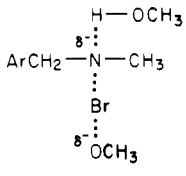
base concentration and be negligible in an aprotic solvent.

Rate data contained in Table IV are also consistent with this interpretation. If the substitution reaction is catalyzed by free methanol, the second-order rate constants for the substitution reaction, k_2^S, would be expected to decrease with increasing MeONa concentration (vide supra). On the other hand, those for the elimination reaction, k_2^E, should remain constant. In agreement, the k_2^E values are invariant but the overall second-order rate coefficients ($k_2 = k_2^S + k_2^E$) decrease with increasing base concentration. Therefore, the transition-state structure for attack of methoxide at bromine in **2** is envisioned as **9** in which a hydrogen-bonded methanol molecule helps to stabilize the developing negative charge on nitrogen.



9

Experimental Section

Benzylidenemethylamines **3**, benzylmethylamines **4**, and *N*-halobenzylmethylamines **1** and **2** and MeONa–MeOH were prepared as described previously.[8] Benzylidene-*tert*-butylamine, benzyl-*tert*-butylamine, *N*-bromobenzyl-*tert*-butylamine (**5**) and *N*-chlorobenzyl-*tert*-butylamine (**6**) were prepared by known methods.[8,17]

Products from reactions of **1** and **2** with MeONa–MeOH were isolated and identified as before.[8] Yields of **3** from reactions of **2** with MeONa–MeOH were determined by comparing the UV absorbances of the reaction products with those for authentic samples.

Reactions of *N*-chloro- and *N*-bromobenzyl-*tert*-butylamines (**6** and **5**, respectively) with MeONa–MeOH were carried out by stirring the solution of **6** or **5** in MeOH (7.26×10^{-2} M, 3.0 mL), MeONa–MeOH (2.28 M, 3.0 mL), and *tert*-butylbenzene (internal standard, 0.2 mmol) for 12 h at room temperature. The solvent was removed in vacuo, and the residue was extracted with diethyl ether and analyzed by gas chromatography on a 20-m Carbowax 20M capillary column with temperature programming from 110–200 °C. The products were benzylidene-*tert*-butylamine (99.5%) from **6** and benzylidene-*tert*-butylamine (26.5%) and benzyl-*tert*-butylamine (73.5%) from **5**, respectively.

The reaction of **6** with EtSNa–MeOH was carried out by the same procedure except that the EtSNa–MeOH was prepared by adding EtSH (13.5 mmol) to MeONa–MeOH (2.28 M, 3.0 mL). In this reaction, benzyl-*tert*-butylamine was obtained in 99.8% yield.

Stability of the *N*-haloamines in MeOH was demonstrated by the previously used method.[8]

Kinetic studies were carried out as before[8] using a Cary 17D UV spectrophotometer. The pseudo-first-order rate constant was divided by the base concentration to afford the second-order rate constant, k_2. For reaction of **2** with MeONa–MeOH, the k_2 values were multiplied by the imine yields to obtain the second-order rate constant for imine formation, k_2^E.

Acknowledgment. This investigation was supported by grants from the Basic Research Institute Program, Korea Ministry of Education (1984), the Peeres Company, and the Korea Science and Engineering Foundation.

Registry No. **1a**, 3555-71-3; **1c**, 70972-89-3; **1d**, 70972-94-0; **1e**, 70972-96-2; **2a**, 98760-21-5; **2c**, 98760-20-4; **2d**, 98760-22-6; **2e**, 98760-23-7; **3a**, 622-29-7; **3c**, 13114-23-3; **3d**, 35003-56-6; **3e**, 877-80-5; **4a**, 103-67-3; **4c**, 702-24-9; **4d**, 67344-77-8; **5**, 98777-15-2; **6**, 33863-73-9; PhCH=NBu-*t*, 6852-58-0; $PhCH_2NHBu$-*t*, 3378-72-1.

(17) Friefedier, M.; Moore, M. B.; Vernstein, M. R.; Stone, G. R. *J. Am. Chem. Soc.* **1958**, *80*, 4320–4323.

Highly Regioselective Ring Cleavage of *N*-Acylaziridines by "Anthracene Hydride" (Anion of 9,10-Dihydroanthracene). Intermediacy of a Carbonyl Adduct. Influence of Nitrogen Inversion on the Ring Opening?[1,2]

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Anthracene hydride AH^- reacts with *N*-acylaziridines by reductive opening of the aziridine ring and/or amidoethylation of AH^-. When the two aziridine carbons are differently substituted, in both reactions only that bond is broken which can form the more stable carbon radical quite in accord with the intermediacy of a radical anion (ketyl) **14** and with the known homolytic cleavage of **14** forming the radical **15**. The extra electron in **14** is provided by AH^- being oxidized to the radical AH·, which can react with **15** either by radical combination or by hydrogen transfer. The reaction of AH^- with *N*-aroylaziridines can be interrupted at the stage of the carbonyl adduct **5** as is shown by the isolation of the ketones **7a,b**. So, **5** (R^4 = aryl) is considered to be in equilibrium with the radical pair AH·/**14**. The conversion of **5** into the final products progresses as expected from its structure apart from the observed retardation by a phenyl substituent in the aziridine ring (**3a**, **4a**). This retardation is tentatively explained by a hypothesis assuming ring opening of **14** to occur in the transition state of nitrogen inversion. The anion X^- of xanthene resembles AH^- in its reactivity. Both carbanions react with *N*-sulfonylaziridines as expected from an S_N2 mechanism.

The anions of dihydroarenes are formally composed of the corresponding arene and a hydride ion. They may therefore be called arene hydrides for convenience. Since they are negatively charged analogues of dihydropyridines,

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Table I. Room Temperature Reactions of AH^- with *N*-Acylaziridines

				isolated yields,[a,b] %									
				amido-ethylation		redn		carbonyl compd		displaced aziridine base		educts and artifacts thereof	
entry	aziridine	molar excess AH^-, %	time										
1	**1a**	25	30 min	25	**8a**	67	**9a**,	1	**7a**				
						>56	A						
2	**1b**	0	30 min	11	**8b**	70	**9b**	3	**7b**				
						(76)	A						
3	**2a**	25	30 min	15	**8c**	78	**9c**						
						(83)	A						
4	**2b**	0	45 min	15	**8d**	82	**9d**						
						(78)	A						
5	**3a**	20	25 min			14	**9e**	52	**7a**	49	**6c**	16	**3a**
6	**4a**	20	25 min			23	**9f**	56	**7a**	52	**6d**	15	**4a**
7	**4a**	20	1 day			96	**9f**						
						>43	A						
8	**2c**	20	4 days	85	**8g**	(3.7)	A						
9	**1d**	0	10 min	26	**8h**							16	**11h**[c]
				48	**10a**								
10	**2d**	25	1 day	73	**8i**	(0.4)	A	14	**7d**				
11	**2d**	25	5 days	72	**8i**			14	**7d**				

[a] Only a part of anthracene was isolated. Yields of anthracene in parentheses are determined from this and from the ^1H NMR spectrum of the isolated mixture of AH_2 and A. AH_2 was always employed in excess. [b] All products satisfactory elementary analyses (C, H, N ±0.3%) or precise elementary composition from MS. [c] Product is characterized in ref 11.

one may expect their reducing properties to be more pronounced than those of common carbanions. One unusual and unexpected result in our work on activated aziridines prompted a study of the reactivity of arene hydrides. We report now on reactions of anthracene hydride AH^- with activated aziridines.

Nucleophilic ring opening of activated aziridines has been shown to follow an S_N2 mechanism.[3] However, for certain weakly activated aziridines a homolytic ring opening was recently proposed[4] and confirmed.[5] Since the first step of the proposed mechanism is a single electron transfer, the symbol SET was used for the characterization of this mechanism. We show now that the reaction of AH^- with some *N*-acylaziridines is also best explained by such a mechanism even in the absence of steric hindrance of an S_N2 reaction.

Results and Discussion

AH^- was generated from 9,10-dihydroanthracene (AH_2) and butyllithium in THF at low temperatures with subsequent warming. Room temperature reactions of 1–4 with this solution resulted in amidoethylations of AH^- and/or reductive ring opening Scheme I, Table I), both reactions always exclusively with bond breaking between nitrogen and the sterically more hindered aziridine carbon ("abnormal" opening[4,5]). We were not able to detect any isomeric product formed through "normal" opening. The observed bond breaking is always in accord with the formation of the more stable radical.

Thus, the *N*-aroylaziridines **1a,b** and **2a,b** afforded high yields of *N*-ethyl- (**9a,b**) and *N*-isobutyl amides (**9c,d**) and as minor products the amidoethyl derivatives **8a–d** of AH_2 (entries 1–4). From **1a** and **1b** we isolated also small amounts of the ketones **7a** and **7b** which only can have formed by protonation of the carbonyl adduct **5** and elimination of the aziridine base **6a**. Although carbonyl attack is well-known for reactions of *N*-acylaziridines with some carbanions,[6,7] we shall discuss this reaction later. Formation of the carbonyl adduct **5** is the major reaction for the phenyl-substituted *N*-aroylaziridines **3a** and **4a** as evidenced by the isolated yields of ketone **7a** and of the aziridine bases **6c,d** (Table I, entries 5 and 6). The only other reaction of **3a** and **4a** was reductive opening (**9e,f**) which became predominant (96% **9f**, no **7a**) after prolonged reaction (entry 7). There is a reaction path from **5** to **9** and also from **5** to **8** as will be shown later. Exclusive amidoethylation of AH^- was found with **2c** (entry 8) the carbonyl function of which is not conjugated with an aryl group ($R^4 \neq$ aryl). Also exclusive amidoethylation occurred with **1d** (entry 9), while with **2d** the amidoethylation product **8i** was accompanied by some diphenylamide **7d**, which must have originated from the corresponding **5**. Since the yield of **7d** did not decrease with time (entries 10 and 11), there is no reaction path from **5** to **8** or **9** for $R^4 = NPh_2$. Formation of **7d** and reaction of **1d** will be discussed later.

