

Indirect Electrochemical Reduction of Vinyl Halides and Related Compounds

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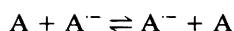
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Gatti, N., Jugelt, W. and Lund, H., 1987. Indirect Electrochemical Reduction of Vinyl Halides and Related Compounds. – Acta Chem. Scand., Ser. B41: 646–652.

Some substituted vinyl halides and related compounds have been reduced indirectly by electrolysis using anion radicals as mediators. The rate of the electron transfer from the electron donors to the electron acceptors has been measured by cyclic voltammetry, and the solvent and bond reorganization energy, λ , has been extracted from the data using the Marcus equation. The λ values for the vinyl and cyclopropyl halides were found to be closer to those for aryl halides than those for alkyl halides. The method was used preparatively for selective dehalogenation of vinyl halides, including derivatives of 10-bromo-5*H*-dibenz[*b,f*]azepine.

The indirect reduction of alkyl halides,^{1a,2} benzyl halides^{1b} and vicinal dihalides^{1c} has been reported previously, and the rate of electron transfer from the electron donors to the substrates was measured by electroanalytical methods.³ Aromatic and heteroaromatic anion radicals, together with dianions of dihydroaromatic compounds and certain anions, were used as electron donors; it was shown that the rate-determining step in some of the nucleophilic substitution reactions of the dianions and anions with sterically hindered alkyl and benzyl halides was the transfer of an electron, more specifically an outer-sphere electron transfer, and that the reduction of some vicinal dihalides by an enolate ion also involved an outer-sphere electron transfer.

These results have been discussed in terms of the Marcus theory for electron transfer; the use of the Marcus equation in organic chemistry has been discussed recently.⁴ According to the Marcus theory, the free energy of activation in an electron transfer depends on, among other parameters, the solvent and bond reorganization energy λ . In the above-mentioned investigation it was found that the solvent and bond reorganization energy $\lambda(0)$ for the self-exchange reaction

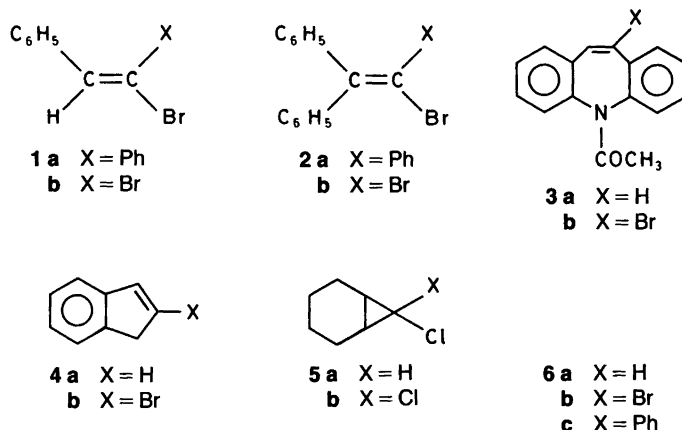


for alkyl and benzyl halides varied somewhat, but in all cases $\lambda(0)$ was >100 kcal mol⁻¹. $\lambda(0)$ was calculated from the solvent and bond reorganization energy, λ , for the reaction between an aromatic anion radical and the halide by assuming $\lambda'(0)$ for the aromatic compounds to be 10 kcal mol⁻¹. A $\lambda(0)$ value of >100 kcal mol⁻¹ was taken as evidence for considerable stretching of the C–X bond in the transition state of the electron transfer reaction, i.e. dissociative ET.

Vinyl and cyclopropyl halides have, in some respects, properties which place them between aryl and alkyl halides. Some aryl-substituted vinyl bromides have previously been investigated by electrolysis and polarography in *N,N*-dimethylformamide (DMF), and addition of an electron to the π -electron system was suggested as the primary step;⁵ fast loss of bromide ion and transfer of a second electron followed by uptake of a proton from solvent gave the product.

