-**4b** (100)
3[a]	(*Z*,*Z*)-**5a** (57)	(*Z*,*Z*)-**5a**
	(*E*,*Z*)-**5b** (12)	(*E*,*Z*)-**5b** (12)
	(*Z*,*E*)-**5c** (17)	(*Z*,*E*)-**5c** (74)
	(*E*,*E*)-**5d** (14)	(*E*,*E*)-**5d** (14)
4[b]	(*E*,*Z*)-**5b** (100)	(*Z*,*E*)-**5c** (64)
		(*E*,*E*)-**5d** (36)
5[b]	(*Z*,*Z*)-**5a** (57)	(*Z*,*Z*)-**5a**
	(*E*,*Z*)-**5b** (12)	(*E*,*Z*)-**5b**
	(*Z*,*E*)-**5c** (17)	(*Z*,*E*)-**5c** (73)
	(*E*,*E*)-**5d** (14)	(*E*,*E*)-**5d** (27)
6[c]	(*Z*)-**6a** (70)	(*Z*)-**6a**
	(*E*)-**6b** (30)	(*E*)-**6b** (100)
7[d]	(*Z*,*Z*)-**7a** (58)	(*Z*,*E*)-**8a** (72)
	(*E*,*Z*)-**7b** (15)	(*E*,*E*)-**8b** (28)
	(*Z*,*E*)-**7c** (14)	(*Z*,*E*)-**5c** (72)
	(*E*,*E*)-**7d** (13)	(*E*,*E*)-**5d** (28)

[a] Experiment carried out in DMF–TBAOH at room temperature for 3 days. [b] Exhaustive electrolysis of indene **2** in the presence of an equimolar amount of the mixture of indan isomers **5**. [c] Exhaustive electrolysis of **3** in the presence of an equimolar amount of the mixture of indan isomers **6**. [d] Exhaustive electrolysis of **2** in the presence of an equimolar amount of the mixture of deuterated indans **7**.

at δ 3.57 is cis to the methyl group and trans to the other proton at δ 4.54.

As far as (*E*,*Z*)-**5b**, no enhancement is observed after irradiation of the methyl resonance at δ 1.51; on the contrary, irradiation of the methine proton at δ 3.94 causes a 9.9% enhancement of the proton resonance at δ 4.68. The opposite experiment gives a 8.2% enhancement. It follows that the methine protons are in a cis configuration, while the methyl group is trans to both.

Isomerization. Two different sets of isomerization experiments were carried out in order to evaluate the relative thermodynamic stability of the isomeric indans formed in the electrolyses and to obtain information about the stereochemistry of the reduction process.

(a) **Isomerization in the Presence of Tetrabutylammonium Hydroxide (TBAOH).** DMF solutions either of pure indan isomers or of mixtures of isomers, as obtained by electrolysis, were stirred at room temperature in the presence of aqueous TBAOH for 3 days. Under these conditions, a mixture of isomers **4a**–**c** (in the ratio as obtained by electrolysis of **1** without added proton donors) showed complete isomerization only of the isomer (*Z*,*Z*)-**4a** into (*Z*,*E*)-**4b** (see experiment 1, Table V), whereas the others remained unchanged. This was in agreement with the result of experiment 2 carried out by using only the pure isomer (*Z*,*Z*)-**4a**.

Analogously, when a mixture of isomers **5a**–**d** (in the ratio as obtained by electrolysis of **2** in the presence of phenol) was treated under the same experimental conditions complete isomerization only of (*Z*,*Z*)-**5a** into (*Z*,*E*)-**5c** was observed, the other isomers remaining unaffected (experiment 3).

No isomerization was observed for a mixture of isomers (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the ratio 50:50 and of isomers (*Z*)-**6a** and (*E*)-**6b** in the ratio 70:30, which were recovered unchanged at the end of the experiment.

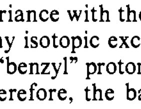
(b) **Isomerization under Electrolysis Conditions.** The possibility that the isomerization of the reduction products occurred during the electrolysis was tested by reducing indenes **1**–**3** in the presence of equimolar amounts of their reduction products. No isomerization was observed for indans **5a**–**d** and **6a**–**b** in the electrolyses in the presence of phenol and for indans **4a**–**c** both in the presence and in the absence of phenol. On the other hand, exhaustive electrolysis of **2** in the presence of equimolar amounts of (*E*,*Z*)-**5b** and water (0.3 M) gave a mixture of isomers (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the ratio 36:64 (experiment 4), thus indicating a complete isomerization of (*E*,*Z*)-**5b** into (*E*,*E*)-**5d**. Exhaustive electrolysis of **2** in the presence of a mixture of isomers **5a**–**d** (experiment 5) afforded a mixture of (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the ratio 73:27, which indicates complete isomerization of (*Z*,*Z*)-**5a** and (*E*,*Z*)-**5b** into (*Z*,*E*)-**5c** and (*E*,*E*)-**5d**, respectively. Moreover, the isomerization of (*Z*,*Z*)-**5a** and (*E*,*Z*)-**5b** under these conditions is a very fast process: complete isomerization was indeed observed after only 4 min of electrolysis.

