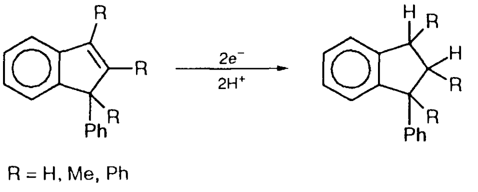
Reactivity of Unsaturated Substrates under Reductive Electron Transfer Conditions. Part 1. Reduction of 1,2,3-Triphenyl-1*H*-indene with Sodium Metal in Various Solvents

Stefano Gotta,[a] **Mauro Marchetti,**[a] **Mario Branca**[b] **and Giovanni Melloni***[,b]
[a] *Istituto CNR per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, Via Vienna 2, I-07100 Sassari, Italy*
[b] *Dipartimento di Chimica, Università di Sassari, Via Vienna 2, I-07100 Sassari, Italy*

The reduction of 1,2,3-triphenyl-1*H*-indene **1** with sodium metal in various solvents was carried out in order to compare the results with those previously obtained in the electrochemical reduction of **1** (Hg cathode, dimethylformamide, $Bu_4N^+ClO_4^-$ as supporting electrolyte). The most general reaction observed was reduction of the double bond of the pentatomic cycle to afford the corresponding indanes of different configurations. In two cases (1,2-dimethoxyethane, dioxane) this reaction was accompanied by reduction of the C(1)–H bond of **1** with formation of the corresponding anion and hydrogen. No rearrangement or cleavage of groups was observed. In a protic solvent (pentan-1-ol) the results are consistent with a reduction process occurring *via* protonation of the radical anion of **1**, affording quantitatively the isomeric indanes with a slight preference for those of *cis*-configuration around the C(2)–C(3) bond. In liquid ammonia, in contrast, the results are indicative of a reduction process occurring *via* protonation of dianionic species, leading to the almost exclusive formation of indanes of *trans*-configuration around the C(2)–C(3) bond. The self-protonation reaction, which is the characteristic process of reduction of **1** under electrochemical conditions in the absence of specific proton donors, was found to be followed only in the case of tetrahydrofuran, where a pseudo-unimolecular decay of a paramagnetic species, likely the radical anion of **1**, could be followed in an EPR cavity.

The behaviour of aromatic compounds containing a condensed cyclopentadienyl ring, *i.e.*, indenes and fluorenes, toward electron transfer reduction has received attention in the literature for some sixty years.[1] The interest has been mainly focused either on the cleavage of the acidic carbon–hydrogen bond(s) leading to formation of the corresponding anion with evolution of hydrogen[2–5] or on the rearrangement or cleavage of groups bonded to the 1-position of indenes[3,6–8] or to the 9-position of fluorenes.[9] In a recent series of papers, one of us has reported the study of the correlation between mechanisms and stereochemistry of the electrochemical reduction of phenyl-substituted indenes;[10–12] under the conditions exploited [Hg cathode, dimethylformamide (DMF), tetrabutylammonium perchlorate as supporting electrolyte] all the indenes underwent exclusive two-electron two-proton reduction at the double bond of the five-membered ring to afford the corresponding indanes (Scheme 1). The sophisticated electrochemical techniques allowed elucidation of the mechanisms of reduction with different indenyl substrates under a variety of conditions; the cyclic structure of the indane products permitted easy assignment of their configuration.[13]



