chlorobenzyl bromide, 117380-00-4; 4-hydroxy-5-(hydroxymethyl)xanthene, 118143-49-0; 4-hydroxy-5-formylxanthene, 75830-34-1; 4-hydroxy-5-[[(methoxycarbonyl)dithio]methyl]xanthene, 118143-50-3; 4-acetoxy-5-[[(methoxycarbonyl)dithio]methyl]xanthene, 118143-51-4; ethyl *N*-(*tert*-butoxycarbonyl)-*S*-[[(4-acetoxy-5-xanthenyl)methyl]thio]-L-cysteinate, 118143-53-6; bis(1,5-dihydroxy-3-methoxy-2-methyl-9-oxo-9*H*-xanthen-4-yl) sulfide, 118143-55-8; 1,5-dihydroxy-3-methoxy-2-methylxanthone, 118143-54-7; 2,3-dihydroxybenzoic acid, 303-38-8; 2-methyl-3,5-dimethoxyphenol, 50827-64-0; 1,5-dihydroxy-3-methoxy-4-[(methoxycarbonyl)dithio]-2-methylxanthone, 118143-56-9; ethyl *N*-(*tert*-butoxycarbonyl)-*S*-[(1,5-diacetoxy-3-methoxy-2-methyl-9-oxo-9*H*-xanthen-4-yl)thio]-L-cysteinate, 118170-28-8; 1,5-diacetoxy-3-methoxy-4-[(methoxycarbonyl)dithio]-2-methylxanthone, 118143-57-0; 1,5-diacetoxy-3-methoxy-4-mercapto-2-methylxanthone, 118143-58-1; 4-acetoxydibenzothiophene, 118143-59-2; dibenzothiophene, 132-65-0; 4-hydroxydibenzothiophene, 24444-75-5; 4-methoxydibenzothiophene, 24444-74-4; 4-methoxy-6-mercaptodibenzothiophene, 118143-60-5; 4-mercapto-6-hydroxydibenzothiophene, 118143-61-6; 4-[(methoxycarbonyl)dithio]-6-hydroxydibenzothiophene, 118143-62-7; 4-[(methoxycarbonyl)dithio]-6-acetoxydibenzothiophene, 118143-63-8; methyl *N*-(*tert*-butoxycarbonyl)-*S*-[(6-acetoxy-4-dibenzothiophene-yl)thio]-L-cysteinate, 118143-65-0; 4-acetoxydibenzofuran, 101762-27-0; 1-acetoxyphenoxathiin, 118143-71-8; 1,3-dimethoxy-2-methyl-5-acetoxyxanthone, 77834-07-2; 1-acetoxy-2-(methylthio)naphthalene, 118143-74-1; 1-acetoxy-2-[(methylthio)methyl]benzene, 54810-48-9; ethyl *N*-acetoxy-*S*-[[(4-hydroxy-5-xanthenyl)methyl]thio]-L-cysteinate, 118143-75-2; 2-[(methoxycarbonyl)dithio]phenol, 118143-46-7; methyl *S*-[(2-hydroxyphenyl)thio]-L-cysteinate, 118143-47-8; methyl *S*-[[2-[(benzyloxycarbonyl)-L-alanyloxy]phenyl]thio]-L-cysteinate, 118143-48-9.

Supplementary Material Available: Listings of final positional and thermal parameters and bonds and angles for **15** (20 pages). Ordering information is given on any current masthead page.

Reductive Ring Opening of *N*-Benzoylaziridine by Anthracene Hydride (Anion of 9,10-Dihydroanthracene) via Base-Induced Fragmentation of the Intermediate Carbonyl Adduct[1-3]

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Received August 8, 1988

As previously reported, reaction of anthracene hydride (AH^-), or of its oxa analogue xanthenyl anion (X^-), with *N*-benzoylaziridines **1a,b** can result in amidoethylation (**2a,b** and **3a,b**) of the carbanion, in reductive opening (**4a,b**) of the aziridine ring, and in attack on the carbonyl group of **1a,b**. We now show with **1a** that both the rate of ring opening and the amount of reductive opening are significantly enhanced by an excess of AH^-Li^+ while the initially formed (90%) carbonyl adduct **6a** survives with a deficit of AH^-Li^+. Both effects due to carbanion excess are absent with X^-Li^+ but are much stronger with AH^-Na^+. These results point to a rapid process that is triggered off by deprotonation at position 10 of the carbonyl adduct **6**. A concerted or subsequent homolytic fragmentation is proposed to generate the ketyl **5** of **1**, followed by homolytic ring opening of **5** to yield the radical **12**, which is reduced to the carbanion **14**. The latter forms **4** by capturing a proton from dihydroanthracene. Inaccessibility of reductive ring opening for a trialkylacetyl-activated aziridine is demonstrated again (**18**).