Apart from the formation of **5** and the reaction of **1d**, the ring openings of Table I are clearly in accord with the proposed SET mechanism[4,5] via the radical intermediates **14** and **15**. The exclusively abnormal ring opening and particularly the reductive ring opening[5] are good evidence for the homolytic cleavage of a "ketyl" **14**. The regioselectivity or perhaps even regiospecificity of reductive opening of **2a,b** rules out a direct nucleophilic ring opening by a hydride transfer.[8] To investigate further the reactivity of *N*-acylaziridines toward hydride attack we used sodium borohydride in methanol, conditions which are

(1) Reactions with Aziridines. Part 33. Arene Hydrides. Part 1. The major part of this work was taken from the Doctoral Dissertation of A. Sommer.

(2) Reactions with Aziridines. Part 32: Buchholz, B.; Stamm, H. *Isr. J. Chem.*, in the press.

(3) Ham, G. E. *J. Org. Chem.* **1964**, *29*, 3051.

(4) Stamm, H.; Assithianakis, P.; Buchholz, B.; Weiss, R. *Tetrahedron Lett.* **1982**, 5021.

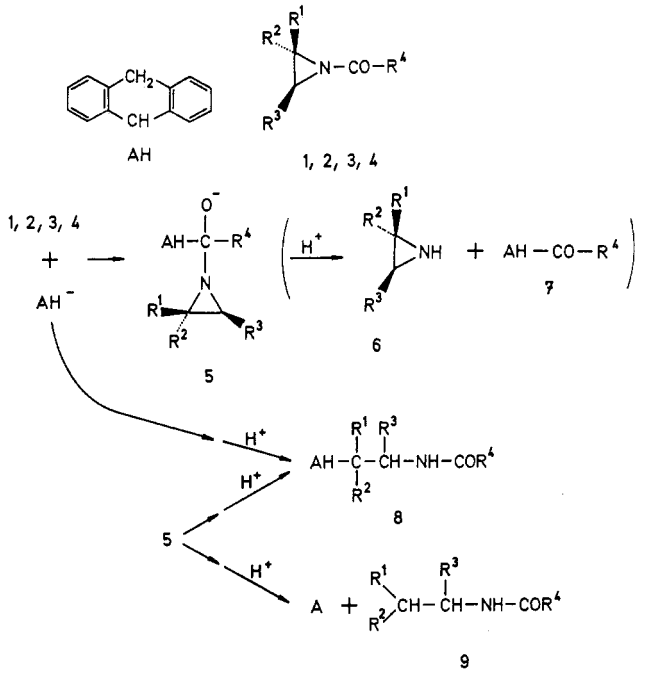
(5) Reactions with Aziridines. Part 31: Stamm, H.; Assithianakis, P.; Weiss, R.; Bentz, G.; Buchholz, B. *J. Chem. Soc., Chem. Commun.* **1984**, 753.

(6) Stamm, H.; Führling, G. *Tetrahedron Lett.* **1970**, 1937. Stamm, H. *Tetrahedron Lett.* **1971**, 1205. Stamm, H.; Wiesert, W. *Chem. Ber.* **1978**, *111*, 2665. Wattanasin, S.; Katawala, F. G. *Tetrahedron Lett.* **1984**, 811. *N*-(Ethoxycarbonyl)aziridine and phenylmagnesium bromide gave benzophenone: Stamm, H.; Führling, G., unpublished results.

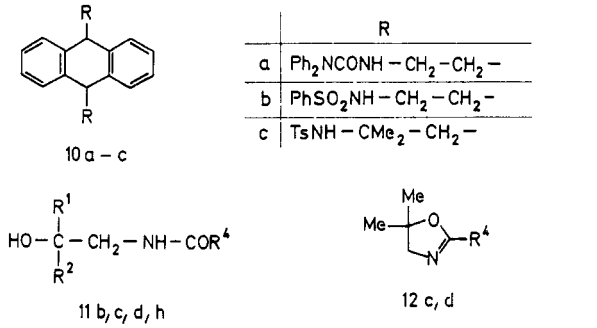
(7) Hassner, A.; Kascheres, A. *Tetrahedron Lett.* **1970**, 4623.

(8) For N-substituted acridans which are isosters of AH^- a hydride transfer mechanism in reductions of quinones has been considered: Colter, A. K.; Plank, P.; Bergsma, J. S.; Lahti, R.; Quesnel, A. A.; Parsons, A. G. *Can. J. Chem.* **1984**, *62*, 1780.

Scheme I[a]



	R
a	$Ph_2NCONH-CH_2-CH_2-$
b	$PhSO_2NH-CH_2-CH_2-$
c	$TsNH-CMe_2-CH_2-$

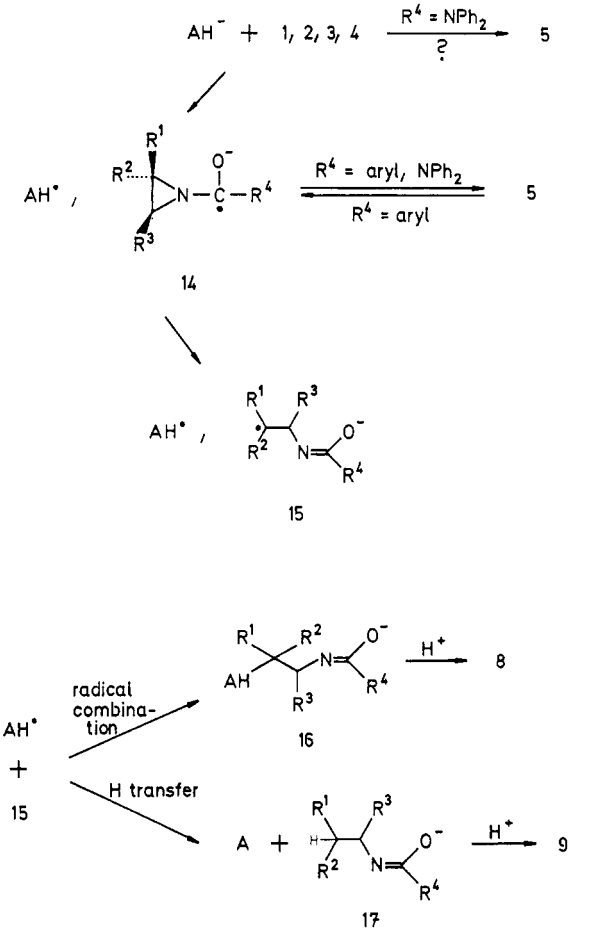


	R^1	R^2	R^3	1-5, 7	R^4
1, 6a	H	H	H	a	
2, 6b	Me	Me	H	b	
3, 6c	Ph	H	H	c	CMe_3
4, 6d	Ph	H	$PhCH_2$	d	NPh_2

8, 9, 11-13	R^1	R^2	R^3	R^4
a	H	H	H	
b	H	H	H	
c	Me	Me	H	
d	Me	Me	H	
e	Ph	H	H	
f	Ph	H	CH_2Ph	
g	Me	Me	H	CMe_3
h	H	H	H	NPh_2
i	Me	Me	H	NPh_2

[a] AH_2 = 9,10-dihydroanthracene, AH^- = anion of AH_2, AH· = radical of AH_2, A = anthracene.

Scheme II



reported[7] to effect reductive opening of *N*-(ethoxycarbonyl)aziridine. In our experiments **2a** was not attacked in 2 days at room temperature, while **1a** gave 46% benzyl alcohol, 43% methyl benzoate, and 10% **9a** after 1 day. This can be rationalized by attack at the carbonyl function forming successively benzaldehyde and benzyl alcohol. An accompanying attack on the ring would yield the anion of **9a**, which immediately generates methoxide. The latter attacks the carbonyl group of **1a** forming methyl benzoate.

As will be shown later, **5** is an intermediate in the reaction of each *N*-aroylaziridine studied. So, the reactions in Table I (except **1d**, entry 9) may be rationalized by the modified mechanism depicted in Scheme II. A homolysis equilibrium between **5** (R^4 = aryl) and the geminate radical pair AH·/**14** accounts for the product dependence on reaction conditions. The assumption that this equilibrium is entered from the left side via a primary SET step is consistent with previous results[4,5] and leads to a uniform and simple mechanistic picture which also allows for cases of ring opening without intermediacy of **5** as, e.g., with **2d**.

This primary step in the reaction of AH^- with **1a,b** and **2a,b** is very fast since 1 equiv of *N*-aroylaziridine immediately decolorizes the intensely brown-red solution of AH^-. How can this fast SET step be reconciled with the known [4] slow SET amidoethylation of common nucleophiles by **1a**? AH^- is a very strong base (pK_a 30.3[9]) that forms one of the most stable simple radicals (AH·) on electron detachment.[10] The ability of AH^- to transfer an electron

(9) Streitwieser, A.; Berke, C. M.; Robbers, K. *J. Am. Chem. Soc.* **1978**, *100*, 8271.