When an equimolar mixture of **3** and the isomers (*Z*)-**6a** and (*E*)-**6b** was electrolyzed exhaustively (experiment 6), indan (*E*)-**6b** was recovered as the only product, the isomer (*Z*)-**6a** being transformed completely into the more stable one.

The results of the isomerization experiments described above have to be related to the different basicity of the two reaction media. In the presence of TBAOH the isomerization is slow and affects only the least thermodynamically stable (*Z*,*Z*) isomers. On the contrary, under electrolysis conditions in the presence of water the isomerization is a much faster process, due to the presence of carbanionic intermediates, and affects quantitatively the isomers bearing "cis" configurations around the C_2–C_3 bond. Indans **4** seem to make exception to this behavior; this can be ascribed to the relatively strong acidity of **1** with respect to water, which prevents the formation of a highly basic medium. The same consideration can be applied to the absence of isomerization in the electrolyses in the presence of a strong proton donor such as phenol.

In order to obtain information on the pathways through which the isomerization can take place, the following experiments were carried out. Exhaustive electrolysis of **2** in the presence of water and of an equimolecular amount of a mixture of deuterated indans **7a**–**d** (experiment 7) afforded a mixture of isomers (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the expected ratio 72:28 along with an equimolar amount of a mixture of indans (*Z*,*E*)-**8a** and (*E*,*E*)-**8b** deuterated only at C_2, in the same ratio (eq 19).

$$2 + 7\text{a–d} \xrightarrow[H_2O]{2e^-} (Z,E)\text{-5c} + (E,E)\text{-5d} + \qquad (19)$$



(*Z*,*E*)-8a + (*E*,*E*)-8b

The presence among the reaction products of the two isomers (*Z*,*E*)-**8a** and (*E*,*E*)-**8b** in the ratio 72:28 clearly indicates a complete deuterium exchange only at C_3, with quantitative transformation of (*Z*,*Z*)-**7a** and (*E*,*Z*)-**7b** into (*Z*,*E*)-**8a** and (*E*,*E*)-**8b**, respectively.

It must be pointed out that, at variance with the C_3 position, the C_2 position is not involved in any isotopic exchange, in accordance with the lower acidity of a "benzyl" proton with respect to a "diphenylmethyl" proton. Therefore, the base-promoted isomerization of indans goes through exclusive inversion of configuration at C_3.

Discussion

The kinetic data reported above indicate that two different mechanistic pathways are followed in the electrochemical reduction of indenes **1**–**3**, depending on the acidity of the proton donor present in the reaction medium; both pathways involve the formation of a radical anion as the first intermediate and may be summarized as follows:

pathway A

$$2\text{Ind} \xrightleftharpoons{+2e^-} 2\ \text{Ind}^{-\cdot} \rightleftharpoons \text{Ind} + \text{Ind}^{2-} \xrightarrow{\text{HS}} \text{IndH}^- \xrightarrow{\text{HS}} \text{IndH}_2$$

pathway B

$$\text{Ind} \xrightleftharpoons{+e^-} \text{Ind}^{-\cdot} \xrightarrow{\text{HS}} \text{IndH}\cdot \xrightarrow[\text{and/or } +e^-]{+\text{Ind}^{-\cdot}} \text{IndH}^- \xrightarrow{\text{HS}} \text{IndH}_2$$

It is noteworthy that pathways A and B are commonly followed in the electrochemical dihydroreduction of unsaturated hydrocarbon.[21]

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(21) See ref 6 and Becker et al. [Becker, J. Y.; Ginzburg, G.; Willer, I. *J. Electroanal. Chem.* **1980**, *108*, 355–368] and references therein in regards to pathway A and ref 14 and 15 and references therein in regards to pathway B.

Pathway A consists of a single mechanism (direct disproportionation mechanism). In case of pathway B, two different mechanisms can be operating, depending on whether the neutral radical IndH· is reduced at the electrode (ecec mechanism) or homogeneously by a radical anion (disp 1 mechanism); in both cases the rate determining step is the first protonation reaction.

Pathway A is followed in the case of the reduction of **2** and **3** in the presence of water. The disp 1 mechanism of pathway B is followed in the case of the reduction of **1**–**3** in the presence of phenol. As to the reduction of **1** in the absence of specific proton donors, where self-protonation occurs, owing to the impossibility of carrying out homogeneous kinetic experiments and to the lack of voltammetric theoretical treatments we cannot decide, at the present stage of the research, which pathway is followed.

In order to find possible correlations between these mechanisms and the observed stereochemistry of the reduction products it is essential to verify whether such pathways are followed also under potentiostatic macroscale electrolysis conditions.

In the case of the reduction of indenes **2** and **3** in the presence of water there is no doubt that pathway A is followed also in the macroscale electrolyses: in this case the experimental conditions are similar to those of the homogeneous kinetic experiments, with the intervention of the electrode only in the primary fast heterogeneous electron-transfer step. The effect of the higher concentration of substrate used in macroscale electrolyses, if any, favors disproportionation, due to the higher concentration of the radical anion formed at the electrode.

