Cathodic Oligomerisation of Bis(diazo) Compounds of the Indenofluorene Series Part 2.[1] Kinetic and Mechanistic Aspects

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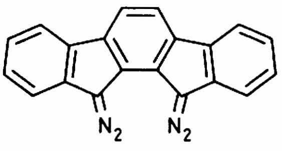
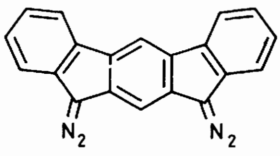
The time dependence of the disappearance of diazo groups during the constant-current electrolysis in-dimethylformamide solution at a platinum cathode of two bis(diazo)indenofluorenes (**1**) and (**2**) giving oligomeric polyazines has been investigated. The form of the diazo group concentration *vs.* time curves shows that chain reactions are involved and the slopes place limits on the chain lengths. By interruption of the current after partial reaction it was possible to show, using an adaptation of methodology previously developed to explain the electrochemical reduction of 9-diazofluorene, that for (**1**) the chain-termination process is kinetically of the first order in the chain carrier; kinetic parameters for the propagation and termination processes in homogeneous solution were obtained. The discrepancy between the observed concentration/time curve for continuous electrolysis and that calculated from these kinetic parameters provides information on the initiation step, yielding a consistent picture of a chain carrier formed from four monomer units. Similarly it has been shown that the results for (**2**) best fit a reaction scheme involving, in the early stages, a trimeric chain carrier which is partitioned between chain transfer to monomer and termination by dimerisation. Details of these processes are discussed, and the way in which the mechanistic schemes permit interpretation of the differing molecular-weight distributions in the final products from (**1**) and (**2**) are explained. Supporting evidence is provided by voltammetric experiments on the related monodiazo compound (**5**) and thermolytic studies of (**1**)–(**3**) in solution.

It was shown in part 1[1] that cathodic reduction of three isomeric bis(diazo)indenofluorenes (**1**), (**2**), and (**3**) in dimethylformamide solution at a platinum cathode led to the formation of oligomeric polyazines, the average chain length ranging from 3–4 for (**1**) to around 16 for (**2**) and (**3**). Evidence was presented which showed that a chain mechanism was involved since up to 10 diazo groups were consumed for each electron introduced. In this paper we report a more detailed study of the kinetic and mechanistic aspects of the oligomerisation of 11,12-bis(diazo)-11,12-dihydroindeno[2,1-*a*]fluorene (**1**) and 10,12-bis(diazo)-10,12-dihydroindeno[2,1-*b*]fluorene (**2**), together with some additional observations that provide support for our interpretation.



(**1**)



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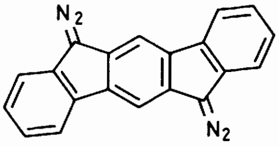


(**3**)

Results

Constant-current Electrolysis.—Diazo compounds (**1**) and (**2**) were subjected to constant-current electrolysis as previously described,[1,2] using *ca.* 3 mmol dm^{-3} solutions in dimethylformamide containing 0.1 mol dm^{-3} tetramethylammonium tetrafluoroborate as the supporting electrolyte. The concentration of unchanged diazo groups was determined by i.r. spectroscopy as a function of time. In separate experiments, the current was interrupted by disconnecting the working electrode, and the further disappearance of diazo groups monitored over a period of up to two hours. The results for (**1**) are shown graphically in Figure 1 and those for (**2**) in Figure 2.

It can be seen that in both cases the behaviour is as expected for a chain process initiated by electron transfer at the cathode; several diazo groups are decomposed for each electron injected into the system. In the case of (**1**) the disappearance of diazo groups shows the expected acceleration initially, reaching a value of about six diazo groups per electron. After consumption of *ca.* 75%, the current efficiency shows a fairly abrupt drop, and each electron then brings about the destruction of only a single diazo function. Eventually the efficiency drops still further, and the disappearance of the diazo peak in the i.r. spectrum is only completed by prolonged electrolysis. For (**2**) a broadly similar pattern is observed, but here the disappearance of diazo groups is initially more rapid (close to ten diazo groups per electron) and decelerates more smoothly to close to one per electron. In both cases, after interruption of the current, decomposition continues, becoming very slow after a period of fifteen to twenty minutes.