The stereochemical outcome of the reduction in DMF of (*Z*)- and (*E*)-3-iodo-3-hexenes has been studied;⁶ it was found that (*E*)-3-hexene was the major product obtained from both compounds, although it was formed in higher yield from the (*Z*) compound than from the (*E*)

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Scheme 1.

isomer. The stereochemical results were independent of addition of phenol, which was suggested as indicating that isomerization takes place in the vinyl radical rather than in the vinyl anion. The difference in yield of (*E*)-3-hexene obtained from the two iodohexenes could be explained by assuming comparable rates for the second electron transfer and the isomerization. Similar isomerization has been observed in the reduction of bromomaleic acid in aqueous solution.⁷

An indirect electrochemical reduction can often compare favourably with a direct one with respect to selectivity and/or current density; an investigation of the indirect reduction of vinyl halides and related compounds was therefore made using preparative electrolysis and cyclic voltammetry (CV). The latter data were used for calculation of the rate of the electron transfer from the mediator to the halide and of the solvent and bond reorganization energy, λ , associated with this reaction.

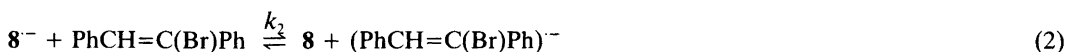
The following compounds were investigated: (*E*)-1-bromo-1,2-diphenylethene (**1a**), 2,2-dibromo-1-phenylethene (**1b**), 2-bromo-1,1,2-triphenylethene (**2a**), 2,2-dibromo-1,1-diphenylethene (**2b**), 5-acetyl-10-bromo-5*H*-dibenz[*b,f*]azepine (**3b**), 2-bromoindene (**4b**), 7,7-dichlorobicyclo[4.1.0]heptane (**5b**), 2-bromophenylacetylene (**6b**) and 1,1-dichloroethane (**7**).

ene (**2b**), 5-acetyl-10-bromo-5*H*-dibenz[*b,f*]azepine (**3b**), 2-bromoindene (**4b**), 7,7-dichlorobicyclo[4.1.0]heptane (**5b**), 2-bromophenylacetylene (**6b**) and 1,1-dichloroethane (**7**).

Results and discussion

(*E*)-1-Bromo-1,2-diphenylethene (**1a**; $E_p = -1.33$ V vs. Ag/AgI at $\nu = 0.4$ Vs⁻¹) was studied by CV, and measurements of the rate of the electron transfer from a number of aromatic anion radicals to **1a** were attempted using the technique employed previously.^{1,3} According to this the ratio of the anodic peak current i_p^a to the cathodic peak current i_p^c was measured for different ratios of the concentrations of **1a** and the mediator, and the results were compared with simulated values. However, no consistent rate constants could be extracted from the measured data by employing the usual treatment,^{1,3} and a kinetic complication was therefore suspected.

Preparative indirect reduction of **1a** using dimethyl terephthalate (**8**) as mediator yielded a mixture of equal amounts of stilbene (*trans* + *cis*) (**9**) and diphenylacetylene (**6c**). These products are proposed to be formed through the sequence



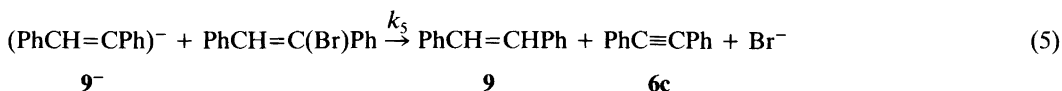


Table 1. Rate constants (k_{SET}) and free energies of activation (ΔG^\ddagger) for electron transfer from electrochemically generated anion radicals (A^-) to some vinyl halides (BX) and related compounds in DMF/0.1 M TBABF₄ measured by cyclic voltammetry; reference electrode Ag/AgI, 0.1 M I⁻. $T = 25^\circ\text{C}$.