In the case of the reduction in the presence of phenol the macroscale electrolysis conditions might favor, with respect to voltammetric conditions, the reductions of the neutral radical IndH· at the electrode (ecec mechanism), due to the lower rate of diffusion of the radical anion away from the electrode. As regards this problem, one should consider that the competition between disp 1 and ecec mechanisms under exhaustive potentiostatic electrolysis conditions depends, in our case, on the value of the parameter $\log (k_6 k_{17}{}^{-3/2}[\mathrm{PhOH}]^{-3/2}[\mathrm{Ind}]D^{1/2}\delta^{-1})$[22] where D is the diffusion coefficient and δ the thickness of the diffusion layer. On the basis of the experimental values of k_{17}, [Ind] and [PhOH], assuming k_6 diffusional (see voltammetric section) and using typical values of D and δ (10^{-5} cm^2 s^{-1} and $5 \cdot 10^{-3}$ cm, respectively),[22] the disp 1 mechanism may be calculated to prevail over the ecec mechanism for at least 90–95% in the case of the reduction of **1** and **2**. On the other hand, in the case of **3**, which shows a higher value of k_{17}, the ecec mechanism may be calculated to operate for ca. 30%.

As for the reduction of **1** in the absence of phenol the uncertainty in ascertaining which pathway is followed under voltammetric conditions has to be obviously extended to macroscale electrolyses; however, the observed very fast decay of the radical anion suggests the occurrence of a direct protonation of this intermediate (pathway B). If this is the case, the disp 1 mechanism is expected to predominate because of the lower proton donating ability of **1** with respect to phenol.[23]

Looking up at the results of macroscale electrolyses (Table II), two stereochemical behaviors are evident: an exclusive, formal anti addition of hydrogen to the double bond in the case of the reduction of **2** and **3** in the presence of water and a prevalent (in one case exclusive) formal syn addition in the case of the reduction of **1**–**3** in the presence of phenol and also of **1** under self-protonating conditions.

At the first sight it would seem easy to draw a correlation between the two mechanistic pathways A and B and the two different stereochemical courses; actually, things are less straightforward if one considers that both pathways have in common, besides the formation of the radical anion, the formation of the last intermediate, the indanyl anion. In order to decide whether such correlation is correct, the following factors have to be taken into consideration: (i) the site of the first protonation step both of radical anions and dianions; (ii) the relative rates of the first and the second protonation steps, in relation to kinetic or thermodynamic control of the process; (iii) the effect of the electrode, regarded not as a specific effect (adsorption), which was never observed as such in our experiments but, in a broader sense, as a heterogeneity effect on the proton-transfer processes.

(i) Owing to the intrinsic difficulty to discriminate between the two protonation steps, which rapidly occur in the reaction conditions for both pathways A and B, we were unable to determine directly the site of the first protonation. We suggest, however, that this occurs at C_2 in both cases on the basis of the following considerations.

For the protonation of radical anions literature data on EPR spectra and MO calculations indicate a higher electron density at C_2 for the radical anion of 1,1-dimethylindene:[25] considering that in our indenyl substrates both 2- and 3-positions are occupied by the same substituents (phenyl groups) we may infer that no considerable variations may occur and reasonably exclude, anyway, an inversion of the electronic distribution with respect to the model. As far as dianions, it is reasonable to consider the negative charge at the "benzylic" C_2 position less delocalized than that at the diphenyl-substituted C_3 position. Further support to these predictions comes from considerations on the relative stabilities of the two possible species formed upon protonation at C_2 or C_3. In the case of protonation of the radical anion intermediate these are neutral radical species, whereas indanyl anions are formed from the dianion intermediate; for both intermediates protonation at C_2 would afford the most stable species, i.e., a diphenylmethyl radical and a diphenylmethyl anion, respectively.

(ii) On the basis of the relative basicity of the intermediates involved in electron-transfer reductions of unsaturated hydrocarbons, it is generally accepted that the rate of protonation of a dianion (the most basic intermediate) is higher than the rate of protonation of the corresponding monoanion, whereas the rate of protonation of a radical anion (the least basic intermediate) is lower.[26] In our case this sequence is less straightforward, owing to the fact that the dianion is protonated by a weak proton donor (H_2O),[27] whereas the radical anion is protonated by stronger proton donors (phenol or indene **1**). Following this consideration and on the basis of the experimental values of the protonation rate constants of radical anions and dianions we may infer that the protonation of the indanyl anion by phenol (pathway B) is the fastest protonation step, whereas the protonation of the indanyl anion by water (pathway A) is the slowest. These facts must have a strong influence on the stereochemistry of our reactions, which often afford kinetically controlled products. In fact, in the reaction occurring by pathway B we have observed prevalent or exclusive kinetic control of both protonation steps; in the case of mechanism A only the first protonation step is kinetically controlled (see the reduction of **2**), whereas the second appears to be thermodynamically[28] controlled (see the reduction of **2** and **3**).

Under these circumstances, an explanation which accounts for the apparent contradiction that the two pathways, though occurring through the formation of the same last intermediate, give opposite stereochemical results could be the following. In the second protonation step of pathway B the indanyl anion is rapidly protonated to the final product in its original (or in a very similar) configuration; on the other hand, in mechanism A the indanyl

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(22) Amatore, C.; Savéant, J. M. *J. Electroanal. Chem.* **1981**, *123*, 189–201.

