

Aziridines. 76 [1]

Neglected Aspects of Anthracenide (Anthracenidyl) Chemistry – Reactions with two *N*-Benzoylaziridines

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Abstract. Reaction of anthracenide $A^{\cdot-}$ with *N*-benzoylaziridines **1a,b** forms charged radicals **3a,b** by single electron transfer and homolytic ring opening. Reactions follow that are known or expected as *e.g.* coupling with position 9 of $A^{\cdot-}$ forming dihydroanthracene anions **9a,b** that yield amidoethylated dihydroanthracenes **10a,b**, or react with **1a,b** giving finally 9,10-bis-amidoethylated dihydroanthracenes **11a,b**. Results depend on experimental conditions and on the counter ions Na^+ or Li^+ . Coupling is not regioselective: contributions by positions 2 and 1 reach 29% or 4%, respectively, of total coupling with the primary radical **3a**; much

higher contributions are possible with Li . Product **21s** (probably 3,3'-disubstituted tetrahydrobianthryl) may arise by hydrogen detachment from the first intermediate (**29**) of coupling with position 2 and dimerization of the formed 2-substituted $A^{\cdot-}$ (**30**). Coupling products may be fully aromatized or may be hydroxylated in one of the benzylic positions. With counter ion Li^+ a non-SET reaction of **1a** with the dimer of $A^{\cdot-}$ is indicated by the isolation of 9-benzoyl-dihydroanthracene **15** and by 19% yield of **16a** (aromatized **10a**). Reaction of **3b** with anthracene is indicated by 10,10'-disubstituted tetrahydrobianthryl **37**.

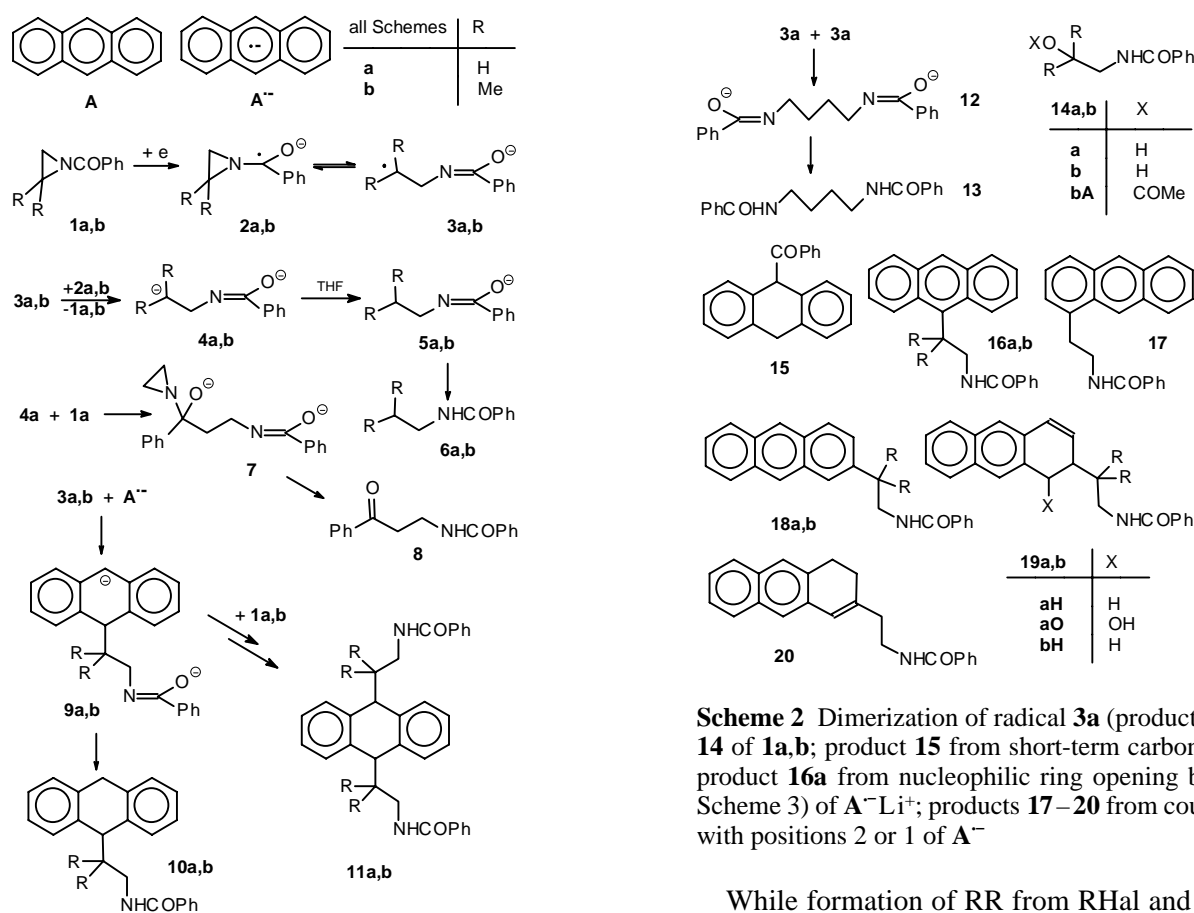
Single electron transfer (SET) reactions of *N*-acylaziridines with radical anions and other electron sources were prompted by a mechanistic problem [2]. Usually aziridino ketyls arise and homolyze to amidatoalkyl radicals [2–7]. The final result can depend on substituents of the aziridine ring, on the acyl group and on the radical anion. 2-Phenylaziridines present a special case [6–7]. Reactions with *N*-pivaloylaziridines were reported both with naphthalenidyl $N^{\cdot-}$ (naphthalenide) and with $A^{\cdot-}$ [3], reactions of *N*-aroylaziridines with $N^{\cdot-}$ only [5]. After a very short notice [2], reactions of **1a,b** with $A^{\cdot-}$ are now fully described with steps and types of products usually ignored or even unknown in $A^{\cdot-}$ chemistry and therefore of possible importance for reactions with alkylating agents RX [8] (*cf.* introduction in [3]) that give alkylation in position 9 (and 10) of $A^{\cdot-}$ besides reduction ($\rightarrow RH$) and multi-step dimerization ($\rightarrow RR$) (Scheme 1).

Results and Discussion

Tables 1 and 2 present the most important ones of many experiments with **1a,b** and $A^{\cdot-}$. Main products (Scheme 1) are **6a,b**, **8**, **10a,b** and **11a,b**. In contrast to RX above, **1a** (Table 1) provided more **6a** (corresponding to RH) than **10a** and **11a** taken together. It had been concluded

[3] that the amidatoalkyl radicals (here **3a,b**) are reduced to the carbanions (here **4a,b**) by the aziridino ketyl (here **2a,b**), a path not possible with RX . Subsequent steps to **6a,b** and **8** are known from reactions with other electron sources [5]. Since **6a** and ketone **8** are very difficult to chromatographically separate from one another run 1 includes a laborious technique to overcome this problem. A question-mark for the yield of **13** in Table 1 indicates that this nearly insoluble product may have been lost during work-up [5]. This does not disturb a discussion of the other products. Counter ion Na^+ has been replaced by Li^+ in runs 6 and 7 that are dealt with separately.

