Electrostatic repulsion by the charged tail of a radical controls the stereochemistry of coupling with anthracenide. Reversibility of benzylic fragmentation[1,2]

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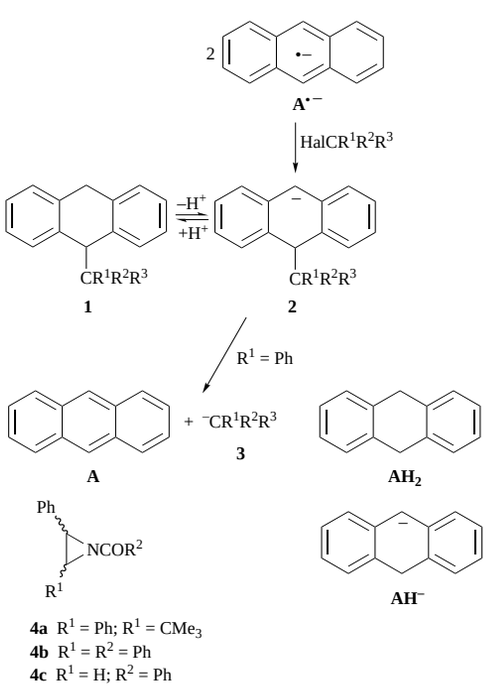
Reaction of anthracenide $A^{\bullet -}$ with 1-pivaloyl-2,3-diphenylaziridines *cis*-4a and *trans*-4a yield the same products, namely $PhCH_2CHPhNHCOCMe_3$ (11) and AH–CHPhCHPhNHCOCMe$_3$ (6) (AH = dihydroanthryl). The steric differentiation is lost when the two ketyls 12 formed from 4a undergo homolytic ring cleavage forming the same anionic radical 13. Extremely short reactions (≤10 s) give 6 as the *erythro* isomer exclusively or nearly so. Coupling of 13 with $A^{\bullet -}$ does not form the precursor (*threo*-8) of *threo*-6 owing to electrostatic repulsion between $A^{\bullet -}$ and the anionic tail of 13 in the preferred conformation of the latter. Radical coupling is not completed within this short time so 11 can be formed directly from 13 *via* 10, the amide anion of 11. Reduction of 13 to carbanion 9 by outer-sphere electron transfer or *via* 8 and its benzylic fragmentation (BFR) is the other path to 11. Extending the time to 1 or 2 min has the following effects. Coupling of 13 with $A^{\bullet -}$ is completed at the expense of 11. Second, more than a trace of *threo*-6 is detected indicating that BFR 8→9 + A (A = anthracene) is reversible and that addition of dianion 9 to A proceeds without pronounced stereochemical preference. With even more time the *erythro*:*threo* ratio changes in favour of *threo*-6 and finally can even reach a value slightly less than 1. Simultaneously the amount of 11 increases slowly at the expense of the total 6 indicating that part of BFR which becomes irreversible by carbanion protonation 9 + THF→10. With much longer reaction times imidate ion 10 eliminates (*E*)-stilbene. Both isomers of 6 have been independently synthesized from the two isomers of 4a and anthracene hydride AH^-.

Introduction

The base induced fragmentations (FR) of 9-substituted 9,10-dihydroanthracenes **1** (Scheme 1) are observed when the leaving



Scheme 1

carbanion **3** (heterolytic FR) or ketyl **3** ($R^2 = O^-$, homolytic FR) is stabilized. Stabilization is usually due to the phenyl group (R^1 = Ph) giving the leaving species a benzyl structure and providing the practical term 'benzylic FR' (BFR) when this reaction was detected and studied at Heidelberg. Deprotonation at position 10 and elimination of the benzyl species have been shown to be discrete steps.[4,5] The intermediate carbanion **2** (R^1 = Ph) resembles the intermediate **2** (R^1, R^2, $R^3 \neq$ Ar) formed in reactions of anthracenide $A^{\bullet -}$ with alkyl halides Hal-$CR^1R^2R^3$ or similar reagents.[6] While **1** was the main product in the reactions of $A^{\bullet -}$, so far **1** with R^1 = Ar has been found in low yields only twice. Beckwith and Waters[7] obtained **1** (R^1 = Ph, $R^2 = R^3$ = H) from $A^{\bullet -}$ and benzyl chloride in ether together with other products including $PhCH_2CH_2Ph$ whose formation may now be interpreted to result from BFR followed by S_N2 reaction of the benzyl anion with benzyl chloride. This would be the first BFR although it was unrecognized as such. In the second case[5] the short lifetime of **2** obtained from $A^{\bullet -}$ and **4c** in THF was attributed to BFR followed by typical reactions of the benzyl anion **3**.

The classic papers on reactions of aromatic radical anions have not considered the possibility of BFR although they revealed a different behaviour of alkyl and benzyl halides in reactions with naphthalenide.[8] Benzylic halides never yielded substituted naphthalenes or dihydronaphthalenes. This may also be explained by BFR of a naphthalene analogue of **2**. A recent paper[9] described a homolytic BFR in the reaction of naphthalenide with a benzoylaziridine: benzoylnaphthalenes were obtained after a very short reaction time only. Thus, BFR is probably a general phenomenon, but is most important in the anthracene series for obvious reasons.