(23) Though the acidities of **1** and phenol are quite similar in terms of p*K*'s in Me_2SO (15.2[24a] and 16.4,[24b] respectively), the voltammetric behavior shows that the protonation of the radical anion by phenol is faster than that by **1**, probably because of steric effects (vide infra).

(24) (a) Bordwell, F. G.; Drucker, G. E. *J. Org. Chem.* **1980**, *45*, 3325–3328. (b) King, E. J. "Physical Chemistry of Organic Solvent Systems"; Covington, A. K., Dickinson T., Eds.; Plenum Press: London, 1973; p 367.

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(26) (a) Reference 16, p 229. (b) Dietz, R. "Organic Electrochemistry"; Baizer, M. M., Ed.; Marcel Dekker: New York, 1973; p 259. (c) Szwarc, M.; Streitweiser, A.; Mowery, P. C. "Ions and Ion Pairs in Organic Reactions"; Szwarc, M., Ed.; Wiley: New York, 1974; Vol. 2; p 221.

(27) pK_a 31.4 in Me_2SO. Olmstead, W. N.; Margolin, Z.; Bordwell, F. G. *J. Org. Chem.* **1980**, *45*, 3295–3299.

(28) Throughout this paper the word "thermodynamic" refers to the most stable isomers obtained under our experimental conditions.

anion can have the time to reach the most stable configuration prior to protonation or through the isomerization process.

(iii) On the basis of the electrochemical evidences, adsorption phenomena can be reasonably excluded. Other heterogeneity effects induced by the electrode can play a role depending on the type of mechanism occurring.

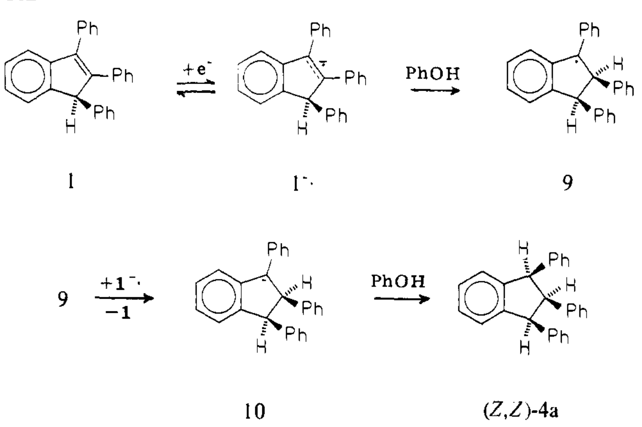
As regards mechanism A, the slow decay of the radical anions via disproportionation implies that the protonation of the dianion and of the indanyl anion takes place far away from the electrode, i.e., under homogeneous conditions, and hence without any effect by the electrode. The same considerations hold also in the case of the disp 1 mechanism of pathway B, where the protonation of the radical anion to neutral radical should not occur close to the electrode, since the reduction of the latter takes place homogeneously. On the other hand, in the ecec mechanism (pathway B), implying the reduction of the neutral radical at the electrode, it is reasonable to assume that protonation both of the radical anion and of the indanyl anion, preceding and following the second heterogeneous electron transfer, takes place near the electrode surface. On these bases, a different stereochemical pattern could be expected, in principle, depending on the route followed in pathway B.

In this respect, particular relevance is assumed by the quenching experiments where the whole process takes place under homogeneous conditions, following a disp 1 type mechanism (eq 17, 6, 18). As far as indene **2**, the stereochemical results of the macroscale electrolysis and the quenching experiment are practically identical; it follows that the disp 1 mechanism, which prevails under macroscale electrolysis conditions, is not affected by the electrode. On the other hand, with indene **3** significantly different stereochemical results are obtained in the macroscale electrolysis and in the quenching experiment: this can be reasonably imputed to a participation of the ecec mechanism under electrolysis conditions.

We are now able to draw a rationalization of our results, particularly from a stereochemical point of view. The most significant result of this work is the prevalent formation, independently of the pathway followed, of the indan isomers bearing the hydrogen at C_2 in a position trans to the phenyl group bonded at C_1. This is indicated by the formation (70–100%) of the isomers having the *Z* configuration around the C_1–C_2 bond, i.e., (*Z*,*Z*)-**4a**[29] in the reductions of **1** and (*Z*,*Z*)-**5a** and/or (*Z*,*E*)-**5c** in the reductions of **2**. Furthermore, another significant result is the prevalent formation (57–100%), in the reactions occurring by pathway B, of the isomers having the three (two in the case of indans **6**) phenyl groups cis to each other. This is indicated by the prevalent formation of (*Z*,*Z*)-**4a** in the reduction of **1**, of (*Z*,*Z*)-**5a** in the reduction of **2**, and of (*Z*)-**6a** in the case of **3**. A third significant stereochemical result is the exclusive formation, in the reactions occurring by mechanism A, of the indan isomers having the *E* configuration around the C_2–C_3 bond, i.e., with the phenyl groups at C_2 and C_3 trans to each other. This is indicated by the formation of (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the reduction of **2** and of (*E*)-**6b** in the case of **3**.

