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Electrochemical Reduction of Activated Carbon–Carbon Double Bonds. 3. 1,2 Phenyl Migration in the Reduction of Some 1,1-Diphenyl-Substituted Indenes

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Abstract: The reduction at a Hg electrode in DMF of 1,1,3-triphenylindene (**1**), 2-methyl-1,1,3-triphenylindene (**2**), and 1,1,2,3-tetraphenylindene (**3**) was carried out in order to check the occurrence of rearrangements of the reaction intermediates. The two-electron two-proton reduction involved exclusively the pentatomic cycle and afforded both unrearranged indans (having the same framework of the starting indenes) and, in the case of indenes **1** and **2**, rearranged indans derived from a 1,2 phenyl shift. Voltammetric and kinetic experiments indicate that the shift occurs exclusively at the level of the dianions produced at the electrode at the potential of the second reduction step and, in the case of **2**, formed also by disproportionation of the radical anion produced at the potential of the first reduction step. Competition between rearrangement and protonation of the dianions as well as between disproportionation and protonation of the radical anions was observed; accordingly, in the presence of added proton donors (water, phenol) unrearranged products were exclusively obtained. The fast rearrangement of the dianions of indenes **1** and **2** is discussed in terms of a 1,2 cationotropic shift and attributed to a gain of stabilization in the rearranged dianions due to electronic and steric effects.

In the current interest in electron transfer induced reactions special attention is devoted to the structural reorganizations, which may precede, accompany, or follow the electron transfer. Significant examples in the electrochemical field have been reported and rationalized in terms of conformational and configurational changes, migration of substituents, and changes in bonding mode.[2]

In our previous investigations on the correlation between mechanism and stereochemistry of the electrochemical reduction of substituted indenes to indans,[3] no structural reorganization was observed; the indanyl products maintained in any case the framework of the starting indenes. In order to test the occurrence of structural reorganizations, in the prosecution of our study, we have taken into consideration the reduction of indenes different from those previously investigated, such as 1,1-diphenyl-substituted indenes, which are known to give 1,2 migration of a phenyl group under a variety of conditions, i.e., under thermal,[4] photochemical,[5] oxidative,[6] and reductive[7] conditions.

A correct rationalization of the migration occurring under oxidative and reductive conditions, which imply multistep processes, requires to ascertain which intermediate undergoes rearrangement. In particular, for the rearrangement occurring under reductive conditions it is an open question whether the phenyl migration occurs at the level of the radical anion or the dianion. In their early work on the reduction of phenyl-substituted indenes with alkali metals in THF, Miller and Boyer[7a] suggested that the rearrangement might occur at the level of either intermediates; subsequent work by Kiesele[7b,c] showed that the rearrangment of 1,1,3-triphenylindene under electrochemical conditions in THF with Na^+ as a counterion occurs exclusively at the dianion level. It should also be pointed out that in the complex reduction process leading to the final indanyl products other intermediates, besides the radical anion and the dianion, could undergo migration of the phenyl group, such as a neutral radical, formed by protonation of the radical anion, or a carbanion, formed either by reduction of the neutral radical or by protonation of the dianion. Examples of 1,2 phenyl shifts occurring via radicals[8] or carbanions[9] are known.

Table I. Standard Potentials[a] in DMF–0.1 M TBAP at −37 °C

indene	$-E^\circ_1$, V	$-E^\circ_2$, V	$-E^\circ_3$, V	$-E^\circ_4$, V
1	2.46	>3.0[b]	1.95	<1.63[b]
2	2.65	>3.1[b]	2.09	1.62
3	2.16	2.50	*c*	*c*

[a] Referred to a SCE. [b] The chemical irreversibility of the peak does not allow determination of E°. [c] The corresponding peak couple was not observed.

Following these premises, it seemed interesting to investigate the behavior of these intermediates under our usual electrochemical conditions.[3] We report here the results obtained in the reduction at a Hg electrode in DMF, with tetra-*n*-butylammonium perchlorate as a supporting electrolyte, of 1,1,3-triphenyl-substituted indenes **1–3**, bearing different substituents at the 2-position.

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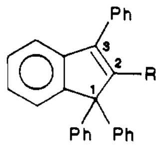


1: R = H
2: R = Me
3: R = Ph

Results

Voltammetric Behavior. In dry solution the electrochemical reduction of 1,1,2,3-tetraphenylindene (**3**) takes place, in cyclic voltammetry, in two one-electron steps corresponding to the formation of the radical anion ($\text{Ind}^{\bullet-}$) and the dianion (Ind^{2-}) of the indene (Ind):

$$\text{Ind} + e^- \overset{E^\circ_1}{\rightleftharpoons} \text{Ind}^{\bullet-} \qquad (1)$$

$$\text{Ind}^{\bullet-} + e^- \overset{E^\circ_2}{\rightleftharpoons} \text{Ind}^{2-} \qquad (2)$$

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

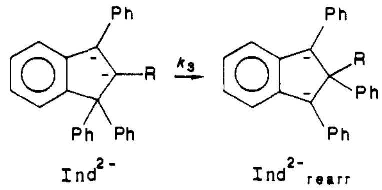
As previously observed for 2,3-diphenyl-substituted indenes,[3c] the first reduction step appears completely reversible, whereas a quasi-reversible heterogeneous electron transfer is involved in the second step. Furthermore, the chemical reversibility of the second peak is affected by the presence of weak proton donors (e.g., water) able to protonate the dianion but not the less basic radical anion.