The product of two-fold SET (**6a**) was always the main product of Table 1 in contrast to the results from reactions of $A^{\cdot-}$ with RX [8] or with *N*-pivaloylaziridines [3]. This is in accord with the electron source **2a** for the conversion **3a** \rightarrow **4a** since **2a** has a longer lifetime than aliphatic aziridino ketyls and can better compete with $A^{\cdot-}$. This SET from **2a** to **3a** may further profit from the reported [5] reversible dimerization of **2a** if one ketyl of the separating pair undergoes ring opening before it diffuses away. The yields of **6a** (and also of **6b** in Table 2) may be a bit low in long term runs since **5a,b** and analogous precursors can eliminate [5] the *N*-substituent as olefine (ethene from **5a**) when Na^+ is the counter ion.



Scheme 1 Formation of main products: 1) SET from $A^{\bullet-}$ to **1**; 2) homolytic ring opening **2** \rightarrow **3**; 3) either reduction of radicals **3** to carbanions **4** or coupling of **3** with $A^{\bullet-}$ to yield **9** and finally products **10** and **11**; 4) **4a,b** are protonated by THF to **5a,b** yielding finally products **6a,b** although part of **4a** forms product **8** via carbonyl attack (intermediate **7**) on **1a**

Scheme 2 Dimerization of radical **3a** (product **13**); artifacts **14** of **1a,b**; product **15** from short-term carbonyl attack and product **16a** from nucleophilic ring opening by dimer (see Scheme 3) of $A^{\bullet-}Li^+$; products **17–20** from coupling of **3a,b** with positions 2 or 1 of $A^{\bullet-}$

While formation of RR from RHal and an aromatic radical anion proceeds by reduction of the radical R^{\bullet} ($\rightarrow R^-$) and SET reaction of the generated carbanion R^- with RHal providing a radical pair that collapses to RR [9], the precursor **12** of dimer **13** arises by a direct dimerization of radical **3a** without intermediacy of **4a** [5]. The highest yield of **13** comes from a run (9) that favours a high conversion **1a** \rightarrow **2a**. Encounter of **4a**

Table 1 Reactions of **1a** with $A^{\bullet-}$ in THF^{a)} at room temperature. Influence of experimental conditions.

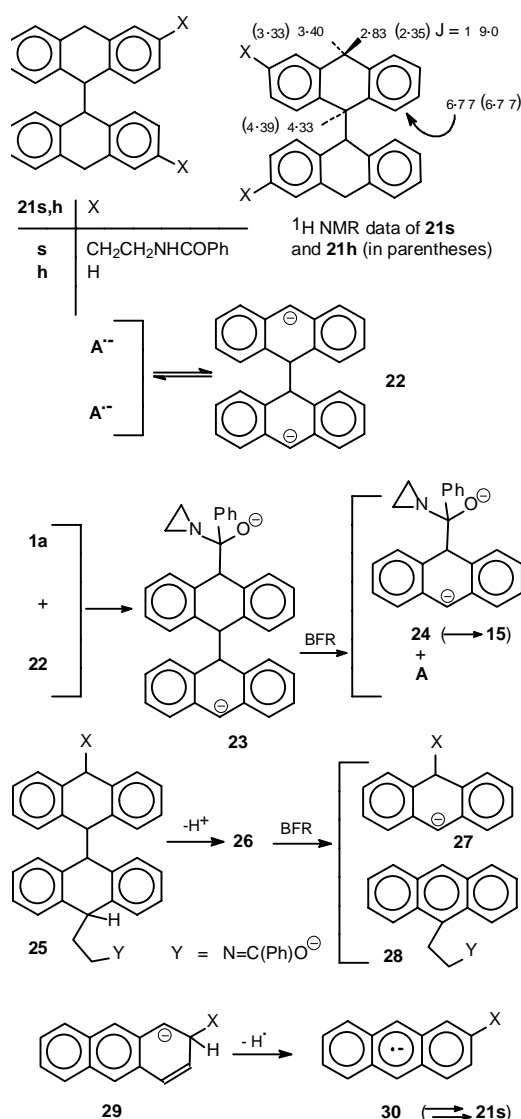
run	mmol of reagents			time ^{b)}	yields ^{c)} of products					further products	
	metal	A	1a		6a	8	10a	11a	13		1a ^{d)}
1	15 Na	15	15	15 min ^{e)} /40 h	37	19					
2	6.3 Na	6	3.2	30 min/30 min	(39)	(5)	(6)	(11)	?		
3	6.3 Na	6	5.6	30 min/30 min	(36)	(18)	4	(16)	(5)		
4	5.4 Na	7.5	4	2 layers ^{f)} /2 h	(34)	(1)	14	(4)	–	39 14a	
5	6 Na	6.5	5.2	ca.10 s ^{g)} /–	(24)	(17)	2	(11)	6	29 1a , 3 14a	
6	6 Li	6.5	5.3	ca.10 s ^{g)} /–	11	tr	2	–	–	67 1a , 9 14a	7 15
7	17 Li	20	6.8	inj. ^{h)} /3 d	57	10	(1)	–	?		19 16a , (1) 17 , (>0.5) 18a , (1) 19aH , (4) 19aO ⁱ⁾ , (0.3) 20 (0.5) 17 , >4 19aO ⁱ⁾
8	17 Na	20	6.8	inj. ^{h)} /1 d	>28 ^{j)}	tr	(2)	15	4		
9	12 Na	14	2	36 min/–	(41)	(13)	(18)		17		1 16a , 17 , 19aH , 19aO ⁱ⁾ , 2 20 , (4) 21s

^{a)} Anthracene **A** and metal in 100 ml, **1a** in 20 or 30 ml. ^{b)} Specification before the slant is the time required for the addition (dropwise unless otherwise stated) of **1a**. Reactions were quenched (except run 1) with MeCO₂H. ^{c)} Yields in parentheses are from ¹H NMR of product mixtures. tr = trace. A product number without yield in the last column indicates a trace. For „?“ see text. ^{d)} And artifacts of **1a**. ^{e)} At –10 °C. ^{f)} **1a** solution slowly poured over $A^{\bullet-}$ solution, no stirring. ^{g)} Fastest possible flux from a dropping funnel. ^{h)} Rapid injection of **1a** solution. ⁱ⁾ Mixture of diastereomers α -**19aO** and β -**19aO** where the former predominated. ^{j)} 28–29%.