Ring opening of *N*-aroylaziridines, e.g., **1a,b** by anthracene hydride (AH^-) (or xanthenyl anion (X^-)) can provide[4] amidoethylated dihydroanthracenes such as **2a,b** (or amidoethylated xanthenes, e.g., **3a,b**) and products of reductive opening, e.g., **4a,b** (Chart I). Both types of products were proposed to arise by homolytic ring opening of an intermediate ketyl, **e.g., 5a,b**.[4] Ring opening was preceded by the formation of a carbonyl adduct such as **6a,b** (or **7a,b**) as evidenced by the isolation of ketones of type **8** or **9** in high yield when the reaction could not go to completion.[4] A strong influence of the gegenion (Li^+ or Na^+) of X^- was described in a recent paper[3] together with a trapping of AH^-, X^-, and **1a** under reaction conditions that normally give the ketones **8** or **9**. Consequently, the carbonyl adducts **6a** and **7a** are reversibly formed by a classic ionic mechanism and the equilibrium concentrations of **1a** and X^- (and by analogy of **1a** and AH^-) are responsible for the ring-opening reactions: amidoethylation (forming **3a** and by analogy **2a**) and, to a negligible extent (ratio **3a:4a** = 8:1),[3] reductive opening. The latter is a slow process and proceeds most likely by single-electron transfer (SET) from X^- to **1a** forming **5a** and the radical $X^\bullet$ (analogously AH^- may form **5a** and the radial $AH^\bullet$). The respective conclusions can be applied to other *N*-benzoylaziridines. Since the dimethylaziridine **1b** undergoes only abnormal opening (**2b, 3b, 4b**),[4] this points to an SET mechanism[5] at least in this case where steric hindrance slows down the S_N2 ring opening.[5] On the other hand, the S_N2 path to **2a** and **3a** cannot be ruled out. Now, there are two findings that point to a different behavior of AH^- and X^-, which is not accounted for by the previous[4,3] interpretations. In the first reported[4] ring-fission reactions of **1a,b**, reductive opening was the main event with AH^-, but it was a side reaction with X^-. Second, the reported ring opening of **1a** proceeded much faster[3] with AH^-Li^+ than with X^-Li^+. We now present evidence that base-induced fragmentation of the carbonyl adduct

(1) Reactions with Aziridines. 49. Arene Hydrides. 6.
(2) Reactions with Aziridines. 48; see: Stamm, H.; Onistschenko, A.; Buchholz, B.; Mall, T. *J. Org. Chem.* **1989**, *54*, 193–199. 47: Stamm, H.; Speth, D. *Arch. Pharm. (Weinheim)*, in press. 46: Mall, T.; Stamm, H. *Chem. Ber.* **1988**, *121*, 1353–1355.
(3) Arene Hydrides. 5. Reactions with Aziridines. 45: Mall, T.; Stamm, H. *Chem. Ber.* **1988**, *121*, 1349–1352.
(4) Stamm, H.; Sommer, A.; Woderer, A.; Wiesert, W.; Mall, T. *J. Org. Chem.* **1985**, *50*, 4946–4955.
(5) Stamm, H.; Assithianakis, P.; Buchholz, B.; Weiss, R. *Tetrahedron Lett.* **1982**, 5021–5024.

