N-S Cleavage Is Faster Than Homolytic Ring Opening in Single-Electron Transfer to Some *N*-Sulfonylaziridines. Competition between S_N2 and SET†,[1]

Konstantinos Bellos, Helmut Stamm,* and Dieter Speth

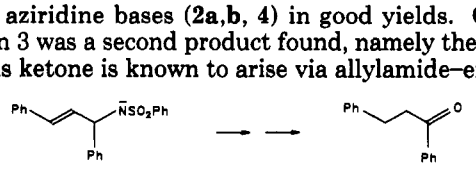
Pharmazeutisch-Chemisches Institut, Faculty of Pharmacy, Im Neuenheimer Feld 346, D-6900 Heidelberg, Germany

Received April 2, 1991

The radical anions of the *N*-sulfonylaziridines, **1a,b** and **3** undergo N-S cleavage in place of homolytic ring opening as is demonstrated by reactions with anthracenide $A^{\bullet-}$. Nucleophilic ring opening of the sulfonylaziridines **1a,b** and **3** by the carbanions AH^-, X^-, and Fl^- of dihydroanthracene, xanthene, and fluorene, respectively, proceeds with the expected regioselectivity and is slow enough to allow some competition by a single-electron transfer (SET) initiated N-S cleavage, which provides the desulfonated aziridines and bixanthenyl X-X or bifluorenyl Fl-Fl, respectively. The SET path is favored by light. The competition is in favor of SET to the exclusion of the nucleophilic opening when trityl anion reacts with **1a**. The twice-found byproducts **11** and **12** require the azirine intermediate **15**, which is, at least formally, generated by elimination of TsH from **1a** in a non-SET reaction.

Substitutive ring opening of 2,2-dimethylaziridines by nucleophiles can switch in regioselectivity from "normal opening" with sulfonyl activation to an "abnormal" one with acyl activation.[4,5] This marked change in a high regioselectivity of ring opening will sometimes be caused by a change from a sterically decelerated S_N2 to a single-electron transfer (SET) mechanism with homolytic ring opening and radical combination.[2] The tendency of *N*-acylaziridines to undergo homolytic ring opening has been demonstrated in reactions with aromatic radical anions[3,6] or with tributyltin hydride/azobisisobutyronitrile,[7] while an *N*-sulfonylaziridine did not react with the latter combined reagent. Nothing is known about the behavior of *N*-sulfonylaziridines in SET reactions. A preliminary experiment with 1-tosyl-2,2-dimethylaziridine and 2 equiv of anthracenide $A^{\bullet-}$ provided as nonvolatile and water insoluble materials only anthracene A and dihydroanthracene AH_2 in a quantitative yield. This was the first indication of an N-S cleavage since this tosyl aziridine is recoverable and since any products possessing a tosylamide structure would be isolable. N-S cleavage must have provided 2,2-dimethylaziridine, which is volatile and easily soluble in water. A substantiation of this interpretation should be possible when the expected aziridine base is easier to isolate or to detect (Chart I).

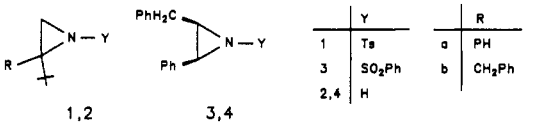
Indeed, the reactions of **1a,b** or **3** with $A^{\bullet-}$ (entries 1-3 of Table I) show beyond doubt that SET results in N-S cleavage, which is well-known[8] for other sulfonamides. No products of homolytic ring opening could be detected. The respective radical anions $1^{\bullet-}$ and $3^{\bullet-}$ obviously undergo N-S cleavage much faster than homolytic ring opening quite in contrast to their *N*-acyl analogues[2,7,9] and in contrast to the general behavior of three-membered rings with an attached radical center. The reactions furnished the expected aziridine bases (**2a,b**, **4**) in good yields. Only in reaction 3 was a second product found, namely the ketone **6**. This ketone is known to arise via allylamide-enamide

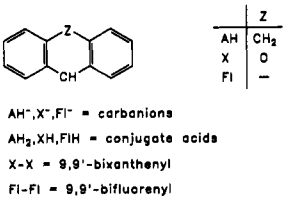


5 6

isomerization from **5**, which is formed by eliminative fission of **3**. The fission is induced by deprotonation of the benzylic methylene group.[10] The reaction mixture in our experiment certainly can make available the required base so that the formation of **6** poses no problem. We see at least three candidates for this base: first, the anion of **4**; second, the dianion of A formed by disproportionation of $A^{\bullet-}$; and third, but most likely, the dimer of $A^{\bullet-}$ (i.e., the dianion of tetrahydrobianthracene), which is in equilibrium with $A^{\bullet-}$ (see the thorough discussion in ref 14) and which is in effect a substituted AH^- (see below) and will resemble $A^{\bullet-}$ in reactivity (compare entry 4). An alternative SET path cannot explain the formation of **6** since homolytic ring cleavage[7] would split the wrong N-C bond of **3** and could therefore produce only positional isomers of **5** and **6** at best.