BX	A	$-E_A/\text{V}$	$k_{\text{SET}}/\text{M}^{-1} \text{ s}^{-1}$	$\log k_{\text{SET}}$	$\Delta G^\ddagger/\text{kcal mol}^{-1}$
2a	Azobenzene	0.879	18.8	1.27	13.3
	4-Benzoylpyridine	0.976	582	2.76	11.2
	2,4'-Dimethoxyazobenzene	0.991	529	2.72	11.3
	1,4-Diacetylbenzene	1.006	1.64×10^3	3.21	10.6
	Tetracene	1.097	2.94×10^4	4.46	8.9
	Dimethyl terephthalate	1.191	8.46×10^4	4.93	8.3
	Quinoxaline	1.200	2.38×10^5	5.38	7.7
2b	2-Chloroazobenzene	0.735	7.4	0.87	13.8
	4-Chloroazobenzene	0.783	66	1.82	12.5
	4-Nitroanisole	0.786	68	1.83	12.5
	Azobenzene	0.879	265	2.42	11.7
	2-Methoxyazobenzene	0.898	442	2.65	11.4
	2-Methoxyazobenzene	0.898	5.4	0.73	14.0
3b	4-Benzoylpyridine	0.976	150	2.18	12.0
	2,4'-Dimethoxyazobenzene	0.991	2.1×10^2	2.32	11.8
	1,4-Diacetylbenzene	1.006	2.9×10^2	2.46	11.6
	Tetracene	1.097	6.5×10^3	3.81	9.8
	Acenaphthylene	1.189	8.3×10^4	4.92	8.3
	Dimethyl terephthalate	1.191	7.9×10^4	4.90	8.3
	Quinoxaline	1.200	5.1×10^4	4.71	8.6
4b	9,10-Diphenylanthracene	1.404	9.3	0.97	13.7
	Anthracene	1.488	143	2.16	12.1
	Pyrene	1.618	1.16×10^3	3.07	10.8
	Tetraphenylethene	1.652	3.37×10^3	3.53	10.2
	Methyl benzoate	1.777	4.1×10^4	4.61	8.7
6b	Anthraquinone	0.400	92	1.96	12.3
	2,2'-Azopyridine	0.532	291	2.46	11.7
	2-Methoxycarbonylazobenzene	0.611	299	2.48	11.6
	Nitrobenzene	0.688	614	2.79	11.2
	2-(Trifluoromethyl)-azobenzene	0.702	974	2.99	10.9
	4-Chloroazobenzene	0.783	1.5×10^3	3.18	10.7
5b	Tetraphenylethene	1.652	29	1.47	13.0
	4-Methoxyacetophenone	1.737	5×10^2	2.69	11.3
	Methyl benzoate	1.777	1.2×10^3	3.08	10.8
	Chrysene	1.813	3.5×10^3	3.54	10.2
	Diphenylacetylene	1.854	1.0×10^4	4.01	9.5
	Phenanthrene	1.999	1.6×10^5	5.21	7.9
	7	Benzophenone	1.320	13	1.11
7	9,10-Diphenylanthracene	1.404	61	1.78	12.6
	Anthracene	1.488	2.7×10^2	2.44	11.7
	Pyrene	1.618	1.16×10^3	3.05	10.8
	Methyl benzoate	1.777	1.29×10^4	4.11	9.4
	Chrysene	1.813	2.64×10^4	4.42	9.0
	Diphenylacetylene	1.854	5.45×10^4	4.72	8.5

of reactions shown in Scheme 1. The kinetic complication in the cyclic voltammetric determination of k_2 is thus probably the elimination of hydrogen bromide from the substrate **1a** by the stilbene carbanion 9^- . Preliminary data⁸ obtained using LSV suggest that the rate of elimination (k_3) is high compared to k_2 .

Addition of water or phenol (as proton donors) to the catholyte in the preparative reduction of **1a** suppressed the formation of **6c** partially (H_2O) or nearly completely ($PhOH$) and increased the yield of **9**. It is interesting that the rate of elimination (k_3) is so high that a significant amount of the substrate diffusing toward the electrode is intercepted by and reacts with 9^- before it reaches the electrode.