The benzyl anion **3** arises in the presence of anthracene **A** and may attack it resulting in a reverse BFR. This has not yet been observed but may be expected since addition of alkyllithium species to **A** has been described.[10] Search for direct evidence of this reversibility and the possibility of diastereoselectivity (see below) stimulated a study of reactions with the *cis–trans* pair of **4a**. The pivaloylaziridines **4a** were selected rather than the benzoylaziridines **4b** in order to avoid complicating carbonyl reactions and to shorten the lifetime of the ketyl. In spite of the very unfavourable reduction potentials of **A** (−1.98 V)[11] and of a pivaloylaziridine (about −2.7 V),[12,13] single election transfer (SET) to a pivaloylaziridine has previ-

Table 1 Reactions[a] of *trans*-**4a** with $\mathbf{AH}^-$

	Reagents (mmol/cm³ THF)				Yields[b] of products	
Run	$\mathbf{AH_2}$	BuLi	*trans*-**4a**	Time	*erythro*-**6**	**11**
1	6.25/70	5	4.8/40	5 min	82	
2	7.5/70	5	1/20	30 min	(53)	(28)
3	7.5/70	5	1.26/25	17 h		100
4	30/150	25	4.96/50	5 min	(57)	(31)

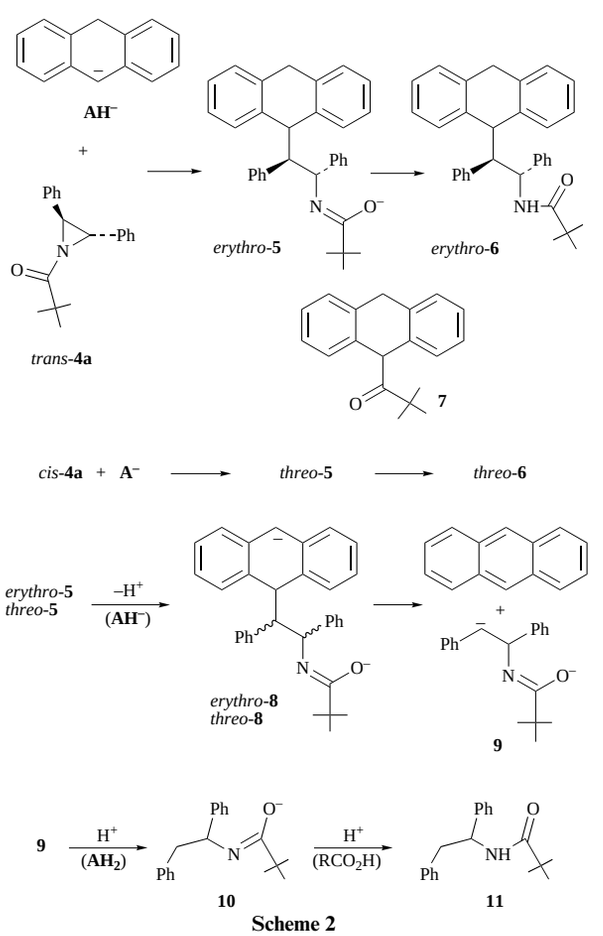
[a] The solution of $\mathbf{AH_2}$ in THF was cooled to −160 °C and BuLi (in hexane) was added; stirring was begun as soon as possible and continued until quenching; the solution of **4a** in THF was added dropwise within 3 min (4 min in run 1, 5 min in run 4) at room temperature. The reactions were quenched with acetic acid. [b] Yields in parentheses were calculated from ^{1}H NMR spectra of product mixtures.

ously been observed.[13] The general problem of unfavourable potentials in SET reactions has already been discussed by Bank and Juckett,[11] but with acylaziridines an essential aspect may be the interaction of the counter ion with the acylaziridine before, during and after SET.

The possibility of diastereoselectivity was considered since **1** with an enantiomeric excess has been obtained from optically active alkylating agents.[6]

Results and discussion

S_N2-like ring-opening of *cis*-**4a** and *trans*-**4a** by $\mathbf{AH}^-$ appeared to be a simple way to prepare pure samples of the two diastereomeric dihydroanthracenes **6** required as authentic material



Scheme 2

(Scheme 2). Synthesis of *erythro*-**6** from *trans*-**4a** (Table 1) was easy with a small excess of $\mathbf{AH}^-$ and a short reaction time (run 1). Runs 2–4, carried out with a large excess of $\mathbf{AH}^-$, *viz*. 5:1, show the expected BFR, yielding **11**, and its dependence on time and on the concentration of $\mathbf{AH}^-$. Both effects counteract in runs 2 and 4 to give nearly the same result.

The IR carbonyl bands[14] confirm the expectation that *cis*-**4a** (1683 cm^{-1}) has a steeper nitrogen pyramid than *trans*-**4a** (1664 cm^{-1}). The S_N2-reactivity of acylaziridines decreases when the steepness of the nitrogen pyramid increases.[15] This is borne out by the reactions of *cis*-**4a** with $\mathbf{AH}^-$ (Table 2). No run in Table 2 produced exclusively *threo*-**6** although this was the main product in runs 1–3. Keeping the excess of $\mathbf{AH}^-$ small (run 1 and 2) did not completely prevent the formation of **11** *via* BFR and also provided the ketone **7**. The attack on the carbonyl group of **4a**, despite severe steric hindrance, was possible because the steep pyramid in *cis*-**4a** not only slows down the competing ring-opening, it also makes the carbonyl group susceptible to nucleophilic attack. Such carbonyl attack is reversible and this explains the lack of ketone **7** in the other runs where **4a** was consumed by the competing reaction. The equilibrium concentration of the carbonyl adduct vanishes when **4a** disappears. Run 5 illustrates the time-dependence of BFR.