Chart I





Nucleophiles can act as reducing agents for electrophiles when the competing nucleophilic attack on the electrophile is slow and when the difference in redox potentials between nucleophile and electrophile is not too unfavorable.[11]

† Dedicated to Professor Hans Suschitzky on the occasion of his 75th birthday.

(1) Reactions with Aziridines. 55. For parts 54 and 53, see refs 2 and 3.
(2) Reactions with Aziridines. 54: Werry, J.; Lin, P.-Y.; Bellos, K.; Assithianakis, P.; Stamm, H. *J. Chem. Soc., Chem. Commun.* **1990**, 1553.
(3) Reactions with Aziridines. 53: Stamm, H.; Falkenstein, R. *Chem. Ber.* **1990**, *121*, 2227.
(4) Stamm, H.; Assithianakis, P.; Buchholz, B.; Weiss, R. *Tetrahedron Lett.* **1982**, *23*, 5021.
(5) Stamm, H.; Sommer, A.; Woderer, A.; Wiesert, W.; Mall, T.; Assithianakis, P. *J. Org. Chem.* **1985**, *50*, 4946.
(6) Stamm, H.; Assithianakis, P.; Weiß, R.; Bentz, G.; Buchholz, B. *J. Chem. Soc., Chem. Commun.* **1984**, 753.
(7) Werry, J.; Stamm, H.; Lin, P.-Y.; Falkenstein, R.; Gries, S.; Irngartinger, H. *Tetrahedron* **1989**, *45*, 5028.
(8) Ji, S.; Gortler, L. B.; Waring, A.; Battisti, A.; Bank, S.; Closson, W. D.; Wriede, P. *J. Am. Chem. Soc.* **1967**, *89*, 5312. Closson, W. D.; Ji, S.; Schulenburg, S. *J. Am. Chem. Soc.* **1970**, *92*, 650.
(9) Bellos, K.; Speth, D.; Stamm, H. Unpublished results.
(10) Stamm, H.; Speth, D. *Chem. Ber.* **1989**, *123*, 1795.

0022-3263/91/1956-6846$02.50/0

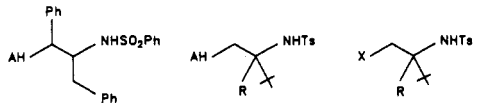
Table I. Reactions of 1a,b and 3 in THF[a] at Room Temperature

entry	mmol of reagents			time[b]	% yields of products (yields in parentheses are from ^1H NMR)
1	3, **1a**	7, A	6, Na	4 h	86, **2a**
2	2.2, **1b**	7, A	6, Na	4 h	68, **2b**
3	2.6, **3**	7, A	6, Na	4 h	51, **4**; 33, **6**
4	2, **3**	5, AH_2	4, BuLi	2 h	14, **4**; (21), **6**; (30), **7**; (34), **3**
5	2, **3**	18, AH_2	16, BuLi	1 h	39, **4**; (42), **7**
6	3, **1a**	7, AH_2	6, BuLi	5 d	17, **2a**; 68, **8a**
7	3, **1b**	7, AH_2	6, BuLi	3 d	69, **8b**
8	3, **1a**	7, Ph_3CH	6, BuLi	6 d	78, **2a**; 15, **1a**
9	4, **1a**	7, XH	6, BuLi	3 d	4, **2a**; 6, X–X; 72, **9a**; (5), **11**[c]
10	3, **1b**	7, XH	6, BuLi	3 d	76, **9b**; (7), X–X
11	3, **1a**	5.5, FlH	4.5, BuLi	5 d	(35), **10a**; (trace), Fl–Fl; (49), **1a**
12	4, **1a**	10, FlH	9, BuLi	5 d	49, **12**; 12, **13**
13[d]	1.5, **1a**	5.5, FlH	5, BuLi	5 d	(1–2), **2a**; (trace), Fl–Fl; (90), **10a**
14[e]	1.5, **1a**	5.5, FlH	5, BuLi	5 d	(28), **2a**; (17), Fl–Fl; (69), **10a**
15	4, **1b**	6.5, FlH	5, BuLi	7 d	75, **10b**