2,2-Dibromo-1-phenylethene (**1b**; $E_p = -1.05$ V vs. Ag/AgI at $\nu = 0.4$ Vs^{-1}) behaved similarly. In the absence of a proton donor, an elimination reaction analogous to that of eqn. (5) took place during the indirect reduction and the electron consumption rose to about $3 F mol^{-1}$, the products being (*Z*)-2-bromostyrene and phenylacetylene (**6a**); 2-bromo-1-phenylacetylene (**6b**) could be detected as an intermediate. **6b** ($E_p = -0.84$ V vs Ag/AgI at $\nu = 0.4$ Vs^{-1}) is more easily reduced than **1b** and is thus reduced further during the reaction; data for the electron transfer from mediators to **6b** are given in Table 1.

In vinyl bromides having no β -hydrogens the reduction was not complicated by an elimination, the products being the debrominated compounds. Indirect reduction of 2-bromo-1,1,2-triphenylethene (**2a**; $E_p = -1.35$ V vs. Ag/AgI at $\nu = 0.4$ Vs^{-1}) with quinoxaline as mediator gave 1,1,2-triphenylethene, and 2,2-dibromo-1,1-diphenylethene (**2b**; $E_p = -1.11$ V vs. Ag/AgI at $\nu = 0.4$ Vs^{-1}) was reduced to 2-bromo-1,1-diphenylethene using azobenzene as mediator. The rate constants, determined by CV, for the electron transfer from a number of mediators to **2a** and **2b** are given in Table 1. The values for **2b**

may be somewhat uncertain as the direct reduction of **2b** may have interfered slightly with the curves of the mediators having the most negative redox potentials. The cleavage of the carbon-halogen bond is considered fast compared to the electron transfer from A'^- to BX for the following reasons: firstly, it has not been possible to see any reversibility in CV at 10^3 Vs^{-1} for any of the compounds **1-7**; secondly, reduction of 2-bromo-2-nitrostyrene becomes reversible at 10^2 Vs^{-1} ; thirdly, cleavage of an anion radical of a halogen compound becomes faster the more negative the reduction potential. The compounds investigated here are reduced at potentials 0.8 V or more negative than that for 2-bromo-2-nitrostyrene.

In the case of 5-acetyl-10-bromo-5*H*-dibenz[*b,f*]azepine (**3b**; $E_p = -1.29$ V vs. Ag/AgI at $\nu = 0.4$ Vs^{-1}), no complications were found due to base-induced elimination of hydrogen bromide, although it has a β -hydrogen; the steric strain involved in introducing a triple bond into the seven-membered ring excludes that possibility. Under preparative conditions, however, a certain degree of base-induced cleavage of the *N*-acetyl groups was observed; this can be prevented by carrying out the indirect reduction in the presence of a proton donor with a suitable pK_a value, so that it protonates the anion of **3a** but not the anion radical of the mediator. Diethyl malonate is suitable for this purpose. [Eqn. (6)].

Indirect electrochemical reduction is a convenient way of reducing **3b** rapidly and completely in a mixture of **3a** and **3b**, and the method could presumably be used in a number of similar cases by employing a suitable mediator and proton donor.

The rates of reaction between **3b** and some anion radicals are given in Table 1. Quinoxaline reacts with **3b** with electron transfer rate constant $k_2 = 5 \times 10^4$ $M^{-1} s^{-1}$, which indicates that quinoxaline is very suitable as mediator for this reduction. Furthermore, the basic properties of quin-