BFR generates the carbanion-imidate ion **9**. Protonation of the carbanionic site by $\mathbf{AH_2}$ was confirmed by experiments with $[^2H_4]\mathbf{AH_2}$ (87–88% ^{2}H in each non-aromatic position). From both isomers of **4a**, **11** was obtained containing (^{1}H NMR) 82% of [^{2}H]**11** ($PhCHDCH_2NHCOCMe_3$).

erythro-**6a** and *threo*-**6a** can easily be differentiated by ^{1}H NMR spectroscopy. Strong ring current effects in the crowded molecules generate remarkable shift differences for all non-aromatic signals except for the pseudo-equatorial H in position 10 of the dihydroanthracene. In particular, the strong singlets for Bu^t are valuable: 0.71 *vs*. 1.33 ppm (1.09 ppm for **11**). Even the aromatic *ortho*-signals of NCCPh were in the olefin region and differed by 0.3 ppm. Thus, expected unseparable mixtures of products in reactions with $\mathbf{A}^{\bullet-}$ can be analyzed by ^{1}H NMR spectroscopy.

A reaction between $\mathbf{A}^{\bullet-}$ and **4a** can only occur by single electron transfer. For an example[6] of SET with simultaneous seemingly S_N2-like reactions of $\mathbf{A}^{\bullet-}$, see below. SET generates the two ketyls *cis*-**12** and *trans*-**12** (Scheme 3) which rapidly form the same amidatoalkyl radical **13**. This could be anticipated. The reaction of **13** with excess $\mathbf{A}^{\bullet-}$ as well as follow-up reactions have been investigated.

The first experiments were performed under conditions that leave as little time as possible for the expected BFR. The surprising results of these extremely short reactions are shown in Table 3 and Scheme 3. No difference in products from either aziridine had been expected and was supported experimentally. The main product was always **11** but **6** was not obtained as a diastereomeric mixture since only (or nearly only)† *erythro*-**6** was found. It is unlikely that about 65% of **11** in these very short reactions had been formed by BFR of an intermediate coupling product *erythro*-**8** or *threo*-**8**. Further results described below generally rule out carbanion **8** as the main precursor of **11** in the runs of Table 3. Considering the strong tendency of excess $\mathbf{A}^{\bullet-}$ to couple with a carbon radical rather than to reduce it to a carbanion,[6,13] it appears reasonable to assume that a

† It is likely that traces of *threo*-**6** arose from a small impurity in **4a**. In the last step of its synthesis **4a** may be ring-opened by chloride ion causing contamination by $PhCHClCHPhNHCOCMe_3$. SET cleavage of the C–Cl bond without deprotonation would provide an uncharged radical, *i.e.* **13** protonated on nitrogen.

Table 2 Reactions[a] of *cis*-**4a** with $\mathbf{AH}^-$

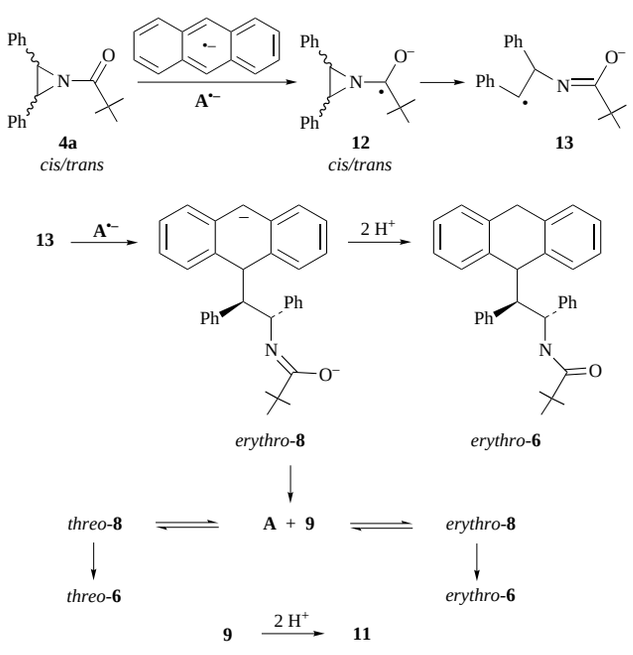
	Reagents (mmol/cm³ THF)				Yields[b] of products			
Run	$\mathbf{AH_2}$	BuLi	*cis*-**4a**	Time	*threo*-**6**	**11**	**7**	*cis*-**4a**
1	7.5/70	6.25	4.73/20	5 min	(49)	(3)	20	21
2	7.5/70	6.25	4.9/30	5 h	(55)	(7)	22	
3	7.5/70	5	1/20	45 min	60	(33)		
4[c]	7.5/70	5	1.37/20	1 d	(26)	(42)		
5[d]	30/150	25	4.93/50	30 min	(22)	(51)		
				1 h	(14)	(63)		
				27 h		98		

[a] The solution of $\mathbf{AH_2}$ in THF was cooled to −160 °C and BuLi (in hexane) was added; stirring was begun as soon as possible and continued until quenching; the solution of **4a** in THF was added dropwise within 5 min (1 min in run 1, 3 min in run 2) at room temperature. The reactions were quenched with acetic acid. [b] Yields in parentheses were calculated from ^{1}H NMR spectra of product mixtures. [c] About 15% of products were lost during workup. [d] 20 cm³ samples were withdrawn after the time given and worked up.