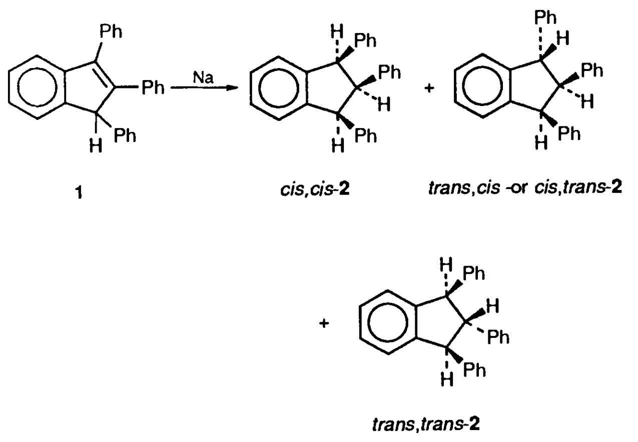
Scheme 1

Two main processes were shown to occur,[10,11] depending on the presence of more or less acidic proton donors. In the presence of strong proton donors the reduction occurred *via* protonation of the radical anion generated in the first electron transfer and led to the preferential formation of the thermodynamically less stable reduction product(s), *i.e.*, indanes with a *cis* configuration around the C(2)–C(3) bond; as a particular case, in the absence of specific proton donors the occurrence of a self-protonation process *via* radical anion was observed with indenes bearing an acidic hydrogen at C(1). In the presence of weak proton donors the reduction occurred *via* protonation of the dianion formed by disproportionation of the radical anion and led to the exclusive formation of the thermodynamically more stable reduction product(s), *i.e.*, indanes with a *trans* configuration around the C(2)–C(3) bond.

As an extension of this work, we have undertaken the study of the reduction of indenyl substrates with alkali metals, feeling that comparison or combination of the information obtained both by electrochemical and 'chemical' means could be useful for a better understanding of reductive electron transfer processes at carbon–carbon double bonds. The usefulness of combining the opportunities of these two methods in order better to understand the mechanisms of electron transfer reactions has been discussed in a recent authoritative review.[14] We refer here to the results obtained in the study of the reduction with sodium metal of a typical self-protonating substrate, namely 1,2,3-triphenyl-1*H*-indene **1**.

Results

The reactions were carried out by allowing to react, with efficient stirring, *ca.* 0.1 mol dm^{-3} solutions of **1** in anhydrous, freshly distilled solvents with a large excess of sodium metal under argon. For the reactions in aprotic or non-dissolving-metal solvents the metal was added in one or two pieces, after it was realised that its form had practically no influence on the reaction. After standard work-up, the significant reaction products, which consisted of 1,2,3-triphenylindanes **2** (Scheme 2) and of unchanged **1**, were isolated by flash chromatography on silica gel and their ratio determined by ^1H NMR



Scheme 2

spectroscopy. The configuration of the three isomeric indanes was assigned by ^{1}H NMR in a previous study.[13]

Reduction in Protic Solvents.—Two systems were investigated: glacial acetic acid at 25 °C and pentan-1-ol (AmOH) at 25 °C and at reflux (138 °C). In the former solvent only a trace of indanes was formed after 24 h, in the latter quantitative formation of indanes **2** was observed in short reaction times. The results are reported in Table 1.

At variance with the work of Miller and Boyer,[6] who reported the isolation of *cis,cis*-**2*** in 66% yield after 2 h reflux in pentan-1-ol, under our conditions a mixture of all three isomers of **2** was obtained in different ratios depending on the reaction temperature, with a slight preference for the *cis,cis*-isomer.

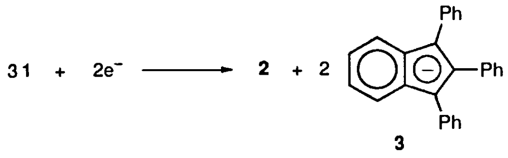
Reduction in Solvents of Very Low Polarity.—Two solvents were used: tributylamine (TBA) and 2,4,4-trimethylpentane (isooctane) at 25 °C; under these conditions, however, the solubility of **1** in both solvents was very poor. Very low conversion into indanes was observed in 24 h (Table 1). Slow evolution of a gas (hydrogen?) was observed.

Reduction in Polar Aprotic Solvents and in Liquid Ammonia.—It is known that DMF is not stable to alkali metals;[15] a study of its reactivity toward sodium metal in liquid ammonia has been reported.[16] Nevertheless, owing to the obvious importance of a direct comparison with the reduction under electrochemical conditions, a preliminary test was carried out. However, **1** was recovered unchanged after 24 h reaction at room temperature;† no evolution of hydrogen was noticed. An identical result was obtained with hexamethylphosphoric triamide (HMPA) as the solvent.