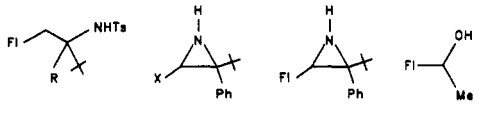
[a] 70–90 mL of THF, 170 mL for entry 5. [b] Reactions were quenched with methanol or with acetic acid (entries 4 and 5). [c] **11** was not obtained in a pure state (mixture with xanthone). It was identified by ^1H NMR comparison with **12**. [d] Performed in the absence of light. Yields were determined from the ^1H NMR spectrum of the crude reaction mixture. [e] Performed exactly like and synchronously with reaction 13 but under irradiation with visible light: daylight (window) and permanent irradiation with a Philipps Prismatic SL-13 lamp (low evolution of heat). Yields were determined as in entry 13.

Nucleophilic attack on the aziridine ring of **1a,b** should be slow due to serious steric hindrance. This hindrance will be less pronounced with **3**. The reactivity of the three aziridines is further diminished by a slow (cis-disubstituted aziridine **3**) or even impossible (**1a,b**) nitrogen inversion. It has been proposed[12] and was experimentally supported[13] that nucleophilic ring opening proceeds most rapidly in or near the planar transition state of nitrogen inversion. Broadening of the NMR singlet (250 MHz) of the phenyl ortho protons in **1a** at 7.55 ppm is caused by a hindered rotation of the phenyl ring and not by nitrogen inversion. At −50 °C these protons give two doublets (J = 8 Hz) of equal intensity separated by 0.7 ppm.

Anions of diarylmethanes are good candidates for SET reactions.[14] Indeed, reaction of **3** with anthracene hydride AH^- showed that SET can compete with nucleophilic ring opening (entries 4 and 5). The latter provided the amidoethylated dihydroanthracene **7** via attack on the phenyl carrying carbon atom, the former provided **4**. In contrast to ring opening by sodium alkoxide,[10] no attack on the benzyl-carrying carbon atom of **3** was observed, i.e., no isomer of **7** could be detected (compare the same S_N2 behavior when **3** is devoid of the benzyl group[5]).



7 8 9



10 11 12 13

Completion of the reaction appears to require a large excess of AH^-: compare entry 4 with entry 5. The two entries seem to further show that the large excess favors SET more than nucleophilic attack. This observation should not be overestimated as long as one cannot be sure that the reaction conditions were strictly identical (vide infra) except for the excess of AH^-. On the other side, at least one of the primary products of the N–S cleavage must undergo further reductions to form products that are stable until workup. The initial SET step (from the carbanion to **1** or **3**) is probably slower than these reductive steps subsequent to the N–S cleavage.

Reaction of **1a** and **1b** with AH^- provided mainly the S_N2 products **8a** and **8b**, respectively, in practically identical yields, but only in entry 6 was a clear evidence for SET found by isolation of **2a** (vide infra for **2b**, which was not detected in experiment 7).

Going from AH^- to the trityl anion Tr^- would be expected to enormously increase the steric hindrance of a nucleophilic attack (compare ref 2). Indeed, the latter was completely suppressed in entry 8, which provided only **2a** from **1a**. This is an outstanding example for the difference in SET reactions of a nucleophile with an activated aziridine since the benzoyl analogue of **1a** exclusively underwent homolytic ring opening[2] in the reaction with Tr^-.

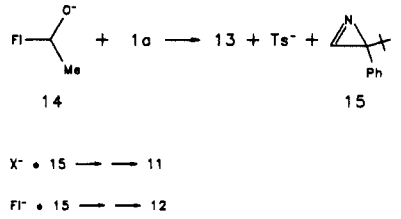
Reactions of the anion X^- of xanthene XH with **1a** (entry 9) and **1b** (entry 10) resembled those of the carba analogous AH^- (entries 6 and 7): mainly S_N2 reaction in similar yields of **9a,b** together with an isolation of an aziridine base (**2a**) from **1a** only. However, the detection of comparable amounts of bixanthyl X–X in both runs indicates comparable SET contributions in both runs. It appears as if **2b** is more difficult to isolate or to detect than **2a**. This may also explain the different yields in entries 1 and 2. Then, it is likely that also with AH^- and **1b** in entry 7 some SET reaction had proceeded. The dimer (corresponding to X–X) of the dihydroanthryl radical $AH^•$, under the strongly basic reaction conditions, is fragmented[14] into one molecule of anthracene A and one molecule of dihydroanthracene AH_2. The amounts of A have not been determined in entries 4–7. The same applies to the secondary products (compare, e.g., ref 14) derived from trityl radical $Tr^•$ in entry 8.