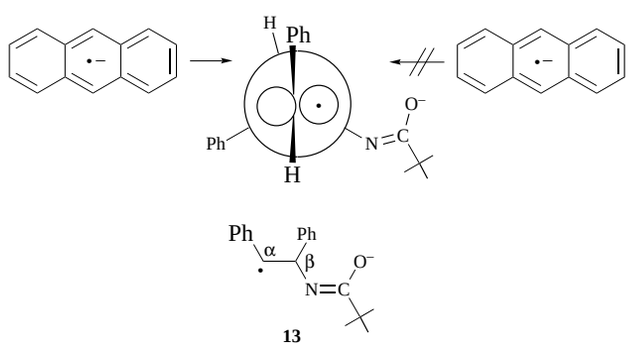
Table 3 Short-term reactions[a] of *cis*-**4a** and *trans*-**4a** with $\mathbf{A}^{\bullet -}$

	Reagents (mmol/cm³ THF)			Time of	Yields (^{1}H NMR) of products		
Run	**A**	Na	**4a**	addition/s	*erythro*-**6**	*threo*-**6**	**11**
1	7/100	5.0	*trans* 1.0/20	7	26	0	65
2	7/100	5.0	*cis* 1.0/20	5	18	Trace	68
3	6/100	4.4	*cis* 1.87/20	7	19	0	66
4[b]	6/100	4.7	*cis* 1.65/20	10	22[c]	Trace	49[d]

[a] **A**, Na and THF were stirred for about 1 day. The solution of **4** in THF was added within the time given. The reactions were immediately quenched with excess acetic acid before air was allowed to enter. [b] Reaction was quenched with CF_3CO_2D. [c] 67% deuterium incorporated in pseudo-axial position 10 of the dihydroanthracene. [d] 63% of **11** contained deuterium as indicated by NCCHDPh.



Scheme 3



Scheme 4

substantial part of the non-coupling amidatoalkyl radical **13** survived until quenching or until workup. The deuterium incorporation (63%) into **11** (49%) in run 4 by quenching with CF_3CO_2D points to dianion **9** as the precursor for 31% of **11** and hence to the partial reduction of radical **13** by $\mathbf{A}^{\bullet -}$ or, more likely,[13] by ketyls **12**. Tentatively, one may also consider deuterium incorporation by an internal deuterium atom transfer with a cyclic six-membered transition state after the imidate part of **13** has accepted a deuteron on the oxygen. Protonation of amide anions occurs first on oxygen.[16] The drawback of this alternative is clear: a rather stable benzyl radical would have to generate a radical N=C–O$^\bullet$ with the unpaired electron in the wrong orbital for resonance stabilization.

How can the very high diastereoselectivity of coupling be explained? The preferred conformation (Scheme 4) of **13** has α-phenyl and β-hydrogen eclipsed. Radical coupling with either lobe of the singly occupied π orbital can only proceed from either side of the plane given by Ph–αC–βC–H. Only a little steric disparity of these two sides may arise from the 'radical tail' βCHPh (imidate). However, this tail must create a very pronounced electrostatic disparity. Formation of the *threo* product from coupling of **13** with $\mathbf{A}^{\bullet -}$ will be hindered by charge repulsion. The observed stereoselectivity results clearly from a SET reaction of $\mathbf{A}^{\bullet -}$. In contrast, the reported[6] small to moderate stereoselectivity probably does not come from a reaction of $\mathbf{A}^{\bullet -}$ itself. An S_N2 reaction of its dimer or rather of one carbanion site of this dimer followed by BFR would easily explain the excess of Walden inversion in reactions with optically active alkylating agents. A similar explanation is not possible for the present results.

Thus, coupling of a charged radical ‡ with a radical anion can be controlled by an electrostatic effect exerted by the 'tail' of the charged radical. This novel stereoselectivity principle should be more effective and more useful when the reacting anionic radical is not a benzylic radical whose coupling with $\mathbf{A}^{\bullet -}$ is followed by BFR. Another drawback of this particular case may be an easy reduction of **13** as expected from its

‡ It appears advisable to differentiate between anionic radicals as **13** and radical anions as $\mathbf{A}^{\bullet -}$. Chemists usually associate the term radical anion with a species whose charge comes from the singly occupied MO (*cf. e.g. Radical Ions*, ed. E. T. Kaiser and L. R. Kevan, Interscience, New York, 1968, part of the series: Reactive Intermediates in Organic Chemistry).

Table 4 Product ratios *erythro*-**6**:*threo*-**6**:**11**:(*E*)-stilbene from reactions of *cis*-**4a** and *trans*-**4a** with $\mathbf{A}^{\bullet -}$

Run	Reagents (mmol/cm^3 THF)[a] **A**	Na	**4a**	Time	Molar ratios of products (see text)
1	17.5/100	15.0	*cis* 3.0/40	2 min	54:9:37:—
				5 min	46:17:38:—
				30 min	36:21:42:—
				1 h	34:20:46:—
				6.5 h	7:6:40:43
2	15.0/150	13.5	*cis* 4.99/50	2 min	66:8:26:—
				30 min	50:20:30:—
				3 h	31:17:35:17
				6 h	17:10:37:36
				10 h	7:5:43:45
3	12.0/150	8.8	*cis* 3.96/50	1 min	39:7:54:—
				5 min	34:8:58:—
				10 min	19:9:72:—
				20 min	6:10:84:—
				30 min	6:8:87:—
4	9.0/100	6.0	*trans* 3.11/40	2 min	51:5:44:—
				15 min	40:8:52:—
				30 min	30:10:60:—
				1 h	28:12:60:—
				10 h	0:0:0:100 (93%)
5	7.0/100	3.5	*cis* 2.92/40	1 min	15:6:78:—
				5 min	7:10:83:—
				30 min	4:8:88:—