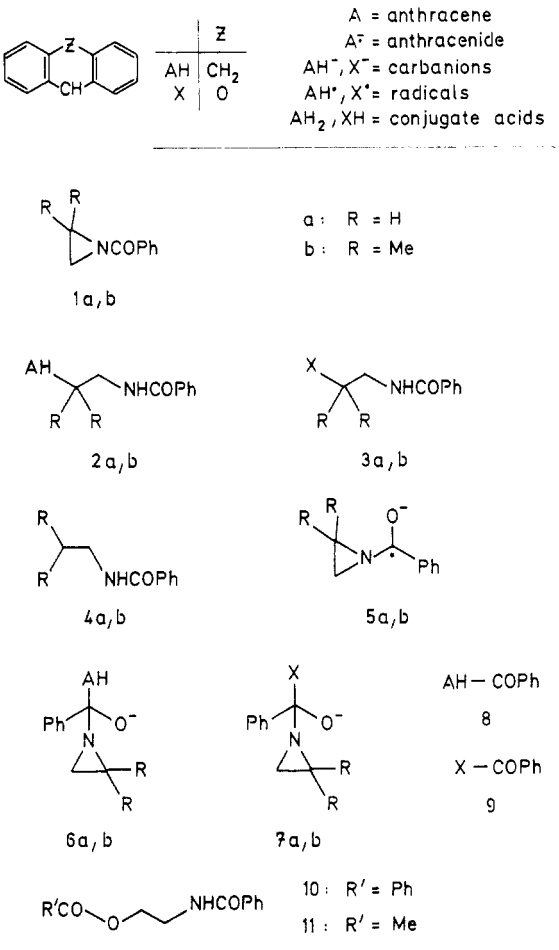
0022-3263/89/1954-1603$01.50/0

Table I. Reactions of AH^-Li^+, X^-Li^+, and AH^-Na^+ with Aziridine 1a in THF

	mmol reactant					% yields of products[b] relative to 1a							
entry	AH_2	XH	base	1a	min	2a	3a	4a	8	9	10	11	1a
1	7.5		6.25 BuLi	5	20	25		73	0		0	0	0
2	7.5		5 BuLi	5	20	10		(23)	37		(9)		
3	7.5		4 BuLi	5	20	0		0	54		17	12	10
4	7.5		5 BuLi	2	1	0		0	93				
5		7.5	6.25 BuLi	5	20		5	0		83			
6		75.5	5 BuLi	5	20		3	0		83		1	
7		7.5	4 BuLi	5	20		0	0		63		25	
8	7.5		7 $NaNH_2$	5	60	0		95	0				
9	10		8 $NaNH_2$	4	60	0		98	0				
10	7		4.5 $NaNH_2$	8	1/60[c]	0		(42)	(14)		0	(4)	(32)

[a] Time between end of addition of 1a and quenching with acetic acid. Time of addition of 1a (dissolved in 15 mL of THF) was 1 min for entries 1–3, 10–15 s for entries 4 and 10, and 2 min for the other entries. [b] Yields in parentheses are from ^1H NMR analysis of mixtures. [c] The time for the addition of 1a was longer.[a]

Chart I



6a can account for an accelerated conversion of the latter and for the predominance of reduction (e.g., 4a) over amidoethylation (e.g., 2a) as first reported.[4]

Results and Discussion

The experiments in Table I demonstrate that the outcome of the reaction between AH^- and 1a in THF depends pronouncedly on experimental conditions. We first restricted our experiments to lithium as the gegenion. An excess of AH^-Li^+ (entry 1) gave reduction (4a) and amidoethylation (2a) in the ratio 74:26. This is practically the same ratio as obtained previously[4] (73:27) under very similar reaction conditions except for the time needed for the addition of 1a. In the present experiments the solution of 1a in THF was added rapidly to the solution of AH^-Li^+ in THF. As in previous work, the reactions were quenched with acetic acid. Repeating the first run (entry 1) with equimolar quantities of AH^-Li^+ and 1a (entry 2) did not significantly change the ratio of 4a:2a (70:30) but substantially reduced their yields in favor of both ketone 8 and benzoate 10. The fact that 8 was the main product indicated that, contrary to entry 1, a large portion of the first-formed carbonyl adduct 6a survived until quenching. The trend observed in entries 1 and 2 reached its possible maximum when these runs were repeated with a deficit of AH^-Li^+ (entry 3): no 4a and 2a but 54% of 8 was obtained. A large portion of that part of 1a that had not formed 8 was recovered or converted to the acetate 11 by reaction with acetic acid after quenching. This conversion of 1a into 11 (as well as into 10) was not intended. Since it is slow under the experimental conditions (vide infra), it must depend on these conditions.[3,6]

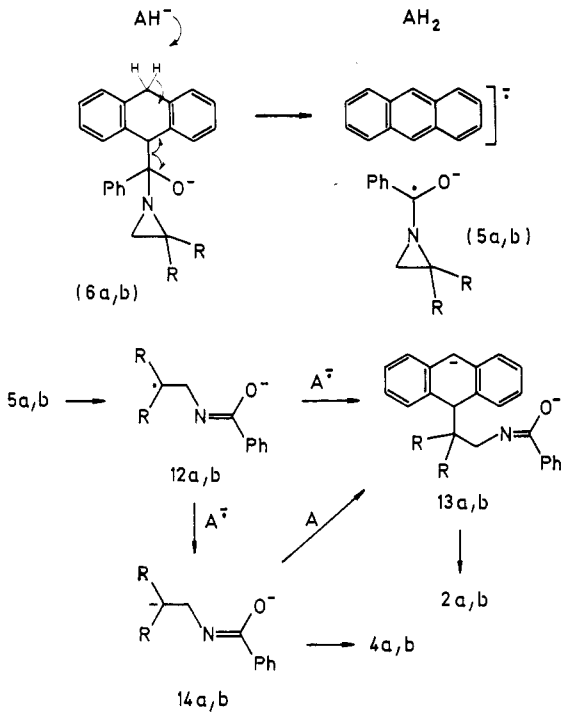
The above results suggest that in entry 1 the carbonyl adduct 6a was transformed to 4a and 2a neither via the mentioned classic ionic equilibrium with AH^- and 1a nor via the first-proposed[4] homolytic cleavage of 6a into AH• and ketyl 5a. Both pathways should be independent of the ratio AH^-:1a. A short time experiment (entry 4) confirmed that 6a is indeed initially formed in a very high yield.[7]