Substitution of the phenyl group at C(2) with a hydrogen or a methyl group shifts both reduction steps toward more negative potentials, according to a diminished delocalization of the negative charge both in the radical anion and in the dianion. Indeed, 1,1,3-triphenylindene (**1**) and 2-methyl-1,1,3-triphenylindene (**2**) show, in cyclic voltammetry, a first reversible one-electron reduction peak at potentials more negative than that of indene **3** (Table I) and a second reduction peak close to the discharge of the supporting electrolyte (see Figures 1 and 2). Whereas the first peak is chemically reversible even at the lowest sweep rates investigated (100 mV s^{-1}), the second peak appears chemically irreversible also at high sweep rates (100 V s^{-1}) and low temperatures (−55 °C).

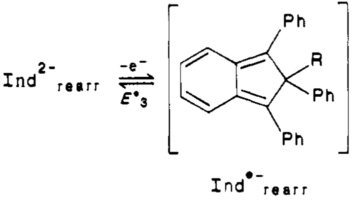
For the indenes considered in previous work,[3] the irreversibility of the second step was attributed exclusively to the protonation of the dianion by acidic species (in traces or appropriately added) and the anodic peak detected in the range −1.0 to −1.2 V was related to the oxidation of the indanyl anion (IndH^-) thus formed. On the other hand, for indenes **1** and **2** two new oxidation peaks, O_3 and O_4, are detectable when the second reduction step R_2 is involved in the cathodic sweep (Figures 1 and 2). These oxidation peaks are not detectable when only the first reduction peak is involved in the sweep, even if the potential is maintained at the inversion value for a few seconds (15 or more) before reversing the sweep. For both indenes **1** and **2** the oxidation peak O_3 shows the corresponding reduction peak R_3; the difference between the peak potentials indicates that a quasi-reversible one-electron transfer is involved. On the other hand, only for indene **2**, the oxidation peak O_4 shows the corresponding reduction peak R_4 (Figure 1), with a difference between the peak potentials indicating a reversible one-electron step. For indene **1** this reduction peak was never observed, even at the highest sweep rates investigated (100 V s^{-1}).

On the basis of the voltammeric behavior and the results of macroscale electrolyses (see below) and in agreement with the attribution of Kiesele,[7b,c] we can impute peak O_3 for both indenes to the oxidation of the species obtained by 1,2 phenyl migration in the dianion electrochemically generated at R_2, according to eq 3 and 4.

Peak O_4 can be attributed to the oxidation of the radical anion formed at O_3, with formation of the rearranged indene ($\text{Ind}_{\text{rearr}}$), having an isoindene structure (eq 5).



(3)



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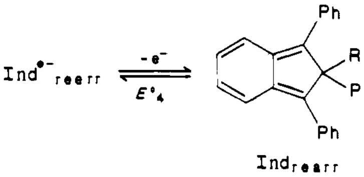
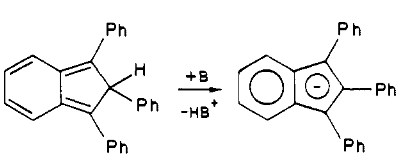


(5)

As regards indene **1** (R = H), the chemical irreversibility of O_4 can be likely attributed to easy loss of the acidic hydrogen at C(2) (due to the aromatic character of the indenyl anion thus formed)[5a] in the highly basic environment in which the rearranged indene is produced (eq 6). According to this fact, when peak O_4 is involved in subsequent voltammetric sweeps, the breakdown of the peak couple O_3/R_3 is observed for indene **1** but not for indene **2** (compare Figures 2 and 3).



(6)

It should also be pointed out that the chemical irreversibility of O_4 cannot be due to a fast 2,1 hydrogen migration in the rearranged indene, with formation of 1,2,3-triphenyl-1*H*-indene, since the well recognizable reduction peaks of the latter[3c,d] are not observed in subsequent voltammetric sweeps involving O_4; 2,1 phenyl migration with formation of indene **1** can also be excluded since no appreciable variation of the height of R_1 is observed regardless of the involvement of O_4 in subsequent reduction–oxidation cycles.

Examination of the steady-state voltammograms of indene **2** (Figure 3) reveals that the decrease of the height of the reduction peak R_1, observed when the second reduction step R_2 is involved in the sweep, is comparable with the height of the new peaks R_3 and R_4, thus indicating that the decay of the dianion $\mathbf{2}^{2-}$ occurs prevalently via rearrangement. Furthermore, the comparison between the height of the peaks R_1 and R_3 in the steady-state voltammograms of Figures 2 and 3 shows that the dianion $\mathbf{1}^{2-}$ undergoes the rearrangement to a smaller extent than the dianion $\mathbf{2}^{2-}$.

Macroscale Electrolysis. Exhaustive controlled-potential electrolysis of indenes **1**–**3** at the potential of both the first and the second reduction step requires 2 electrons/molecule,[10] with quantitative formation, after quenching, of either "normal" (unrearranged) indans **4**–**6** and/or rearranged indans **7** and **8**, in some cases as mixtures of configurational isomers, according to eq 7.

Electrolysis at the potential of the first reduction step afforded preferentially the unrearranged product **4** in the case of **1** and the rearranged isomeric products **8** in the case of **2** (Table II). In the case of **3**, the consumption of 1 electron/molecule at the

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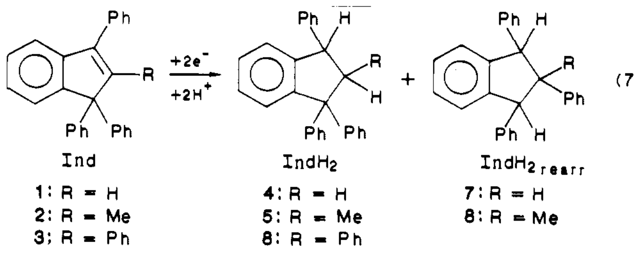
[10] Actually, in the electrolysis of **2** at the potential of the second reduction step only 70–75% of the indene was reduced after the consumption of 2 electrons/molecule. This can be likely imputed to the contemporary discharge of the supporting electrolyte (see Figure 1).