For reasons explained below the interpretation of the results followed an approximate procedure, but one based on the principles laid down in our treatment of the cathodic reduction of 9-diazofluorene, the prototype for compounds (**1**)–(**3**). Thus the processes being followed on the time-scale of these experi-

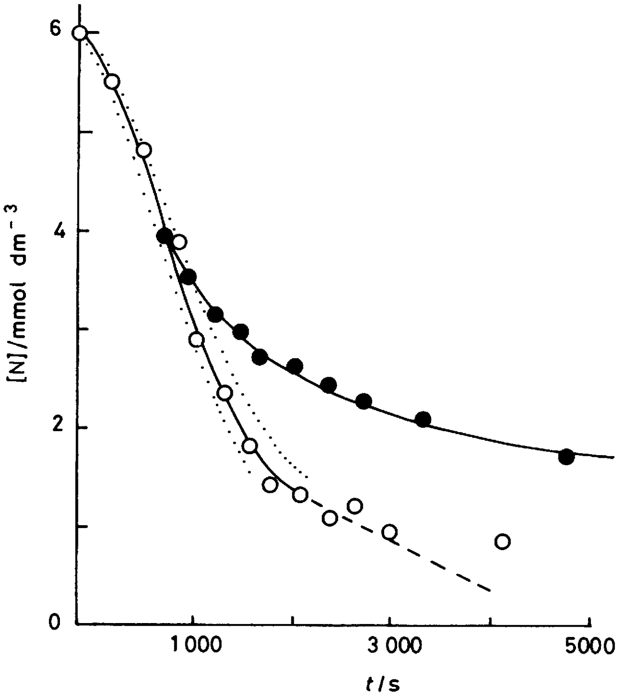


Figure 1. Variation with time of the concentration of diazo groups during constant-current electrolysis of (**1**) (○) and after interruption of the current (●). The points are from typical experiments and the lines are theoretical ($m = 3/2$; $n = 4$; $k_T = 1.6 \times 10^{-4}$ s^{-1}; $k_p = 0.46$ dm^2 mol^{-1} s^{-1}; $v_I = 5.4 \times 10^{-7}$ mol dm^{-3} s^{-1}). The dotted lines show the prediction for $m = 1$ (upper) and $m = 2$ (lower) and the dashed line is drawn assuming the consumption of one diazo group per electron.

ments are assumed to obey kinetic laws appropriate to the homogeneous liquid phase, that is to say, very fast processes that occur in the regions close to the surface of the electrode are not explicitly incorporated in the kinetic scheme. There are good precedents for this,[2,3] especially in stirred solutions and where the rates of the chemical steps of interest are not so fast that they take place in regions where there are ill-defined concentration gradients. Compared with our earlier study of 9-diazofluorene,[2] however, the present investigation poses additional problems: (*i*) The analytical method does not distinguish between the monomeric bis(diazo) compound and polyazines with diazo end groups. (*ii*) Because the polyazines are fully conjugated, the reactivity of species involved in chain extension is likely to be a function of chain length, so that, in principle, a different set of (smaller) rate coefficients should be used after each addition of a monomer unit. (*iii*) The solubility of compounds (**1**), (**2**), and (**3**) in DMF permits initial diazo concentrations of only 3 mmol dm^{-3}, and this makes the rate of consumption of diazo groups in the initiation process at controllable constant currents comparable to that in the propagation sequence.