(10) Compare, e.g., the correlation between carbanion basicity and reductive power: Bordwell, F. G.; Clemens, A. H. *J. Org. Chem.* **1981**, *46*, 1035.

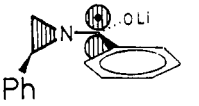
rapidly is shown by the immediate appearance of the blue color of benzophenone ketyl upon addition of benzophenone. Electron attachment onto an *N*-aroylaziridine should similarly be facilitated by spin delocalization in **14** though to a smaller extent than in the rather stable benzophenone ketyl. Generally, the energy of ketyl **14** will be determined by the extent of spin delocalization into R^4. For instance, the ketyl of **1b** has somewhat less energy than the ketyl of **1a**. This explains why more carbonyl adduct **5** survived with **1b** than with **1a** (Table I, entries 1 and 2; compare also experiments described hereinafter).

An irreversible reaction AH·/**14** → **5** may occur with a high energy ketyl **14**. So, in the reaction of **2d**, the carbonyl adduct **5** may be formed as well by this radical combination as by a direct attack of AH^- on the sterically hindered carbonyl group of **2d**. The reluctance of this particular carbonyl group against nucleophilic attack is demonstrated, in the case of **1d**, by its resistance to attack by alkoxide ion,[11] a reaction that is fast for common *N*-acylaziridines.

Homolytic ring opening of **14** is formulated in Scheme II as an irreversible process. The possibility of an equilibrium **14** ⇄ **15**, as suggested by a referee, cannot be excluded. However, there are reasons to assume that such an equilibrium either does not exist or does not exert a disturbing influence that would change the essentials of our mechanistic considerations. E.g., one might expect a change in regioselectivity of opening within the series **2a–d**, where the existence of an equilibrium for the high energy ketyls of **2c,d** is unlikely. How could an equilibrium explain that the conversion of **5** into the final products is faster for **1a** than for **3a** or **4a** and faster for **2a** than for **3a** or **4a**? The equilibrium would, namely, require that the final reaction of **15** with AH· should be about an order of magnitude slower for **3a** or **4a** than for **1a** and could therefore hardly be reconciled with the known[12] small variations in interradical reaction rates. Finally, interradical reactions belong to the fastest reactions known.[12] So, the assumption seems reasonable that the reaction **14** → **15** is rate determining in the formation of **16** and **17** from **14** even if under other conditions (no radical to react with for **15**) the equilibrium may develop[13] and exert an influence.

The substitution in the aziridine moiety of **14** will have little influence if any on the energy of **14** and on the equilibrium[14] **5** ⇄ AH·/**14**. However, this substitution can influence stronly the rate of homolytic ring cleavage. As indicated by the high regioselectivity of ring opening in Table I, an N–CMe_2 bond opens much faster than an N–CH_2 bond and an N–CHPh bond much faster than both N–CH_2 and N–$CH(CH_2Ph)$ in **3a** or **4a**. The stabilities of the carbon radicals to be formed have obviously a strong influence on the relative rates of homolysis. Therefore, R^4 being equal, a ketyl derived from **2** should always open faster than that derived from **1**. With $R^4 = NPh_2$ we still isolated **7d** from **2d** but not from **1d** (entries 9–11). This points to an S_N2-like opening of **1d** quite in accord with the absence of both ketyl stabilization in SET and steric hindrance in S_N2. On the other hand, the similar product distribution in the reactions of **1a,b** and **2a,b** is good support for the SET mechanism even in the sterically unhindered formation of **8a,b**.

Applying the above reasoning to the reaction of **3a** and **4a** leads to an apparent paradox. Within their ketyls the N–CHPh bond is broken much faster than the other bond. However, the N–CHPh bond of these ketyls is broken more slowly than the N–CH_2 bond of the **1a** ketyl as shown by the conversions of **5** (Table I, entries 1, 5–7). This paradox can perhaps be explained as follows. Aziridines with tervalent nitrogen possess a pyramidal conformation, even *N*-acylaziridines,[15] and undergo nitrogen inversion.[16] Ring opening of such aziridines will generally take place most easily in the transition state (TS) of this inversion when the ring strain is maximal (compare the discussion in ref 2). The aziridine ring and acyl function are coplanar in the TS of an *N*-acylaziridine,[16] lowering the activation barrier due to conjugative stabilization of the TS. On the other hand, accumulation of electron density in the nitrogen lone pair by π electron repulsion will increase the barrier by conjugative destabilization of the TS[16] as is supported by the observation of such an effect in *N*-phenylaziridines.[17] So, in **14** with a full elementary charge on the acyl group this barrier should be rather high and may become comparable to, or higher than, the barrier of an inversion with a bisected conformation of the TS (see schematic formula I) that avoids repulsion of two occupied π orbitals.



I

This bisected conformation with the aziridine ring and the p orbital of the N–C–O carbon in the same plane provides good stereoelectronic conditions for the homolytic ring cleavage by pairing of the unpaired ketyl electron with an electron of one N–C bond of the aziridine ring. For the ketyls of **3a** and **4a** a steric crowding in this TS (see schematic formula I)[18] may slow down their inversion provided there is no compensation by a steric destabilization of the ground state (GS).[19] The two GS are unequal for the ketyl derived from **3a** or **4a**, namely cis and trans relative to the phenyl group R^1 (and the benzyl group R^3 of **4a**, which is cis to R^1). These ketyls will exist mainly in the trans GS with no steric destabilization. Thus, their opening cannot profit from the inversion as much as the ketyls of the symmetrical aziridines **1** and **2** with identical invertomers. An investigation of this hypothesis is under way.

Since activated cyclopropanes cannot profit from an inversion, this may be one reason for their slow nucleophilic ring opening compared to that of aziridines with similar strength of activation.[20] The differing opening

(11) Stamm, H.; Schneider, L. *Chem. Ber.* **1974**, *107*, 2870.
(12) Ingold, K. U. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Chapter 2.
(13) For the influence of experimental conditions on the development of a radicalic ring closure–ring cleavage equilibrium, compare: Castaing, M.; Pereyre, M.; Ratier, M.; Blum, P. M.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1979**, 287.
(14) Likewise but a small influence of R^1–R^3 would be expected if the dissociation of **5** is irreversible. If the conversion of **5** into the final products is slow as for **3a** and **4a** (Table I, entries 5–7), an irreversible dissociation of **5** would build up a high concentration of AH·/**14**. The unlikeliness of maintaining a high concentration of this radical pair for a long time strongly supports the reversibility of the dissociation.
(15) Zacharias, H. M.; Trefonas, L. M. *J. Heterocycl. Chem.* **1968**, *5*, 343. Gopalakrishna, E. P. *Acta Crystallogr., Sect. B* **1972**, *B28*, 2754.
(16) Lehn, J. M. *Fortschr. Chem. Forsch.* **1970**, *15*, 313.
(17) Andose, J. D.; Lehn, J.-M.; Mislow, K.; Wagner, J. *J. Am. Chem. Soc.* **1970**, *92*, 4050.
(18) The counterion of a ketyl is probably tightly bound to the oxygen thus increasing the steric demand. Compare: Tanikaga, R.; Maruyama, K.; Goto, R. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 144. For simplicity we ignored the role of the gegen ion although this role may be important for a better understanding of the reactions in our paper.
(19) A steric destabilization of the inversion GS is well-known for simple aziridine bases. Compare ref 16 or the following paper: Brois, S. J. *J. Am. Chem. Soc.* **1967**, *89*, 4242.

Table II. Low-Temperature Reactions of AH^- with *N*-Acylaziridines

entry	aziridine	excess AH^-, %	temp,[a] °C	time, min	isolated yields, % amido-ethylation		redn		carbonyl compd		educts and artifacts thereof[b]	
1	**1a**	20	−65	5					94	**7a**		
2	**1a**	0	−65 → rt	30	10	**8a**	14	**9a**	73	**7a**		
3	**1b**	20	−65	5					77	**7b**	11	**1b**
											5	**11b**
4	**1b**	0	−65 → rt	30					75	**7b**	17	**1b**
											4	**11b**
5	**2a**	20	−65	5					94	**7a**		
6	**2a**	0	−65 → rt	30	28	**8c**	72	**9c**				
7	**2b**	20	−65	5					76	**7b**	(8)	(**11d**)
											(3)	(**12d**)
											(2)	(**13d**)
8	**2b**	0	−65 → rt	60	33	**8d**	48	**9d**				
9	**2c**	20	−65	5							97	**2c**
10	**1d**	20	−65	5	57	**8h**					38	**1d**

[a] rt = room temperature; cooling with a −78 °C bath gave an internal temperature of about −65 °C. [b] Artifacts in parentheses were identified and analyzed in the isolated mixture by ^1H NMR comparison (see Experimental Section). Slow chromatography converts **2b** into a mixture of **11d**, **12d**, and **13d**.