An interesting byproduct was found in entry 9. The new aziridine **11** was not isolated but detected by ^1H NMR and identified by spectral comparison with **12** (vide infra). Structure and formation of **11** are analogous to **12** and will not be discussed separately.

A relatively small excess of the anion Fl^- of fluorene FlH (entry 11) provided the S_N2 product **10a** and a trace of bifluorenyl Fl–Fl. A second run with a large excess of Fl^- surprisingly gave no **10a** but only the new aziridine **12** along with the alcohol **13** (entry 12). The latter must have formed by reaction of Fl^- with acetaldehyde. The anion

(11) SET as general principle: Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; Springer: Heidelberg, 1987.
(12) Buchholz, B.; Stamm, H. *Isr. J. Chem.* **1986**, *27*, 17.
(13) Mall, B.; Stamm, H. *J. Org. Chem.* **1987**, *52*, 4812.
(14) Werry, J.; Stamm, H.; Sommer, A. *Chem. Ber.* **1990**, *123*, 1553.

Scheme I



of acetaldehyde is known to arise by the reaction of butyllithium with THF.[15] Thus, obviously the experimental conditions of routine run 12 must have been accidentally such that at least a part of the butyllithium reacted with the solvent prior to the reaction with fluorene FlH. The protolytic equilibrium with FlH provided then the acetaldehyde required for the reaction with Fl^- to form 14. As entries 13–14 show, neither 12 nor 13 was detected in any other routine run with **1a**. It appears therefore reasonable to relate the formation of both products to one another. It is assumed that 14 acts as base on **1a** and eliminates a proton together with the toluenesulfinate ion Ts^- from **1a** thereby forming the azirine **15**, which adds Fl^- to yield the final product 12 after protonation. To our knowledge, this is a novel way to generate an azirine. The base character of 14 can be expected to be relatively more pronounced than the nucleophilicity of 14. This is not uncommon for an alkoxide and is supported by the stability of **1a,b** toward refluxing methanolic sodium methoxide, i.e., conditions that lead to nucleophilic ring opening of **3**.[10] This stability is not incompatible with the above mechanistic proposal, since the basicity of alkoxides, especially of bulky ones, increases in aprotic polar solvents.

The reducing power of a carbanion can be increased by electronic excitation. In the case of colored carbanions this may be achieved by visible light. Two reactions of Fl^- with **1a** were performed under identical conditions except for exclosure of light in one experiment (entry 13) and supply of extra illumination in the other experiment (entry 14). Indeed, the SET contribution increased on illumination from 1–2% to 28%, while the S_N2 contribution dropped from 90% to 69%.

A routine run of Fl^- with **1b** (entry 15) provided a high yield of the S_N2 product **10b** while no **2b** or Fl–Fl was detected. One must, however, be aware of the possibility that **2b** (and perhaps also Fl–Fl) escaped detection (vide supra).

Entries 4–15 demonstrate for reactions of *N*-sulfonylaziridines with some carbanions a competition of a reductive N–S cleavage with the nucleophilic ring opening of the S_N2 type. From the reactions of **1a** with these carbanions one may derive the following order of decreasing SET preference: $Tr^- > AH^- > X^- > Fl^-$.

Experimental Section

General Methods and Materials. ^1H NMR Spectra ($CDCl_3$) were recorded on a Bruker W 250 (250-MHz) instrument. Chemical shifts are reported in δ (ppm) downfield from internal TMS followed in parentheses by signal multiplicity (s, d, t, q, m, m_c = multiplet centered at), coupling constants J, number of protons if necessary for clarity, and assignment. IR spectra (KBr tablets unless otherwise stated) were recorded on a Perkin-Elmer 283 spectrometer.

All reactions were performed in dry THF with continuous stirring under dry nitrogen (see ref 5 and submethods A and B). The reactions were quenched with acetic acid or with methanol. Subsequent evaporation provided a residue that was taken up in dichloromethane and washed with water. Evaporation of the organic layer yielded a residue whose treatment (column chromatography or NMR analysis) is given below. Column chromatography was performed with 0.063–0.2-mm silica gel (Merck); column dimensions (thickness × length, cm) are given for the specific workup. Method A (entries 1–3): 1.25 g (7 mmol) of anthracene A and 136 mg (6 mmol) of Na were stirred for 1 day in 50–60 mL of THF; **1a,b** or **3** (dissolved in 10 mL of THF) was added dropwise; time of reaction and amounts of **1a,b** and **3** are given in Table I. Method B (entries 4–15): the carbanions were generated in 60–70 mL (80 mL in entry 4, 150 mL in entry 5) of THF as described in ref 5; **1a,b** or **3** dissolved in 10 mL (20 mL in entries 4, 5, 13, and 14) of THF were added dropwise; time of reaction, amounts of the reagents, and other details (light or dark reaction) are given in Table I.