The first two of these problems were overcome by approximation by treating the overall course of the reaction in phases. At the beginning of the electrolysis only monomer is present, and in the first part of the reaction it was assumed that the reaction solution contained only monomer and oligomers that could be treated as a single species of average molecular weight and with average values for the rate coefficients describing the competing reaction pathways. At a later stage in the electrolysis, the reaction solution was taken to contain only the oligomeric bis(diazo)polyazine resulting from the first phase together with a higher oligomer, again with properties that could adequately be represented by average values taken over the range of species actually present. The reaction scheme is thus as shown in equations (1) to (3).

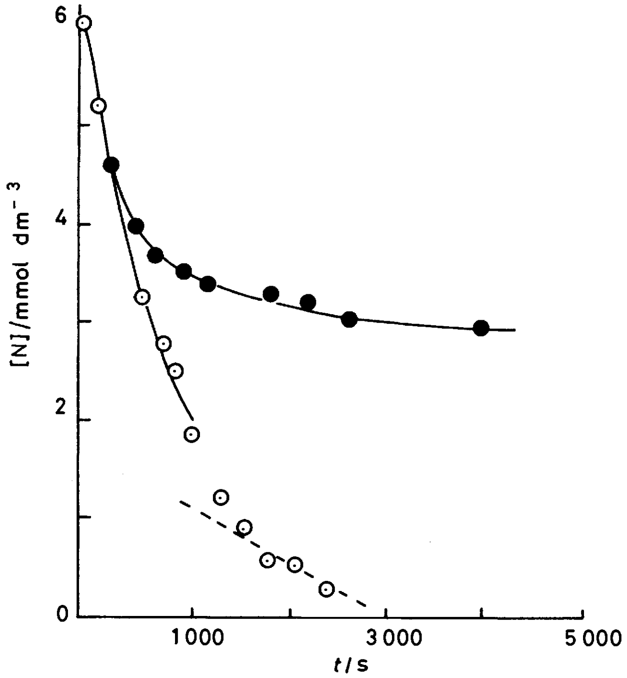


Figure 2. Time variation of the diazo-group concentration during constant-current electrolysis of (**2**) (○) and after interruption of the current (●). Typical experimental points are shown. The lines are theoretical predictions ($m = 2$; $n = 3$; $k_T = 54$ dm^3 mol^{-1} s^{-1}; $k_p = 6.2$ dm^3 mol^{-1} s^{-1}; $v_I = 5.4 \times 10^{-7}$ mol dm^{-3} s^{-1}). The dashed line is drawn assuming the consumption of one diazo group per electron.

Initiation (at the electrode):

$$(m + 1)\mathrm{A} + \mathrm{e} \xrightarrow{v_I} \mathrm{C} \qquad (1)$$

Chain propagation:

$$\mathrm{C} + n\mathrm{A} \xrightarrow{nk_p} \mathrm{D} + \mathrm{C} \qquad (2)$$

Chain termination:

$$m\mathrm{A} + \mathrm{X} \xrightarrow{k_T} \mathrm{P} \qquad (3)$$

Here, A represents the monomer, C the chain carrier (an anion radical), D the oligomeric bis(diazo) compound produced, and P the product of termination (a dianion in the case where X, the reaction partner of C in this process, is another C). The parameter m is the number of azine linkages formed per electron in generating the chain carrier C. The parameter n is the average number of monomer molecules that are transformed in each complete cycle.

In analysing for diazo end groups it was assumed throughout that those in monomer and oligomer molecules would be detected, together with others produced from diazo-anion radicals and dianions by electron transfer to atmospheric oxygen during the spectrometric determination. Hence, if the rate of termination is much slower than that of propagation, the concentration of monomer A is related to the measured end-group concentration [N] by equation (4), where $[\mathrm{A}]_0$ is the initial value.

$$[\mathrm{A}] = (n[\mathrm{N}] - 2[\mathrm{A}]_0)/2(n - 1) \qquad (4)$$

As in the treatment of 9-diazofluorene, the general procedure in the present work involved fitting the decay of the diazo functionality [transposed, using (4), into monomer and oligomer concentrations] after interruption of the constant current to the equations predicted for termination according to kinetic laws either first or second order in C. In this way the termination kinetics are established and values for the rate coefficients for termination (k_T) and propagation (nk_P) obtained, assuming a propagation rate law first order in both C and A. These kinetic parameters are then used to calculate the time dependence of the disappearance of diazo groups under conditions of continuous electrolysis. Because of the rather low solubility of the bis(diazo)indenofluorenes used here, it was necessary to add to the diazo groups consumed in the propagating chains the substantial concentrations removed by the initiation, this computation being done at time intervals of one hundred seconds. The parameter *m* then is derived in this final fitting process.