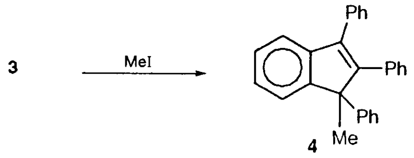
In liquid ammonia at −33 °C the reduction of **1** was complete in *ca.* 1 h; a mixture (*ca.* 32:1) of *trans,trans*- and *trans,cis*-**2** in almost quantitative yield was obtained (Table 1).

Reduction in Ethereal Solvents.—Four different ethers were used: tetrahydrofuran (THF), 1,2-dimethoxyethane (DME), dioxane and diethyl ether; for comparison purposes, all reactions were carried out at 25 °C for 24 h. The results are reported in Table 1.

The reduction in THF afforded a 2:1 ratio of starting **1** and of a mixture of isomeric **2**. The **1**:**2** ratio did not change after prolonged reaction times. Quenching of the reaction mixture with methyl iodide and formation thereby of 1-methyl-1,2,3-triphenyl-1*H*-indene **4** in 65% yield permitted us to ascertain that indene **1** was present at the end of the reaction as the corresponding anion **3**. This is in agreement with the stoichiometry of a self-protonation reaction,[11,17] in which one-third of the starting indene was reduced and two-thirds acted as proton donors (Schemes 3 and 4).



Scheme 3



Scheme 4

In DME and in dioxane the reduction of **1** occurred only to a small extent, affording **2** in 13 and 18% yield, respectively, after 24 h; the main reaction observed was evolution of hydrogen and concomitant formation of the indenyl anion **3**. The latter was the only species present at the end of the reaction, beside the mixture of **2**, as shown by quenching with methyl iodide according to Scheme 4; the exact amount of hydrogen formed was not measured.

The reduction in Et_2O afforded a mixture of indanes **2** and **3**, as shown on quenching with methyl iodide; however, at variance with the reduction in THF, the **2**:**3** ratio was 1. This ratio did not change after prolonged reaction times. This behaviour is not in agreement either with a self-protonation process (Scheme 3) or with a concomitant reduction of the acidic hydrogen. Indeed, in the latter case **3** should form in a higher amount than was found; accordingly, no evolution of hydrogen was observed.

Poor stereoselectivity was observed in all four solvents, with a preference for the formation of the *trans,trans*-isomer in the reduction in Et_2O (Table 1).

EPR Experiments.—The reductions carried out in ethereal solvents were subjected to EPR investigation, in order to obtain information of the presence of intermediate paramagnetic species,‡ possibly of the radical anion of **1**. For the reactions in DME, dioxane and Et_2O no signal was detected, even at different temperatures and concentrations of reagents. In the case of THF an EPR spectrum was obtained with a solution of **1** (initial concentration 0.01 mol dm^{-3}) in the presence of excess sodium metal at 25 °C (Fig. 1); diluting repeatedly the solution and/or lowering the temperature to −70 °C did not produce appreciable changes. Such a spectrum appeared a few min after contact of the solution of **1** with the sodium metal and reached its maximum intensity *ca.* 1 h after mixing. Afterwards, the intensity remained constant for *ca.* 6 h, then slowly decreased;

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* The attribution of the *trans,trans* configuration to this indane isomer reported by Miller and Boyer (ref. 6) proved to be incorrect; see ref. 13 for details.

† Identical behaviour was observed for triphenylethene and *trans*-stilbene, whereas under the same conditions 1,1-diphenylethene afforded a product of insertion of DMF into the carbon–carbon double bond.[15d]

‡ For a thorough discussion of the EPR spectrum of the radical anion of 1,1-dimethylindene see ref. 7.

Table 1 Reduction of **1** with Na metal

Solvent	T/°C	t/h	Total yield of **2** (%)[a,b]	Isomer yield (%)[a,c] (*cis,cis*)-**2**	(*trans,cis*)-**2**[d]	(*trans,trans*)-**2**	Hydrogen evolution
AmOH	25	12	quant.	50	8	42	yes[e]
AmOH	138	1	quant.	40	25	35	yes[e]
AcOH (glac.)	25	24	trace				yes[e]
TBA	25	24	5	80		20	*f*
Isooctane	25	24	2	50		50	*f*
HMPA	25	24	0				no
DMF	25	24	0				no
NH_3 (liq.)	−33	1	98		3	97	no
THF	25	24	33	41	18	41	no
DME	25	24	13	44		56	yes
Dioxane	25	24	18	63	trace	37	yes
Et_2O	25	24	49	27	21	52	no

[a] Average of at least three experiments; reproducibility within 2%. [b] A corresponding amount of unchanged **1**, up to 100%, was also isolated. [c] Determined by integration of the ^{1}H NMR spectrum of the reaction mixture; estimated error *ca.* 2%. [d] Or (*cis,trans*)-**2** (racemic mixture). [e] Reaction of Na metal with the solvent. [f] See text.