The influence of an excess of AH^-Li^+ on the rate of conversion of 6a into 4a and 2a is pronounced and indicates that a rapid reaction sequence is triggered off by an excess of AH^-. In sharp contrast, X^-Li^+ (entries 5–7) shows a very small dependence on analogous changes in experimental conditions. This is in accord with the reported[3] fast reversible formation of 7a–Li^+ and slow irreversible formation of 3a, or its amide anion rather, from the equilibrium concentrations of X^-Li^+ and 1a. Thus, it is obvious that deprotonation of the methylene group of the dihydroanthryl moiety in 6a (which is absent in the xanthenyl pendant 7a) by excess AH^- causes the rapid transformation of 6a into ring-opened products. The essential process in this transformation must be the breaking of the C–C bond between the dihydroanthracene moiety and the 1a moiety. Analogous AH^-Li^+-induced fragmen-

(6) Two extreme findings may illustrate the influence of experimental conditions on the reaction of 1a with carboxylic acids. 1a reacted exothermically with an excess of glacial acetic acid (no other solvent) and gave only 11 within a few minutes. However, equimolar quantities (5 mmol) of 1a and benzoic acid in refluxing benzene (100 mL) reacted slowly according to TLC. A spot for 10 arose slowly and needed 2 days to become comparable to the spot of 1a. After 3 days ^1H NMR analysis of the evaporated solution indicated the presence of 1a and 10 in the ratio 6:94 but no other products.

(7) One of the reviewers regretted that no spectroscopic (NMR, IR) analysis of the solutions was performed in order to determine the extent to which 6a is formed. A proper spectroscopic approach would probably be very fruitful but is beyond our possibilities due to the obvious technical problems.

Scheme I

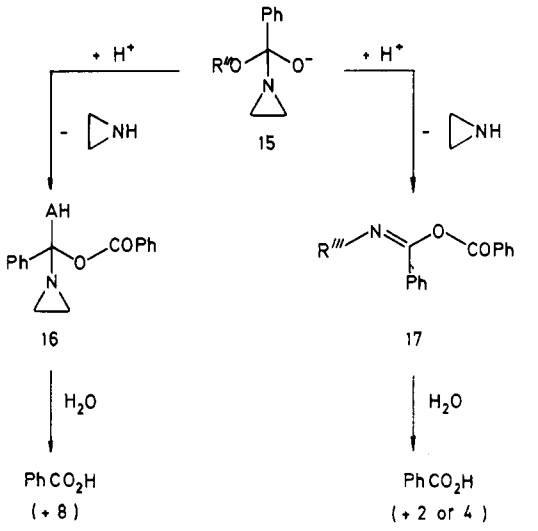


tations of intermediates resembling **6a,b** have previously been reported.[8] It appears that this fragmentation may be a general phenomenon with 9-substituted 9,10-dihydroanthracenes when the dihydroanthracene moiety can aromatize by loss of a fairly stable anionic species. There can be little doubt that this fragmentation will also be involved in reactions of other *N*-aroylaziridines (e.g., **1b**) with excess AH^-Li^+.

The rapid fragmentation of the carbonyl adduct may be depicted for **6a,b** as in the upper part of Scheme I. It may be either concerted or the result of a discrete deprotonation step followed by cleavage of the C–C bond in the second step. Cleavage of the C–C bond may be homolytic, providing ketyl **5** directly, or, as proposed in analogous cases,[8] it may be heterolytic, yielding A and the high energy dianion of **1** that would rapidly transfer an electron back to A with the same result as the homolytic cleavage. The lower part of Scheme I interprets the subsequent events. The generated ketyl **5** undergoes homolytic ring opening[5] to the anionic radical **12**. The latter has two possibilities[9] to react with the generated anthracenide $A^{-\bullet}$, namely, by radical combination yielding **13** (and hence **2**) or by SET yielding dianion **14**. The latter may abstract a proton from AH_2, thus forming the amide anion of **4** or it may form **13** by addition to the generated anthracene molecule A in analogy to the known[10] addition of alkyllithium species to A.