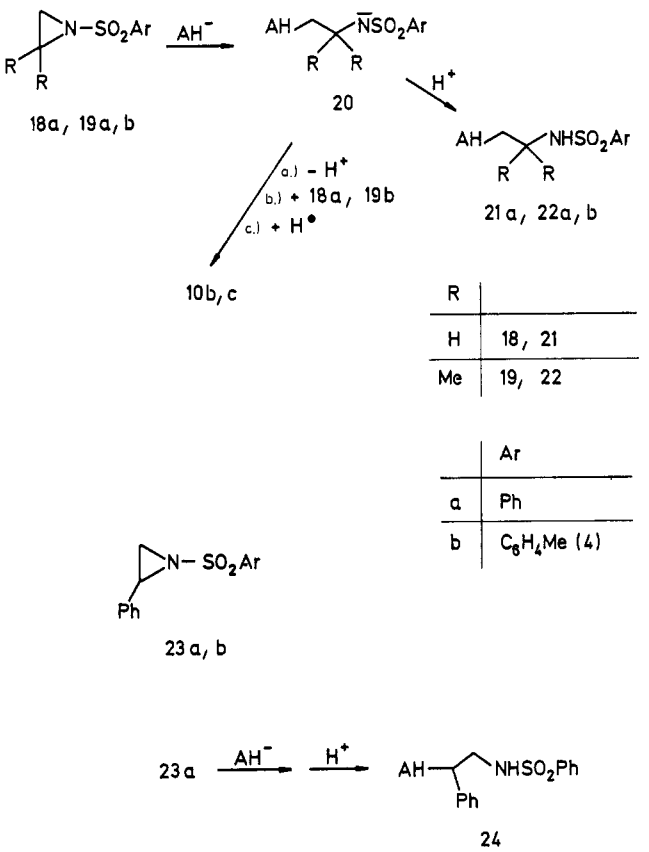
behavior of unsymmetrically substituted cyclopropylcarbinyl radicals[31] and their aziridine counterparts **14** ($R^1 \neq H$) may possibly also be correlated with this inherent difference.

The mechanism depicted in Scheme II and discussed above is corroborated by the low-temperature reactions in Table II. After 5 min at −65 °C only **5** was formed from **1a,b** and **2a,b** (entries 1, 3, 5, and 7) as shown by the high yields of ketones **7a,b**. However, a short warming to room temperature transformed the carbonyl adduct **5** of **1a** partly (entry 2) and the carbonyl adduct of **2a,b** completely (entries 6 and 8) into the ring-opened final products of Table I. Only the carbonly adduct of **1b** withstood the warming up (entry 4) quite in accord with our mechanistic interpretation. The ketyl of **1b** being in equilibrium with **5** has its spin best delocalized and undergoes cleavage more slowly than the ketyls of **2a,b**.

A high-energy ketyl without spin delocalization will form slowly. Thus, **2c** did not react within 5 min at −65 °C (entry 9). Here also the alternative S_N2 attack is slow, owing to weak activation and steric hindrance (compare ref. 4). **1d** with a similar weak activation but no steric hindrance was partly opened (entry 10), obviously by an S_N2 process as already discussed. A fast S_N2 opening of various **1** by a good nucleophile is not unusual.[32]

AH· and **15** can react with one another either by radical combination forming **16** or by hydrogen transfer from AH· to **15** forming **17** and anthracene A. Where determined, the amount of A was found as expected from the amount of aziridine reduction (Table I). The deviations (<±9%)

Scheme III



(20) The strength of activation should depend inversely on the basicity of the leaving group.[2] However cyclopropanes ordinarily require two activating groups.[21] The very effective so-called spiroactivation[22] is simply the result of the long known extremely low basicity of the leaving group; pK_a of Meldrum's acid is ca. 5, i.e., about 9 units lower than diethyl malonate whose deprotonation is unfavorable on entropy grounds.[23] 1,1-Bis(phenylsulfonyl)cyclopropane (pK_a of bis(phenylsulfonyl)methane = 11.2[24]) requires 80 °C for the reaction with the anion of diethyl malonate,[25] while 1-benzoylaziridine (pK_a of benzamide > 19[26]) reacts at room temperature.[27] Diethyl 2,2-dimethylcyclopropane-1,1-dicarboxylate (pK_a of diethyl malonate = 13.3[28a] or 15.2[28b]) reacts with pyrrolidine at 120 °C (40 h) to give 13% abnormal opening,[21] while (a) **2a** reacts at room temperature to give 79% abnormal opening[29] and (b) **19b** (pK_a of tosylamide = 10.17[30]) gives 88% normal opening at room temperature.[29] The possibility of a SET mechanism for an abnormal opening of unsymmetrically substituted activated cyclopropanes ought to be considered as alternative for the discussed heterolytic ring opening.

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(32) Stamm, H.; Wiesert, W. *Chem. Ber.* **1978**, *111*, 502.

Table III. Reactions of AH^- with *N*-Sulfonylaziridines

entry	aziridine	excess AH^-, %	temp,[a] °C	time	isolated yields,[b] %	
1	**18a**	25	rt	15 min	83	**10b**[c]
2	**18a**	50	rt	15 min	50	**21a**
					36	**10b**[c]
3	**18a**	20	−65	5 min	84	**21a**
4	**19a**	20	−65	5 min	87	**22a**
5	**19b**	0	rt	19 h	22	**22b**
					63	**10c**
					14	**19b**
6	**23a**	20	rt	10 min	86	**24**

[a] rt = room temperature; for −65 °C see footnote *a* in Table II. [b] New products gave satisfactory elementary analyses (C, H, N ±0.3%) or precise elementary composition from MS. [c] Cis isomer.

from the expected values are considered to lie within the limits of both methods and workup particularly with respect to the facile oxidation of AH^- by oxygen. The latter is demonstrated by the detection of small amounts of A in the nonreductive reactions of **2c** and **2d** in Table I. Thus, hydrogen abstraction from the solvent THF by **15** can only play a minor role or a mediating role in that intermediate THF radicals abstract subsequently hydrogen from AH·.

The direct hydrogen transfer from AH· to **15** was proven by reaction of **2a** with trideuteriated AH^-. Starting from 9,9,10,10-tetradeuteriated AH_2 (89% deuteriated as determined from the ^1H NMR spectrum) we obtained the monodeuteriated reduction product **9c**-D with a deuterium content of about 77% (determined from the mass spectrum) to 84% (determined from the ^1H NMR spectrum). For both determinations the error may be greater than 5%. Starting from this AH_2 with 11% ^1H in position 9 and 10 and assuming a kinetic isotope effect of **3** for both deprotonation of AH_2 and abstraction of a hydrogen from AH·, a calculation of the statistical distribution of both isotopes leads to a product **9c**-D with an expected deuterium content of about 88%. So, the experimental deuterium content of **9c**-D is compatible with AH· as the nearly exclusive source of hydrogen in the transformation of **15** into **17**.

Changing the aziridine activation from weak (acyl) to strong by going to *N*-sulfonylaziridines (Scheme III, Table III) alters the reactivity drastically, since we found (1) no reductive ring opening in the reaction of AH^- with **18**, **19**, or **23**, (2) only normal or benzylic (vide infra) amidoethylation of AH^-, (3) fast amidoethylation even at −65 °C, and (4) no indication for an intermediate of type **5**. These findings support the assumed[4] change in mechanism with a change in the strength of activation. Obviously, the good leaving group quality[2] of a sulfonamide anion makes the S_N2 opening very fast, faster than the also possible[4] SET step. We regard the well-known benzylic effect in S_N2 reactions as reason for the "abnormal" opening of **23** (entry 6). Although the "stereoelectronic" effect[33] seems to be absent in ring openings of phenyl-substituted three-membered rings,[34] the inductive and mesomeric effects of the phenyl group should be operative, particularly with the good leaving group of **23a**. Nucleophiles seem to attack always the benzylic position of **23a,b**, soft nucleophiles more than hard ones: alkoxides[2] and methylmagnesium bromide[35] predominantly, allylmagnesium bromide[35] and

Scheme IV

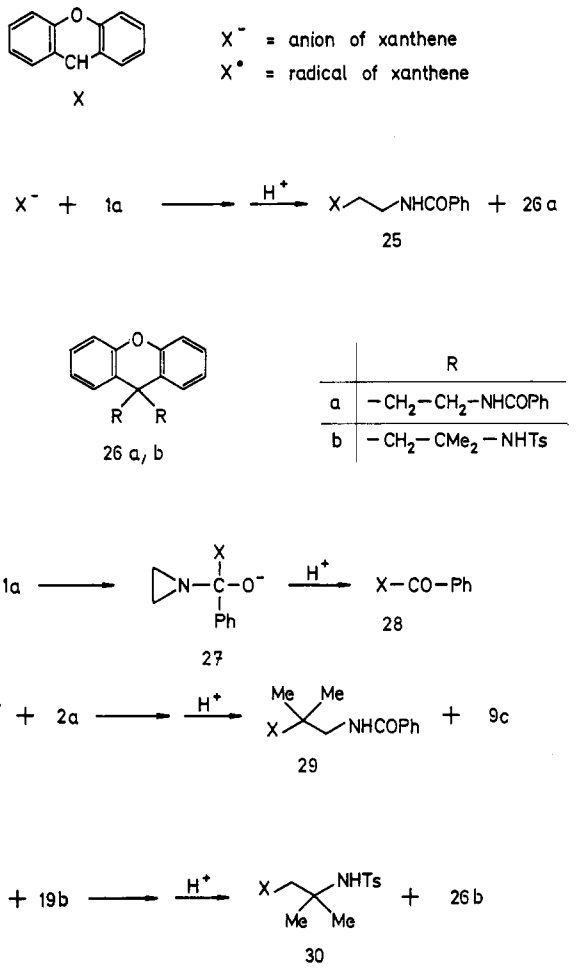

Table IV. Reactions of X^- with Activated Aziridines

entry	aziridine	excess of X^-, %	temp	time	isolated yields of products,[b] %	
1	**1a**	0[c]	30	1 h	39	**25**[d]
					42	**26a**[d]
2	**1a**	0	−65 → rt	50 min	83	**28**
					14	**1a**
3	**2a**	0	rt	8 days	75	**29**
					12	**9c**
					3	**11c**[e]
					2	**12c**[e]
4	**19b**	25	rt	1 day	80	30
					10	**26b**
5	**19b**	0[c]	rt	19 h	44	**30**
					47	**26b**

[a] rt = room temperature; for −65 °C see footnote *a* in Table II. [b] New products gave satisfactory elementary analyses (C, H, N ±0.3%) or precise elementary composition from MS. [c] Sodium salt of xanthene (X^-Na^+). [d] Taken from ref 37. [e] Products are characterized in ref 5.

the anion of diethyl malonate[36] exclusively, the latter with complete inversion.