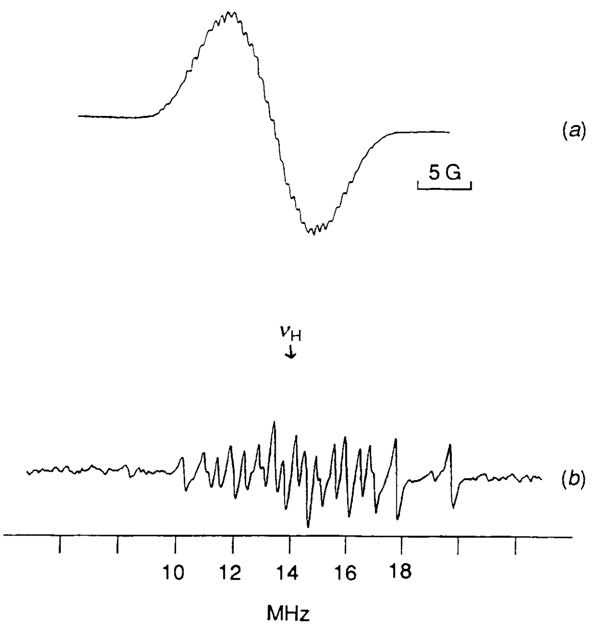


Fig. 1 (*a*) EPR spectrum of $\mathbf{1}^{\bullet -}$ at 25 °C (SW 50 G, CF 3351, db 10); (*b*) ^{1}H ENDOR spectrum at 205 K, hyperfine constant, MHz (G): 0.34 (0.125), 1.18 (0.420), 1.88 (0.673), 2.22 (0.798), 3.20 (1.450), 4.04 (1.850), 5.09 (2.050), 5.71 (2.160), 5.99 (2.300), 7.59 (2.720), 10.17 (3.693), 11.42 (4.092)

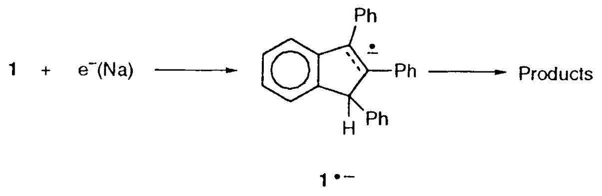
disappearance of the signal occurred after *ca.* 24 h. The poor resolution of the spectrum is likely due to the presence of many non-equivalent protons.

A ^{1}H ENDOR experiment permitted us to determine 12 hyperfine coupling constants, whose values are reported in Fig. 1. Simulation of the EPR spectrum using these constants was successful with various combinations of multiplicity. Therefore, a precise assignment of the coupling constants was impossible. This behaviour, which is characteristic of species having low symmetry and a large number of protons, suggests the presence of the radical anion of **1**. Support for this hypothesis came from the following experiments.

In a preliminary experiment, the reaction was repeatedly checked both by EPR and ^{1}H NMR spectroscopy. This permitted us to observe the simultaneous decay of the paramagnetic species and disappearance of the NMR signal of the proton at C(1) of **1**. In a second experiment, the kinetics of decay of the paramagnetic species was carried out in the EPR cavity at 25 °C. Measurements were obtained shortly after the appearance of the EPR signal, so that **1** was in large excess, thus allowing a pseudo-order treatment. The plot of the values obtained, reported in Fig. 2, showed that the disappearance of the EPR signal followed second-order kinetics, with a pseudo-first-order rate constant of 1.44 × 10^{-2} s^{-1}.