Interruption of the electrolysis of (**1**) after some 30% of the diazo groups had been consumed led to further decomposition. Conversion of values of [N] into concentrations of residual monomer $[A]_\tau$, where τ is the time after interruption of the current, was carried out using (4), assuming values of the parameter $n = 3$ and 4, and the further disappearance of A then was found to fit equation (5), derived on the basis of a termination process first order in C. This treatment yielded a value of k_τ of $(3.5 \pm 0.4) \times 10^{-4}$ s^{-1} for $n = 3$, and, from the observed value of $\ln([A]_i/[A]_\infty)$ and the value of $[C]_i$ calculated from k_τ and the rate of initiation, $nk_P/k_T = 9\,000$ dm^3 mol^{-1}. For $n = 4$, the corresponding values were $(1.60 \pm 0.14) \times 10^{-4}$ s^{-1} and 11 500 dm^3 mol^{-1}. With these parameters the time variation of [N] was calculated using equations (6) and (4) up to the point when all of the monomer had been consumed. Thereafter, with all the monomer originally present now in the form of oligomer of length *n*, further injection of electrons was taken to lead to non-chain destruction of end groups by a process involving loss of one diazo group per electron. In neither of the present cases, however, was the calculated curve in agreement with observation; clearly the disappearance of diazo groups takes place faster during electrolysis than predicted from the transient after interruption. By including a contribution from the removal of diazo groups in the initiation process ($= mv_1$), however, calculation and experiment could be brought into coincidence. The best fit was found with $n = 4$ and $m = 3/2$ as shown by the solid line in Figure 1.

It was immediately evident that for (**2**) the further decay with time of diazofunctionality after interruption of the constant current did not have the form expected if termination followed a first-order kinetic law. Although the concentration of diazo groups appeared to fall to a constant non-zero value as predicted for a termination process first order in the chain carrier, the time dependence of the diazo-group concentration could not be fitted to equation (5) (derived on the assumption of

$$\ln\left[1 - \frac{\ln([A]_i/[A]_\tau)}{\ln([A)_i/[A]_\infty)}\right] = k_T\tau \qquad (5)$$

first-order termination) for values of *n* (equation 4) from 2 to 6, the range of values possible on the basis of the number of end groups consumed per electron. Instead, the results could be fitted to equation (7) derived on the basis of a termination

$$\ln([A]_0/[A]_t) = (nk_Pv_1/k_T)\{t - [1 - \exp(-k_Tt)]/k_T\} \qquad (6)$$

$$\ln([A]_i/[A]_T) = (nk_P/k_T)\ln(k_T[C]_i\tau + 1) \qquad (7)$$

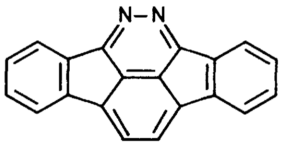
process second order in C, with the following values: $n = 3$; $nk_P/k_T = 0.346$; $k_T[C]_i = 0.005\,0$. Since for such a termination process the value of $[C]_i$ is given by equation (8), k_T and nk_P can be separately obtained by an iterative procedure *viz.*, $k_T = 54$ dm^3 mol^{-1} s^{-1}, $nk_P = 18.6$ dm^3 mol^{-1} s^{-1}.