[a] **A** in THF and Na were stirred for 1 d. Stirring was continued. The solution of **4a** in THF was added from a dropping funnel within 10–15 s. The reactions were quenched with acetic acid after sampling.

structure and the special electron source **12**. A third unfavourable factor is possibly a relatively slow formation of *erythro*-**8**. Coupling of an aromatic radical anion with an alkyl radical is known to be a very fast reaction.[11] In particular, coupling was faster than any other reaction of the intermediate amidatoalkyl radical, a substituted Bu^t radical, in the reaction of 2,2-dimethyl-1-pivaloylaziridine with $\mathbf{A}^{\bullet -}$ where no counterpart of **11** was found under conditions (run 2 of Table 1 in ref. 13) comparable to those of run 3, the run with the smallest excess of $\mathbf{A}^{\bullet -}$ in Table 3. As compared to this previous case, coupling of **13** may be slowed by steric hindrance arising from β-phenyl and by the decrease from 2 to 1 in the statistical factor.

Coupling of unreacted anionic radical **13** with available $\mathbf{A}^{\bullet -}$, as well as BFR of **8**, proceeds with reaction time. Thus, several experiments with varying excesses of $\mathbf{A}^{\bullet -}$ were conducted (Table 4) in a manner that would show the change in products and/or their relative yields with time. Samples, sufficient in size for routine workup, of the reaction solution were withdrawn with a pipette at the times given for each run and worked up. The products **6** and **11** were chromatographically obtained as ternary mixtures that were analyzed by ^{1}H NMR spectroscopy giving the molar ratios of products and approximate values of yields. When the sum of the approximate yields showed a large deficit, the hydrocarbon fraction, mainly anthracene, was analyzed for *trans*-stilbene by ^{1}H NMR spectroscopy giving a crude yield or rather an upper yield limit that made the sum of approximate yields exceed 100%. The amount of stilbene was then adapted to give a total of 100% making the product ratios include stilbene when necessary after long-term sampling. Formation of stilbene should produce the same amount of pivaloylamide that, however, was obviously lost during workup owing to volatility and solubility in water. The same problem is already known from pivaloylamide carrying short alkyl groups.[13] Most runs of Table 4 were performed with *cis*-**4a** since *cis*-**4a** is obtained in a pure state much easier than *trans*-**4a**. Summarizing, the experimental precision is not so high as in the runs of Tables 1–3 but the product ratios listed in Table 4 depend on time and other details in a manner that allows reasonable interpretations and mechanistic conclusions.

Run 1, conducted with the same ratio of reactants (5:1) as in run 1 of Table 3, provided *erythro*-**6** as the main product after 2 min, in accord with an incomplete coupling of **13** in the runs given in Table 3. Detection of ⩽9% of *threo*-**6** after 2 min is evidence for a reversible BFR of *erythro*-**8**. This reverse BFR (Scheme 3, bottom) can be discussed with the help of Scheme 4 when one simply replaces $\mathbf{A}^{\bullet -}$ by **A** and radical **13** by carbanion **9**. An electrostatic repulsion that hinders formation of *threo*-**8** does not exist between carbanion **9** and neutral **A**. One even may suspect that **9** and **A** for steric reasons prefer to form *threo*-**8** since internal electrostatic repulsion will push away the charged oxygen from the carbanion site (*cf*. the conformation in Scheme 4) and thus create or increase the steric disparity that favours the *threo* product. Summing up, the reverse BFR should produce both diastereomers but perhaps more *threo* than the *erythro* product. Indeed, with increasing reaction time, the *erythro*–*threo* ratio for **6** gradually changed from 54:9 to 7:6 in run 1.

The yield of **11** dropped from about 65% (Table 3) to ⩽37% in the 2 min sample of run 1. This indicates that in the very short runs of Table 3 about half of **11** arose directly from radical **13** without intermediacy of carbanion **9**. After 2 min, radical **13** should have completed its coupling with excess $\mathbf{A}^{\bullet -}$ leaving only the carbanion **9** as a precursor of **11**. The other samples of run 1 show that carbanion **9** reacts faster with **A** than with THF. This follows from a comparison of *erythro*–*threo* isomerization with the increase in amount of **11** and fits nicely with the previous finding[5] that the benzylic anion formed from **4c** reacted faster with the carbonyl group of available **4c** than with the solvent THF. Thus, the BFR path leading to **9** really contributes little to the formation of **11** in the short-term samples of run 1. Direct reduction of radical **13** to carbanion **9** by $\mathbf{A}^{\bullet -}$ or **12** is probably the main path leading to **11** in run 1 of Table 4. The competition between coupling and reduction of **13** as measured by the product quantities deviates from the corresponding competition known[13,6] for $\mathbf{A}^{\bullet -}$ and alkyl radicals. Reasons for this deviation are found in the above discussions but a different behaviour of alkyl and benzyl radicals cannot be excluded. A very slow process, recognizable after 6 h and possibly at work already after one hour, is the elimination of *trans*-stilbene from amide anion **10**. This will be discussed below.