Replacement of the methylene bridge of AH^- by a bridge without hydrogen should influence the interradical hydrogen transfer only. The anion X^- of xanthene and **1a**

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have been reported to yield **25** and **26a**[37] (SchemeIV, Table IV, entry 1). When we repeated this reaction at −65 °C, the expected benzoylxanthene **28** was the sole product (entry 2). Room temperature reaction of X^- with **2a** led exlusively to abnormal opening of **2a**, predominantly to amidoethylation (**29**, entry 3). The small amount of reductive opening (**9c**) is the result of hydrogen abstraction from the solvent THF by **15**.[5] The 12% reduction may be regarded as the upper limit for hydrogen abstraction from THF by **15** in the reaction of **2a** with AH^-, quite in accord with the deuterium experiment.

The mechanistic behavior of AH^- and X^- is obviously very similar apart from the incapability of the xanthenyl radical X· to provide a hydrogen atom for the transfer. The mechanistic analogy between AH^- and H^- holds for the reaction with an *N*-sulfonylaziridine too: X^- gave exclusively normal amidoethylation (entries 4 and 5). The differing product ratios **30**/**26b** may reflect not only the influence of an excess of X^- but also that of the gegen ion (entry 5; Na^+). The lithium salt of X^- can be generated as described for AH^-. Both anions can be obtained with sodium as gegen ion by deprotonation of a THF solution of the CH acid with sodium naphthalenide or sodium biphenylide at room temperature or with sodium amide under reflux.

Experimental Section

General Methods and Materials. ^1H NMR spectra ($CDCl_3$) were recorded on a Bruker HX-90E spectrometer (90 MHz) unless otherwise stated. Some spectra were recorded on a Bruker W 250 (250 MHz) or on a Varian T60-A (60 MHz) spectrometer. Chemical shifts are reported in δ (ppm) downfield from internal Me_4Si followed in parentheses by peak multiplicity (s, d, t, q, m; mc = 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. Mass spectra and exact *m/e* of molecular ions (M^+) were obtained from a Varian MAT 311 spectrometer.

THF (Merck) was heated under reflux over a mixture of sodium and potassium until benzophenone gave a blue color. It was distilled from this apparatus immediately prior to use. Nitrogen was bubbled through a wash bottle containing sodium and naphthalene in THF; absence of oxygen and moisture was secured as long as the dark green color of the naphthalenide radical anion held. Column chromatography was performed with silica gel 0.063–0.2 mm (Merck); column dimensions (thickness × length, cm) are given for the specific workup. TLC was performed with TLC plates silica gel F_{254} (Merck), preparative TLC with 2-mm PLC plates silica gel 60 F_{254} (Merck). The *n*-butyllithium concentration (1.6 M in hexane, EGA Chemie) was determined by the classic double-titration method of Gilman. 9,10-Dihydroanthracene (AH_2, Janssen Chimica) was recrystallized from dichloromethane. Deuteriated AH_2 was prepared from 5 g of AH_2 in 10 g of hot (bath temperature 85 °C) Me_2SO-d_6 (Aldrich, 99+ atom % D) by addition of a catalytic amount of potassium *tert*-butoxide,[38] quenching with D_2O (99 atom % D), filtering, and recrystallizing from ethanol. Xanthene (Aldrich) was used without further purification.

The activated aziridines were prepared from the corresponding aziridine base **6** and the respective acyl or sulfonyl chloride according to a known procedure.[39] The aziridine bases **6** were prepared by using described methods: **6b**,[40] **6c**,[41] and **6d**.[42] The following activated aziridines are described in the literature: **1a**, **1d**,[11] **2a**,[2] **18a**, **19b**,[2] and **23b**.[2]

1-(4-Phenylbenzoyl)aziridine (1b): Yield, 63%; mp 108–109 °C; IR 1659 cm^{-1}; NMR (60 MHz) δ 2.35 (s, 2 CH_2), 7.30–7.75 (m, Ph and meta H of benzoyl), 7.95–8.23 (m, ortho H of benzoyl); mass spectrum, calcd for M^+ of $C_{15}H_{13}NO$ *m/e* 223.0997, found *m/e* 223.0997.

2,2-Dimethyl-1-(4-phenylbenzoyl)aziridine (2b): yield, 55%; mp 66–67 °C; IR 1660 cm^{-1}; NMR (60 MHz) δ 1.33 (s, 2 Me), 2.37 (s, CH_2), 7.33–7.78 (m, Ph and meta H of benzoyl), 7.96–8.20 (m, ortho of benzoyl); mass spectrum, calcd for M^+ of $C_{17}H_{17}NO$ *m/e* 251.1310, found *m/e* 251.1310.

2,2-Dimethyl-1-pivaloylaziridine (2c): yield, 58%; bp 30 °C (0.01 torr); IR (film) 1673 cm^{-1}; NMR δ 1.23 (s, CMe_3), 1.34 (s, 2 Me), 2.15 (s, CH_2); mass spectrum, calcd for M^+ of $C_9H_{17}NO$ *m/e* 155.1310, found *m/e* 155.1310.

2,2-Dimethyl-1-(diphenylcarbamyl)aziridine (2d): yield, 75%; mp 114–115 °C; IR 1667 cm^{-1}; NMR (60 MHz) δ 0.93 (s, 2 Me), 2.06 (s, CH_2), 7.21 (mc, 2 Ph); mass spectrum, calcd for M^+ of $C_{17}H_{18}N_2O$ *m/e* 266.1419, found *m/e* 266.1420.

1-Benzoyl-2-phenylaziridine (3a): yield, 90% (without purification); oil; IR (film) 1680 cm^{-1}; NMR δ 2.40 (d, *J* = 3.3 Hz, cis 3-H), 2.96 (d, *J* = 6.0 Hz, trans 3-H), 3.45 (dd, *J* = 6.2 Hz, *J* = 3.5 Hz, 2-H), 7.14–7.48 (m, Ph and meta, para H of benzoyl), 7.86–8.04 (m, ortho H of benzoyl); mass spectrum, calcd for M^+ of $C_{15}H_{13}NO$ *m/e* 223.0997, found *m/e* 223.0997.

1-Benzoyl-2-benzyl-3-phenylaziridine (4a): yield, 98%; mp 94–95 °C; IR 1672 cm^{-1}; NMR (250 MHz) δ 2.63 (dd, *J* = 14.7 Hz, *J* = 7.9 Hz, 1 benzyl H), 2.99 (dd, *J* = 14.7 Hz, *J* = 5.4 Hz, 1 benzyl H), 3.19 (ddd, *J* = 7.9 Hz, *J* = 6.2 Hz, *J* = 5.4 Hz, 2-H), 3.78 (d, *J* = 6.2 Hz, 3-H), 6.93–7.00 (m, 2 H), 7.14–7.24 (m, 3 H), 7.29–7.52 (m, 8 H), 7.97–8.03 (m, ortho H of benzoyl); mass spectrum, calcd for M^+ of $C_{22}H_{19}NO$ *m/e* 313.1467, found *m/e* 313.1467.

1-(Phenylsulfonyl)-2,2-dimethylaziridine (19a): yield, 82%; mp 77–78 °C; IR 1308, 1315, 1160 (all SO_2N) cm^{-1}; NMR δ 1.56 (s, 2 Me), 2.46 (s, CH_2), 7.49–7.61 (m, meta, para H of Ph), 7.90–8.01 (m, ortho H of Ph); mass spectrum, calcd for M^+ of $C_{10}H_{13}NO_2S$ *m/e* 211.0667, found *m/e* 211.0667.

Reactions with 9-Lithio-9,10-dihydroanthracene or 9-Lithioxanthene. The reactions were conducted in THF under nitrogen. The solution of AH_2 or xanthene (7.5–10 mmol; 10–50 mol % excess over *n*-butyllithium) in 70–150 mL of THF was cooled to −65 °C or until freezing of THF, butyllithium (mol % excess relative to the aziridine as given under "excess AH^- (X^-)" in Tables I–IV) added, and the mixture warmed to room temperature under stirring. There developed an intense brown-red color. For reactions at −65 °C this solution was subsequently cooled again before adding the aziridine. The activated aziridine (5–10 mmol, 5 mmol unless otherwise stated) dissolved in 10–20 mL THF was added dropwise. The reactions were quenched under nitrogen by neutralization with glacial acetic acid. The solvent was removed under reduced pressure and the residue taken up in CH_2Cl_2 and washed with water. On concentrating the dried CH_2Cl_2 solution, anthracene (A) crystallized sometimes and was removed by filtration. Further workup was done with column chromatography according to the details noted for the specific reaction.

Table I, Entry 1. A (0.5 g) was removed by filtration. The filtrate was chromatographed (3 × 25). Elution with toluene removed a mixture of A and AH_2 followed by 14 mg (1%) of **7a**. Elution with CH_2Cl_2/ethyl acetate (10:1) yielded 406 mg (25%) of **8a** and (1:2) 502 mg (67%) of **9a**.