with **1a** would not lead to **12** but give ketone **8** via **7** [5] as is also supported by the influence (runs 2–3) of the molecular ratio A^- : **1a** that needs to be ≥ 2 :1 for the products **6a** and **10a** (from coupling of **3a** with A^-) but only 1:1 for **8** and **11a**. An „addition“ of dissolved **1a** to dissolved A^- nearly without mixing describes run 4; slowing bimolecular reactions by thermal diffusion across the interface makes **3a** live long enough [5] to form **5a** with THF and to react with A^- when this is regenerated from **A** by SET. Formation of **11a** (bis-imidate) proceeds by fast (cf. short-term run 5 with high concentrations of **1a** and **9a** during rapid mixing) nucleophilic ring opening of **1a** through **9a** (counter ion Na^+) that possibly is preceded by an even faster reversible attack of **9a** (carbanionic site) on the carbonyl group of **1a** [10, 11]. Run 9 shows that this reaction can be suppressed by a large excess of A^- combined with slow dropwise addition of **1a**, conditions that simultaneously favour strongly the reaction of **30** with A^- (total coupling reaches 25%). In contrast, moderate excess, long reaction time and very fast mixing (run 8) provided the highest yield ratio (7.5) of **11a**: **10a** in Table 1. The pivaloyl analogue of **1a** yielded under similar conditions no analogue of **10a** at all but 26% of the analogue of **11a** [3] in accord with a reaction time of three days. From runs 5 and 9 follows that even with counter ion Na^+ the carbanion **4a** reacts much faster with **1a** than with THF taking into account the difference in concentrations. **14a** arose by hydrolytic ring opening of unreacted **1a**.

Elaborate chromatography in runs 7–9 led to the detection of several by-products where the benzamidoethyl chain is attached to position 1 or 2 of the anthracene ring system. Apart from two pivaloyl analogues of **18a** [3] this seems to be without precedence in A^- chemistry. Most of these by-products are not obtained in a pure state but their structures are deduced from unambiguous 1H NMR signals. Protons in positions 9 and 10 of anthracene compounds show singlets near 8.4 ppm, a region usually without signals. Two singlets of equal intensity at 8.42 and 8.69 ppm indicate structure **17** since the downfield shift for one of these protons points to a substituent in the neighbouring position 1. Isomer **16a** is one of the main products in Li run 7. Pure isomer **18a** shows the two singlets at 8.37 and 8.42 ppm. The structure of **19aH** follows from signals of the olefinic double bond and from a multiplet at 3.1 ppm (NCCCH=C=C). The 3,4-dihydro isomer **20** shows a C=CH singlet at 6.52 ppm. The hydroxy compound **19aO** is found as two diastereomers α and β . Their structure was deduced, among others, from the OCH signals. Signals for ArH and CH_2CH_2NH are always seen but usually difficult to distinguish from one another and from signals of other products.

Coupling of A^- with a radical is clearly not regiospe-



Scheme 3 Proposed structure of by-product **21s** and 1H NMR comparison with known **21h**; dimerization of A^- and reaction of the dimer **22** with **1a** forming either **23** (and hence **15**) or **25** ($X = H$ or CH_2CH_2Y) and hence **28** and **16a**.

cific, and run 8 shows that at least coupling in position 2 cannot be neglected since it reached 29% (much higher in the Li run 7, see below) of the total coupling with **3a** but only 4% for position 1. The 2 isomer of **9a** is certainly not so stable as **9a** and may easily be oxygenated when oxygen enters the reaction vessel during quenching. Dehydration of the final product **19aO** would form **18a**. An analogous path to **17** is possible (for an alternative path to **17** and **18a** see below) but **16a** may arise from a special mechanism discussed below. Of course, one cannot exclude a hydroxylation during work-up. The assigned structure of product **21s** will be dealt with later.

Na run 5 and Li run 6 have been performed identically except for the counter ion. A comparison shows that

the SET step **1a** → **2a** as well as the reaction of **1a** both with **4a** (→→ **8a**) and **9a** (→→ **11a**) proceeds more slowly with Li, the latter due to a deactivating carbanion stabilization. **15** was found only with Li after a very short reaction time (run 6) but not in the long-term Li run 7. One reaction of **A⁻**, namely its (reversible) dimerization (Scheme 2), is usually ignored or even denied in spite of Schlenk's evidence (mol. mass after carbonization and methylation of the dicarbonic acid) [12], later independent confirmation [13] and theoretical arguments for a special behaviour of this radical anion. The equilibrium will be shifted by Li⁺ in favour of the dimer **22** due to the carbanion stabilization by Li⁺. The lowered concentration of monomer **A⁻** may explain the slow SET step at least in part as well as the decrease of coupling (at most ca. 1% of **16a** in run 7 may have been formed by radical coupling, see run 9). This dimerization explains the formation of **15** in run 6 and the high yield of **16a** in run 7. Fast attack of the lithiated „monomeric **22⁻**, *i.e.* of 9-lithio-9,10-dihydroanthracene, on the carbonyl of **1a** is known [10,11]. Thus, formation of **23** from **22** can be expected, followed by heterolytic (Scheme 3) benzylic fragmentation (BFR) to give **A** and **24** that yields **15** if the time until quenching is too short for a homolytic BFR of **24** that would provide **A⁻** and **2a**. Lack of **15** in the long term Li run 7 may be considered evidence that this inner-sphere SET path to **2a** [11b] plays a role and perhaps even an important role with Li. This is underlined by the high yields of **6a,b** in Li runs 6, 7 and 13 (Table 2): the yield in run 6 is 46% of converted **1a**. Homolytic BFR of **24** (counter ion Li⁺) and its dimethyl analogue gives much more **6a,b** than **10a,b** [11].

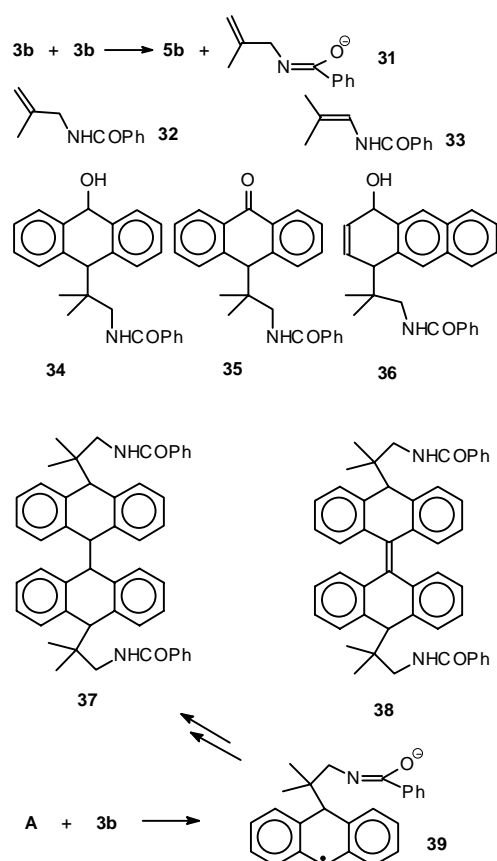
The high yield of **16a** in run 7 can be explained in a similar manner with a slight modification, already described for the pivaloyl analogue of **16a** [3]. The rapid injection of **1a** in run 7 may enable a reaction of both carbanion sites in **22** forming **25** that by deprotonation in the lower part (H indicated in the formula) gives carbanion **26** that undergoes heterolytic BFR yielding **27** and **28**, the precursor of **16a**. The fate of **27** depends on X. **27** arises from **22** and **1a** either by carbonyl attack or by ring opening. More likely appears the path **23** → **25** to **27** that in this long-term run would undergo homolytic BFR to **A⁻** and **2a**.