Ind: 1: R = H; 2: R = Me; 3: R = Ph

IndH2: 4: R = H; 5: R = Me; 6: R = Ph

IndH2rearr: 7: R = H; 8: R = Me

(7)

potential of the first reduction step led to quantitative accumulation of $3^{\bullet-}$, due to its very slow decay compared to that of $1^{\bullet-}$ and $2^{\bullet-}$. This required, in order to complete the reduction, the application of the potential of the second step, thus leading to the same results of the reduction carried out entirely at the latter potential[11] (Table II).

Electrolysis at the potential of the second reduction step afforded preferentially the unrearranged products **4** in the case of **1** and the rearranged isomeric products **8** in the case of **2**; the unrearranged products **6** were exclusively formed in the case of **3** (Table II). It should be stressed that the percentage of rearranged products obtained from **2** is higher than that obtained from **1**, in agreement with the voltammetric behavior; furthermore, for both indenes **1** and **2** the amount of rearranged products is higher than that observed in the reduction carried out at the potential of the first reduction step.

For comparison purposes, electrolyses of **1** and **2** were also carried out in the presence of phenol at the potentials of the single reduction peak. Consumption of 2 electrons/molecule and quantitative formation of unrearranged products **4** and **5**, respectively, were observed (Table II). Similar results were obtained in the electrolyses of **1** and **2** carried out in the presence of added water at the potential both of the first and of the second reduction steps.

Homogeneous Kinetics. The decay of radical anions $1^{\bullet-}$ and $2^{\bullet-}$, produced by electrolysis of **1** and **2** at the potential of the first reduction peak, was followed by an amperometric method. Kinetic measurements were driven at −37 °C in the presence of the parent indene in excess with respect to $\mathrm{Ind}^{\bullet-}$ to allow a pseudoorder treatment.

The decay of both $1^{\bullet-}$ and $2^{\bullet-}$ is accompanied by half-regeneration of the corresponding indene, according to the involvement of 1 electron/molecule in the formation of the radical anion and of 2 electrons/molecule in the overall reduction process.

The decay of $1^{\bullet-}$ is first order in its concentration, with an apparent first-order rate constant k_{I} decreasing with an increasing amount of indene electrolyzed before the kinetic run. Significant values of k_{I} after the reduction of 30, 50, and 70% indene (initial concentration 5×10^{-2} M) are 1.5×10^{-3}, 5×10^{-4}, and 3×10^{-4} s^{-1}, respectively.

On the other hand, the decay of $2^{\bullet-}$ follows a mixed first- and second-order decay in its concentration. Considering eq 8 and assuming k_{I} and k_{II} constant throughout the kinetic run, we obtain, after integration, eq 9.

$$\mathrm{d}[\mathrm{Ind}^{\bullet-}]/\mathrm{d}t = k_{\mathrm{I}}[\mathrm{Ind}^{\bullet-}] + k_{\mathrm{II}}[\mathrm{Ind}^{\bullet-}]^2 \qquad (8)$$

$$\frac{[\mathrm{Ind}^{\bullet-}]}{[\mathrm{Ind}^{\bullet-}]_0} = \frac{k_{\mathrm{I}} \exp(-k_{\mathrm{I}}t)}{k_{\mathrm{II}}[\mathrm{Ind}^{\bullet-}]_0[1 - \exp(-k_{\mathrm{I}}t)] + k_{\mathrm{I}}} \qquad (9)$$

Data treatment by a nonlinear least-squares method allows the determination of k_{I} and k_{II}. As in the case of $1^{\bullet-}$ the value of k_{I} decreases with an increasing amount of indene electrolyzed; significant values of k_{I} after the reduction of 30, 50, and 70% indene (initial concentration 5×10^{-2} M) are 1.4×10^{-4}, 7×10^{-5}, and 4×10^{-5} s^{-1}, respectively. On the other hand, the value of k_{II} increases with a decreasing concentration of indene in different kinetic runs. In particular, a linear plot is obtained by reporting $1/k_{\mathrm{II}}$ versus indene concentration (Figure 4).

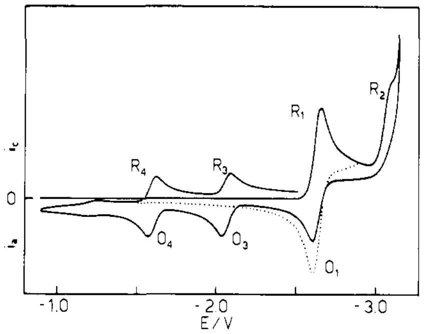


Figure 1. Cyclic voltammograms of indene **2** (2.0 mM) at −55 °C. Voltage sweep rate 0.25 V s^{-1}.

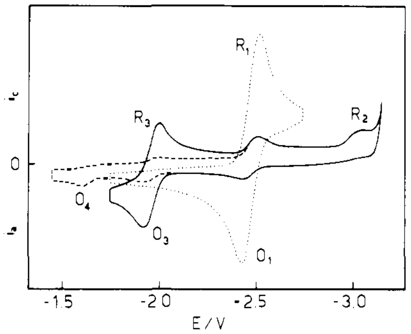


Figure 2. Steady-state voltammograms of indene **1** (2.0 mM) at −55 °C, involving different values of the reversing potentials. Voltage sweep rate 20 V s^{-1}.