Table I, Entry 2. Chromatography (3 × 25) with toluene afforded a mixture of A and AH_2 followed by 0.06 g (3%) of **7b**. Elution with ethyl acetate provided a mixture (1.14 g), which yielded 0.23 g (11%) of **8b** and 0.78 g (70%) of **9b** through a second chromatography (2 × 60; 10:1 CH_2Cl_2/ethyl acetate).

Table I, Entry 3. A (0.56 g) was removed by filtration. The filtrate was chromatographed (3 × 60). After eluting A and AH_2 with CH_2Cl_2, elution with ethyl acetate provided a mixture (0.96 g), which yielded 0.27 g (15%) of **8c** and 0.69 g (78%) of **9c** through

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(42) Kotera, K.; Miyazaki, S.; Takahashi, H.; Okada, T.; Kitahonoki, K. *Tetrahedron* **1968**, *24*, 3681.

a second chromatography (3 × 60; 5:1 CH_2Cl_2/ethyl acetate).

The same reaction (1.5 h) with deuteriated AH_2 was performed on a 2.5-mmol scale. The second chromatography was preparative TLC.

Table I, Entry 4. A (0.44 g) was removed by filtration. Chromatography (2 × 60; CH_2Cl_2) of the filtrate yielded successively a mixture of A and AH_2, 0.33 g (15%) of **8c**, and 0.69 g (82%) of **9c**.

Table I, Entry 5. Chromatography (2 × 60) with toluene afforded first a mixture of A and AH_2 and then 0.74 g (52%) of **7a**. Elution with CH_2Cl_2/ethyl acetate (1:1) yielded 0.16 g (14%) of **9e** and 0.18 g (16%) of **3a**; elution with ethyl acetate yielded 0.29 g (49%) of **6c**.

Table I, Entry 6: 2.4 mmol of 4a. Chromatography (2 × 60) with toluene provided a mixture of A and AH_2, 0.38 g (56%) of **7a**, and 0.11 g (15%) of **4a**. Subsequent elution with ethyl acetate gave a mixture (0.47 g) which yielded 0.17 g (23%) of **9f** and 0.26 g (52%) of **6d** through a second chromatography (3 × 25; 5:1 CH_2Cl_2/ethyl acetate).

Table I, Entry 7. A (0.38 g) was removed by filtration. Chromatography (3 × 60) provided a mixture of A and AH_2 (toluene) and then 1.50 g (96%) of **9f** (ethyl acetate).

Table I, Entry 8. On concentrating the CH_2Cl_2 solution 0.67 g (40%) of **8g** crystallized. Chromatography (3 × 25) of the filtrate with toluene provided AH_2 containing a small amount of A. Elution with ethyl acetate yielded another 0.77 g (45%) of **8g**.

Table I, Entry 9: 3.75 mmol of 1d. Chromatography (3 × 60) provided AH_2 (CH_2Cl_2), 0.41 g (26%) of **8h** (CH_2Cl_2), 0.73 g (48%) of **10a** (ethyl acetate), and 0.20 g (16%) of **11h**[11] (acetone).

Table I, Entry 10. Chromatography (2 × 60) with CH_2Cl_2 provided AH_2, 0.26 g (14%) of **7d**, and 1.32 g (60%) of **8i**. Elution with ethyl acetate yielded another 0.29 g (13%) of **8i**.

Table I, Entry 11. Workup was as described for entry 10.

Table II, Entry 1. Chromatography (2 × 60; toluene) provided AH_2 and 1.33 g (94%) of **7a**.

Table II, Entry 2. Chromatography (2 × 60) and elution with toluene provided a mixture of A and AH_2 and then 1.03 g (73%) of **7a** and elution with CH_2Cl_2/ethyl acetate (1:2) 0.16 g (10%) of **8a** and 0.10 g (14%) of **9a**.

Table II, Entry 3: 4 mmol of 1b. Chromatography (3 × 25) provided AH_2 (toluene) and 1.11 g (77%) of **7b** (toluene), 0.10 g (11%) of **1b** (ethyl acetate), and 0.05 g (5%) of **11b** (acetone).

Table II, Entry 4. Workup was as described for entry 3.

Table II, Entry 5. Chromatography (2 × 60; toluene) provided AH_2 and 1.34 g (94%) of **7a**.

Table II, Entry 6. Chromatography (2 × 60) after removing crystalline A and elution with CH_2Cl_2 provided a mixture of A and AH_2 and then 0.51 g (28%) of **8c** and elution with ethyl acetate 0.63 g (72%) of **9c**.

Table II, Entry 7: 4 mmol of 2b. Chromatography (3 × 25) and elution with toluene provided AH_2 and 1.10 g (76%) of **7b** and elution with acetone provided 0.14 g of a mixture whose ^1H NMR spectrum showed the presence of 8% **11d**, 3% **12d**, and 2% **13d**. An authentic sample of **11d** was prepared by treating a THF solution of **2b** with 70% aqueous $HClO_4$ for 20 min, adding water, extracting with CH_2Cl_2, evaporating, and recrystallizing from CCl_4. An authentic sample of **12d** was prepared[26] by treating a benzene solution of **2b** with $AlCl_3$ for 10 min, adding ice, and extracting with CH_2Cl_2. An authentic sample of **13d** was prepared by heating **2b** to 146 °C and recrystallizing from CCl_4.

Table II, Entry 8. Chromatography (2 × 60; CH_2Cl_2) provided AH_2 and A, a mixture (0.95 g), and 0.40 g (33%) of **9d**. A second chromatography (3 × 60; 10:1 CH_2Cl_2/ethyl acetate) separated the mixture into 0.71 g (33%) of **8d** and 0.19 g (15%) of **9d**.

Table II, Entry 9: 5.16 mmol of 2c. Chromatography (3 × 60) provided AH_2 (toluene) and 0.78 g (97%) of **2c** (ethyl acetate).

Table III, Entry 1. Chromatography (3 × 60) provided AH_2 (CH_2Cl_2) and 1.13 g (83%) of **10b** (ethyl acetate).

Table III, Entry 2: 4 mmol of 18a. Chromatography (3 × 25) provided AH_2 (toluene), 1.09 g (50%) of **21a** (CH_2Cl_2), and 0.52 g (36%) of **10b** (ethyl acetate).

Table III, Entry 3. Chromatography (2 × 60; CH_2Cl_2) provided AH_2 and 1.52 g (84%) of **21a**.

Table III, Entry 4. Chromatography (3 × 25) provided AH_2 (toluene) and 1.69 g (87%) of **22a** (CH_2Cl_2).

Table III, Entry 5. Chromatography (3 × 60) provided 159 mg (14%) of **9b** (CH_2Cl_2), 437 mg (22%) of **22b** (CH_2Cl_2), and 988 mg (63%) of **10c** (1:1 ethyl acetate/acetone).

Table III, Entry 6. Chromatography (2 × 60; CH_2Cl_2) provided AH_2 and 1.90 g (86%) of **24**.

Table IV, Entry 2. Chromatography (2 × 60) provided xanthene (toluene), 1.19 g (83%) of **28** (toluene), and 0.10 g (14%) of **1a** (ethyl acetate).

Table IV, Entry 3: 10 mmol of 2a. Crystallization from CCl_4 yielded 2.21 g (62%) of **29**. The mother liquor was chromatographed (3 × 60). Elution with CH_2Cl_2/ethyl acetate (20:1) provided xanthene, 456 mg (13%) of **29**, 208 mg (12%) of **9c**, and 40 mg (2%) of **12c**. Elution with ethyl acetate yielded 60 mg (3%) of **11c**.

Table IV, Entry 4. Chromatography (3 × 60) provided xanthene (CH_2Cl_2), 1.63 g (80%) of **30** (CH_2Cl_2), and 0.16 g (10%) of **26b** (ethyl acetate).

Table IV, Entry 6. Xanthene, (0.82 g, 4.5 mmol), 0.31 g (4 mmol) of sodium amide dispersion (50%), and 48 mL of THF were refluxed for 2 h. After the mixture cooled to room temperature a solution of 0.90 g (4 mmol) of **19b** in 12 mL of THF was added dropwise. After the usual workup chromatography (3 × 60; CH_2Cl_2) provided xanthene, 711 mg (44%) of **30**, and 592 mg (47%) of **26b**.

Reaction of 1a with $NaBH_4$. $NaBH_4$ (5 mmol) was added to a solution of 5 mmol of **1a** in 40 mL of ethanol. The mixture obtained after workup was analyzed by ^1H NMR.

Characterization of Products. 9-Benzoyl-9,10-dihydroanthracene (7a): mp 101 °C (lit.[43] 101 °C); IR 1671 cm^{-1}; NMR δ 3.92 (d, J = 18.4 Hz, 10-H pseudo eq), 4.47 (d br, J = 18.4 Hz, 10-H pseudo ax), 5.98 (s, 9-H pseudo eq), 7.08–7.53 (m, 11 H, aryl H of AH_2, meta, para H of benzoyl), 7.98–8.08 (m, nearly d with J = 8.1 Hz, ortho H of benzoyl).