The aziridines **3** and **4** are known;[16] for **2a,b** see ref 7. **1a,b** were prepared from **2a,b** and tosyl chloride according to the proven two-phase method described in ref 17 (the internal temperature during the addition of the chloride was held at −4 °C to −5 °C).

2-*tert*-Butyl-2-phenyl-1-(4-tolylsulfonyl)aziridine (1a): yield 80%; mp 156–157 °C; IR 1323, 1164 cm^{-1} (both SO_2); ^1H NMR δ 0.96 (s, tBu), 2.42 (s, Me of Ts), 2.58 (s, 1 H of NCH_2), 2.79 (s, 1 H of NCH_2), 7.25 (d, J = 8.2 Hz, 2 meta H of Ts), 7.20–7.36 (m, 2 meta H and 1 para H of Ph), 7.55 (s br, 2 ortho H of Ph), 7.72–7.80 (d, J = 8.2 Hz, 2 ortho H of Ts). Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.22; H, 7.11; N, 4.27.

2-Benzyl-2-*tert*-butyl-1-(4-tolylsulfonyl)aziridine (1b): yield 82%; mp 91–93 °C; IR 1328, 1310, 1165 cm^{-1} (all SO_2); ^1H NMR δ 0.89 (s, tBu), 2.43 (s, Me of Ts), 2.50 (s, 1 H of NCH_2), 2.85 (s, 1 H of NCH_2), 3.57 (d, J = 15.7 Hz, 1 benzylic H), 3.63 (d, J = 15.7 Hz, 1 benzylic H), 7.19–7.36 (m, 7 aromatic H), 7.82–7.89 (m, 2 ortho H of Ts). Anal. Calcd for $C_{20}H_{25}NO_2S$: C, 69.9;4 H, 7.34; N, 4.08. Found: C, 69.75; H, 7.39; N, 4.09.

Preliminary Experiment with 1-Tosyl-2,2-dimethylaziridine. Method A. A 2.14-g (12-mmol) portion of A, 0.23 g (10 mmol) of Na, and 1.13 g (5 mmol) of 1-tosyl-2,2-dimethylaziridine dissolved in 20 mL of THF. After 4 h the reaction was quenched with water. Workup provided 2.15 g of a mixture (^1H NMR) of A and AH_2.

Entry 1. Method A. Chromatography (60 × 3) provided (dichloromethane) 1.22 g of hydrocarbons (A, AH_2) and (ethyl acetate) 450 mg (86%) of **2a**.

Entry 2. Method A. Chromatography as in entry 1 provided 1.15 g hydrocarbons and 284 mg (68%) of **2b**.

Entry 3. Method A. Chromatography (60 × 3) provided (dichloromethane) 1.19 g of hydrocarbons, 180 mg (33%) of **6**, and (ethyl acetate) 280 mg (51%) of **4**. Ketone **6** was identified by comparison (mp, IR, ^1H NMR) with authentic material.[10]

Entry 4. Method B. Chromatography (15 × 3) provided (petroleum ether) 1.00 g of a mixture consisting (^1H NMR) of 496 mg of AH_2, 25 mg of A, 240 mg (34%) of **3**, 146 mg of **7**, and 6 mg of anthraquinone. Subsequent elution with dichloromethane yielded 167 mg (total 313 mg corresponding to 30%) of **7**. With ethyl acetate 60 mg (14%) of **4** were obtained.

***erythro*-9-[1,3-Diphenyl-2-(phenylsulfonamido)propyl]-9,10-dihydroanthracene (7):** mp 251–253 °C; IR 3370 (NH), 1364, 1320, 1166 cm^{-1} (all SO_2); ^1H NMR δ 2.16 (dd, J = 14.2/10.9 Hz, 1 H of benzylic CH_2), 3.27 (dd, J = 14.2/2.9 Hz, 1 H of benzylic CH_2), 3.33–3.42 (m, overlapping with dd at 3.27, NCH), 3.54 (dd, J = 10.6/4.1 Hz, NCCH), 3.82 (d, J = 18.5 Hz, 10-H pseudo eq), 3.91 (d, J = 7.2 Hz, NH), 4.23 (d, J = 18.6 Hz, 10-H pseudo ax), 4.50 (d, J = 10.4 Hz, 9-H pseudo eq), 6.54–6.61 (m, 2 ortho H of C-Ph), 6.84–6.95 (m, 4 aromatic H), 6.98–7.41 (m, 15 aromatic H), 7.44–7.52 (m, 2 ortho H of SO_2Ph). Anal. Calcd for $C_{35}H_{31}NO_2S$: C, 79.36; H, 5.90; N, 2.64. Found: C, 79.10; H, 5.92; N, 2.56.