Discussion

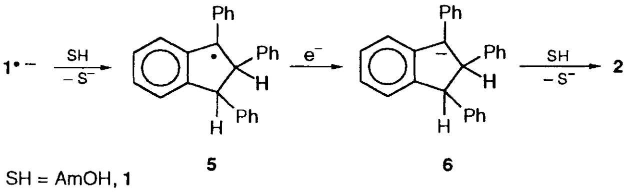
On the basis of the results of this work, the reduction of **1** with sodium metal likely occurs in most cases through the initial formation of the radical anion $\mathbf{1}^{\bullet -}$ (Scheme 5), whose decay to indanes follows different courses depending on the solvent and the reaction conditions.



Scheme 5

In the previous electrochemical work,[10,11] the intermediacy of $\mathbf{1}^{\bullet -}$ was proven by various means; in the present work, on the contrary, proof of formation of $\mathbf{1}^{\bullet -}$ was not equally definite. However, an unambiguous result, such as the self-protonation process observed in THF,* and the results of the spectroscopic experiments, where the simultaneous disappearance of a paramagnetic species and of the starting indene suggests the decay of a radical anion by protonation, provide support for the intermediacy of $\mathbf{1}^{\bullet -}$.

According to this hypothesis, the formation of products **2** in a good proton-donor solvent (reduction in AmOH) or under



Scheme 6

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* A self-protonation process *via* dianion was shown not to occur in the electrochemical reduction of **1** and other acidic hydrocarbons in THF, due to the successful competition by the fast homogeneous electron-transfer process; see ref. 5.

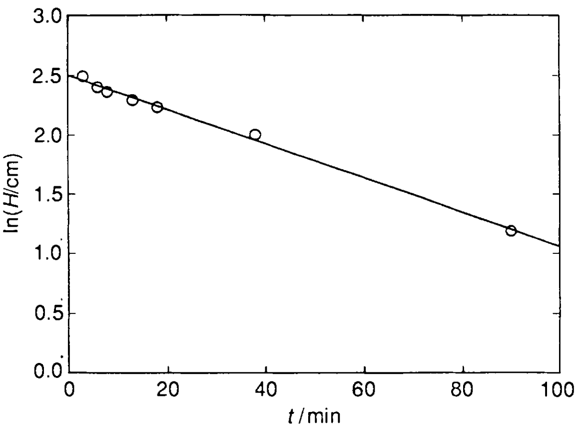


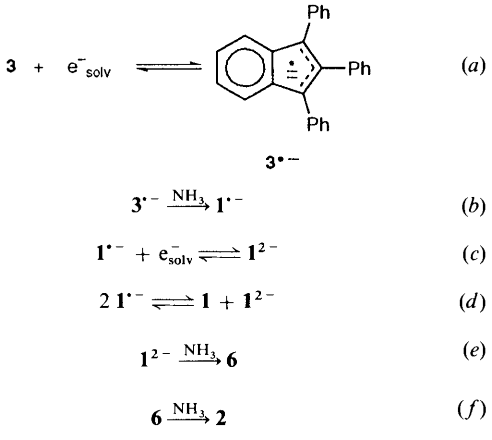
Fig. 2 Time dependence of ln height of the EPR signal: $y = 2.4992 - 0.014\,399\,x$ ($R^2 = 0.996$)

strict self-protonating conditions (reduction in THF) can be rationalised by a mechanistic scheme analogous to that invoked for the electrochemical reduction of **1** in the presence of an added proton-donor[10] or under self-protonating conditions[11] (Scheme 6).

In the electrochemical reduction of **1** in DMF this process led to exclusive (in the presence of phenol) or predominant (in case of self-protonation) formation of *cis,cis*-**2**, with high *syn* stereoselectivity.[10,11] The poor stereoselectivity observed in the present work (see Table 1) can be explained as follows. Under the present reaction conditions the intermediates undergoing protonation, namely $\mathbf{1}^{\bullet -}$ and **6**, exist as ion pairs with the sodium cation. The structure of such ion pairs strictly depends on the solvent and likely leads to conformational equilibria different from those existing in DMF with Bu_4N^+ as a counterion; the direction, as well as the rate, of attack of the proton donor is therefore affected in a different way. Indeed in AmOH, where protonation should be a fast process, a slight *syn* stereoselectivity was observed.