Run 2 performed with a reactant ratio of 2.7:1 resembled run 1 in all ways. In both runs the colour of the solution after addition of **4a** remained dark-green. In run 3, with a reactant ratio of 2.2:1, this dark-green colour changed slowly to light yellow–green indicating an insufficient excess of $\mathbf{A}^{\bullet -}$ which explains the low extent of coupling. The molar amount of **11** was always high, higher than that of both isomers of **6** taken together, whereby the reaction time was obviously not long enough to observe conversion of **10** to stilbene. Perhaps favoured by the small amount of *erythro*-**6** formed after 1 min, later on slightly more *threo*-**6** than *erythro*-**6** was found. This correlates better with the *erythro–threo* rate difference of BFR than with the rate difference in reverse BFR. Generally, there is good reason to assume that the rate of BFR depends on the stereochemistry of **8**. The steric situation for BFR is different for *erythro*- and *threo*-**8**. Steric crowding in **2** had even suppressed BFR in another case.[17]

Run 4 with *trans*-**4a** and a reactant ratio of 1.9:1 showed also the trends already described but a comparison with run 3 reveals some differences in quantities of products that may be related to *cis–trans* isomerism. The rates of steps **4**→**12** and **12**→**13** may be different for *cis* and *trans*. The first step should be faster for the *cis* isomer owing to the steep nitrogen pyramid that makes *cis*-**4a** resemble a ketone while *trans*-**4a** has more amide character. A kind of stereoelectronic effect should accelerate the second step for *trans*-**12** since generation of a stabilized benzylic radical demands coplanarity of PhC–C, which is possible only for *trans*-**12**. A shorter lifetime of *trans*-**12** means less time for reduction of **13** explaining the difference of ratios in runs 4 and 3.

In order to verify the proposed non-carbanion path for **13** to **11**, run 5 was performed with a reactant ratio of 1.2:1, *i.e.* with practically equimolar quantities. In comparison to the other runs of Table 4, the formation of both **6** was a minimum with all samples in accord with the requirement of two equivalents of $\mathbf{A}^{\bullet -}$. The ratio of coupling and non-coupling resembles the respective ratios in Table 3. An alternative path to **6** can be excluded although Beckwith and Waters have described the addition of benzyl radical to **A**, but the observed main reactions of the arising dihydroanthryl radical were dimerization and coupling with a second benzyl radical.[7] Neither of these products were found in run 5. The high amounts of **11** in run 5 can only have arisen by hydrogen abstraction **13**→**10**, certainly from THF in these relatively long reaction times.

Elimination of olefines in SET reactions of acylaziridines have previously been described and possible mechanisms discussed.[18] Direct elimination from a precursor of type **10** was verified leaving some doubts about whether this is the whole explanation. The counter ion may have some influence. It was recently shown[4] that the sulfonyl counterpart of **9** with counter ion Li^+ immediately provided stilbene without any intermediate proton abstraction from $\mathbf{AH_2}$. The results shown in Table 4 exclude cleavage of **9** and **13** and leave the internal proton transfer in **10** as the route to the formation of stilbene under the present conditions.

Experimental

Characterization of products was accomplished by ^{1}H NMR spectroscopy (Bruker W250 instrument, $CDCl_3$ solution, signal multiplicity given, m_c = multiplet centred at; *J* values in Hz) and IR (Perkin-Elmer 283 instrument; KBr tablets unless otherwise stated).

All reactions were performed in dry, continuously stirred THF under nitrogen whose quality was secured with a THF solution of sodium naphthalenide.

Starting materials

Aziridines *cis*-**4a** and *trans*-**4a** are known.[14] $[^2H_4]\mathbf{AH_2}$ was prepared from $\mathbf{AH_2}$ and $[^2H_6]DMSO_6$ as described in ref. 19.

Reactions with anthracene hydride AH^-

These reactions were performed using the previously[19] described technique. Necessary details are given in Tables 1 and 2. The residue obtained by evaporation was taken up in dichloromethane and washed with water. Evaporation left a residue, which was subjected to chromatography (silica gel Merck, 0.063–0.200 mm, thickness × length column in cm and other details are given with each run). Preparative layer chromatography (PLC) was performed on plates 20 × 20 cm, 2 mm thick (Merck 5717, silica gel 60F254).

Run 1, Table 1. Chromatography (3 × 50 cm) with CH_2Cl_2 removed hydrocarbons. Elution with CH_2Cl_2–ethyl acetate (10:1) provided *erythro*-**6** (1.813 g, 82%), mp 193–194 °C (Found: C, 86.0; H, 7.3; N, 3.0. $C_{33}H_{33}NO$ requires C, 86.2; H, 7.2; N, 3.1%); ν_{max}/cm^{-1} 3400 (NH), 1648 (amide I) and 1522 (amide II); δ 0.71 (s, Bu^t), 2.09 (d, *J* 19.0, 10-H pseudo ax), 3.18 (d, *J* 19.0, 10-H pseudo eq), 3.60 (dd, *J* 2.8 and 11.5, NCCH), 4.18 (s br, 9-H pseudo eq), 5.41 (d, *J* 8.0, NH), 5.53 (dd, *J* 8.0 and 11.5, NCH), 6.33–6.36 (m, 2 × *o*–H of NCCPh), 6.94–6.96 (m, 4 × ArH), 7.09–7.28 (m, 6 × ArH), 7.37–7.42 (m, 2 × ArH), 7.51–7.57 (m, 2 × ArH) and 7.70–7.73 (m, 2 × ArH).