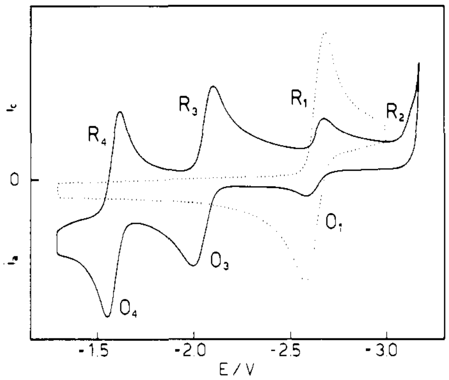


Figure 3. Steady-state voltammograms of indene **2** (2.0 mM) at −55 °C, involving different values of the reversing potentials. Voltage sweep rate 20 V s^{-1}.

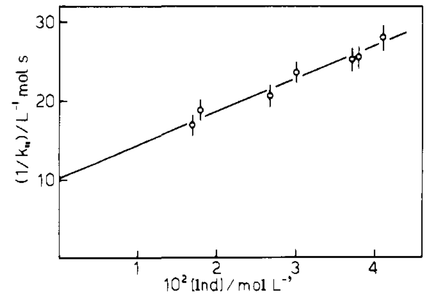


Figure 4. Plot of $1/k_{\mathrm{II}}$ vs [Ind] for indene **2** at −37 °C.

According to these facts, to voltammetric evidences, and to the results of macroscale electrolyses, we can reasonably assume that the first- and second-order decay of the radical anions are attributable to direct protonation and to disproportionation, re-

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[11] It has to be pointed out that the dianion 3^{2-} undergoes no rearrangement nor appreciable protonation but comproportionation with the substrate, so that the corresponding radical anion accumulates in solution, even at the potential of the second reduction step, until the substrate is completely consumed.

Table II. Results of Macroscale Potentiostatic Electrolyses in DMF-0.1 M TBAP, at -37 °C

			yield,[c] %			
indene[a]	electrolysis potentials[b]	proton donor	unrearranged products		rearranged products	
			4		(*E*,*E*)-**7**[d]	
1	-2.65[e]		97		3	
1	-3.1[f]		68		32	
1	-2.6[g]	PhOH[h]	100			
			(*Z*)-**5**	(*E*)-**5**	(*Z*,*Z*)-**8**[i]	(*E*,*E*)-**8**[i]
2	-2.8[e]			24	2	74
2	-3.3[f]			8	35	57
2	-2.6[g]	PhOH[h]	10	90		
			(*Z*)-**6**	(*E*)-**6**		
3	-2.3/-2.8[j]		44	56		
3	-2.8[f]		44	56		

[a] [Indene] = 5×10^{-2} M; 2 electrons/molecule are generally required for the exhaustive electrolyses, with the exception of the electrolysis of **2** at -3.3 V (see text, under Macroscale Electrolysis). [b] Referred to a SCE. [c] Determined by integration of the ^{1}H NMR spectrum of the reaction mixture; estimated error ca. 2%. [d] The (*Z*,*Z*) and (*Z*,*E*) isomers were not detected. [e] Corresponding to the first reduction step. [f] Corresponding to the second reduction step. [g] Corresponding to the single reduction step. [h] [PhOH] = 0.25 M. [i] The (*Z*,*E*) [or (*E*,*Z*)] isomer was not detected. [j] See text, under Macroscale Electrolysis.

spectively, according to the following competitive[12] mechanisms I and II:

Mechanism I

$$\mathrm{Ind}^{\bullet-} \xrightarrow[k_{10}]{+\mathrm{HS}} \mathrm{IndH}^{\bullet} \tag{10}$$

$$\mathrm{IndH}^{\bullet} + \mathrm{Ind}^{\bullet-} \xrightarrow{\text{fast}} \mathrm{IndH}^{-} + \mathrm{Ind} \tag{11}$$

$$\mathrm{IndH}^{-} \xrightarrow{+\mathrm{HS}} \mathrm{IndH}_2 \tag{12}$$

$$2\mathrm{Ind}^{\bullet-} \xrightarrow{+2\mathrm{HS}} \mathrm{Ind} + \mathrm{IndH}_2 \tag{13}$$

Mechanism II

$$2\mathrm{Ind}^{\bullet-} \underset{k_{-14}}{\overset{k_{14}}{\rightleftharpoons}} \mathrm{Ind}^{2-} + \mathrm{Ind} \tag{14}$$

$$\mathrm{Ind}^{2-} \xrightarrow[k_{15}]{+\mathrm{HS}} \mathrm{IndH}^{-} \tag{15}$$

$$\mathrm{IndH}^{-} \xrightarrow{+\mathrm{HS}} \mathrm{IndH}_2 \tag{12}$$

$$\mathrm{Ind}^{2-} \xrightarrow{k_3} \mathrm{Ind}^{2-}{}_{\mathrm{rearr}} \tag{3}$$

$$\mathrm{Ind}^{2-}{}_{\mathrm{rearr}} \xrightarrow{+\mathrm{HS}} \mathrm{IndH}^{-}{}_{\mathrm{rearr}} \tag{16}$$

$$\mathrm{IndH}^{-}{}_{\mathrm{rearr}} \xrightarrow{+\mathrm{HS}} \mathrm{IndH}_{2\,\mathrm{rearr}} \tag{17}$$

$$2\mathrm{Ind}^{\bullet-} \xrightarrow{+2\mathrm{HS}} \mathrm{Ind} + \mathrm{IndH}_2/\mathrm{IndH}_{2\,\mathrm{rearr}} \tag{18}$$