$$[C]_i = (v_1/k_T)^{\frac{1}{2}} \tanh (v_1k_T)^{\frac{1}{2}}t_i \qquad (8)$$

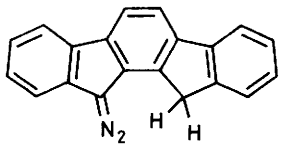
$$-\Delta[A]/\Delta t = mv_1\Delta t + (nk_P/k_T)\Delta \ln\{\cosh[(v_1k_T)^{\frac{1}{2}}t]\} \qquad (9)$$

With these parameters known, the time dependence of the disappearance of diazo groups during constant-current electrolysis was fitted to equation (9) using integral values of *m*, and steps (Δt) of 100 s. The line drawn in Figure 2 is that computed for $m = 2$, and the fit can be seen to be excellent over the first 65% of reaction, at which point all the monomeric bis(diazo) compound should, on average, be in the form of trimeric bis(diazo) compound (after chain transfer) or tetrameric dianion (after termination by dimerisation of C). Thus in each cycle, three monomer molecules are transformed, with loss of four diazo groups, into trimeric bis(diazo) compound; each termination product molecule, however, involves the destruction of six diazo functions. On average, the cycle turns twice before termination for each electron.

Further progress of the reaction according to the approximate treatment involves the transfer of an electron at the cathode to the trimeric product of the first phase of the oligomerisation. At this stage roughly three diazo groups are consumed per electron, and this number is progressively decreased until it approaches unity, the result expected for an EC or EC$_{\text{dim}}$ process. The latter electrochemical mechanism has been established for 9-diazofluorene under voltammetric conditions,[4] and related to azine formation *via* a tetrazine dianion intermediate.[5] In the present context such behaviour would correspond to a step-growth polymerisation, with dimerisation of the diazoalkane anion radical being followed by sequential electron transfer and loss of a molecule of nitrogen. A new azine linkage would thus link two formerly separate bis(diazo) compounds.



(**4**)



(**5**)

Thermal and Photochemical Decomposition of (**1**), (**2**), *and* (**3**).—Thermal and photochemical decomposition of diazo compounds gives rise to carbenes. In the case of (**1**) we have previously reported[6] that photolysis at cryogenic temperatures in a glassy matrix gives rise to a monocarbene, and this behaviour has also been found with (**2**) and (**3**).[7] As part of the present investigation the three bis(diazo) compounds were decomposed in solution in mesitylene, a compound which rather readily gives up hydrogen atoms to carbenes. Rates of disappearance of diazo groups, corresponding to the rate of carbene formation, were measured spectrophotometrically as before, and obeyed a first-order kinetic law over at least the first 50% of the reaction [*ca.* 80% in the case of (**1**)], yielding the kinetic parameters in the Table. Notwithstanding the fairly low precision and narrow temperature range used, activation parameters were derived for comparison with that reported in the literature for 9-diazofluorene under the same conditions.[8] It is immediately apparent that (**1**) is much the most reactive of the three bis(diazo) compounds, perhaps reflecting the close

Table. Kinetic parameters for the thermal decomposition of (**1**), (**2**), and (**3**) in mesitylene solution.

		k_{obs}/s^{-1}				
Compound	T/K	363	373	383	$\Delta H^{\ddagger}$/ kcal mol^{-1} [b]	$\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1} [b]
(**1**)			2.6	6.0	22	15
(**2**)		0.34	1.5		38	26
(**3**)		0.16	0.60		34	14
9-Diazofluorene			0.10		33	0[a]

[a] Assumed. [b] 1 cal = 4.184 J

proximity of the diazo groups. Moreover, whereas (**2**) and (**3**) yielded ill-defined mixtures of highly coloured species with molecular weights (by mass spectrometry and gel-permeation chromatography) in the range 500 to 600, (**1**) affords the aromatic cyclic azine (**4**) in 63% yield, attesting to the remarkable facility of the monocarbene from (**1**) to attack the terminal nitrogen of the adjacent diazo group, even in the presence of a good H-atom donor. It is to be noted that (**4**) was not detected in the products of cathodic reduction of (**1**).