Entry 5. Method B. Chromatography (40 × 3.5) provided (petroleum ether) 926 mg of hydrocarbons then (dichloromethane) 70 mg of a mixture consisting (^1H NMR) of 30 mg of anthraquinone, 13 mg (4%) of A, 27 mg of **7**, and finally 493 mg of a mixture consisting (^1H NMR) of 421 mg of **7** and 72 mg of anthraquinone followed by 57 mg of unknown products. Elution

(15) Maercker, A. *Angew. Chem.* **1987**, *99*, 1002.

(16) Stamm, H.; Speth, D. *Arch. Pharm. (Weinheim)* **1989**, *322*, 277.

(17) Woods, C. W.; Borkovec, A. B.; Hart, F. M. *J. Med. Chem.* **1964**, *7*, 371.

with ethyl acetate yielded 162 mg (39%) of 4. The total yield of 7 was 448 mg (42%).

Entry 6. Method B. Chromatography (60 × 3) with dichloromethane provided 0.85 g of AH_2 and 1.04 g (68%) of **8a**. Elution with ethyl acetate yielded 91 mg (17%) of **2a**.

9-[3,3-Dimethyl-2-phenyl-2-(4-tolylsulfonamido)butyl]-9,10-dihydroanthracene (8a): mp 130–132 °C; IR 3325 (NH), 1315, 1154 cm^{-1} (both SO_2); ^1H NMR δ 0.75 (s, tBu), 2.42 (s, Me of Ts), 2.60 (dd, J = 15.1/9.5 Hz, 1 H of $NCCH_2$), 3.04 (dd, J = 15.1/5.8 Hz, 1 H of $NCCH_2$), 3.81 (d, J = 17.7 Hz, 10-H pseudo eq), 4.30 (d, J = 17.4 Hz, 10-H pseudo ax), 4.54 (dd, J = 9.5/5.8 Hz, 9-H pseudo eq), 4.95 (s, NH), 6.53–6.63 (m, 2 ortho H of Ph), 6.86–7.36 (m, 13 aromatic H), 7.88–7.95 (m, 2 ortho H of Ts). Anal. Calcd for $C_{33}H_{35}NO_2S$: C, 77.76; H, 6.92; N, 2.75. Found: C, 77.84; H, 6.89; N, 2.74.

Entry 7. Method B. Chromatography (60 × 3) with dichloromethane yielded 0.81 g of AH_2 and 1.08 g (68%) of **8b**.

9-[3,3-Dimethyl-2-benzyl-2-(4-tolylsulfonamido)butyl]-9,10-dihydroanthracene (8b): mp 143–145 °C; IR 3355 (NH), 1318, 1312, 1308, 1155 cm^{-1} (all SO_2); ^1H NMR δ 0.96 (s, tBu), 1.84 (dd, J = 14.9/7.6 Hz, 1 H of nonbenzylic $NCCH_2$), 2.10 (dd, J = 14.9/4.1 Hz, 1 H of nonbenzylic $NCCH_2$), 2.39 (s, Me of Tos), 3.07 (d, J = 13.9 Hz, 1 H of benzylic $NCCH_2$), 3.26 (d, J = 14.2 Hz, 1 H of benzylic $NCCH_2$), 3.71 (d, J = 17.7 Hz, 10-H pseudo eq), 3.80 (d, J = 17.3 Hz, 10-H pseudo ax), 4.21 (dd, J = 7.6/4.1 Hz, 9-H pseudo eq), 4.49 (s, NH), 6.74–6.81 (m, 2 ortho H of Ph), 6.92–6.98 (m, 1 aromatic H), 7.07–7.47 (m, 15 aromatic H). Anal. Calcd for $C_{34}H_{37}NO_2S$: C, 77.97; H, 7.12; N, 2.67. Found: C, 77.89; H, 7.10; N, 2.68.

Entry 8. Method B. Chromatography (60 × 3) with dichloromethane provided 1.65 g of triphenylmethane and 150 mg (15%) of **1a**. Elution with ethyl acetate yielded 410 mg (78%) of **2a**.