Run 7 and 8 have been performed identically except for counter ion and reaction time that certainly was unnecessarily long in run 7. Material balance (ca. 94%) and yield of **6a** are high in run 7. Lower yield and poorer balance in run 8 point to the mentioned ethene elimination from **5aNa⁺** [5]. **5aLi⁺** in run 7 is much more stable as already shown by the yields of **6a** [11]. The excess of **A⁻** and the rapid injection of **1a** in runs 7 and 8 are unfavourable for the formation of **8** since carbanion **4a**, once it is formed, will find only small concen-

trations of **1a** in contrast to the situation in run 9. The result is more pronounced in run 8. The 10% yield in run 7 may be ascribed to the stabilization of **4a** by Li⁺ that retards the protonation much more than the carbonyl attack which perhaps even may be faster with the lithiumorganic reagent. Surprising are the high contributions of coupling with positions 2 and 1 in the Li run 7. The above given maximum estimate (1%) of **16a** arising from coupling *via* **9a** gives a total of 8.8% for all coupling products. This total coupling is then composed of the contributions 23%, 66% and 11% for coupling in position 9, 2 and 1, respectively. It appears as if the spin distribution in **A⁻** changes markedly on going from Na⁺ to Li⁺. This may be correlated to changes in the fast equilibria between different kinds of **A⁻** ion pairs including that one of the paramagnetic dimer of **A⁻** [14].

A late chromatographic fraction of run 9 contained **8** together with a further product. Its ¹H NMR spectrum (see Scheme 3) showed two 19.0 Hz doublets and a singlet at 4.33 ppm pointing to a dihydroanthracene compound substituted in position 9 by a substituent Z that does not show vicinal coupling. The shift rules out Z = CPh and Z = OH, OR but all these signals as well as a kind of doublet at 6.77 ppm of this uncommon product, proposed structure **21s**, match nicely the respective signals in **21h** [15] except for 10-H *pseudo ax*. This shift difference may arise from the side chain CH₂CH₂NHCOPh in **21s** whose CH₂ signals (for an easier understanding discussed here for one half of this symmetrical molecule only) show diastereotopism as expected from structure **21s**: multiplets at 2.16 ppm (1H of NCCH₂), 2.62 ppm (1H of NCCH₂), 3.15 ppm (1H of NCH₂) and 3.60 ppm (1H of NCH₂). Additionally, these multiplets, NCH₂ less clear than NCCH₂, appear as doubled more simple sub-multiplets of unequal intensity within each sub-multiplet pair. This doubling is compatible with an unequal mixture of *meso*-**21s** and *rac*-**21s**. If the assumed structure is correct, how can it arise? A reasonable sequence follows. Coupling of **3a** with **A⁻** is favoured in run 9 (see above) and should form some carbanion **29**. This is less stable than isomer **9a** and should be a good hydrogen donor in reactions with a radical, *e.g.* **3a**. The high yield of **13** simultaneously indicates particularly high concentrations of **3a** in this run. Thus, abstraction of the allylic hydrogen atom in **29** by **3a** may generate **30** whose dimerization gives the tetra-anion of **21s**, both when the side chains point in the same or in the opposite direction during dimerization. The reverse dimerization would be less effective than the conversion **22** → **A⁻** if it is slowed down by some stabilizing interaction of the side chain from one half to the other half in the charged precursor of **21s**, *e.g.* by chelating the counter ion of the carbanion. The hydrogen detachment from **29** or its 1-isomer may also be a simple path to products **18a** and **17** when

the arising **30** (or its 1-isomer) transfers the unpaired electron to **A**. Due to the high excess of \mathbf{A}^- in run 9 would this SET be less effective thus allowing some dimerization. A positional isomer of **21s** can be ruled out by the following arguments. Coupling in position 1 of \mathbf{A}^- is generally less important than in position 2. Moreover, ^1H NMR signal (4H) at 6.77 ppm excludes substitution in positions 1, 1', 8 or 8' while substitution in positions 4, 4', 5 or 5' should influence the 19.0 Hz doublets relative to **21h** more than observed. Substitu-



Scheme 4 Disproportionation of **3b** forming **32** and in part **33**; artifacts **34–36** of coupling products; addition of radical **3b** to anthracene **A** and dimerization of the adduct **39** yielding finally **37** and its artifact **38**.

tion in positions 2, 2', 7 or 7' would make the signal at 6.77 ppm a singlet with perhaps some fine splitting and could for steric reasons not exert the observed shift of the 2.35 doublet in **21h** to 2.83 ppm in the new product.

Some reactions of **1b** are listed in Table 2. Except for run 13, **6b** was not the main product, even taken together with **32** and **33**. The tertiary radical **3b** does not dimerize; its self reaction is disproportionation to **5b** and **31**, the precursor of **32** and **33** (via slow base catalyzed isomerization of **31** [16]). It is not clear how much of **32** is an artifact of **1a**. Product **33** in run 13 indicates that here at worst only a part of **32** is an artifact. **10b** is always the main or the second important product. Surprising is the formation of **11b** that even is the main product in the equimolar long-term run 10. No pivaloyl analogue of **11b** has previously been found, although a nucleophilic ring opening of the pivaloylaziridine is faster than that one of **1b** [17]. Anions of 9-substituted dihydroanthracenes are known to prefer the *cis* conformation [18]. We suspect therefore that the pivaloyl analogue (Ph replaced by *t*-Bu) of **9b** exerts a stronger shielding of the carbanionic centre than **9b** does. The slowness of the reaction of **9b** with **1b** can be recognized from a comparison of runs 10 and 11. **11b** may exist as *cis* or *trans* isomer. It was isolated in three runs, showing the same melting point and mixed melting point but indicating two isomers by the ^1H NMR spectra.

Again, several „irregular“ products were detected. **18b** and **19bH** are recognizable from ^1H NMR comparison with **18a** or **19aH**, respectively. An olefinic doublet of doublet at 6.17 ppm ($J = 9.9/3.8$ Hz) indicates that there is only one vicinal aliphatic proton in **19bH**. Lack of **16b** in the Li run 13 contrasts with the high yield of **16a** in run 7. This is expected from steric hindrance of a nucleophilic ring opening by **22** (cf. [17]). Part of **10b** in run 13 was found hydroxylated (**34**) giving rise to *cis*–*trans*–isomerism. One isomer (α -**34**) was obtained pure while β -**34** was only found in mixture with **36** from which a single crystal could be picked out. The CHO singlet of α -**34** is downfield from that of β -**34** indicating that this H stands *pseudo-axial* in α -**34** as expected for the *cis*-isomer. The rather high yield of