Three stages in Scheme I involve carbanions whose behavior should depend on the gegenion. Alkyllithium species are less polar, less basic in the kinetic sense, and more prone to undergo addition reactions than their sodium counterparts. Reactions of **1a** with AH^-Na^+ are

Scheme II



presented in entries 8–10 of Table I. Most remarkably, ring opening provided exclusively **4a** and was much faster (entry 10) than that with AH^-Li^+. Ketone **8**, indicative of the amount of carbonyl adduct **6a** present before quenching, was detected as a byproduct after a very short reaction time and under avoidance of an excess of AH^-Na^+ (entry 10). These findings and the pronounced gegenion effect are in accord with Scheme I, excluding step **12a** → **13a**. Addition reactions, forming **6a** and **13a**, are favored by lithium; deprotonation reactions, between AH^- and **6a** or between **14a** and AH_2, are faster with sodium. Similar gegenion effects could not be expected if **2a** and **4a** were formed from the radical **12a** without intervention of the carbanion **14a**.

While the acetate **11** certainly arises from **1a** after the reaction is quenched with acetic acid, the mechanistic origin of the benzoate **10** is not clear, although a similar reaction between **1a** and benzoic acid may appear likely. The problem is that benzoic acid cannot arise directly from **1a** and the acetic acid used for quenching.[11] As suggested by one reviewer and in support of the picture that we had obtained from many isolated findings, we investigated the reaction of **1a** with benzoic acid or acetic acid in separate experiments. These experiments confirmed the stated[3] influence of workup conditions. Stirring a solution of **1a** (2.5 mmol) and benzoic acid (2.5 mmol) or acetic acid (2.5 mmol) in THF (100 mL) for 2 h did not affect **1a**. Subsequent treatment that mimicked the workup of the reactions in Table I produced mixtures of **1a** and **10** (42:58) or **1a** and **11** (78:22), respectively. No **10** and no benzoic acid could be detected in the reactions with acetic acid. Thus, the direct route from **1a** to **10** or benzoic acid is definitely ruled out. **10** forms faster than **11** in accordance with the higher yield of **10** in entry 3 of Table I and in many unpublished results. This faster reaction was confirmed in a competition experiment with both carboxylic acids (1.25 mmol each). A mixture of **1a**, **10**, and **11** in the ratio 67:19:14 resulted. A possible way to benzoic acid under the experimental conditions is as follows (Scheme II). Reversible addition of an oxide ion $R''O^-$ (**6a** or the

(8) Stamm, H.; Sommer, A.; Onistschenko, A.; Woderer, A. *J. Org. Chem.* **1986**, *51*, 4979–4983. Sommer, A.; Stamm, H.; Woderer, A. *Chem. Ber.* **1988**, *121*, 387–389.

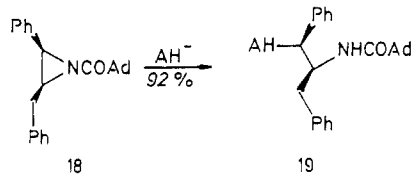
(9) Compare reactions of intermediate alkyl radicals with naphthalenide in reactions of naphthalenide with alkyl halides: Garst, J. F. *Acc. Chem. Res.* *4*, 400–406.

(10) Harvey, R. G.; Davis, C. C. *J. Org. Chem.* **1969**, *34*, 3607–3609. Brinkmann, A. W.; Gordon, M.; Harvey, R. G.; Rabideau, P. W.; Stothers, J. B.; Ternay, A. L., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 5912–5916.

(11) There is no precedence for such a reaction. Moreover, it is at least difficult to construct a respective mechanism, above all since reaction and workup are performed under mild conditions. The only reaction that can be expected from literature[12] and from experience in this laboratory is formation of **11** and perhaps little isomerization of **1a** to 2-phenyloxazoline.

(12) Dermer, O. C.; Ham, E. G. *Ethylenimine and other Aziridines*; Academic Press: New York, 1969; pp 257–260.

Scheme III



18 19

Ad = 1-adamantyl

imidate ions of **2a** and **4a**) to **1a** can yield an intermediate of type **15** before quenching. Protonation during quenching may eliminate ethylenimine from **15**, forming reactive benzoic acid derivatives of type **16** or **17**. Now hydrolysis during workup can rapidly yield benzoic acid that dissolves in the organic layer together with **1a**. The *O*-acyl-*O*,*N*-ketal **16** would simultaneously liberate **8**, while the *O*-acylimidates **17** would liberate **2a** or **4a**.