Entry 9. Method B. Chromatography (60 × 3) with dichloromethane provided first 240 mg of (^1H NMR) 151 mg of XH, 89 mg (6%) of X–X, and thereafter 1.47 g (72%) of **9a**. Elution with dichloromethane/ethyl acetate (10:1) provided 400 mg of a mixture of (^1H NMR) 332 mg of xanthone and 68 mg (5%) of **11**. Elution with ethyl acetate yielded 31 mg (4%) of **2a**.

9-[3,3-Dimethyl-2-phenyl-2-(4-tolylsulfonamido)butyl]-xanthene (9a): mp 127–129 °C; IR 3310 (NH), 1314 (SO_2), 1249 (COC), 1155 cm^{-1} (SO_2); ^1H NMR δ 0.75 (s, tBu), 2.43 (s, Me of Ts), 2.63 (dd, J = 15.1/11.2 Hz, 1 H of $NCCH_2$), 2.93 (dd, J = 15.1/3.7 Hz, 1 H of $NCCH_2$), 4.52 (dd, J = 11.1/3.6 Hz, NCCCH), 5.15 (s, NH), 6.19–6.23 (m, 2 ortho H of Ph), 6.80–7.00 (m, 7 aromatic H), 7.07–7.24 (m, 3 aromatic H), 7.97–8.04 (m, 2 ortho H of Ts). Anal. Calcd for $C_{32}H_{33}NO_3S$: C, 75.12; H, 6.50; N, 2.74. Found: C, 75.14; H, 6.57; N, 2.65.

2-*tert*-Butyl-3-(9-fluorenyl)-2-phenylaziridine (11). Only in mixture with xanthone: ^1H NMR δ 0.87 (s, tBu), 2.40 (d, J = 8.5 Hz, NCH), 3.13 (d, J = 8.5 Hz, NCCH), NH not detectable, aromatic signals hidden under those of xanthone.

Entry 10. Method B. Chromatography (60 × 3) with dichloromethane provided first 440 mg of a mixture of (^1H NMR) 364 mg of XH and 76 mg (7%) of X–X and thereafter 1.21 g (76%) of **9b**.

9-[3,3-Dimethyl-2-benzyl-2-(4-tolylsulfonamido)butyl]-xanthene (9b): mp 182–184 °C; IR 3330 (NH), 1323 (SO_2), 1251 (COC), 1160 cm^{-1} (SO_2); ^1H NMR δ 0.83 (s, tBu), 1.81 (dd, J = 15.2/7.1 Hz, 1 H of nonbenzylic $NCCH_2$), 2.04 (dd, J = 15.2/4.7 Hz, 1 H of nonbenzylic $NCCH_2$), 2.40 (s, Me of Ts), 3.00 (d, J = 14.1 Hz, 1 H of benzylic CH_2), 3.42 (d, J = 14.1 Hz, 1 H of benzylic CH_2), 4.14 (dd, J = 7.0/4.7 Hz, NCCCH), 4.49 (s, NH), 6.87–7.03 (m, 4 aromatic H), 7.07–7.29 (m, 10 aromatic H), 7.39–7.51 (m, 2 ortho H of Ts and 1 other aromatic H). Anal. Calcd for $C_{33}H_{35}NO_3S$: C, 75.40; H, 6.92; N, 2.6. Found: C, 75.30; H, 6.74; N, 2.66.

Entry 11. Method B. Chromatography (60 × 3) with dichloromethane provided 685 mg of hydrocarbons (FlH and a trace of Fl–Fl) and 702 mg of a mixture of (^1H NMR) of 527 (35%) and **10a** and 175 mg (18%) of **1a**. Finally, 311 mg (total yield 486 mg corresponding to 49%) of **1a** were obtained. The above mixture was recrystallized from toluene to give a sample of pure **10b**.

9-[3,3-Dimethyl-2-phenyl-2-(4-tolylsulfonamido)butyl]-fluorene (10a): mp 162–164 °C; IR 3400 (NH), 3340 (NH), 1319, 1158 cm^{-1} (both SO_2); ^1H NMR δ 0.94 (s, tBu), 2.31 (dd, J = 15.2/11.1 Hz, 1 H of $NCCH_2$), 2.35 (s, Me of Ts), 3.35 (dd, J = 15.3/3.6 Hz, 1 H of $NCCH_2$), 4.33 (dd, J = 11.1/3.6 Hz, NCCCH), 5.29 (s, NH), 5.87 (d, J = 7.7 Hz, 1 aromatic H), 6.50–6.59 (m, 1 aromatic H), 7.04–7.39 (m, 10 aromatic H), 7.44–7.59 (m, 1 aromatic H), 7.56–7.61 (m, 1 aromatic H), 7.65–7.71 (m, 1 aromatic H), 7.85–7.91 (m, 2 ortho H of Ts). Anal. Calcd for $C_{32}H_{33}NO_2S$: C, 77.54; H, 6.71; N, 2.82. Found: C, 77.75; H, 6.62; N, 2.55.