Table 2 Reactions of **1b** with \mathbf{A}^- in THF at room temperature. Influence of experimental conditions

run	mmol of reagent/ml of THF		time ^{a)}	yields ^{b)} of products					further products
	metal + A /THF	1b /THF		6b	32	33	10b	11b	
10	15 Na + 15/150	15/30	15 min ^{d)} /40 h	(18)	(7)	–	21	40	
11	5.6 Na + 7.5/100	5/30	15 min/1d	(15)	(10)		32	9	12 Oxa ^{e)} 12 14bA
12	11 Na + 20/150	10/20	inj. ^{f)} /2d	4	8	–	13	5	3 Oxa ^{e)} (1) 14b
13	15 Li + 18/150	6/10	inj. ^{f)} /1d	34	4	3	17	0	6 18b , 10 α - 34 , 1 β - 34 , 0 35 , 0.5 36

^{a)} Specification before the slant is the time required for the addition of dissolved **1b**. Addition was dropwise unless otherwise stated. Reactions were quenched (except run 1) with acetic acid (run 2) or methanol (run 3 and 4). ^{b)} Yields in parentheses are from ^1H NMR of product mixtures. ^{c)} Artifacts of **1b**. ^{d)} At -10 °C. ^{e)} Oxa = 5,5-Dimethyl-2-phenyl-4,5-dihydrooxazole. ^{f)} Rapid injection of dissolved **1b**.

34 may result from the carbanion stability of **9b**(Li⁺)₂ that slows protonation by methanol used to quench this run. Anthrone **35** in run 12 may arise from **34** or its peroxidic precursor. The only 1-substituted anthracene product obtained from **1b** was **36**. Its most characteristic and structure proving ¹H NMR signals are those for the olefinic double bond: doublets of doublets at 6.37 ppm and 6.48 ppm (*J* = 10.4/5.2 Hz). The total coupling of **3b** with **A**^{•−} in the Li run 13 amounted to 34.5% with a distribution of 81%, 17% and 1.4%, respectively, for positions 9, 2 and 1.

A real surprise were the dimeric products **37** and **38**. ¹H NMR showed a slow conversion **37** → **38** of the crystals during storage or handling. The structures were deduced from ¹H NMR and MS, the dimeric nature proven by a FAB spectrum of **37**. How can **37** arise? A path similar to that one proposed for **21s** is obviously unlikely. However, 2-cyano-2-propyl radical (Me₂C–CN radical), structurally resembling **3b**, is known [19] to add to position 9 of **A**; one reaction of the arising substituted dihydroanthryl radical is dimerization to yield an analogue of **37**. Thus, we propose that **3b** and **A** form **39** which dimerizes to the *N*-deprotonated **37**.

This paper shows that reactions of **A**^{•−} with substituting reagents can strongly depend on the counter ion, that they may include reactions of dimerized **A**^{•−}, that generated radicals may couple with **A**^{•−} not exclusively in position 9 and that position 2 is more prone to coupling than position 1. **A**^{•−}Li⁺ may couple even more in position 2 than 9. Furthermore, the products may be fully aromatized. Even bianthryl derived products may arise and radical addition to **A** may occur.

Experimental

¹H NMR: Bruker WM 250, AC 200, AC 300, CDCl₃. – IR: Perkin-Elmer 283, KBr tablets unless otherwise stated. – MS: Varian MAT 311-A. Chromatography: silica gel Merck, 0.063–0.2 mm, column dimensions in cm are given with each run, mixtures analyzed by ¹H NMR. Abbreviations: Chr. (chromatography), dic. (CH₂Cl₂), EA (ethyl acetate), B (benzene), T (toluene).

General Procedure

See Tables. All reactions were performed in dry THF under dry N₂ (Ar with Li) with continuous stirring (except run 4). The mixture of **A**, THF, and metal was stirred for 0.5–1 d (2 d with Li). Addition of **1a** or **1b** and quenching is stated in the Tables. On evaporation of THF usually some **A** precipitated that was removed. The residue of evaporation was taken up in dic., washed with water and evaporated. Further treatment is given below. Some products are known: **8**, **13** and **33** [5]; **6a**, **6b**, **10a**, **10b**, and **15** [11]; **11a** [20]; **32**, Oxa [21].

Run 1

Chr. (35 × 3, dic.) provided hydrocarbons and a mixture of **6a**

and **8** that was dissolved in CCl₄ and 5 times washed with water. Evaporation of the organic layer yielded 360 mg (19%) of **8**. The wash water was twice extracted with dic. to give 830 mg (37%) of **6a**.

Run 2

Chr. (80 × 2, dic.) removed hydrocarbons. Elution with EA provided 363 mg of a mixture consisting of 189 mg (39%) of **6a**, 20 mg (5%) of **8**, 66 mg (6%) of **10a** and 87 mg (11%) of **11a**.

Run 3

Chr. (40 × 3, dic.) provided hydrocarbons and 70 mg (4%) of **10a**. Elution with dic./EA 1:1 yielded 642 mg of a mixture consisting of 302 mg (36%) of **6a**, 129 mg (18%) of **8** and 211 mg (16%) of **11a**. Elution with MeOH gave 178 mg of a mixture that was boiled out with EA/MeOH 3:1. Hot filtration yielded an extract containing (calibrated ¹H NMR) 41 mg (5%) of **13**.

Run 4

Chr. (40 × 3, dic.) removed hydrocarbons. Elution with dic./EA 10:1 yielded 182 mg (14%) of **10a**. Elution with dic./EA 1:1 gave 247 mg of a mixture consisting of 206 mg (34%) of **6a**, 7 mg (1%) of **8** and 34 mg (4%) of **11a**. Elution with MeOH yielded 259 mg (39%) of **14a**.

N-(2-Hydroxyethyl)benzamide (**14a**)

m.p. 55–57 °C (Lit. ca. 58 °C [22]). – ¹H NMR δ/ppm = 2.48 (s br, OH), 3.61–3.70 (m, NCH₂), 3.82–3.90 (m, OCH₂), 6.62 (s br, NH), 7.38–7.55 (m, *m*-H and *p*-H of Ph), 7.74–7.84 (m, *o*-H of Ph).

Run 5

Chr. (40 × 3, T) removed hydrocarbons. Elution with dic./EA 25:1 yielded 220 mg (29%) of **1a**. Elution with dic./EA 10:1 gave 39 mg (2%) of **10a** and 79 mg of unknown products. Elution with EA provided 433 mg of a mixture consisting of 184 mg (24%) of **6a**, 111 mg (17%) of **8** and 138 mg (11%) of **11a**. Elution with MeOH gave 102 mg of a mixture containing (calibrated ¹H NMR) 43 mg (6%) of **13** and 26 mg (3%) of **14a**.

Run 6

Chr. (40 × 3, T) provided hydrocarbons and 107 mg (7%) of **15**. Elution with dic./EA (25:1) yielded 519 mg (67%) of **1a** and (10:1) 35 mg (2%) of **10a** and 65 mg unknown products. Elution with EA provided 89 mg (11%) of **6a** containing traces of **8** and unknown products. Elution with MeOH yielded 78 mg (9%) of **14a**.