A special finding in the first report[4] may now have a simple explanation: the pivaloyl analogue ($COCMe_3$ in place of benzoyl) of **1b** underwent neither reductive opening nor carbonyl attack with AH^-Li^+. The only product detected after a long reaction time was the pivaloyl analogue of **2b**, probably as a result of the reaction sequence SET, homolytic ring opening, and radical combination. We now assume that this result was primarily caused by steric hindrance to carbonyl attack, thus closing the major path (Scheme I) to reductive opening. Using excess of AH^-Li^+ on aziridine **18**, we are now able to add a second example of this phenomenon (Scheme III). Again we found exclusive amidoethylation (**19**) while the benzoyl analogue of **18** had previously[4] undergone reductive opening (96%). It thus seems that with trialkylacetyl activation the minor, nonfragmentation pathway to reductive opening is also not available. The existence of this minor route, probably starting with SET between acylaziridine and carbanion, is known from the above-mentioned reaction of X^- with the benzoyl aziridines **1a**[3] and **1b**.[4] For **18** the observed regioselectivity itself would be compatible with both a S_N2 mechanism and a SET process, but **19** consisted of one diastereomer only. This diastereomeric purity of **19** is difficult to reconcile with the radical combination of $AH^\bullet$ and an intermediate of type **12**. It, therefore, appears reasonable to assign the erythro configuration (in one eclipsed conformation the two hydrogen atoms side by side as well as the similar substituents AH and benzyl) to **19**. This configuration would arise by configurational inversion of the reacting aziridine carbon.

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 4). Column chromatography was performed with 0.063–0.2 mm silica gel (Merck, Germany); column dimensions (thickness × length, cm) are given for the specific workup.

18 was prepared from *cis*-2-benzyl-3-phenylaziridine[13] and 1-adamantylcarbonyl chloride according to a proven procedure.[14]

***cis*-1-(1-Adamantylcarbonyl)-2-benzyl-3-phenylaziridine (18)**: yield 72%; mp 76–77 °C; IR (KBr) 1678 cm^{-1} (C=O); ^1H NMR δ 1.67 (m_c, s-like, 3 CH_2 of adamantyl far from position 1), 1.96 (m_c, s-like, 3 CH and 3 CH_2 of adamantyl next to position 1), 2.46 (dd, J = 14.7 Hz, J = 8.0 Hz, 1 H of benzylic CH_2), 2.87 (dd, J = 14.7 Hz, J = 5.0 Hz, 1 H of benzylic CH_2), 3.03 (ddd, J = 8.0 Hz, J = 6.2 Hz, J = 5.1 Hz, 2-H of aziridine), 3.68 (d, J = 6.2 Hz, 3-H of aziridine), 6.89–6.94 (m, 2 ortho H of Ph), 7.09–7.23 (m, 3 Ar H), 7.28–7.41 (m, 5 Ar H). Anal. Calcd for $C_{26}H_{29}NO$: C, 84.06; H, 7.87; N, 3.77. Found: C, 84.24; H, 8.04; N, 3.94.

Reactions with 9-Lithio-9,10-dihydroanthracene or 9-Lithioxanthene. Generation of AH^-Li^+ (or X^-Li^+) from AH_2 (XH) in 70 mL of THF and *n*-butyllithium (hexane solution) followed by addition of **1a** dissolved in 15 mL of THF (20 mL of THF for entries 5–7) at room temperature was performed as described in ref 4 and Table I. The reactions were quenched with a small excess (ca. 10–30%) of glacial acetic acid. THF was removed under reduced pressure and the residue taken up in CH_2Cl_2 and washed with water. The concentrated CH_2Cl_2 solution was subjected to column chromatography (3 × 20). After removal of AH_2, A, and **8** (or **9**) with toluene, the other compounds were eluted with ethyl acetate and chromatographed again (1.5 × 70, CH_2Cl_2/ethyl acetate 10:1), providing **2a** (or **3a**), **4a**, **10**, and **11** in this sequence either in a pure state or as binary mixtures that were analyzed by ^1H NMR. The mixture containing **8** (or **9**) was chromatographed again (1.5 × 70, toluene), providing **8** (or **9**) as last eluate.

Reactions with 9-Sodio-9,10-dihydroanthracene. AH_2, sodium amide (30% suspension in toluene), and 100 mL of THF were refluxed for 2 h. After being cooled to room temperature, the solution of **1a** in 15 mL of THF was added dropwise within 2 min (in a fast flow within 10–15 s in entry 10). Quenching and workup was performed as in entries 1–7. Chromatography (3 × 60) with CH_2Cl_2 provided a mixture consisting of AH_2, A, and **8** (yield determined by ^1H NMR analysis). Subsequent elution with ethyl acetate yielded **4a** or (entry 10) a mixture consisting of **1a**, **4a**, and **11**. The latter mixture was analyzed by ^1H NMR.