The mechanisms shown in Scheme 6, valid for a good proton donor (SH), do not seem to operate in the case of the reduction in liquid ammonia, where either **1** and the eventually formed anion **3** are quantitatively reduced to **2**. In principle, liquid ammonia may act as a proton donor; it is well known, however, that, owing to its low acidity ($pK_a = 34$), it may protonate only highly basic species.[18] It should not be able, therefore, to protonate either the indenyl anion **3**, which is the conjugated base of a quite acidic hydrocarbon* or the radical anion $\mathbf{1}^{\bullet -}$, which was shown in previous work to be weakly basic (at least in DMF);[10,11] on the other hand, ammonia should be able to protonate the anion **6**, whose basicity may be considered similar to that of a diphenylmethyl anion. Nevertheless, the almost complete reduction of **1** to **2** clearly indicates that ammonia furnishes the two protons necessary to the completion of the reduction process. These facts suggest that the reduction occurs through the formation of highly basic dianionic species, such as $\mathbf{3}^{\bullet -}$ [Scheme 7(*a*)] and $\mathbf{1}^{2-}$ [Scheme 7(*c*) and (*d*)]. Protonation of $\mathbf{3}^{\bullet -}$ and $\mathbf{1}^{2-}$ by ammonia affords the radical anion of **1** [Scheme 7(*b*)] and the indanyl anion **6** [Scheme 7(*e*)], respectively; the latter is subsequently protonated to **2** [Scheme 7(*f*)].

Formation of dianionic species may be possible owing to the homogeneous electron transfer conditions and the highly negative potential of the solvated electron in liquid ammonia.[18,20] Examples of radical dianions of cyclopentadienylic hydrocarbons are reported in the literature.[21] Support for this hypothesis is given by the almost exclusive *anti* stereoselectivity



$$\mathbf{3}^{\bullet -} \xrightarrow{NH_3} \mathbf{1}^{\bullet -} \qquad (b)$$

$$\mathbf{1}^{\bullet -} + e^-_{solv} \rightleftharpoons \mathbf{1}^{2-} \qquad (c)$$

$$2\,\mathbf{1}^{\bullet -} \rightleftharpoons \mathbf{1} + \mathbf{1}^{2-} \qquad (d)$$

$$\mathbf{1}^{2-} \xrightarrow{NH_3} \mathbf{6} \qquad (e)$$

$$\mathbf{6} \xrightarrow{NH_3} \mathbf{2} \qquad (f)$$

Scheme 7

observed, which is the peculiar behaviour of the reduction of phenyl-substituted indenes occurring *via* dianion.[10]

The results of the reduction of **1** in Et_2O appear somewhat puzzling and of difficult rationalisation. At first sight they would seem the outcome of a disproportionation reaction, occurring by protonation during the quenching,[10] of a quantitatively formed radical anion $\mathbf{1}^{\bullet -}$, leading to **1** and **2** in a 1:1 ratio (Scheme 8).

$$2\,\mathbf{1}^{\bullet -} \xrightarrow{\text{SH (quenching)}} \mathbf{2} + \mathbf{1}$$

Scheme 8

This is ruled out by the quenching experiments, which showed that the products of the reaction before quenching were equal amounts of indenyl anion **3** and of indanes **2**. Furthermore, the EPR experiments showed that no radical species were present in appreciable concentration during the reaction. At the present stage of the research we cannot offer a definite rationale for this result. However, the partial *anti* stereoselectivity observed suggests the presence of the dianion $\mathbf{1}^{2-}$, whose formation in Et_2O may be favoured by the occurrence of tight ion pairs.[22]

A last comment must be given to the reactions occurring with a low conversion of **1** into **2**, such as the reactions in dioxane, DME and in solvents of very low polarity. In the last case the results obtained should be related to poor solubility of **1** and/or to a generally low reactivity. In contrast, in the case of dioxane and DME, the reduction to indanes is accompanied by hydrogen evolution. The results of these reactions, therefore, can be rationalised in terms of a competition between reduction at the double bond of **1** to afford indanes and reduction at the acidic hydrogen at C(1) to afford the indenyl anion **3**. Since the latter reaction was secondary compared with the whole of our results, it was not studied in detail. Indeed, such reaction is well known and has been used in several cases for synthetic purposes;[2,3] its mechanism for cyclopentadienyl substrates, however, has been much debated but still remains obscure.[4,5,17] According to a mechanistic proposal advanced for the reduction of the parent indene,[3,4] hydrogen gas could be formed by loss of a hydrogen atom at C(1) from the π-radical anion, affording directly the indenyl anion. In the case of **1** this process would correspond to Scheme 9.