Since specific effects by the electrode have been excluded, a reasonable explanation for the high syn stereoselectivity observed may be found in steric effects, which favor the attack of the protonating agent on the less hindered side of the anionic intermediates.[30] This seems more likely if one considers that the protonating agents used in this work, i.e., phenol, water, as well as indene **1** in the self-protonation reaction, are practically undissociated in DMF.[31] Following this point of view, a rationalization of the exclusive formation of (*Z*,*Z*)-**4a** in the reduction of **1** in the presence of phenol (pathway B, disp 1 mechanism), which is the most clear-cut result obtained, is reported in Scheme I.

Scheme I



This scheme may be successfully extended, with the appropriate variations, to the reduction of **2** and **3** in the presence of phenol and also to the reduction of **1** under self-protonating conditions. In the case of **2** the lower stereoselectivity observed in the first protonation step (74%, corresponding to the sum of the yields of indans (*Z*,*Z*)-**5a** and (*Z*,*E*)-**5c**) may be likely imputed to the presence of the methyl group at C_1, which makes more balanced than in the case of **1** the steric effect on the attack of phenol at C_2. Furthermore, the methyl group at C_1 seems to affect also the direction of attack of the proton donor at C_3, which occurs with a lower stereoselectivity than for **1**. This may be due to an indirect steric effect (different population of conformers in respect to **1**), to a direct steric effect, similar to that exerted toward the attack at C_2, or to a combination of both.

As to the reduction of **3**, which was also studied in order to test the direction of the attack of the proton donor at C_3 without any differential influence by the groups bonded at C_1, the formation of at least 60% of (*Z*)-**6a** again confirms the preferential attack of phenol on the less hindered side of the indanyl anion. The more balanced situation than for **1** is likely due to the absence of a phenyl group at C_1 and, probably, to a difference in conformation due to a diminished steric interaction between one of the methyl groups at C_1 and the phenyl group at C_2 in respect to both indenes **1** and **2**.

The lower stereoselectivity (70%) observed in the reduction of **1** under self-protonating conditions may be imputed to a slower protonation of the intermediates by the indene **1**, with respect to phenol, which would allow both the radical anion $\mathbf{1}^{-\cdot}$ and the indanyl anion **10** to assume more stable conformations prior to protonation, with a trans arrangement (or at least a staggering) of the phenyl groups.

Following the same line of reasoning, a steric effect on the direction of protonation can also be invoked for the reductions occurring by mechanism A. In this case two facts must be taken into consideration: the prevalent attack of the proton donor at C_2 on the opposite side of the phenyl group at C_1 in the reduction of **2** (72%, corresponding to the indan isomer (*Z*,*E*)-**5c**) and the exclusive trans arrangement of the two hydrogens around the C_2–C_3 bond in the reduction both of **2** and **3**. Both of these findings may be rationalized as reported in Scheme II, which shows the path of formation of isomers (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the reduction of **2** in the presence of water.

As in the case of the protonation of $\mathbf{2}^{-\cdot}$ by phenol, also the protonation of $\mathbf{2}^{2-}$ by water occurs preferentially on the less hindered side of the molecule, namely on the side bearing the methyl group at C_1; the close analogy between these two steps may not be casual if one considers the similarity in the percentage of the isomers having the *Z* configuration around the C_1–C_2 bond observed for both reactions: 74% (sum of the yields of (*Z*,*Z*)-**5a** and (*Z*,*E*)-**5c**) for the reaction occurring via protonation of the radical anion and 72% (yield of (*Z*,*E*)-**5c**) for the reaction occurring via protonation of the dianion. As regards the second protonation step, the thermodynamic control leading to 100% anti

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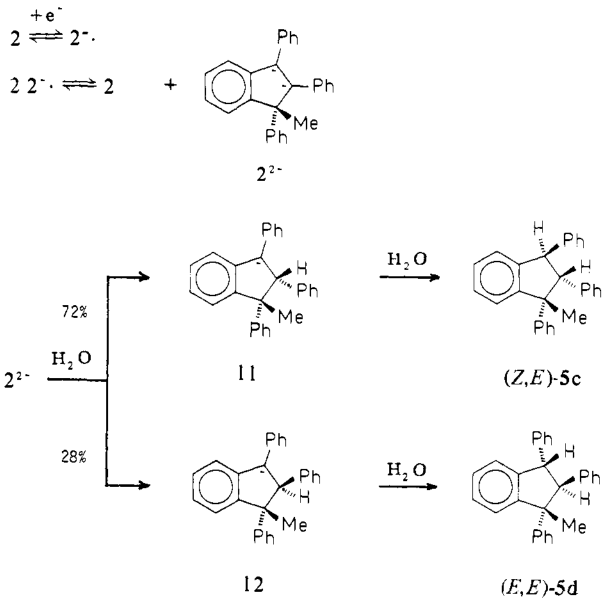
[29] As regards (*Z*,*E*)-**4b**, which is undistinguishable from the (*E*,*Z*) isomer, it is impossible to distinguish between syn and anti addition.

[30] A similar rationalization has been proposed by Zimmerman et al. for the stereochemistry of the ketonization reaction of enols. See: Zimmerman, H. E.; Mariano, P. S. *J. Am. Chem. Soc.* **1968**, *90*, 6091–6096 and previous papers of the series.