The products **2a**, **3a**, **4a**, **8**, and **9** have been characterized previously.[3,4]

2-Benzamidoethyl benzoate (10): mp 85–88 °C (lit.[15] mp 88–89 °C); IR (KBr) 3260 (NH), 1723 (ester C=O), 1641 (amide I), 1563 cm^{-1} (amide II); ^1H NMR δ 3.83 (m_c, q-like, NCH_2), 4.52 (m_c, t-like OCH_2), 6.97 (s br, NH), 7.35–7.58 (m, 4 meta H and 2 para H of 2 Ph), 7.76–7.80 (m, 2 ortho H of PhCON), 8.01–8.05 (m, 2 ortho H of $PhCO_2$). Anal. Calcd for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20. Found: C, 71.25; H, 5.62; N, 5.01.

2-Benzamidoethyl acetate (11): mp 45–46 °C; IR (KBr) 3360 (NH), 1735 (ester C=O), 1642 (amide I), 1534 cm^{-1} (amide II); ^1H NMR δ 2.05 (s, Me), 3.68 (m_c, q-like, NCH_2), 4.26 (m_c, t-like, OCH_2), 7.07 (s br, NH), 7.36–7.48 (m, meta H and para H of Ph), 7.77–7.80 (m, ortho H of Ph). Anal. Calcd for $C_{11}H_{13}NO_3$: C, 63.75; H, 6.32; N, 6.76. Found: C, 64.01; H, 6.45; N, 6.60.

Reaction of **1a** with benzoic acid (mimicked workup). A solution of **1a** and benzoic acid (2.5 mmol each) in 100 mL of THF was stirred for 2 h. TLC (silica gel, dichloromethane/ethyl acetate 10:1) indicated only starting material. The solution was evaporated (10 min, bath temperature 55–58 °C). After 30 min, the residue was dissolved in 50 mL of dichloromethane and washed twice with water (50 mL each time). The organic layer was concentrated (bath temperature about 40 °C). TLC (as above) indicated **1a**, **10**, and benzoic acid. A sample was evaporated and analyzed by means of the ^1H NMR spectrum.

The reaction of **1a** with acetic acid (or with equimolar amounts of benzoic and acetic acid) was performed in precisely the same manner.

***N*-[1-Benzyl-2-(9,10-dihydroanthr-9-yl)-2-phenylethyl]-adamantanecarboxamide (19).** A solution of 901 mg (5 mmol) of AH_2 in 50 mL of THF was cooled to freezing (about −110 °C). After addition of 3.8 mmol of *n*-butyllithium (hexane solution), the mixture was allowed to warm up under stirring. At room temperature a solution of 1.115 g (3 mmol) of **18** in 20 mL of THF

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was added dropwise. After 16 h the reaction was quenched with acetic acid. Evaporation under reduced pressure provided a residue that was taken up in CH_2Cl_2 and washed with water. Chromatography (3 × 30) with petroleum ether removed the hydrocarbons. Subsequent elution with CH_2Cl_2 yielded 1.52 g (92%) **19**: mp 202–203 °C; IR (KBr) 3395 (NH), 1641 (amide I), 1510 cm^{-1} (amide II); ^1H NMR δ 1.74 (m_c, 3 CH_2 of adamantyl far from position 1), 1.87 (m_c, 3 CH_2 of adamantyl next to position 1), 2.06 (m_c, s-like, 3 CH of adamantyl), 2.17 (d, J = 19.1 Hz, 10-H pseudo ax), 2.45 (dd, J = 14.0 Hz, J = 7.8 Hz, 1 H of benzylic CH_2), 2.81 (dd, J = 14.0 Hz, J = 4.1 Hz, 1 H of benzylic CH_2), 3.16 (dd, J = 10.5 Hz, J ca 2.5 Hz, NCCH), 3.23 (d, J = 19.0 Hz, 10-H pseudo eq), 4.46 (d, J = 2.3 Hz, 9-H pseudo eq), 4.58–4.75 (m, NCH), 5.52 (d, J = 9.0 Hz, NH), 6.33 (m_c, d-like, 2 ortho H of nonbenzylic Ph), 6.90–7.03 (m, 6 Ar H), 7.11–7.30 (m, 9 Ar H), 7.49 (m_c, d-like, 1 Ar H). Anal. Calcd for $C_{40}H_{41}NO$: C, 87.07; H, 7.49; N, 2.54. Found: C, 87.09; H, 7.53; N, 2.27.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemie. This support is gratefully acknowledged. We thank Professor Hans Suschitzky for his help in improving the English.

Registry No. **1a**, 7646-66-4; **2a**, 98943-73-8; **3a**, 70686-42-9; **4a**, 614-17-5; **8**, 50688-77-2; **9**, 98943-92-1; **10**, 16180-99-7; **11**, 92367-87-8; **18**, 119297-89-1; **19**, 119297-90-4; AH_2, 120-12-7; XH, 92-83-1.