Run 7

Chr. (40 × 4, T/EA 10:1) provided hydrocarbons, 392 mg of **16a** and 85 mg of a mixture consisting of 21 mg (1%) of **10a**, 21 mg (total 413 mg, 19%) of **16a**, 21 mg (1%) of **17** and 21 mg (1%) of **19aH**. Treatment of the next fraction (36 mg) with a little MeOH left 18 mg of crystals consisting of 12 mg (0.5%) of **18a** and 6 mg (0.3%) of **20**; evaporation of the extract gave 18 mg of rather pure **19aO** (mainly α). The same treatment of the next fraction (210 mg) left a mixture of **18a** and unknown products undissolved while evaporation of the MeOH gave 72 mg (total 90 mg, 4%) of **19aO** (mainly α). Continued elution yielded 100 mg (10%) of **8**. Elution with

T/EA/MeOH 10:4:1 provided 567 mg (57%) of **6a** containing a trace of **8**.

9-(2-Benzamidoethyl)anthracene (**16a**)

m.p. 265–267 °C. – IR ν/cm^{-1} = 3308, 1642. – $^1\text{H NMR}$: δ/ppm = 3.84 (m_c , NCCH_2), 4.02 (m_c , NCH_2), 6.19 (s br, NH), 7.22–7.58 (m, Ph and 2-H, 3-H, 6-H, 7-H), 8.03 (m_c , 4-H, 5-H), 8.40 (m_c , 1-H, 9-H), 8.42 (s, 10-H). – MS (174 °C): m/z = 325 (23, M^+), 204 (100, $M - \text{PhCONH}_2$), 191 (62), 189 (20), 105 (69, PhCO), 77 (30, Ph).

$\text{C}_{23}\text{H}_{19}\text{NO}$ Calcd.: C 84.89 H 5.89 N 4.30
(325.41) Found: C 84.85 H 6.09 N 4.57.

1-(2-Benzamidoethyl)anthracene (**17**)

Only in mixture with **10a**, **16a** and **19aH**. – For $^1\text{H NMR}$ see text.

2-(2-Benzamidoethyl)anthracene (**18a**)

m.p. 236–238 °C. – IR: ν/cm^{-1} = 3310, 1638. – $^1\text{H NMR}$: δ/ppm = 3.16 (t, J = 6.7, NCCH_2), 3.88 (q, J = 6.7, NCH_2), 6.18 (s br, NH), 7.32–7.50 (m, m -H and p -H of Ph), 7.51 (m_c , 3-H), 7.65–7.76 (m, o -H of Ph, 3-H, 6-H, 7-H), 7.83 (s, 1-H), 8.00 (m_c , 4-H, 5-H, 8-H), 8.37 (s, 10-H), 8.43 (s, 9-H). – MS (149 °C): m/z = 325 (12, M^+), 204 (100, $M - \text{PhCONH}_2$), 191 (16), 189 (10), 105 (49, PhCO), 77 (28, Ph).

$\text{C}_{23}\text{H}_{19}\text{NO}$ Calcd.: C 84.89 H 5.89 N 4.30
(325.41) Found: C 84.68 H 6.13 N 4.13.

2-(2-Benzamidoethyl)-1,2-dihydroanthracene (**19aH**)

Only in mixture with **10a**, **16** and **17**. – $^1\text{H NMR}$ (recognizable signals only): δ/ppm = 3.10, m_c ($\text{NCCCH}=\text{C}$), 6.08 (dd, J = 10.1/4.5, $\text{NCCC}=\text{CH}=\text{C}$), 6.63 (d, J = 10.1, $\text{NCCC}=\text{CH}=\text{C}$).

2-(2-Benzamidoethyl)-1-hydroxy-1,2-dihydroanthracene (**19aO**)

Impure mixture of isomers α and β . – IR: ν/cm^{-1} = 3100 br, 1638. – MS (139 °C): m/z = 325 (25, $M - \text{H}_2\text{O}$), 204 (100, $325 - \text{PhCONH}_2$), 191 (14, $235 - \text{PhCONHCH}_2$), 189 (8), 105 (33, PhCO), 77 (19, Ph). – $^1\text{H-NMR}$: δ = (α) 1.65–2.19 (m, NCCH_2), 3.08–3.74 (m, NCH_2CCH), 4.83 (d, J = 5.8, OCH), 6.00 (dd, J = 9.6/4.6, $\text{NCCCCH}=\text{C}$), 6.31 (t br, J \approx 6, NH), 6.70 (d, J = 9.9, $\text{NCCCC}=\text{CH}$), 7.15–7.76 (m, ArH), 7.97 (m_c , o -H of PhCO), 8.26 (s, 9-H), 8.32 (s, 10-H); (β , only signals differing from the α signals) 5.26 (d, J = 6.6, OCH), 6.17 (dd, J = 9.8/4.7, $\text{NCCCCH}=\text{C}$), 8.07 (m_c , o -H of PhCO).

$\text{C}_{23}\text{H}_{21}\text{NO}_2$ Calcd.: C 80.44 H 6.16 N 4.08
(343.43) Found: C 80.95 H 6.28 N 4.27.

2-(2-Benzamidoethyl)-3,4-dihydroanthracene (**20**)

Only in mixture with **18a**. – $^1\text{H NMR}$: δ/ppm = 2.31 (t, J = 7.1, $\text{C}=\text{CCH}_2$), 2.59 (t, J = 6.8, NCCH_2), 3.02 (t, J = 7.0, $\text{C}=\text{CCCCH}_2$), 3.72 (q, J = 6.7, NCH_2), 6.52 (s, $\text{C}=\text{CH}$), 7.82 (s, 10-H), 7.99 (s, 9-H), other signals coincide or overlap with the respective ones of **18a**; assignment for the two CH_2CH_2 parts from decoupling.

Run 8

Chr. (40 \times 4, T/EA 10:1) provided hydrocarbons, unknown products and 76 mg of a mixture containing (calibrated $^1\text{H NMR}$) 36 mg (2%) **10a** and 11 mg (0.5%) **17**. Elution with T/EA (5:2) gave 95 mg (4%) of impure **19aO** (mainly α) and 39 mg of a mixture containing α -**19aO**. Further elution provided 57 mg of a mixture consisting of **6a** (main component), **8** and **11a**. The next fraction was 309 mg of a mixture consisting of 131 mg of **6a** and 178 mg of **11a**. Further elution provided 239 mg of a mixture consisting of 130 mg (total >286 mg, >28%) of **6a**, 67 mg (total 243 mg, 15%) of **11a** and 42 mg (4%) of **13**.

Run 9

Chr. (33 \times 3, B/EA 9:1) provided hydrocarbons, 53 mg of unknown products, 85 mg of **10a** containing a trace of **19aH**, 32 mg (total >117 mg, >18%, see next fraction) of **10a** containing a trace of **19aO**, 17 mg of a mixture consisting of **10a** (main component), anthraquinone and some **18a**. Further elution yielded 31 mg of unknown products containing some **20** and a trace of **17**. Continued elution gave 31 mg of a mixture consisting of **20** (main component) and unknown products. The combined last two fractions contained (calibrated $^1\text{H NMR}$) 16 mg (2%) of **20**. Further elution provided 22 mg of a mixture consisting of 10 mg of **8** and 12 mg (4% if structure is correct) of **21s**. Continued elution yielded 146 mg of a mixture consisting of 122 mg (41%) of **6a** and 24 mg (total 36 mg, 13%) of **8**. Further elution gave 49 mg (17%) of **13**.