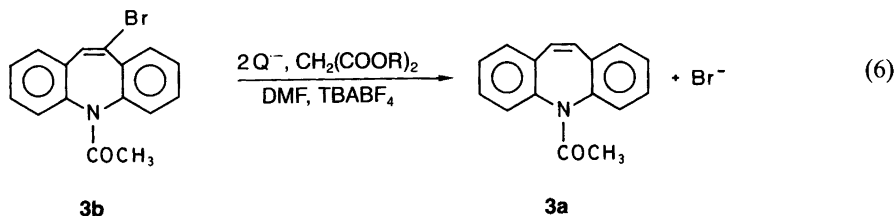


Table 2. Calculated $\lambda(0)$ values, E_p at 400 mV s⁻¹ and calculated E° values (V vs. Ag/AgI, 0.1 M I⁻) for 2-bromo-1,1,2-triphenylethene (**2a**), 5-acetyl-10-bromo-5*H*-dibenz[*b,f*]azepine (**3b**), 2-bromoindene (**4b**), 7,7-dichlorobicyclo[4.1.0]heptane (**5b**) and 1,1-dichloroethane (**7**).

BX	E_p/V	E°/V	$\lambda/kcal\ mol^{-1}$	$\lambda(0)^{BX}/kcal\ mol^{-1}$
2a	-1.35	-1.43	19	28
3b	-1.29	-1.48	17	24
4b	-2.11	-1.77	35	61
5b	<-2.3	-2.12	25	40
7	<-2.3	-0.87	73	135

oxaline make it easy to separate it from **3a**; **3a** is not reduced by quinoxaline anion radical.

The rates of reaction between 2-bromoindene (**4b**; $E_p = -2.11$ V vs. Ag/AgI at $\nu = 0.4$ Vs⁻¹) and some anion radicals are included in Table 1; 1-bromoacacenaphthylene (**1**; $E_p = -1.0$ V vs. Ag/AgI at $\nu = 0.4$ Vs⁻¹) was investigated in the same manner, but the reaction between **10** and anion radicals with redox potentials a little less negative than E_p of **10** was too slow to give useful results in CV.

The bonds in a cyclopropane ring bear some resemblance to π -bonds, and halogen-substituted cyclopropanes might therefore show electro-

chemical characteristics similar to those of vinyl halides; for this reason 7,7-dichlorobicyclo[4.1.0]heptane (**5b**) was included in the investigation. Indirect electrochemical reduction of **5b** using phenanthrene as mediator gave a 2:1 mixture of *cis* and *trans* 7-chlorobicyclo[4.1.0]heptane (**5a**). The rates of reaction between **5b** and a series of mediators are given in Table 1 together with similar data for 1,1-dichloroethane (**7**).

The data in Table 1 can, in principle, be used to extract E° for the compounds, and the solvent and bond reorganization energies (λ) for the electron transfer between mediator and substrate, if the validity of the Marcus equation is accepted