[31] (a) Peover, M. E. *Electroanal. Chem.* **1967**, *7*, 29. (b) Reference 26b, pp 258–259.

Scheme II



stereoselectivity has been already discussed before.

Our stereochemical data suggest a planar (or almost so) structure of the radical anions and indanyl anions at least as soon as they are formed, in agreement with the literature.[32,33] In fact, if they were not planar, one could imagine, for both intermediates, as the most probable a trans arrangement of the phenyl groups, which would imply protonation(s) from the most hindered side with inversion of configuration at least at C_2. Furthermore, the striking similarity in the stereochemistry of the protonation of $\mathbf{2}^{-\cdot}$ and $\mathbf{2}^{2-}$ would suggest an almost planar structure also for the dianion.

As regards possible effects of the counter ion n-Bu_4N^+ on the stereochemistry of the reaction, we do not expect a significant influence, since no tight ion pairs are generally involved under these conditions. Furthermore, preliminary experiments with different cation, e.g., Me_4N^+, did not show different stereochemical results.

The above discussion does not take into consideration any effect of the electrode on the stereochemical course of the reaction; this was reasonably excluded from all of our experiments, except in the case of the reduction of **3** in the presence of phenol, where the small, but significant, difference in the stereochemistry of electrolysis and quenching experiment was ascribed to the intervention of both disp 1 and ecec mechanisms under electrolysis conditions. In the last mechanism, the occurrence of all steps of the process in vicinity of the electrode surface could favor both protonations to take place on the same side, leading to a higher yield of (*Z*)-**6a**.

Experimental Section

Materials. The purification of dimethylformamide (DMF) and the preparation of tetrabutylammonium perchlorate (TBAP) were carried out as previously described.[6] Twice-distilled water and phenol (R. P. Carlo Erba) were used as proton donors in the electrochemical experiments. Neutral alumina (Merck, activity grade I) was activated by heating at 350 °C overnight under vacuum and then stored under dry nitrogen.

Melting points are uncorrected. ^{1}H NMR spectra were taken on Varian EM 360A and Bruker-Spectrospin WP 60 spectrometers operating at 60 MHz and on a Bruker WP 200 SY spectrometer at 200 MHz, using $CDCl_3$ as a solvent; chemical shifts are given in δ relative to Me_4Si as internal standard. NOE experiments were performed on a WP 200 SY Bruker spectrometer in sealed tubes freed from oxygen by repeated freeze–thaw cycles.

Electrochemical Apparatus. Electrochemical measurements were performed with a Princeton Applied Research (PAR) Model 175 Universal programmer connected to a PAR Model 173 potentiostat-galvanostat equipped with a PAR Model 179 digital coulometer using positive feedback to compensate for the ohmic drop.

Polarographic and amperometric data were directly displayed on a Hewlett-Packard Model 7040 A X-Y recorder, while voltammetric measurements were previously recorded on a PAR Model 4203 Signal Averager. A three-electrode cell was employed, and measurements were carried out under nitrogen. The temperature of the solution was kept constant (±0.2 °C) by circulation of thermostated water or ethanol through the double wall of the cell.

The working electrode was a platinum sphere sealed into glass, electrolytically covered by a thin layer of silver and then amalgamated by dipping in mercury. Mechanical renewal of the diffusion layer was achieved in potentiostatic measurements.

Electrolyses were carried out with a mercury-pool cathode. Ag-AgCl-tetramethylammonium chloride (saturated solution) in 3:1 acetonitrile–DMF was used as reference electrode; however, potential data are referred to a saturated calomel electrode.

A platinum wire in a DMF–TBAP solution was used as counter electrode. A plug of methylcellulose gel, made with the latter solution, served as the separator of both electrodes.

Electrochemical Procedure. All measurements were carried out in DMF with TBAP (0.1 M). Before each experiment the solution was cycled through a column of activated alumina; water or phenol was then added to the solution when required.

Homogeneous kinetic runs in the presence of water were carried out by monitoring the decrease of the limiting oxidation current of the radical anions of the indenes produced by electrolysis, at a fixed potential ca. 300 mV more positive than the reversible potential of the Ind–Ind$^{-\cdot}$ pair.

As regards the voltammetric kinetics in the presence of water, the values of the anodic to cathodic peak currents (i_a/i_c) were calculated by the method proposed by Nicholson and co-workers.[34] The i_a/i_c working curve was chosen for each kinetic measurement, taking into account the shape of the electrode and the experimental conditions.[13]

Voltammetric kinetics in the presence of phenol were carried out by the method proposed by Savéant and co-workers,[15] measuring the dependence of the peak potential on the voltage sweep rate and on phenol concentration under pure kinetic conditions.

Exhaustive controlled-potential electrolyses were carried out in correspondence either of the first or of the single polarographic reduction wave. Electrolysis conditions are reported in Table II. Electrolyzed solutions were worked up as follows. After concentration under reduced pressure, the solid products were precipitated by dropwise addition of twice-distilled water, filtered off, washed several times with water to remove completely the supporting electrolyte and other water-soluble compounds (e.g., phenol, acetic acid) where present, and dried. Product ratios were determined by ^{1}H NMR spectroscopy on this crude reaction residue.