As to mechanism I,[13] step 10 can be considered rate determining and practically irreversible since step 11 is thermodynamically favored and extremely fast.[3c] As to mechanism II,[14] in the likely assumption of a steady state for the reactive dianion and of a constant concentration of indene throughout each kinetic run, the following rate law is obtained

$$-\frac{\mathrm{d}[\mathrm{Ind}^{\bullet-}]}{\mathrm{d}t} = \frac{2k_{14}(k_3 + k_{15})}{k_{-14}[\mathrm{Ind}] + k_3 + k_{15}}[\mathrm{Ind}^{\bullet-}]^2 = k_{\mathrm{II}}[\mathrm{Ind}^{\bullet-}]^2 \tag{19}$$

and hence the equation

$$1/k_{\mathrm{II}} = \frac{1}{2k_{14}} + \frac{[\mathrm{Ind}]}{2K_{14}(k_3 + k_{15})} \tag{20}$$

where K_{14} $(=k_{14}/k_{-14})$ represents the equilibrium constant of the disproportionation reaction (eq 14) and k_{15} the pseudo-first-order rate constant of protonation of the unrearranged dianion (eq 15).

For indene **2** the linear plot of $1/k_{\mathrm{II}}$ versus [Ind] (Figure 4) is in agreement with the kinetic law 20; from the value of the intercept (10 ± 2 L^{-1} mol s at -37 °C), we obtain $k_{14} = (5 \pm 1) \times 10^{-2}$ L mol^{-1} s^{-1}.

In the likely hypothesis that k_{-14} is close to the diffusion limit[3c] we obtain $K_{14} \cong 2 \times 10^{-11}$, which corresponds to a $E°_1 - E°_2$ value of about 500 mV. This value is higher than the observed difference between the peak potentials of the first and the second reduction step, in agreement with the positive shift of the second peak due to the chemical processes involving the dianion formed at the electrode (rearrangement and protonation).

On the basis of the estimated value of K_{14} and of the experimental value of the slope of the linear plot of Figure 4 (425 ± 20 s), we obtain, from eq 20, $k_3 + k_{15} \cong 6 \times 10^7$ s^{-1}. Considering that the formation of rearranged and unrearranged products derives from the protonation of $\mathrm{Ind}^{2-}{}_{\mathrm{rearr}}$ and Ind^{2-}, respectively, the value of the ratio k_3/k_{15} should be equal to the ratio between rearranged and unrearranged products obtained in the electrolysis carried out at the potential of the second reduction step (92:8); in this way we obtain $k_3 \cong 5.5 \times 10^7$ s^{-1} and $k_{15} \cong 5 \times 10^6$ s^{-1}. Since k_{15} should depend on the amount of proton donors still present in the reaction medium, as observed for k_{I}, its value can be considered as a mean throughout the electrolysis. However, being $k_{15} < k_3$, the variation of k_{15} in different kinetic runs can be neglected.

According to the proposed mechanisms, addition of proton donors should favor protonation of the radical anion (mechanism I) with respect to disproportionation (mechanism II) and protonation of the unrearranged dianion (eq 15) with respect to rearrangement (eq 3), leading therefore to unrearranged products. This is in agreement with the experiments carried out in the presence of water or phenol, in which disappearance of peaks O_3 and O_4 in the voltammetric experiments and exclusive formation of unrearranged products in the macroscale electrolyses were observed.

Discussion

The results of the voltammetric experiments clearly indicate that under our experimental conditions the rearrangement of indenes **1** and **2** occurs exclusively at the level of the corresponding dianions, whereas it does not occur in the case of indene **3**. Such behavior is supported by the results of the macroscale electrolyses in the case of indene **1**, which affords rearranged products practically only at the potential of the second reduction step, and also in the case of indene **3**, which does not afford rearranged products at all. On the other hand, there seems to be a contradiction in the behavior of indene **2**, which affords large amounts of rearranged products even at the potential of the first reduction peak, whereas in voltammetric experiments no evidence for the rearrangement of the radical anion $\mathbf{2}^{\bullet-}$ was obtained. This behavior can be explained on the basis of the following considerations.

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(12) A mixed first- and second-order decay of radical anions has been recently evidenced in the case of the reductive fragmentation of 9,9-diarylfluorenes and explained in terms of competitive radical anion and dianion cleavage. Walsh, T. D. *J. Am. Chem. Soc.* **1987**, *109*, 1511-1518.

(13) A similar mechanism was observed for the decay of indenyl radical anions in the presence of strong proton donors (phenol, acetic acid, or the indene itself if self-protonating),[3] whereas disproportionation of the radical anions followed by protonation of the dianions took place in the presence of weaker proton donors (water).[3c] The highly basic character of radical anions bearing no phenyl groups at C(2),[3d] as $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$, makes mechanism I feasible also in the presence of weak proton donors.

(14) An alternative mechanism involving a very slow rearrangement of radical anions followed by the thermodynamically favored (see $E°$'s in Table I) and hence very fast homogeneous electron transfer $\mathrm{Ind}^{\bullet-}{}_{\mathrm{rearr}} + \mathrm{Ind}^{\bullet-} \rightarrow \mathrm{Ind}^{2-}{}_{\mathrm{rearr}} + \mathrm{Ind}$ implies a first-order decay of radical anions, at variance with the second-order decay observed in case of formation of rearranged products.