Electrochemical Kinetics of the Reduction of 11-*Diazo*-11,12-*dihydroindeno*[2,1-a]*fluorene* (**5**).—Electrochemical kinetic studies of the type that we have successfully employed previously in mechanistic work on, 9-diazofluorene were not possible with (**1**), (**2**), or (**3**) because of problems of adsorption which distorted the voltammetric response. It proved possible, however, to make some preliminary measurements on the monodiazoalkane (**5**), related to (**1**), by linear-sweep voltammetry, at low concentration (*ca.* 1 mmol dm^{-3}) in acetonitrile. The results yielded a value of dE^{p}/dlog v of 20 mV per decade consistent with an EC_{dim} mechanism as found for the prototype 9-diazofluorene.

Discussion

The approximate kinetic treatment indicates that the cathodically initiated decomposition of (**1**) and (**2**) fits the pattern expected for an electron-transfer chain mechanism with rather short chains (relative to those observed with 9-diazofluorene in acetonitrile solution), but ones that involve the decomposition of several diazo groups in each cycle. An interesting feature, however, is revealed by the comparison of the observed molecular-weight distributions of the products from (**1**) and (**2**) and the chain lengths derived from the kinetics. Thus, in the case of (**1**), the products appear to consist largely of oligomeric azines derived from 3 or 4 bis(diazo) molecules, and the kinetic simulation suggests that the chain mechanism is best described by a cycle in which, after a rapid growth of the chain to a length corresponding to 4 monomer units, chain transfer to monomer or termination by a first-order process stops further chain extension. The oligomeric bis(diazo) compound that results from electron transfer from the growing chain to a monomer molecule is apparently incapable of further growth, and, when all the monomer has been consumed, the resultant anion radicals follow only the termination pathway.

For (**2**), which has less directly conjugated diazo groups, the kinetic chain is similarly short, but the final product is apparently of much higher molecular weight (*ca.* 16 monomer units). Here, however, the process that competes with chain transfer is second order in the chain carrier and this is plausibly a dimerisation, yielding a dimeric dianion that is presumably less able to bring about the destruction of further diazo groups than the shorter-chain anion radicals. When all the monomeric bis(diazo) compound has been consumed, reaction continues with lower current efficiency and the electron-transfer chain process dies away; dimerisation of oligomeric bis(diazo) anion radicals is then left as the principal mode of chain extension. The extended conjugation must ultimately slow down this process too, in relation to side reactions with adventitious protic impurities or traces of oxygen, thus limiting the degree of polymerisation.

This interpretation of the decomposition of (**1**) and (**2**) suggests that there are two different chemical processes by which azine linkages are created in the homogeneous propagation phase of the reaction. The first is by diazoalkane anion radical dimerisation which is most important in the late stages of the reaction of (**2**) and represents a clear example of step-growth condensation polymerisation. The other is that responsible for the rapid consumption of 3,4 bis(diazo)alkane in each cycle of the chain, prior to the rate-limiting electron transfer to monomeric (**1**) or (**2**). This process can be envisaged as attack by a radical centre at the terminal nitrogen of a bis(diazo)alkane anion radical on a diazo carbon atom of a monomeric bis(diazo) alkane with subsequent extrusion of N_2. Although this constitutes a condensation process, the product of such a step is another bis(diazo) polyazine anion radical like its precursor but extended by a monomer unit (minus two nitrogen atoms); the process has some of the character of a linear polymerisation. Prototypes of both these processes have been discussed in relation to the electrochemical conversion of 9-diazofluorene into fluorenone azine.[2,5]