Reagents and Products. 1,2,3-Triphenyl-1*H*-indene (**1**) and 1,1-dimethyl-2,3-diphenyl-1*H*-indene (**3**) were prepared following literature methods.[35] 1-Methyl-1,2,3-triphenyl-1*H*-indene (**2**) was synthesized according to the following reaction scheme:

$$\mathbf{1} \xrightarrow[\text{THF, room temp}]{n\text{-BuLi}} \xrightarrow[\text{THF}]{\text{CH}_3\text{I}} \mathbf{2}$$

To a solution of **1** (0.65 g, 1.9 mmol) in 20 mL of anhydrous THF, 0.86 mL (1.9 mmol) of a 20% hexane solution of n-butyllithium was added dropwise by means of a syringe under nitrogen at room temperature. A red color with green-yellow fluorescence developed immediately. The solution was stirred for about 20 min and then a solution of 0.27 g (1.9 mmol) of CH_3I in 10 mL of anhydrous THF was added. The reaction mixture immediately decolored to pale yellow and, after stirring for 1 h, was neutralized with diluted hydrochloric acid and extracted with ether. The organic layer was anhydrified over $CaCl_2$ and after stripping of the solvent under reduced pressure the residue was chromatographed on silica gel. Elution with light petroleum–benzene (8:1) gave 0.64 g of **2** (95%), which was recrystallized from ethanol, mp 97 °C. The ^{1}H NMR spectrum showed a complex multiplet at δ 7.2–6.7 (19 H, aromatic) and a singlet at δ 1.73 (3 H, methyl).

Anal. ($C_{28}H_{22}$) C; H: calcd, 6.18; found, 6.08.

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(32) The carbon–carbon double bond of tetraphenylethylene is not destroyed when the corresponding radical anion is formed (see ref 11, p 99). On this basis we can reasonably assume that a planar structure around the double bond is maintained also in the case of the radical anions of our substrates.

(33) 3-Indanyl anions are similar to the carbanions derived from 9,10-dihydrophenanthrenes, for which a planar structure is assumed as the most stable. See: Lewis, F. D.; De Voe, R. J. *J. Org. Chem.* **1982**, *47*, 888–891.

(34) Olmstead, M. L.; Hamilton, R. G.; Nicholson, R. S. *Anal. Chem.* **1969**, *41*, 260–267.

(35) (a) Maroni, R.; Melloni, G.; Modena, G. *J. Chem. Soc., Perkin Trans. 1* **1974**, 353–356. (b) Uffman, K. R.; Ullman, E. F. *J. Am. Chem. Soc.* **1967**, *89*, 5629–5633.

The synthesis and characterization of 1,2,3-triphenylindans **4a–c** have been previously reported.[18]

1-Methyl-1,2,3-triphenylindan ((*E*,*Z*)-5b). Catalytic hydrogenation of **2** (0.500 g, 1.38 mmol) in absolute ethanol (100 mL) in the presence of 10% Pd supported on carbon (0.090 gr), at 50 atm and 25 °C for 90 h, afforded quantitatively a mixture of the two isomers (*E*,*Z*)-**5b** and (*Z*,*Z*)-**5a** in the ratio 87:13, as determined by integration of the two methyl signals in the ^{1}H NMR spectrum of the crude reaction mixture. The more abundant of the two isomers, indan (*E*,*Z*)-**5b**, was isolated as a pure compound by fractional crystallization from 95% ethanol, mp 166 °C; ^{1}H NMR data are reported in Table IV.

Anal. ($C_{28}H_{24}$) C; H: calcd, 6.71; found, 6.65.

The (*E*,*Z*) configuration to this compound was assigned on the basis the ^{1}H NMR data and confirmed by NOE (see Stereochemical Assignments).

1-Methyl-1,2,3-triphenylindan ((*Z*,*E*)-5c). Exhaustive electrolysis of indene **2** in the presence of water afforded quantitatively a mixture of the isomers (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the ratio 72:28, as determined by integration of the methyl signals in the ^{1}H NMR spectrum of the crude reaction mixture. After crystallization from ethanol the mixture of the two isomers gave correct analytical data.

Anal. ($C_{28}H_{24}$) C, H.

The isomer (*Z*,*E*)-**5c** was isolated from this mixture as a pure compound by repeated fractional crystallizations from 95% ethanol, mp 101 °C; ^{1}H NMR data are reported in Table IV.

Anal. ($C_{28}H_{24}$) C; H: calcd, 6.71; found, 6.80.

The (*Z*,*E*) configuration to this isomer was assigned on the basis of the ^{1}H NMR data and confirmed by NOE (see Stereochemical Assignments).

Exhaustive electrolysis of **2** in the presence of PhOH afforded quantitatively a mixture of the four possible isomers **5a–d** (see Table II). This mixture, purified by crystallization from ethanol, gave correct analytical data.

Anal. ($C_{28}H_{24}$) C, H.

1,1-Dimethyl-2,3-diphenylindan ((*E*)-6b). Exhaustive electrolysis of **3** in the presence of water afforded quantitatively indan (*E*)-**6b**, which was recrystallized from ethanol, mp 148 °C; ^{1}H NMR data are reported in Table IV.