The Philicity of *tert*-Butoxy Radicals. What Factors Are Important in Determining the Rate and Regiospecificity of *tert*-Butoxy Radical Addition to Olefins?

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Received April 15, 1988

The relative rates of addition of *tert*-butoxy radicals to substituted styrenes have been evaluated by means of competition experiments. The data demonstrate that *tert*-butoxy radicals show electrophilic character (ρ = −0.30). An explanation for the apparently anomalous behavior shown by *tert*-butoxy radicals in their reactions with fluoro olefins is proposed in terms of the ability of α-fluorine substituents to stabilize the incipient C–O bond.

Tedder's "rules"[1] for radical addition reactions indicate that, while regiospecificity is controlled mainly by steric factors, the rate of radical addition to the unsubstituted terminus of 1-substituted or 1,1-disubstituted olefins is determined largely by polar factors. This is in accordance with the finding that trends in the reactivities of radicals toward monomers can often be rationalized in terms of the nucleophilic (e.g. methyl,[1] *n*-hexyl, cyclohexyl, *tert*-butyl[2,3]) or electrophilic (e.g. trifluoromethyl,[1] hydroxy,[4] benzoyloxy[5]) character of the attacking radical.

tert-Butoxy radical reactions have been widely studied.[6] Most work has been devoted to hydrogen atom abstraction, for which *tert*-butoxy radicals have a marked propensity. Studies on the rates of abstraction of benzylic hydrogens from substituted toluenes and subsequent analysis of the data by way of a Hammett correlation indicate that *tert*-butoxy radicals are slightly electrophilic (small negative ρ, see Table I).[7-11] Zavitsas and Pinto,[9] and later, Levin and Abul'khanov,[12] disputed that tert-butoxy radicals have any marked electrophilic character. They suggested that the correlation with Hammett σ was fortuitous and proposed that changes in the C–H bond dissociation

Table I. ρ and ρ^+ Parameters for Reactions of Oxygen- and Carbon-Centered Radicals

	addition to styrene		abstraction from toluene	
radical	ρ^+	ρ	ρ^+	ρ
$(CH_3)_3C^\bullet$	1.1,[a]			0.49[b]
$c\text{-}C_6H_{11}^\bullet$	0.68[a]			
$n\text{-}C_6H_{13}^\bullet$	0.45[a]			
$n\text{-}C_{11}H_{23}^\bullet$				0.45[c]
$CH_3^\bullet$			−0.1[e]	−0.12 (−0.21)[d,e]
$CCl_3^\bullet$	−0.42[f]	−0.43[f]	−1.46[g]	−1.46 (−1.67)[d,g]
$(CH_3)_3CO^\bullet$	−0.27[h]	−0.31[i]	−0.35[j]	−0.34 (−0.36)[d,j]
$(CH_3)_3COO^\bullet$			−0.56[k]	−0.78 (−0.76)[d,k]

[a] 42 °C, ρ increases with decreasing temperature.[2] [b] 80 °C, Pryor, W. A.; Tang, F. Y.; Tang, R. H.; Church, D. F. *J. Am. Chem. Soc.* **1982**, *104*, 2885–2891. See also: Dutsch, H. R.; Fischer, H. *Int. J. Chem. Kinet.* **1982**, *14*, 195–200. Pryor, W. A.; Davis, W. H.; Staneley, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 4754–4756. [c] 80 °C, Henderson, R. W.; Ward, R. D. *J. Am. Chem. Soc.* **1974**, *96*, 7556–7557. See also: Pryor, W. A.; Davis, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 7557–7559. Zavitsas, A. A.; Hanna, G. M. *J. Org. Chem.* **1975**, *40*, 3785–3783. [d] Values in parentheses are those recalculated by Pryor et al.[30] with data for meta-substituted toluenes only. [e] 100 °C, Pryor, W. A.; Tonellato, U.; Fuller, D. L.; Jumonville, S. *J. Org. Chem.* **1969**, *34*, 2018–2020. [f] 70 °C, meta-substituted styrenes only.[36] [g] 50 °C, Huyser, E. S. *J. Am. Chem. Soc.* **1960**, *82*, 394–396. [h] 60 °C, present work see Figure 2. [i] 60 °C, present work, meta-substituted styrenes only, see Figure 1. [j] 45 °C, chlorobenzene (value of ρ shows a small solvent dependence).[7] [k] 30 °C, Howard, J. A.; Chenier, J. H. B. *J. Am. Chem. Soc.* **1973**, *95*, 3054–3055.

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