As regards indene **1**, the first-order decay of $\mathbf{1}^{\bullet-}$ and the preferential formation of unrearranged products in macroscale electrolysis at the potential of the first reduction step indicate that the phenyl shift does not take place at the radical anion level (or, at least, that it does not compete with the slow protonation of the radical anion itself) and also that neither the neutral radical $\mathrm{IndH}^{\bullet}$, formed by protonation of $\mathrm{Ind}^{\bullet-}$, nor the anion IndH^{-}, formed by reduction of $\mathrm{IndH}^{\bullet}$, undergo the rearrangement.[15]

At variance with the behavior of $\mathbf{1}^{\bullet-}$, the decay of the radical anion $\mathbf{2}^{\bullet-}$ follows mixed first- and second-order kinetics, and the macroscale electrolysis of **2** at the potential of the first reduction step affords a 76:24 mixture of rearranged and unrearranged products. The first-order contribution can be likely ascribed to mechanism I, thus leading, by analogy with $\mathbf{1}^{\bullet-}$, to the formation of unrearranged products. On the other hand, the second-order decay of $\mathbf{2}^{\bullet-}$ (disproportionation) leads to the formation of the dianion $\mathbf{2}^{2-}$, which is in part protonated as such, affording the unrearranged products **5**, but prevalently rearranges to the more stable dianion $\mathrm{Ind}^{2-}{}_{\mathrm{rearr}}$, affording products **8**. Therefore, the above ratio should reflect in good approximation the ratio between second- and first-order contributions in the decay of $\mathbf{2}^{\bullet-}$. This ratio depends on the rate constants and on the concentration of the radical anion, according to eq 21. Since the values of k_{II} and

$$r = \frac{k_{\mathrm{II}}[\mathrm{Ind}^{\bullet-}]^2}{k_{\mathrm{I}}[\mathrm{Ind}^{\bullet-}]} = \frac{k_{\mathrm{II}}}{k_{\mathrm{I}}}[\mathrm{Ind}^{\bullet-}] \qquad (21)$$

k_{I} change during the electrolysis, taking as mean values (corresponding to 50% electrolysis) 5×10^{-2} L mol^{-1} s^{-1} for k_{II} (see Figure 4) and 7×10^{-5} s^{-1} for k_{I} (see Results), the mean value of the ratio, r_{m}, is given by eq 22 where $[\mathbf{2}^{\bullet-}]_{\mathrm{m}}$ represents the mean

$$r_{\mathrm{m}} = 7 \times 10^{2}[\mathbf{2}^{\bullet-}]_{\mathrm{m}} \qquad (22)$$

value of the concentration of the radical anion $\mathbf{2}^{\bullet-}$ during the electrolysis. Therefore, $7 \times 10^{2}[\mathbf{2}^{\bullet-}]_{\mathrm{m}} \cong 76/24$ and, finally, $[\mathbf{2}^{\bullet-}]_{\mathrm{m}} \cong 4.5 \times 10^{-3}$ M. This value is meaningful if one considers that the concentration of $\mathbf{2}^{\bullet-}$, determined by polarographic measurements during electrolysis, is in the range $3\text{–}7 \times 10^{-3}$ M, thus indicating a good accordance between kinetic data and results of the macroscale electrolysis.

As to the different modes of decay of $\mathbf{1}^{\bullet-}$ and $\mathbf{2}^{\bullet-}$, the following considerations can be put forward: (i) the apparent first-order rate constant for the decay of $\mathbf{2}^{\bullet-}$, k_{I}, is about 1 order of magnitude smaller than that for the decay of $\mathbf{1}^{\bullet-}$ (see Results), in agreement with an easier protonation of a radical anion bearing a hydrogen at C(2) with respect to one bearing a methyl group;[16] (ii) the separation between the first and the second voltammetric peak is larger for indene **1** than for indene **2** under the same experimental conditions, thus suggesting a smaller disproportionation equilibrium constant for $\mathbf{1}^{\bullet-}$, and, therefore, for similar values of k_{-14} (both close to the diffusion limit),[3c] a smaller value of k_{14} for $\mathbf{1}^{\bullet-}$ (at least 1 order of magnitude). Taking into account such factors, we may calculate that for $\mathbf{1}^{\bullet-}$ the ratio between disproportionation and protonation is at least 2 orders of magnitude smaller than that for $\mathbf{2}^{\bullet-}$, which means that r_{m} for $\mathbf{1}^{\bullet-}$ could reach a top value of about 3×10^{-2}. Hence, a maximum amount of rearranged products of ca. 3% should be expected, in agreement with the results of the macroscale electrolysis (see Table II), to whom it corresponds a second-order kinetic contribution too small to be determined.

Indenes **1** and **2** show different behaviors also in the electrolyses carried out at the potentials of the second reduction step, where $\mathbf{2}^{2-}$ affords an amount of rearranged products larger than that afforded by $\mathbf{1}^{2-}$. On the likely assumption that the influence of the comproportionation reaction (backward of eq 14) can be neglected,[17] this can be imputed to a faster protonation of the dianion $\mathbf{1}^{2-}$ compared with that of $\mathbf{2}^{2-}$, based on the same factors that favor protonation of $\mathbf{1}^{\bullet-}$ in comparison with that of $\mathbf{2}^{\bullet-}$.

In summary, looking at the behavior of indenes **1** and **2** as a whole, we can observe that under our experimental conditions the corresponding radical anions prefer to undergo protonation or disproportionation, even if very slow, rather than rearrangement, whereas the dianions undergo rearrangement despite the competition of relatively fast reactions such as protonation or comproportionation.