Anal. ($C_{23}H_{22}$) C, H.

The *E* configuration was assigned on the basis of the ^{1}H NMR data (see Stereochemical Assignments).

Exhaustive electrolysis of **3** in the presence of PhOH afforded quantitatively a mixture of the two isomers **6a** and **6b** (see Table II). After crystallization from ethanol this mixture gave satisfactory elemental analyses.

Anal. ($C_{23}H_{20}$) C; H: calcd, 7.43; found, 7.51.

Various attempts to separate the two isomers in pure form by fractional crystallization failed.

Deuteration of Indene 2. Electrolysis of **2** (10 mL of a 0.1 M solution) in the presence of CD_3COOD (0.5 M) afforded a mixture of four isomeric 2,3-dideuterio-1-methyl-1,2,3-triphenylindans (**7a–d**) in a ratio very close to that observed in the electrolysis in the presence of phenol (see Table II), under the same experimental conditions. The ^{1}H NMR spectrum of the residue showed four singlets at δ 1.28, 1.51, 1.84, and 1.87 (methyl groups), but no signals were detected in the field of benzylic and diphenylmethylic proton resonances, indicating a complete deuteration at the 2- and 3-positions of the five-member ring of the indanyl moiety.

Isomerization Experiments in the Presence of TBAOH. Solutions of indans **4–6**, either as pure isomers or mixtures of isomers as obtained by electrolysis, in DMF (0.05 M) were stirred for 3 days at room temperature in the presence of TBAOH (0.1 M) and water (2 M). The solutions were then worked up following a procedure identical with that used for the electrolytical reductions. The results of the experiments were valued on the basis of the ^{1}H NMR spectrum of the crude reaction residue and are reported in Table V.

Isomerization Experiments under Electrolysis Conditions. Exhaustive electrolysis (about 2 h) of indenes **1–3** (0.05 M) was carried out in the presence of equimolar amounts of their reduction products, namely indans **4**, **5** (or **7**), and **6**, respectively, and in the presence of water (0.3 M). After workup following the usual procedure, the reaction residues were examined by ^{1}H NMR spectroscopy in order to evaluate the extent of the isomerization. Results are reported in Table V. Appropriate corrections were made to account for the products deriving directly from the reduction of the indenes present as starting material.

In the case of electrolysis of **2** (0.01 M) in the presence of an equimolar amount of the isomeric mixture of deuterated indans **7a–d**, as obtained from the deuteration experiment described above, and in the presence of water (0.3 M), the ^{1}H NMR spectrum of the reaction mixture taken at 200 MHz showed, besides a complex multiplet between δ 6.40 and 7.40, two singlets at δ 1.87 and 1.28 (ratio ca. 2.5:1), doublets at δ 3.57 and 4.54 ($^3J_{HH} = 11.5$ Hz) at δ 3.87 and 4.88 ($^3J_{HH} = 11.4$ Hz), and badly resolved triplets at δ 4.53 and 4.87 ($^3J_{HD}$ not determinable), slightly shifted at higher field because of isotope effect. The integral ratio between the signals centered at δ 3.57 and 3.87 and those centered at δ 4.53–4.54 and δ 4.87–4.88 was ca. 1:2. This indicates the presence in the reaction products of a mixture of the two isomers (*Z*,*E*)-**5c** and (*E*,*E*)-**5d** in the expected ratio 72:28 and of an equal amount of a mixture of the two isomers (*Z*,*E*)-**8a** and (*E*,*E*)-**8b**, deuterated only in the 2-position, in the same ratio.

Quenching Experiments. Radical anions of indenes **2** and **3** were produced and quenched with the following procedure: 10 mL of a 0.1 M solution of the indene in DMF was electrolyzed exhaustively under anhydrous conditions at −30 °C, at the potential of the first polarographic reduction wave, to accumulate the radical anion, as indicated by polarographic investigations, with the consumption of 1 F mol^{-1} of indene. A 1 M solution of phenol in DMF (5 mL) was then added under vigorous stirring. The disappearance of the deep blue color of the radical anion was observed within a few seconds. The solution was then worked up in the usual way. In any case, 50% of the radical anion was transformed into reduction products, and the remaining 50% gave back the starting material (see Table II).

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Registry No. 1, 38274-35-0; **2**, 81747-64-0; **3**, 18949-22-9; (*Z*,*Z*)-**4a**, 72343-28-3; (*Z*,*E*)-**4b**, 70550-46-8; (*E*,*E*)-**4c**, 62677-53-6; (*Z*,*Z*)-**5a**, 81768-01-6; (*E*,*Z*)-**5b**, 81768-00-5; (*Z*,*E*)-**5c**, 81767-99-9; (*E*,*E*)-**5d**, 81747-65-1; (*Z*)-**6a**, 22256-20-8; (*E*)-**6b**, 22256-19-5; (*Z*,*Z*)-**7a**, 91365-72-9; (*E*,*Z*)-**7b**, 91422-71-8; (*Z*,*E*)-**7c**, 91422-72-9; (*E*,*E*)-**7d**, 91422-73-0.