Run 2, Table 1. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with ethyl acetate provided a mixture (322 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-**6** (242 mg, 53%) and **11** (80 mg, 28%).

Run 3, Table 1. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with ethyl acetate yielded **11** (356 mg, 100%), mp 141–142 °C (Found: C, 81.2; H, 8.1; N, 5.1. $C_{19}H_{23}NO$ requires C, 81.1; H, 8.2; N, 5.0%); ν_{max}/cm^{-1} 3350 (NH), 1631 (amide I) and 1531 (amide II); δ 1.09 (s, Bu^t), 3.07 (dd, *J* 7.8 and 13.7, 1 H of CH_2), 3.12 (dd, *J* 6.5 and 13.7, 1 H of CH_2), 5.26 (m_c, NCH), 5.95 (d, *J* 7.2, NH), 7.04–7.07 (m, 2 × ArH) and 7.15–7.32 (m, 8 × ArH).

Run 4, Table 1. Only 20 cm^3 (withdrawn with a pipette) of the solution were quenched and worked up. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with ethyl acetate yielded a mixture (172 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-**6** (129 mg, 57%), **11** (43 mg, 31%) and anthraquinone (12 mg).

Run 1, Table 2. Chromatography (1.5 × 90 cm) with toluene removed hydrocarbons and then **7** (246 mg, 20%), mp 128–130 °C (Found: C, 86.3; H, 7.6. $C_{19}H_{20}O$ requires C, 86.3; H, 7.6%); ν_{max}/cm^{-1} 1703 (C=O); δ 1.28 (s, Bu^t), 3.81 (d, *J* 18.0, 10-H pseudo eq), 4.75 (d, *J* 17.9, 10-H pseudo ax), 5.53 (s, 9-H pseudo eq) and 7.12–7.35 (m, 8 × ArH). Elution with CH_2Cl_2–ethyl acetate (10:1) provided *cis*-**4a** (287 mg, 21%) and a mixture (1.092 mg) consisting (^{1}H NMR spectroscopy) of *threo*-**6** (1.055 g, 49%) and **11** (37 mg, 3%).

Run 2, Table 2. Chromatography (1.5 × 90 cm) with toluene removed hydrocarbons and then **7** (290 mg, 22%). Elution with CH_2Cl_2–ethyl acetate (10:1) yielded a mixture (1.338 g) consisting (^{1}H NMR spectroscopy) of *threo*-**6** (1.240 g, 55%) and **11** (98 mg, 7%).

Run 3, Table 2. Chromatography (1.5 × 90 cm) with CH_2Cl_2 removed hydrocarbons and then *threo*-**6** (347 mg, 60%), mp 216–217 °C (Found: C, 86.1; H, 7.2; N, 3.0. $C_{33}H_{33}NO$ requires C, 86.2; H, 7.2; N, 3.1%); ν_{max}/cm^{-1} 3400 (NH), 1646 (amide I) and 1522 (amide II); δ_H 1.33 (s, Bu^t), 1.93 (d, *J* 18.8, 10-H pseudo ax), 3.18 (d, *J* 19.0, 10-H pseudo eq), 3.45 (dd, *J* 2.2 and 11.7, NCCH), 4.66 (s br, 9-H pseudo eq), 5.66 (dd, *J* 9.6 and 11.7, NCH), 6.19 (d, *J* 9.4, NH), 6.04–6.07 (m, 2 *o*–H of NCCPh), 6.65–6.71 (m, 2 × ArH), 6.86–7.41 (m, 13 × ArH) and 7.68–7.71 (m, 1 × ArH). Elution with CH_2Cl_2–ethyl acetate (1:1) yielded a mixture (141 mg) consisting (^{1}H NMR spectroscopy) of **11** (116 mg, 33%) and anthraquinone (25 mg).

Run 4, Table 2. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with CH_2Cl_2–ethyl acetate (10:1) provided a mixture (395 mg) that was separated by PLC with CH_2Cl_2–ethyl acetate (50:1) into *threo*-**6** and a mixture. Scratching out and eluting with hot ethyl acetate yielded (*i*)

pure *threo*-**6** (130 mg) and (*ii*) a mixture (197 mg) consisting (^{1}H NMR spectroscopy) of *threo*-**6** (34 mg, total 164 mg, 26%) and **11** (163 mg, 42%).

Run 5, Table 2. At the times given in Table 2, 20 cm^3 were withdrawn from the solution with a pipette, quenched and worked up. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with ethyl acetate provided the following results (^{1}H NMR spectroscopy). The 30 min sample gave a mixture (136 mg) consisting of *threo*-**6** (50 mg, 22%), **11** (71 mg, 51%) and anthraquinone (15 mg). The 1 h sample gave a mixture (135 mg) consisting of *threo*-**6** (32 mg, 14%), **11** (87 mg, 63%) and anthraquinone (16 mg). The 27 h sample gave pure **11** (136 mg, 98%).