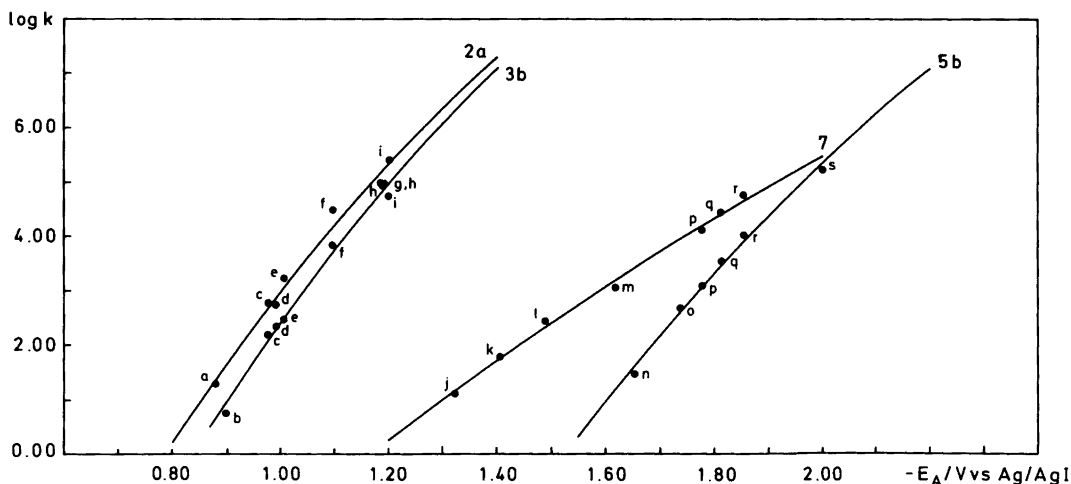


Fig. 1. Dependence of rate constants M⁻¹ s⁻¹ for the reaction between different anion radicals (A⁻) and 2-bromo-1,1,2-triphenylethene (**2a**), 5-acetyl-10-bromo-5*H*-dibenz[*b,f*]azepine (**3b**), 7,7-dichlorobicyclo[4.1.0]heptane (**5b**) and 1,1-dichloroethane (**7**) on the redox potential of the A-compound. A-compounds: a, azobenzene; b, 2-methoxyazobenzene; c, 4-benzoylpyridine; d, 2,4'-dimethoxyazobenzene; e, 1,4-diacetylbenzene; f, tetracene; g, acenaphthylene; h, dimethyl terephthalate; i, quinoxaline; j, benzophenone; k, 9,10-diphenylanthracene; l, anthracene; m, pyrene; n, tetraphenylethene; o, 4-methoxyacetophenone; p, methyl benzoate; q, chrysene; r, diphenylacetylene; s, phenanthrene; T = 25 °C.

for halide reductions. The determination of λ and E° cannot be made with satisfactory accuracy using this technique, since no values of k_2 close to the diffusion limit can be obtained; however, it is possible to determine the magnitude of λ and an approximate E° value. Some values extracted from the data using the same non-linear least-squares iteration program as used previously¹ are given in Table 2. Treatment of the experimental data in the manner used for data for aromatic halides⁹ gives approximately the same value for E° and λ as those listed in Table 2.

The experimental data for **2a**, **3b**, **5b** and **7** are depicted in Fig. 1. The slope of the curves gives an indication of λ for the reaction

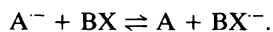
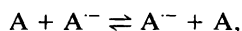


Fig. 1 clearly shows that the slope for **5b** is much closer to those for **2a** and **3b** than to that for **7**. The slope for **7** is in the range found for other aliphatic halides.

A significant part of the activation energy for the electron transfer to halides is probably associated with the stretching of the carbon-halogen bond in the transition-state (TS). Aromatic hydrocarbons have $\lambda(0)^A$ values of ~ 10 kcal mol⁻¹ for the self-exchange reaction



while $\lambda(0)^{AX}$ for aromatic and heteroaromatic halides AX has been evaluated⁹ using Hush (23–33 kcal mol⁻¹) or Marcus theory (46–66 kcal mol⁻¹); a $\lambda(0)^{AX}$ value of 25–50 kcal mol⁻¹ is thus taken as typical for these halides. The λ values for the reaction between aromatic anion radicals and aliphatic halides BX have been extracted¹ from the $\log k - E_\lambda^\circ$ plots, and by using $\lambda = \frac{1}{2}[\lambda(0)^A + \lambda(0)^{BX}]$ and assuming $\lambda(0)^A = 10$ kcal mol⁻¹, the $\lambda(0)^{BX}$ for aliphatic halides have been calculated [$\lambda(0)^{BX} \sim 120$ – 150 kcal mol⁻¹].

The $\lambda(0)$ values for **2a**, **3b**, **4b**, **5b** and **7** are given in Table 2 together with E_p and E° values. E_p is relatively close to the calculated E° , as also found for aromatic halides; the $\lambda(0)$ values are also close to those for aromatic halides. If the connection between $\lambda(0)$ and the stretching of the C–X bond in the TS is accepted then it may be concluded that vinyl and cyclopropyl halides display approximately the same stretching of the C–X bond in the TS as the aromatic halides, and

that the electron is accepted mainly in the π -electron system.