The inaptitude of these radical anions to undergo the rearrangement, described as a suprafacial 1,5 sigmatropic shift,[18a] was found in accordance with theoretical predictions based on orbital- and spin-symmetry considerations stating forbiddenness of pericyclic reactions of neutral and ionic radicals.[7b,18] However, forbiddenness seems to be predicted for the corresponding dianions as well.[18b] Actually, the rearrangement of dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ may not be considered as a 1,5 sigmatropic shift, taking into account that the conjugated chain undergoing reorganization is virtually interrupted due to the loss of π-character of the C(2)–C(3) bond.[19] Following this assumption, the rearrangement observed herein should be considered as a 1,2 cationotropic shift similar to those observed in monoanionic systems.[9]

A MO treatment of 1,2 carbon to carbon migrations, developed by Zimmerman[20] for cations, radicals, and carbanions, predicts energetically difficult rearrangements for carbanions and free radicals; however, this forbiddenness is partially removed in the case of a migrating phenyl group.[20] In our case, the 1,2 phenyl migration in dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ should be further facilitated by electrostatic repulsion between the two negative charges in close proximity and by the lack of delocalization of the negative charge at C(2). Indeed, the rearranged dianions gain stability in that the two negative charges at C(1) and C(3) are equally delocalized both by a phenyl group and by the condensed aromatic ring. The migration is also favored by diminishing crowding at C(1). Accordingly, the lack of rearrangement in dianion $\mathbf{3}^{2-}$ has to be imputed to a sufficient delocalization of the negative charge at C(2) by the phenyl group, coupled with the steric hindrance exerted by the latter against the phenyl group potentially shifting. Analogous effects can explain the lack of rearrangement of the other 2-phenyl-1,1-disubstituted indenes, which we had previously investigated.[3c]

Independently of the occurrence of the rearrangement, the final reduction products here obtained retain in all cases the indanyl structure, in agreement with our previous results; besides, no dimerization or fragmentation is observed, at variance with the results of the reduction carried out with alkali metals.[7b] The stereochemistry of the reduction (see Table II) is in good accord with that previously observed in the electrochemical reduction of di- and triphenyl-substituted indenes in the absence of strong proton donors,[3c] where the predominant or exclusive formation of indan isomers having a trans arrangement of the bulky substituents, corresponding to the thermodynamically most stable structures, was imputed to isomerization under the highly basic reaction conditions.

Taken as a whole, the results of the present work and those obtained in THF with Na^{+} as a counterion[7b,c] seem to indicate that the inertness of the radical anions and, conversely, the great

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[15] This is in agreement with the preferential protonation at C(2) of the indenyl radical anions, as well as of the dianions, due to both electronic and thermodynamic factors.[3c,d]

[16] In previous work[3d] we found that protonation at C(2) of the radical anion of 1,3-diphenylindene is faster than protonation at C(2) of the radical anion of 1,3-diphenyl-2-methylindene.

[17] The very fast decay of dianions $\mathbf{1}^{2-}$ and $\mathbf{2}^{2-}$ due to rearrangement and protonation (eq 3 and 15) does not allow them to diffuse far away from the electrode and hence to react with the substrate (comproportionation), the concentration of the latter near to the electrode surface being very low under electrolysis conditions. In the case of indene **2**, for example, the value of $k_3 + k_{15}$, ca. 6×10^{7} s^{-1}, is presumably higher than the value of $k_{-14}[\mathbf{2}]$, k_{-14} being ca. 10^{9} L mol^{-1} s^{-1} and $[\mathbf{2}]$ being lower than 10^{-3} M in the reaction layer close to the electrode surface.

[18] (a) Kiesele, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 254–255. (b) Kiesele, H. *Tetrahedron Lett.* **1981**, *22*, 1097–1100.

[19] In the reduction of tetraphenylethylene it has been shown that the π-character of the original double bond is maintained in the radical anion but destroyed in the dianion. Szwarc, M.; Jagur-Grodzinsky, J. In *Ions and Ion Pairs in Organic Reactions*; Szwarc, M., Ed.; Wiley-Interscience: New York, 1974; Vol. 2, p 99.

[20] Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393–401.

aptitude of the dianions toward rearrangement, observed under both experimental conditions, are not attributable to ion-pairing phenomena but to intrinsic properties of the intermediates themselves.

Experimental Section

Materials. The purification of dimethylformamide (DMF) and tetra-*n*-butylammonium perchlorate (TBAP) was previously described,[21] as well as the activation of alumina.[3c] Phenol (R. P. Carlo Erba) and twice-distilled water were used as proton donors in some experiments.

Melting points are uncorrected. ^{1}H NMR spectra were taken on a Bruker WP 200 SY spectrometer at 200 MHz, with $CDCl_3$ as a solvent; chemical shifts (δ) are given relative to Me_4Si as internal standard. Coupling constants are given in hertz and might refer to peak separations measured directly from the instrument in spectra not of first order. NOE experiments were performed on a Bruker WP 200 SY spectrometer in sealed tubes freed from oxygen by repeated freeze–thaw cycles.

Electrochemical Apparatus and Procedure. Instruments, cell, and electrodes are as previously reported.[3c]

All measurements were carried out in DMF with TBAP 0.1 M; dry conditions were obtained by cycling the solution several times through a column of activated neutral alumina before each experiment; water or phenol was then added to the solution when required.

Homogeneous kinetic runs were carried out by monitoring the decrease of the limiting oxidation current of the radical anions produced by electrolysis, at a fixed potential ca. 250 mV more positive than the reversible potential of the redox couple $\mathrm{Ind}/\mathrm{Ind}^{\bullet-}$.

Exhaustive controlled-potential electrolyses under dry conditions or in the presence of added water were carried out in correspondence either of the first or of the second reduction peak, whereas electrolyses in the presence of phenol were performed at the potential of the single reduction wave. Electrolysis conditions are reported in Table II. Workup of electrolyzed solutions after quenching with acetic acid was carried out as previously described.[3c]

Reagents and Products. 1,1,3-Triphenyl-1*H*-indene (**1**),[4] 2-methyl-1,1,3-triphenyl-1*H*-indene (**2**),[22] and 1,1,2,3-tetraphenyl-1*H*-indene (**3**)[23] were synthesized following literature methods.