$$\mathbf{1}^{\bullet -} \longrightarrow \mathbf{3} + H^{\bullet}(H_2\uparrow)$$

Scheme 9

According to this interesting hypothesis the competition observed in the reductions in DME and dioxane would

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* The reported pK_a values of **1** are: DME, 17.8;[19a] Me_2SO, 15.2.[19b]

correspond to two different modes of decay of the same radical anion intermediate. The reason(s) why this competition is so much solvent-dependent remains, however, open to question.

Experimental

^1H NMR (300 MHz) spectra of $CDCl_3$ solutions were recorded using a Varian VXR 300s spectrometer. The chemical shifts are reported in ppm downfield from internal Me_4Si; *J*-Values are given in Hz. EPR and ^1H ENDOR spectra were recorded using a Bruker 220 D-SRC spectrometer equipped with a 300 W rf power amplifier and controlled by an Aspect 2000 computer. The temperature of the sample was controlled by means of a Bruker VT 4111 variable temperature unit.

Materials.—All products and reagents were of the highest commercial quality and were further purified by distillation or recrystallisation. AmOH was distilled from Na under argon. Ethereal solvents and isooctane were carefully dried over Na or $LiAlH_4$ according to standard procedures and distilled under argon into the reaction vessel immediately prior to use. TBA was distilled over KOH pellets under vacuum and redistilled from $LiAlH_4$. DMF was purified as previously described.[10] Liquid NH_3 was first distilled over Na and redistilled into the reaction vessel from sodium benzophenone ketyl. Hexamethylphosphoramide (HMPA) (**CAUTION**: carcinogenic agent)[23] was purified according to a standard procedure.[24] 1,2,3-Triphenyl-1*H*-indene **1** and 1-methyl-1,2,3-triphenyl-1*H*-indene **4** were prepared as previously described.[10] The characterisation of isomeric 1,2,3-triphenylindanes **2** was reported previously.[13]

EPR Measurements.—For the EPR and ^1H ENDOR measurements the paramagnetic species were generated by treatment of **1** with Na metal in the appropriate solvent in a high vacuum line using a standard technique.[25] The ^1H ENDOR experiment was carried at 205 K, using mw power = 30 mW, rf power at 14 MHz = 100W and md = 100 KHz.

General Procedure for the Reduction of **1**.—To a solution of **1** (0.3 g, 0.87 mmol) in the appropriate dry solvent (20 cm^3) under argon was added the freshly cut Na metal (0.6 g, 0.026 mol) in one or a few pieces, and the mixture was stirred in the presence of sharp glass fragments at the temperature and for the time indicated in Table 1. At the end of the pre-determined time, the mixture was chilled to 0 °C and quenched by slow dropwise addition of glacial acetic acid (5 cm^3) with stirring (**CAUTION**!). After a few minutes stirring, water was added and the resulting mixture was worked up following standard procedures. In the case of non-dissolving-metal solvents the excess of Na was removed mechanically before quenching; in the case of dissolving-metal solvents the quenching was carried out with water (**CAUTION**!). In the case of liquid NH_3, the ammonia was evaporated to dryness under argon and the reaction mixture quenched by dropwise addition of saturated NH_4OH, followed by addition of water (**CAUTION**!). After evaporation of the solvent, the crude reaction mixture was checked by ^1H NMR and then flash-chromatographed on silica (230–400 mesh) with light petroleum (b.p. 40–60 °C)–Et_2O (9:1) as the eluent. Yields were calculated by weight.

In the case of the reductions in Et_2O and THF the quenching with MeI was performed by adding dropwise a large excess of MeI (11.4 g, 80 mmol) to the reaction mixture at room temperature after removal of the excess metal; after 2 h stirring, work-up was performed as reported above.

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