3,3'-Bis-(2-benzamidoethyl)-9,9',10,10'-tetrahydro-bi-9,9'-anthryl (**21s**), proposed structure

Only in mixture with **8**. Structure proposed on the basis of $^1\text{H NMR}$ data in the text and in Scheme 3.

Run 10

Chr. (35 \times 3, dic.) removed hydrocarbons and yielded mixture a. Elution with acetone provided mixture b. Chr. (40 \times 3, dic.) of mixture a provided some unknown products and impure **10b**, that on recrystallization from cyclohexane yielded 1140 mg (21%) of **10b**. Chr. (35 \times 3, dic./EA) of mixture b yielded small fractions with unknown products and 680 mg of a mixture consisting of 489 mg (18%) of **6b** and 191 mg (7%) of **32**. Acetone yielded **11b** that was recrystallized (CCl_4 , refrigerator) to give 1590 mg (40%) of pure **11b**.

Run 11

Chr. (40 \times 4; dic.) removed hydrocarbons. Elution with dic./EA 10:1 provided 567 mg (32%) of **10b** and 215 mg of a mixture consisting of 131 mg (15%) of **6b** and 84 mg (10%) of **32**. Continued elution yielded 340 mg of mixture a and 107 mg (12%) of Oxa (see Table 2). Chr. (15 \times 1.5, dic./EA 3:1) of mixture a yielded 123 mg (9%) of **11b** and 143 mg (12%) of **14bA**.

2-Benzamido-2-methylpropylacetate (**14bA**)

Oil. – IR (film): ν/cm^{-1} = 3340, 1739, 1650, 1540. – $^1\text{H NMR}$: δ/ppm = 1.49 (s, CMe_2), 2.04 (s, MeCO), 3.70 (d, J = 6.1, NCH_2), 7.20–7.50 (m, NH, m -H and p -H of Ph), 7.75–7.90 (m, o -H of Ph).

$\text{C}_{13}\text{H}_{17}\text{NO}_3$ Calcd.: C 66.36 H 7.28 N 5.95
(235.28) Found: C 66.23 H 7.07 N 5.64.

Run 12

Chr. (30 × 3, T/EA 9:1) yielded hydrocarbons and 314 mg of **10b** and 233 mg of a mixture consisting of 164 mg (total 478 mg, 13%) of **10b** and 69 mg of **19bH**. Further elution gave 43 mg of a mixture consisting of 29 mg (total 98 mg, 3%) of **19bH** and 14 mg (1%) of **18b**. The next fraction was a mixture of 81 mg of **32** and 8 mg of **6b**. Further elution gave 169 mg of a mixture consisting of 93 mg of **35**, 18 mg of **6b**, 46 mg of **32** and 12 mg of **37**. Further elution yielded 84 mg of a mixture consisting of 27 mg of **6b**, 11 mg (total 138 mg, 8%) of **32**, 26 mg (total 119 mg, 3%) of **35**, 7 mg (total 19 mg, 0.5%) of **37** and 13 mg of **38**. The next fraction (153 mg) consisted of 92 mg (total 105 mg, 3%) of **38**, 46 mg (3%) of Oxa (see Table 2) and 15 mg (total 68 mg, 4%) of **6b**. Further elution yielded 132 mg (5%) of **11b** and 201 mg of unknown products.

9,10-Bis-(2-benzamido-1-methyl-2-propyl)-9,10-dihydroanthracene (**11b**)

m.p. 215–217 °C (run 10 and 11, after washing with B/CCl₄). – IR: ν/cm^{-1} = 3 335, 3 320, 1 648, 1 527, 1 522.

11b from run 11. – ¹H NMR: δ/ppm = 1.21 (s, 4 Me), 3.61 (d br, *J* = 5.4, 2NCH₂), 4.06 (s, 9-H, 10-H), 5.93 (t br, *J* ca. 5.5, 2NH), 7.20–7.30 (m, 2-H, 3-H, 5-H, 6-H), 7.30–7.49 (m, *m*-H and *p*-H of 2Ph), 7.49–7.65 (m, 1-H, 4-H, 5-H, 8-H, 4 *o*-H of 2Ph).

C₃₆H₃₈N₂O₂ Calcd.: C 81.48 H 7.22 N 5.28
(530.70) Found: C 81.67 H 7.13 N 5.44.

11b from run 12. – ¹H NMR: δ/ppm = 1.21 (s, 4Me), 3.61 (d br, *J* = 5.4, 2NCH₂), 4.06 (s, 9-H, 10-H), 5.93 (t br, *J* ca. 5.5, 2NH), 7.20–7.30 (m, 2-H, 3-H, 5-H, 6-H), 7.30–7.49 (m, *m*-H and *p*-H of 2Ph), 7.49–7.65 (m, 1-H, 4-H, 5-H, 8-H, 4 *o*-H of 2Ph). – MS (203 °C): *m/z* = 530 (0.1, M⁺), 355 (2, M – 32), 354 (2), 219 (1, anthranylCMe₂), 176 (99, A), 105 (100, PhCO).

C₃₆H₃₈N₂O₂ Calcd.: C 81.48 H 7.22 N 5.28
(530.70) Found: C 81.56 H 7.30 N 5.24.

2-(2-Benzamido-1-methyl-2-propyl)-1,2-dihydroanthracene (**19bH**)

Only in mixture with either **10b** or **18b**. – ¹H NMR: δ/ppm = 1.04 (s, 2Me), 2.49 (m_c, NCCCCH), 3.08 (m_c, NCH₂), 3.46 (m_c, 1H of NCCCCH₂), 3.83 (m_c, 1H of NCCCCH₂), 6.10 (s br, NH), 6.17 (dd, *J* = 9.9/3.9, 3-H), 6.77 (d br, *J* = 9.9, 4-H), 7.30–7.73 (m, ArH indistinguishable from signals of **10b** or **18b**).

9-(2-Benzamido-1-methyl-2-propyl)-10-oxo-9,10-dihydroanthracene (**35**)

Only in mixture with **6b**, **32** and **37**. – ¹H NMR: δ/ppm = 0.76 (s, 2Me), 3.34 (d, *J* = 6.4, NCH₂), 4.06 (s, 9-H), 6.18 (t br, *J* ca 6, NH), 7.62 (m_c, 1-H, 8-H), 8.15 (m_c, 4-H, 5-H), other ArH cannot be assigned in the mixture. – MS (158 °C): *m/z* = 194 (33, anthrone), 176 (39, Oxa-H⁺), 105 (100, PhCO).