Information on the initiation process comes from our finding that the progress of constant current electrolysis cannot be satisfactorily predicted from the kinetic parameters of propagation and termination derivable from the transient behaviour after interruption of the current. The initiation multiplier m that is necessary to make the observed and calculated courses of the reaction equal is to some extent dependent on the correct assignment of the value of n, but for a given n-value the decrease in [N] is a fairly sensitive function of m (see Figure 1). Taking our best estimates of m at face value it can be seen that, for (**1**), 3 diazo groups are consumed in the initiation process for each electron introduced. Since the formation of an azine linkage necessarily causes expenditure of two diazo groups, the implication is that two electrons are required to generate each chain carrier. In this way six diazo groups are consumed, giving three azine linkages connecting the hydrocarbon moieties from four bis(diazo)alkane molecules. Such an interpretation is self-consistent at least, and suggests that the bis(diazo)alkane anion radicals first generated at the electrode probably dimerise as previously observed with 9-diazofluorene and now with (**5**), the close relative of (**1**), in quiet solutions. Such a process seems particularly likely with (**1**) since, if the initially formed anion radical were to react only by attack on a diazo function, it would be expected to do so most readily intramolecularly to yield (**4**), as is found with the analogous carbene. We speculate that growth from the dimeric dianion could then be by electron transfer to monomer followed by combination of the resultant anion radical pair or by further reaction of anion radical with a neutral bis(diazo)alkane molecule. For **(2)** the preferred value of *m* is 2, indicating that on average four diazo groups are converted into two azine links per electron introduced into the system. This is consistent with our observation that *n* is on average 3, with propagation by anion radical + neutral bis(diazo) compound, and with anion radical dimerisation as the principal path by which chains are terminated for this compound.

Despite the encouraging self-consistency of the schemes that we have proposed, we stress that what we have is a framework for further investigation of electron-transfer chain reactions of this type. Additional work is in progress on related systems to investigate the extent of the relationship between conjugation of the end-groups and kinetic behaviour, and to examine the possibility of using anodic initiation to polymerise bis(diazo)-alkanes.

Experimental

The preparation of the bis(diazo)alkanes **(1)**, **(2)**, **(3)**, and **(5)** has been detailed in part 1,[1] together with the experimental procedures used for electrochemical reduction at constant current, including the i.r. spectroscopic analysis for diazo groups.

Preparation of 11,12-*diazaindeno*[1,2,3-cd]*fluoranthene* **(4)**.—The cyclic azine **(4)** was prepared by heating **(1)** (48 mg) in degassed mesitylene (50 cm^3) in a sealed Pyrex tube for 3.5 h at 100 °C. Removal of mesitylene under reduced pressure left a residue which on recrystallisation from tetrahydrofuran afforded **(4)** (27 mg 63%) as orange crystals, m.p. 309.0–309.5 °C Found: C, 86.65; H, 3.6; N, 9.95. $C_{20}H_{10}N_2$ requires C, 86.33; H, 3.60; N, 10.07%).

Photolysis using a high-pressure mercury arc of **(1)** (172 mg) dissolved in nitrogen-purged tetrahydrofuran (85 cm^3) for 100 min, completely destroyed the diazo groups (i.r.). Concentration of the solution led to deposition of the cyclic azine **(4)** (51.2 mg). The mother liquor on t.l.c. (CH_2Cl_2) was found to contain additional **(4)** together with a fast moving component (R_F = 0.71). Separation by column chromatography yielded further **(4)** (31.5 mg; overall yield 49%) and an intractable brown material that was not characterised.

Thermal Decomposition of **(1)**–**(3)** *in Mesitylene*.—The solvent was purified by distillation from calcium hydride. Aliquots of solutions of the diazo compound (*ca.* 0.5 cm^3 of a 3 mmol dm^{-3} solution) were freed of dissolved oxygen by freeze–pump–thaw cycles, sealed in glass tubes, and heated in a thermostatically controlled bath. Tubes were removed at intervals and the reaction arrested by plunging them into solid CO_2–acetone. Residual diazo end groups were then determined by i.r. spectroscopy. Rate coefficients were determined from the equation $-d[N]/dt = k_{obs}[N]$.

The instrumentation and procedure used for the LSV experiments were as previously described.[4]

Acknowledgements

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