9-(4-Phenylbenzoyl)-9,10-dihydroanthracene (7b): mp 161–162°C; IR 1665 cm^{-1}; NMR δ 3.93 (d, J = 18.4 Hz, 10-H pseudo eq), 4.51 (d br, J = 18.4 Hz, 10-H pseudo ax), 6.00 (s, 9-H pseudo eq), 7.04–7.69 (m, 15 H, aryl H of AH_2, Ph, meta H of benzoyl), 8.07–8.16 (m, nearly d with J = 8.4 Hz, ortho H of benzoyl).

***N,N*-Diphenyl-9,10-dihydroanthracene-9-carboxamide (7d):** mp 203 °C; IR 1670 cm^{-1}; NMR δ 3.80 (d, J = 18.0 Hz, 10-H pseudo eq), 4.64 (d br, J = 18.0 Hz, 10-H pseudo ax), 5.26 (s, 9-H pseudo eq), 6.90–7.33 (m, 18 H, aryl H).

9-[2-(Benzoylamino)ethyl]-9,10-dihydroanthracene (8a): mp 113–114 °C; IR 3320, 1634, 1538 cm^{-1}; NMR δ 1.80–2.03 (m, nearly q, $NCCH_2$), 3.13–3.53 (m, nearly q, NCH_2), 3.84 (d, J = 18.5 Hz, 10-H pseudo eq), ca. 4 (hidden, 9-H pseudo eq), 4.08 (d br, J = 18.5 Hz, 10-H pseudo ax), 6.06 (t br, J = 6.0 Hz, NH), 7.11–7.77 (m, 13 H, aryl H).

9-[2-((4-Phenylbenzoyl)amino)ethyl]-9,10-dihydroanthracene (8b): mp 176–177 °C; IR 3340, 1635, 1536 cm^{-1}; NMR δ 1.81–2.05 (m, nearly q, $NCCH_2$), 3.30–3.52 (m, nearly q, NCH_2), 3.86 (d, J = 18.5 Hz, 10-H pseudo eq), ca. 4 (hidden, 9-H pseudo eq), 4.09 (d br, J = 18.5 Hz, 10-H pseudo ax), 6.14 (t br, J = 6.0 Hz, NH), 7.14–7.82 (m, 17 H, aryl H).

9-[2-(Benzoylamino)-1,1-dimethylethyl]-9,10-dihydroanthracene (8c): mp 148–149 °C; IR 3320, 1634, 1545 cm^{-1}; NMR δ 0.97 (s, 2 Me), 3.43 (d, J = 6.2 Hz, NCH_2), 3.82 (d, J = 19.1 Hz, 10-H pseudo eq), 3.87 (s, 9-H pseudo eq), 4.23 (d br, J = 19.1 Hz, 10-H pseudo ax), 5.18 (t br, J = 6 Hz, NH), 7.08–7.66 (m, 13 H, aryl H).

9-[1,1-Dimethyl-2-((4-phenylbenzoyl)amino)ethyl]-9,10-dihydroanthracene (8d): mp 227–228 °C; IR 3420, 1649, 1535 cm^{-1}; NMR δ 1.00 (s, 2 Me), 3.46 (d, J = 6.2 Hz, NCH_2), 3.84 (d, J = 19.1 Hz, 10-H pseudo eq), 3.88 (s, 9-H pseudo eq), 4.26 (d br, J = 19.1 Hz, 10-H pseudo ax), 5.81 (t br, J = 6 Hz, NH), 7.19–7.69 (m, 17 H, aryl H).

9-[1,1-Dimethyl-2-(pivaloylamino)ethyl]-9,10-dihydroanthracene (8g): mp 159 °C; IR 3400, 1649, 1538 cm^{-1}; NMR δ 0.89 (s, 2 Me), 1.00 (s, CMe_3), 3.21 (d, J = 6.1 Hz, NCH_2), 3.78 (s, 9-H pseudo eq), 3.78 (d, J = 19.0 Hz, 10-H pseudo eq), 4.21 (d br, J = 1.90 Hz, 10-H pseudo ax), 5.27 (t br, J = 6 Hz, NH), 7.14–7.36 (m, 8 H, aryl H).

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9-[2-(3,3-Diphenylureido)ethyl]-9,10-dihydroanthracene (8h): mp 158 °C; IR 3330, 1653, 1508 cm^{-1}; NMR (250 MHz) δ 1.74–1.83 (m, nearly q, $NCCH_2$), 3.22–3.30 (m, nearly q, NCH_2), 3.84 (d, J = 18.4 Hz, 10-H pseudo eq), 3.93 (t, J = 7.5 Hz, 9-H pseudo eq), 4.07 (d br, J = 18.4 Hz, 10-H pseudo ax), 4.41 (t br, J = 5.9 Hz, NH), 7.15–7.35 (m, 18 H, aryl H).

9-[1,1-Dimethyl-2-(3,3-diphenylureido)ethyl]-9,10-dihydroanthracene (8i): mp 170 °C; IR 3440, 1667, 1490 cm^{-1}; NMR δ 0.76 (s, 2 Me), 3.20 (d, J = 6.2 Hz, NCH_2), 3.68 (s, 9-H pseudo eq), 3.73 (d, J = 19.0 Hz, 10-H pseudo eq), 4.14 (d br, J = 19.0 Hz, 10-H pseudo ax), 4.41 (t br, J = 6 Hz, NH), 7.10–7.55 (m, 18 H, aryl H).

***N*-Ethylbenzamide (9a)**: mp 67 °C (lit.[44] mp 67 °C); IR 3330, 16351 1547 cm^{-1}; NMR δ 1.20 (t, J = 7.0 Hz, Me), 3.28–3.64 (m, CH_2), 9.9 (s br, NH), 7.16–7.60 (m, meta, para H of benzoyl), 7.73–7.96 (m, ortho H of benzoyl).

***N*-Ethyl-4-phenylbenzamide (9b)**: mp 170 °C; IR 3340, 1642, 1548 cm^{-1}; NMR δ 1.27 (t, J = 7.3 Hz, Me), 3.37–3.68 (m, CH_2), 6.21 (t br, J = 6 Hz, NH), 7.34–7.68 (m, 7 H, Ph, meta H of benzoyl), 7.80–7.89 (m, ortho H of benzoyl).

***N*-Isobutylbenzamide (9c)**: mp 57–58 °C (lit.[45] mp 57 °C); IR 3320, 1642, 1545, 1537 cm^{-1}, NMR δ 0.91 (d, J = 6.6 Hz, 2 Me), 1.73–2.03 (m, CH), 3.20 (t, J_{HCCH} = 6.8 Hz, J_{HNCH} = 6.2 Hz, CH_2), 6.89 (t br, J = 6 Hz, NH), 7.31–7.43 (m, meta, para H of benzoyl), 7.74–7.87 (m, ortho H of benzoyl); MS (100 eV, 40 °C), m/e (relative intensity) 179 (1.11), 178 (10.91), 177 (47.68), 176 (2.64), 162 (9.86), 134 (25.40), 122 (27.26), 106 (17.95), 105 (100).

***N*-(2-Deuterioisobutyl)benzamide (9c-D)**: NMR (250 MHz) δ 0.95 (s, 2 Me; the high-field line of the **9c** doublet is hidden under this singlet, the low-field line is visible), 3.25 (d, J = 6.0 Hz, CH_2), 6.55 (s br, NH), 7.36–7.52 (m, meta, para H of benzoyl), 7.75–7.84 (m, ortho H of benzoyl); MS (100 eV, 40 °C), m/e (relative intensity) 180 (0.45), 179 (4.52), 178 (35.12), 177 (9.91), 176 (0.63), 163 (5.40), 134 (21.45), 123 (17.50), 122 (7.63), 106 (20.12), 105 (100).

***N*-Isobutyl-4-phenylbenzamide (9d)**: mp 167 °C; IR 3320, 1636, 1538 cm^{-1}; NMR δ 0.97 (d, J = 6.6 Hz, 2 Me), 1.68–2.08 (m, CH), 3.29 (t, J_{HCCH} = 6.6 Hz, J_{HNCH} = 6.2 Hz, CH_2), 6.52 (t br, J = 6 Hz, NH), 7.36–7.65 (m, 7 H, Ph, meta H of benzoyl), 7.80–7.90 (m, nearly d with J = 8.4 Hz, ortho H of benzoyl).

***N*-Phenethylbenzamide (9e)**: mp 114 °C (lit.[46] mp 113–114 °C); IR 3350, 1639, 1542 cm^{-1}; NMR δ 2.89 (t, J = 7.1 Hz, $NCCH_2$), 3.55–3.77 (m, nearly q, NCH_2), 6.53 (t br, J = 6 Hz, NH), 7.22 (2, 5 H, Ph), 7.08–7.52 (m, meta, para H of benzoyl), 7.64–7.75 (m, ortho H of benzoyl).

***N*-(α-Benzylphenethyl)benzamide (9f)**: mp 167–168 °C; IR 3360, 1634, 1530 cm^{-1}; NMR δ 2.92 (d, J = 6.8 Hz, 2 CH_2), 4.44–4.84 (m, CH), 5.86 (d br, J = 6 Hz, NH), 7.26 (s, 2 Ph), 7.17–7.45 (m, meta, para H of benzoyl), 7.52–7.63 (m, ortho H of benzoyl).

9,10-Bis[2-(3,3-diphenylureido)ethyl]-9,10-dihydroanthracene (10a): mp 205–206 °C; IR 3440, 3330, 1675, 1655, 1505, 1490 cm^{-1} NMR (250 MHz) δ 1.88–1.97 (m, nearly q, 4 H, N-C-CH_2), 3.46–3.55 (m, nearly q, 4 H, N-CH_2), 3.96 (t, J = 7.3 Hz, 2 H, 9-H 10-H), 4.58 (t br, J = 5.6 Hz, 2 H, NH), 7.15–7.42 (m, 28 H, aryl-H).