Entry 12. Method B. Chromatography (60 × 3) with dichloromethane provided 1.01 g of FlH and 671 mg (49%) of **12**. Elution with ethyl acetate yielded 220 mg (12%) of **13**.

2-*tert*-Butyl-3-(9-fluorenyl)-2-phenylaziridine (12): mp 134–137 °C; IR 3345 cm^{-1} (NH); ^1H NMR δ 1.00 (s, tBu), 2.27 (d, J = 8.6 Hz, NCH), 3.18 (d, J = 8.6 Hz, NCCH), 7.21–7.45 (m, 7 aromatic H), 7.67–7.85 (m, 6 aromatic H); MS (80 eV, 180 °C); m/e (relative intensity) 339 (13, $M^{\cdot+}$), 282 (7, M – tBu), 178 (100, phenanthrene), 174 (28, M – Fl), 165 (21, Fl); molecular mass calcd for $C_{25}H_{25}N$ 339.1991, found 339.1995. Anal. Calcd for $C_{25}H_{25}N$: C, 88.45; H, 7.42; N, 4.12. Found: C, 88.09; H, 7.53; N, 4.02.

1-(9-Fluorenyl)ethanol (13): mp 98–101 °C; IR 3370, 3425 cm^{-1} (both OH); ^1H NMR δ 0.91 (d, J = 6.4 Hz, Me), 2.04 (s, OH), 4.14 (d, J = 5.3 Hz, OCCH), 4.54 (dq, J = 5.3/6.4 Hz, OCH), 7.22–7.43 (m, 4 aromatic H), 7.49–7.54 (m, 1 aromatic H), 7.67–7.78 (m, 3 aromatic H). Anal. Calcd for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.49; H, 6.66.

Entry 13. Method B. No chromatography. The residue (1.33 g) consisted of (^1H NMR) 640 of FlH, 670 mg (90%) of **10a**, and a trace of Fl–Fl.

Entry 14. Method B. No chromatography. The residue (1.29 g) consisted of (^1H NMR) 620 mg of FlH, 84 mg (17%) of Fl–Fl, 513 mg (69%) of **10a**, and 73 mg (28%) of **2a**.

Entry 15. Method B. Chromatography (60 × 3) with dichloromethane yielded 510 mg of FlH and 1.53 g (75%) of **10b**.

9-[2-Benzyl-3,3-dimethyl-2-(4-tolylsulfonamido)butyl]-fluorene (10b): mp 208–210 °C; IR 3320 (NH), 1311, 1155 cm^{-1} (both SO_2); ^1H NMR δ 1.15 (s, tBu), 1.97 (dd, J = 15.4/7.4 Hz, 1 H of nonbenzylic $NCCH_2$), 2.29 (s, Me of Ts), 2.49 (dd, J = 15.2/4.8 Hz, 1 H of nonbenzylic $NCCH_2$), 3.41 (d, J = 14.1 Hz, 1 H of benzylic $NCCH_2$), 3.52 (d, J = 14.1 Hz, 1 H of benzylic $NCCH_2$), 4.36 (m_c, NCCCH), 4.67 (s, NH), 6.96–7.47 (m, 14 aromatic H), 7.64–7.79 (m, 3 aromatic H). Anal. Calcd for $C_{33}H_{35}NO_2S$: C, 77.76; H, 6.92; N, 2.75. Found: C, 78.03; H, 6.83; N, 2.77.

Acknowledgment. Support of this work by the Fonds der Chemie is gratefully acknowledged.

Registry No. **1a**, 136175-22-9; **1b**, 136175-23-0; **2a**, 65855-34-7; **2b**, 126179-50-8; **3**, 121838-18-4; **4**, 1605-08-9; **6**, 1083-30-3; **7**, 136175-24-1; **8a**, 136175-25-2; **8b**, 136175-29-6; **9a**, 136201-62-2; **9b**, 136175-30-9; **10a**, 136175-26-3; **10b**, 136175-31-0; **11**, 136175-27-4; **12**, 136175-28-5; **13**, 3023-49-2; sodium anthracenide, 12261-48-2; anthracenyllithium, 17228-13-6; tritylllithium, 733-90-4; xanthenyllithium, 40102-97-4; fluorenyllithium, 881-04-9; 9,9'-bixanthenyl, 4381-14-0; 9,9'-bifluorenyl, 1530-12-7.