The synthesis and characterization of indans **4–6** and **8** are reported below; the synthesis and characterization of 1,2,3-triphenylindans (**7**) have been previously reported.[24]

The assignment of configuration to the isomeric indans was based, unless otherwise stated, on the following features of the ^{1}H NMR spectra of indanyl systems: (i) 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 trans protons;[25] (ii) the different values of the vicinal coupling constant, $J_{2,3}$, for methylene and methine protons, which are smaller for cis than for trans configurations;[25b] (iii) the lower values of chemical shift generally observed for H(2) with respect to H(1) and H(3);[3c,d,24] (iv) the shielding effect exerted by one or two *cis*-phenyl group(s) on a vicinal methyl group.[3c,24]

1,1,3-Triphenylindan (4). Exhaustive electrolysis of **1** in the presence of phenol afforded quantitatively indan **4**, which was identified by comparison with an authentic sample synthesized by a literature method.[26] ^{1}H NMR (AMX system): δ 2.93 (dd, $J_{AM} = 12.7$, $J_{AX} = 10.5$, 1 H, H-2 trans to H-3), 3.23 (dd, $J_{AM} = 12.7$, $J_{MX} = 6.3$, 1 H, H-2 cis to H-3), 4.20 (dd, $J_{MX} = 6.3$, $J_{AX} = 10.5$, 1 H, H-3), 6.7–7.5 (m, 19 H, aromatic).

(*E*)- and (*Z*)-2-Methyl-1,1,3-triphenylindans (5). The (*E*) isomer was isolated from the reaction mixture of the macroscale electrolysis of **2** in the presence of phenol by fractional recrystallization from light petroleum; mp 142 °C. Anal. ($C_{28}H_{24}$) C, H. ^{1}H NMR: δ 0.85 (d, $J_{\text{H-2,Me}} = 7.0$, 3 H, methyl), 3.3–3.5 (m, 1 H, H-2), 3.67 (d, $J_{2,3} = 11.0$, 1 H, H-3), 6.6–7.5 (m, 19 H, aromatic).

The (*Z*) isomer, formed in small amount together with the (*E*) isomer in the above macroscale electrolysis of **2**, was identified by comparison with an authentic sample independently synthesized as follows. Catalytic hydrogenation of **2** (0.5 mmol) in light petroleum (30 mL) in the presence of 10% Pd supported on charcoal (20 mg), at 50 atm and 27 °C for 117 h, afforded pure (*Z*)-**5** isomer (82% yield), which was purified by recrystallization from light petroleum; mp 167 °C. Anal. ($C_{28}H_{24}$) C, H. ^{1}H NMR: δ 0.25 (d, $J_{\text{H-2,Me}} = 7.3$, 3 H, methyl), 3.4–3.6 (m, 1 H, H-2), 4.76 (d, $J_{2,3} = 6.4$, 1 H, H-3), 7.1–7.7 (m, 19 H, aromatic).

The assignment of configuration to (*E*)- and (*Z*)-**5** was confirmed by NOE experiments.

(*E*)- and (*Z*)-1,1,2,3-Tetraphenylindans (6). These products were obtained in ca. a 1:1 ratio in the macroscale electrolysis of **3** and identified on the basis of the ^{1}H NMR spectrum of their mixture and by comparison with data reported by Kiesele.[7b] ^{1}H NMR: [(*E*)-**6**] δ 4.52 (d, $J_{2,3} = 11.3$, 1 H, H-2), 4.91 (d, $J_{2,3} = 11.3$, 1 H, H-3), 6.3–7.8 (m, 24 H, aromatic); [(*Z*)-**6**] δ 4.70 (d, $J_{2,3} = 6.7$, 1 H, H-2), 5.08 (d, $J_{2,3} = 6.7$, 1 H, H-3), 6.3–7.8 (m, 24 H, aromatic).

(*E*,*E*)- and (*Z*,*Z*)-2-Methyl-1,2,3-triphenylindans (8). These products were obtained in the macroscale electrolyses of **2**, together with the unrearranged product (*E*)-**5**, in different ratios depending on the electrolysis potential (Table II). No evidence was obtained of the presence in the reaction mixtures of the third isomer of (*E*,*Z*) [or (*Z*,*E*)] configuration. The (*E*,*E*) isomer was separated from the mixture by fractional recrystallization from acetone/ethanol, mp 176–177 °C, and identified on the basis of its ^{1}H NMR spectrum; the (*E*,*E*) configuration was confirmed by a single-crystal X-ray analysis. Anal. ($C_{28}H_{24}$) C, H. ^{1}H NMR: δ 0.68 (s, 3 H, methyl), 5.08 (s, 2 H, H-1 and H-3), 6.8–7.5 (m, 19 H, aromatic).

The (*Z*,*Z*) isomer was not obtained in pure form and was therefore identified on the basis of the ^{1}H NMR spectrum of the reaction mixture and by comparison with data reported by Kiesele.[7b]

^{1}H NMR: δ 1.88 (s, 3 H, methyl), 4.68 (s, 2 H, H-1 and H-3), 6.6–7.5 (m, 19 H, aromatic).

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Registry No. 1, 4614-01-1; **2**, 117438-34-3; **3**, 117438-35-4; **4**, 73010-42-1; (*E*)-**5**, 117438-36-5; (*Z*)-**5**, 117438-37-6; (*E*)-**6**, 117438-38-7; (*Z*)-**6**, 117438-39-8; (*E*,*E*)-**8**, 117438-40-1; (*Z*,*Z*)-**8**, 117438-41-2; DMF, 68-12-2; Hg, 7439-97-6; phenol, 2396-01-2.

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