Reactions of 9,10,10-trideutero-AH$^-$ with *trans*-4a and *cis*-4a

[^{2}H$_4$]**AH$_2$** (5.5 mmol) in THF (70 cm^3), BuLi (5 mmol, in hexane) and *trans*-**4a** in THF (20 cm^3) reacted for 22 h and was worked up as described above for reactions given in Table 1. Chromatography (3 × 15 cm) with toluene removed hydrocarbons. Elution with ethyl acetate provided a mixture (335 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-[^{2}H$_3$]**6** (203 mg, 43%) and [^{2}H]**11** (132 mg, 46%). Separation by PLC (CH_2Cl_2–ethyl acetate 50:1) provided the pure products: *erythro*-[^{2}H$_3$]**6** (deuteration ⩽90%), mp 193–195 °C; the ^{1}H NMR data match with those of *erythro*-**6** except for very weak (⩽10% of the required integral) signals for 9-H and both 10-H atoms while the double doublet (dd) at 3.60 ppm had changed to a doublet (d) (*J* 11.5); [^{2}H]**11** (deuteration 82%), mp 140–141 °C; the ^{1}H NMR data match with those of **11** except for very weak signals (⩽10% of the required integral) at 3.07 ppm (1 H of CH_2) and the change of the dd at 3.12 ppm (1 H of CH_2) to d (J 6.5).

[^{2}H$_4$]**AH$_2$** (17.5 mmol) in THF (120 cm^3), BuLi (15 mmol, in hexane) and *cis*-**4a** (3.15 mmol) in THF (40 cm^3) were reacted as described above. A sample (20 cm^3) was withdrawn after 3 h and a second sample (80 cm^3) after 4 d. Workup and chromatography (3 × 17 cm) of the second sample with toluene removed hydrocarbons. Elution with ethyl acetate provided [^{2}H$_1$]**11** (325 mg, 73%), identical with the product described above. Workup of the first sample and chromatography (3 × 17 cm) with toluene removed the hydrocarbons followed (ethyl acetate) by mixture I (75 mg) and mixture II (93 mg). Mixture I consisted (^{1}H NMR spectroscopy) of *threo*-[^{2}H$_3$]**6** (63 mg) and anthraquinone (12 mg). Mixture II consisted (^{1}H NMR spectroscopy) of *threo*-[^{2}H$_3$]**6** (54 mg, total 117 mg, 64%) and [^{2}H]**11** (40 mg, 36%). Recrystallization of mixture I from CCl_4 provided pure *threo*-[^{2}H$_3$]**6**, mp 215–216 °C; the ^{1}H NMR data matched with those of *threo*-**6** except for very weak (⩽10% of the required integral) signals for 9-H and both 10-H, while the dd at 3.45 ppm (NCCH) had changed to a doublet (*J* 11.8).

Reactions with anthracenide A$^{\cdot -}$

These reactions were performed following the previously[13] described techniques. Necessary details are given in Tables 3 and 4. Workup was carried out as described under reactions with **AH$^-$**.

Run 1, Table 3. Chromatography (3 × 20 cm) with toluene removed hydrocarbons. Elution with CH_2Cl_2 provided anthraquinone (75 mg). Elution with ethyl acetate yielded a mixture (303 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-**6** (120 mg, 26%) and **11** (183 mg, 65%).

Run 2, Table 3. Chromatography (3 × 20 cm) with toluene removed hydrocarbons. Elution with CH_2Cl_2–ethyl acetate (2:3) yielded a mixture (276 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-**6** (85 mg, 18%), **11** (191 mg, 68%) and a trace of *threo*-**6**.

Run 3, Table 3. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with CH_2Cl_2 provided anthraquinone (34 mg). Elution with ethyl acetate yielded a mixture (507 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-**6** (162 mg, 19%) and **11** (345 mg, 66%).

Run 4, Table 3. Chromatography (3 × 17 cm) with toluene removed hydrocarbons. Elution with CH_2Cl_2 provided anthraquinone (61 mg). Elution with ethyl acetate yielded a mixture (400 mg) consisting (^{1}H NMR spectroscopy) of *erythro*-**6** (171 mg, 22%, deuterated at position 10-H pseudo-axially to an extent of 67%), [^{2}H]**11** (229 mg, 49%, degree of deuteration, 63%) and a trace of threo-**6**.

Runs of Table 4. The samples (20 cm^3) of the solution were withdrawn by means of a pipette. Keeping the sample and the remaining solution free of air whilst removing samples was difficult and required quick action. The precision of sampling was consequently not high. Each sample was quenched with acetic acid. Evaporation provided a residue that was taken up in CH_2Cl_2 and washed with water. Evaporation gave a residue that was subjected to chromatography (3 × 17 or 3 × 20 cm) with toluene which removed the hydrocarbons. Further elution was performed with ethyl acetate, providing the product mixture, or was performed with CH_2Cl_2–ethyl acetate (2:3), providing anthraquinone, followed by elution with ethyl acetate to give the product mixture. Two samples of run 1 are described with full details. The other samples of all runs were analysed in the same manner.

Run 1, Table 4, sample after 5 min. The product mixture (156 mg) consisted (^{1}H NMR spectroscopy) of *erythro*-**6** (98 mg, 50%), *threo*-**6** (17 mg, 8%) and **11** (41 mg, 34%).

Run 1, Table 4, sample after 6.5 h (volume of sample 60 cm^3). The product mixture (224 mg) consisted (^{1}H NMR spectroscopy) of *erythro*-**6** (42 mg, 7%), *threo*-**6** (36 mg, 7%) and **11** (146 mg, 40%). The hydrocarbon fraction (1.288 g) contained (^{1}H NMR spectroscopy) (*E*)-stilbene (116 mg, ⩽50%) identified by comparison (^{1}H NMR spectroscopy, tlc) with authentic material.

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