It was previously shown^{1a,b} that alkyl and benzyl halides react with the anion of 1,4-dihydro-4-methoxycarbonyl-1-methylpyridine (**10**⁻) with coupling, whereas aromatic halides do not couple with **10**⁻ in DMF. Attempts to couple **2a** with **10**⁻ failed, so that the vinyl halides resemble the aryl halides also in this respect. It should also be noted that the initially formed vinyl radical apparently accepts an electron from A⁻ faster than it abstracts a hydrogen atom from solvent, since the vinyl anion seems to be the base which promotes elimination [eqn. (5)] from the substrate.

Experimental

Materials. (*E*)-Bromostilbene (**1a**). *trans*-Stilbene was brominated¹⁰ and dehydrobrominated in a manner analogous to that for 1,2-dichloro-1,2-diphenylethene.¹¹

2-Bromo-1,1,2-triphenylethene (**2b**). Benzophenone was treated with benzylmagnesium chloride in a manner analogous to the treatment of acetophenone;¹² the alcohol was dehydrated¹³ and the triphenylethene brominated.¹⁴

2,2-Dibromo-1-phenylethene (**1b**) was prepared by a Wittig reaction from benzaldehyde and carbon tetrabromide analogous to the procedure for carbon tetrachloride.¹⁵

5-Acetyl-10-bromo-5H-dibenz[b,f]azepine (**3b**) was prepared from iminostilbene.¹⁶

2-Bromoindene was prepared from indene.¹⁷

2,2-Dibromo-1,1-diphenylethene was prepared from 1,1-diphenylethene by bromination.¹⁸

Apparatus. The previously described equipment¹ was used.

Preparative reductions. *Indirect reduction of 2-bromo-1,1,2-tribromoethene (2a).* **2a** (0.92 g) and quinoxaline (0.1 g) were dissolved in 60 ml of dry DMF/0.1 M TBABF₄ in an H-cell with two diaphragms, and the solution was purged with nitrogen. The potential of the mercury cathode was held at -1.2 V vs. Ag/AgI, i.e. the reduction

potential of quinoxaline. The reduction completed, the catholyte was diluted with 20% aqueous sodium chloride solution, extracted three times with diethyl ether, and the ether layer was washed twice with water and dried. GLC analysis (25 m methylsilicone capillary column, injection temperature 250°C; 150°C for 3 min to 250°C at 10°C min⁻¹) revealed only 1,1,2-triphenylethene and quinoxaline as products.

Indirect reduction of 5-acetyl-10-bromo-5H-dibenz[b,f]azepine (3b). **3b** (0.495 g, 1.5 mmol) and quinoxaline (0.1 g) were reduced as described above; diethyl malonate (0.26 g, 1.62 mmol) was added as proton donor to prevent basic cleavage of the *N*-acetyl group. GLC analysis (same conditions as above, except for a heating rate of 7°C min⁻¹) showed 5-acetylaminostilbene (**3a**) to be the only product; no **3b** or iminostilbene could be detected.

Indirect reduction of (E)-1-bromo-1,2-diphenylethene (1a). **1a** (1.53 g) was reduced as above with 2-benzoylpyridine (0.22 g) as mediator at -1.0 V vs Ag/AgI; to remove impurities of proton donors the DMF/TBABF₄ was dried by passage through a column of activated alumina and pre-electrolysis. GLC analysis (conditions as above, except for 140°C for 5 min to 220°C at 10°C min⁻¹) showed 49.1% diphenylacetylene (**6c**) and 50.9% *cis*- + *trans*-stilbene; the stilbene mixture contained 93.6% *trans* and 6.4% *cis*. When a similar reduction was performed with phenol (1 g) as proton donor, the products were stilbene (94%) and diphenylacetylene (6%); the *cis:trans* ratio in this case was slightly different, viz. 14.5:85.5.

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Received May 4, 1987.