10,10'-Bis(2-benzamido-1-methyl-2-propyl)-9,9',10,10'-tetrahydro-9,9'-bianthryl (**37**)

m.p. 280–281 °C (MeOH). – IR: ν/cm^{-1} = 3 300, 1 640, 1 530. – ¹H NMR: δ/ppm = 1.32 (s, 4Me), 3.90 (d, *J* = 6.4, 2NCH₂),

4.23 (s, 10-H, 10'-H), 4.49 (s, 9-H, 9'-H), 6.28 (t br, *J* ca. 6, 2NH), 6.35 (m_c, 1-H, 1'-H, 8-H, 8'-H), 6.77 (m_c, 2-H; 2'-H, 7-H, 7'-H), 7.21 (m_c, 3-H, 3'-H, 6-H, 6'-H), 7.42–7.60 (m, 4-H, 4'-H, 5-H, 5'-H, *m*-H and *p*-H of 2Ph), 7.67 (m_c, *o*-H of 2Ph). – MS (205 °C): *m/z* = 354 (0.5, M/2 or bianthryl), 219 (4, anthryl-CMe₂ cation), 178 (100, A), 176 (33, Oxa-H⁺), 105 (58, PhCO). – MS-FAB (MNBA + 1% TFA): 709 (M + H⁺).
C₅₀H₄₈N₂O₂ Calcd.: C 84.71 H 6.82 N 3.95
(708.95) Found: C 84.56 H 6.88 N 3.98.

10,10'-Bis(2-benzamido-1-methyl-2-propyl)-9,9',10,10'-tetrahydro-9,9'-bianthrylidene (**38**)

m.p. 311–312 °C (MeOH), the red crystals became non-transparent near 73 °C. – IR: ν/cm^{-1} = 3 350, 3 460, 1 660, 1 650, 1 545, 1 530. – ¹H NMR: δ/ppm = 1.28 (s, 4Me), 3.82 (d, *J* = 6.3, 2NCH₂), 3.93 (s, 9-H, 9'-H), 6.20 (t br, *J* = 6.0, 2NH), 6.71 (t, *J* = 7.4, 2 × 2 ArH), 7.15 (t, *J* = 7.4, 2 × 2 ArH), 7.24 (d, *J* = 7.4, 2 × 2 ArH), 7.35–7.55 (m, 2 × 2 ArH, *m*-H and *p*-H of 2Ph), 7.59 (m_c, *o*-H of 2Ph). – MS (277 °C): *m/z* = 706 (0.07, M⁺), 395 (0.2, bianthrylyl-CMe₂ cation), 354 (9, bianthryl), 176 (92, Oxa-H⁺), 105 (100, PhCO).

C₅₀H₄₈N₂O₂ Calcd.: C 84.71 H 6.82 N 3.95
(708.95) Found: C 84.56 H 6.88 N 3.98.

Run 13

Chr. (30 × 3, T/EA 10:1) provided hydrocarbons and 394 mg of a mixture consisting of 362 mg (17%) of **10b** and 32 mg (3%) of **33**. Further elution gave 127 mg (6%) of **18b** and 436 mg of a mixture consisting of 357 mg (34%) of **6b**, 42 mg (4%) of **32** and 37 mg of α -**34**. Continued elution yielded 189 mg of a mixture consisting of 179 mg (total 216 mg, 10%) of α -**34** and 10 mg of β -**34**. Further elution gave 30 mg of a mixture consisting of 18 mg (total 28 mg, 1%) of β -**34** and 12 mg (0.5%) of **36**.

2-(2-Benzamido-1-methyl-2-propyl)anthracene (**18b**)

m.p. 152–154 °C. – IR: ν/cm^{-1} = 3 300, 1 640, 1 545. – ¹H NMR: δ/ppm = 1.55 (s, 2Me), 3.80 (d, *J* = 6.6, NCH₂), 5.80 (s br, NH), 7.30–7.70 (m, CPh), 7.73 (m_c, 3-H, 6-H, 7-H), 7.95 (s, 1-H), 8.02 (m_c, 4-H, 5-H, 8-H), 8.43 (s, 9-H, 10-H). – MS (134 °C): *m/z* = 353 (30, M⁺), 232 (31, M – PhCONH₂), 219 (M – PhCONHCH₂), 204 (219 – Me), 191 (9), 178 (19, Oxa-H⁺), 105 (25, PhCO).

C₂₅H₂₃NO Calcd.: C 84.95 H 6.56 N 3.96
(353.47) Found: C 84.73 H 6.70 N 4.04.

cis-9-(2-Benzamido-1-methyl-2-propyl)-10-hydroxy-9,10-dihydroanthracene (α -**34**)

m.p. 184–186 °C (MeOH/ether). – IR: ν/cm^{-1} = 3 340, 1 640, 1 535. – ¹H NMR: δ/ppm = 1.21 (s, 2Me), 3.17 (d, *J* = 6.7, NCH₂), 3.87 (s, NCCCCH), 5.84 (s, CHO), 6.89 (t br, *J* ≈ 6, NH), 7.11 (d, *J* = 8.0, 1-H, 8-H), 7.57 (d, *J* = 7.8, 4-H, 5-H), 7.22–7.45 (m, Ph). – MS (161 °C): *m/z* = 353 (0.3, M – H₂O), 178 (91, A), 176 (74, Oxa-H⁺) 105 (100, PhCO).

C₂₅H₂₅NO₂ Calcd.: C 80.83 H 6.78 N 3.77
(371.48) Found: C 80.90 H 6.69 N 3.80.

trans-9-(2-Benzamido-1-methyl-2-propyl)-10-hydroxy-9,10-dihydroanthracene (β -**34**)

m.p. 169–171 °C. – IR: ν/cm^{-1} = 3 340, 1 640, 1 535. –

^1H NMR (in mixture with **36**): δ/ppm = 1.17 (s, 2Me), 3.04 (d, J = 6.8, NCH_2), 3.82 (s, NCCCCH), 5.30 (s, CHO), 7.03 (d, J = 8.0, 1-H, 8-H), 7.54 (d, J = 7.8, 4-H, 5-H), 7.20–7.43 (m, Ph together with Ph of **36**).

$\text{C}_{25}\text{H}_{25}\text{NO}_2$ Calcd.: C 80.83 H 6.78 N 3.77
(371.48) Found: C 80.82 H 6.77 N insufficient material

1-(2-Benzamido-1-methyl-2-propyl)-4-hydroxy-1,4-dihydroanthracene (36)

Only in mixture with β -**34**. – ^1H NMR: δ/ppm = 1.20 (s, 1Me), 1.28 (s, 1Me), 3.23 (m, NCH_2), 3.45 (d br, J = 5.0, NCCCCH), 5.45 (d br, J = 5.0, CHO), 6.37 (dd, J = 10.4/5.1, $\text{NCCCCCH}=\text{C}$), 6.48 (dd, J = 10.4/5.1, $\text{NCCCC}=\text{CH}$), 6.95 (t br, J ca 5, NH), 7.77 (s, 9-H), 7.97 (s, 10-H).

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