9,10-Bis[2-((phenylsulfonyl)amino)ethyl]-9,10-dihydroanthracene (10b): mp 222–223 °C; IR 3310, 1328, 1318, 1170, 1162 cm^{-1}; NMR (250 MHz) δ 1.76–1.85 (m, nearly q, 4 H, $NCCH_2$), 3.02–3.10 (m, nearly q, 4 H, NCH_2), 3.94 (t, J = 7.8 Hz, 2 H, 9-H, 10-H), 4.51 (t br, J = 6.2 Hz, 2 H, NH), 7.13–7.20 (m, 8 H, aryl H of AH_2), 7.49–7.61 (m, 6 H, meta, para H of $PhSO_2$), 7.79–7.83 (m, 4 H, ortho H of $PhSO_2$): NOE difference spectra showed this product to be the cis isomer, absence of NOE for $NCCH_2$ → peri-H, observation of NOE for 9,10-H → peri-H.

9,10-Bis[2-methyl-2-(tosylamino)propyl]-9,10-dihydroanthracene (10c): mp 171 °C; IR 3290, 1322, 1310, 1164, 1150 cm^{-1}; NMR (250 MHz) δ 1.27 (s, 12 H, Me), 2.05 (d, J = 6.3 Hz, 4 H, CH_2), 2.39 (s, 6 H, Me of tosyl), 4.26 (t, J = 6.3 Hz, 2 H, 9-H, 10-H), 4.97 (s br, 2 H, NH), 7.11–7.15 (m, 4 H, 2,3,6,7 of AH_2), 7.32–7.35 (m, 4 H, 1,4,5,8 of AH_2), 7.24 (d, J = 8.1 Hz, 4 H, meta H of tosyl), 7.55 (d, J = 8.1 Hz, 4 H, ortho H of tosyl).

***N*-(2-Hydroxyethyl)-4-phenylbenzamide (11b)**: mp 182–183 °C; IR 3300, 1639, 1634, 1549 cm^{-1}; NMR δ 3.58–3.74 (m, NCH_2, OH), 3.82–3.92 (m, OCH_2), 6.66 (t br, J = 6 Hz, NH), 7.37–7.69 (m, Ph, meta H of benzoyl), 7.82–7.92 (m, ortho H of benzoyl).

***N*-(2-Hydroxy-2-methylpropyl)-4-phenylbenzamide (11d)**: mp 162 °C; IR 3440 sh, 3360, 1633, 1548 cm^{-1}; NMR δ 1.30 (s, Me, Me), 2.46 (s br, OH), 3.50 (d, J = 6.9 Hz, CH_2), 6.76 (t br, J = 7 Hz, NH), 7.23–7.70 (m, Ph, meta H of benzoyl), 7.78–7.93 (m, ortho H of benzoyl).

5,5-Dimethyl-2-(4-biphenylyl)-Δ^2-oxazoline (12d): oil; IR (film) 1640 cm^{-1}; NMR δ 1.49 (s, 2 Me), 3.78 (s, CH_2), 7.15–7.68 (m, 7 H, aryl H), 7.85–8.04 (m, 2 H, ortho H of *p*-phenylene).

***N*-Methallyl-4-phenylbenzamide (13d)**: mp 141 °C; IR 3320, 1639, 1539 cm^{-1}; NMR δ 1.80 (s, Me), 4.04 (d, J = 6.0 Hz, NCH_2), 4.91 (s br, $=CH_2$), 6.45 (t br, J = 6 Hz, NH), 7.25–7.70 (m, Ph, meta H of benzoyl), 7.70–8.03 (m, ortho H of benzoyl).

9-[2-((Phenylsulfonyl)amino)ethyl]-9,10-dihydroanthracene (21a): mp 129–130 °C; IR 3280, 1330, 1168, 1158 cm^{-1}; NMR δ 1.56–1.79 (m, $NCCH_2$), 2.80–3.01 (m, nearly q, NCH_2), 3.77 (d, J = 18.0 Hz, 10-H pseudo eq), 3.90 (d br, J = 18.0 Hz, 10-H pseudo ax), 4.27 (t, J = 7.1 Hz, 9-H pseudo eq), 4.71 (s br, NH), 7.08–7.50 (m, aryl H of AH_2, meta, para H of Ph), 7.73–7.86 (m, ortho H of Ph).

9-[2-Methyl-2-(tosylamino)propyl]-9,10-dihydroanthracene (22b): mp 165 °C; IR 3280, 1325, 1310, 1160, 1140 cm^{-1}; NMR δ 1.14 (s, 2 Me), 1.83 (d, J = 7.0 Hz, $NCCH_2$), 2.38 (s, tosyl Me), 3.80 (d, J = 17.8 Hz, 10-H pseudo eq), 4.00 (d, J = 17.8 Hz, 10-H pseudo ax), 4.26 (t, J = 7.0 Hz, 9-H pseudo eq), 4.57 (s br, NH), 7.09–7.27 (m, aryl H of AH_2, meta H of tosyl), 7.68 (d, J = 8.0 Hz, ortho H of tosyl).

9-[2-((Phenylsulfonyl)amino)-1-phenylethyl]-9,10-dihydroanthracene (24): mp 159 °C; IR 3290, 1334, 1163 cm^{-1}; NMR (250 MHz) δ 2.81 (ddd, J = 10.0 Hz, J = 7.2 Hz, J = 6.0 Hz, CH(Ph)), 3.00 (d br, J = 18.7 Hz, 10-H pseudo ax), 3.28 (ddd, J = 13.3 Hz, J = 10.0 Hz, J = 3.3 Hz, 1 H of NCH_2), 3.47 (ddd, J = 13.3 Hz, J = 9.3 Hz, J = 6.0 Hz, 1 H of NCH_2), 3.52 (d, J = 18.7 Hz, 10-H pseudo eq), 4.08 (d, J = 7.2 Hz, 9-H pseudo eq), 4.15 (dd, J = 9.3 Hz, J = 3.3 Hz, NH), 6.39 (dd, J = 8.0 Hz, J = 0.8 Hz, 2 H, ortho H of CPh), 6.73 (d, J = 7.9 Hz, 1 H, 1-H of AH_2), 6.92–7.25 (m, 7 H, 2,3,4,5,6,7,8-H of AH_2), 7.44–7.69 (m, 5 H, SO_2Ph).

9,9-Bis[2-methyl-2-(tosylamino)propyl]xanthene (26b): mp 162 °C; IR 3380, 3280, 1314, 1160, 1154 cm^{-1}; NMR (250 MHz) δ 0.71 (s, 12 H, Me), 2.40 (d, J = 6.5 Hz, 4 H, $NCCH_2$), 2.41 (s, 6 H, tosyl Me), 3.96 (s br, 2 H, NH), 6.96 (d, J = 8.1 Hz, 2 H, 1-H and 8-H of xanthene), 7.12 (t, J = 8.1 H, 2 H, 3-H and 6-H of xanthene), 7.20 (d, J = 8.3 Hz, 4 H, meta H of tosyl), 7.24 (t, J = 8 Hz, 2 H, 2-H and 7-H of xanthene), 7.41 (d, J = 7.8 Hz, 2 H, 4-H and 5-H of xanthene), 7.51 (d, J = 8 Hz, 4 H, ortho H of tosyl) [additional fine splitting is observed for the multiplets δ 6.96/7.12 (J = 1.4 Hz) and δ 7.41/7.24 (J = 1.6 Hz)].

9-Benzoylxanthene (28): mp 139 °C; IR (1660 cm^{-1}; NMR δ 5.78 (s, 9-H), 6.83–7.46 (m, aryl H of xanthene, meta, para H of benzoyl), 7.86–7.97 (m, ortho H of benzoyl).

9-[2-(Benzoylamino)-1,1-dimethylethyl]xanthene (29): mp 171 °C; IR 3410, 3390, 1640, 1525 cm^{-1}; NMR δ 0.95 (s, 2 Me), 3.13 (d, J = 6.0 Hz, CH_2), 3.67 (s, 9-H), 5.88 (t br, J = 6 Hz, NH), 6.80–7.45 (m, 11 H, aryl H of xanthene, meta, para H of benzoyl), 7.60–7.85 (m, 2 H, ortho H of benzoyl).

9-[2-Methyl-2-(tosylamino)propyl]xanthene (30): mp 131 °C; IR 3280, 1335, 1325, 1160, 1150 cm^{-1}; NMR δ 1.03 (s, 2 Me), 1.91 (d, J = 6.4 Hz, CH_2), 2.35 (s, tosyl Me), 4.30 (t, J = 6.6 Hz, 9-H), 5.15 (s br, NH), 6.94–7.33 (m, aryl H of xanthene, meta H of tosyl), 7.75 (d, J = 8.2 Hz, ortho H of tosyl).

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Registry No. **1a**, 7646-66-4; **1b**, 98943-67-0; **1d**, 52204-95-2; **2a**, 21384-58-7; **2b**, 98943-68-1; **2c**, 56930-49-5; **2d**, 98943-69-2; **3a**, 93638-44-9; *cis*-**4a**, 98943-70-5; **6c**, 1499-00-9; *cis*-**6d**, 1605-08-9;

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7a, 50688-77-2; 7b, 98943-71-6; 7d, 98943-72-7; 8a, 98943-73-8; 8b, 98943-74-9; 8c, 85809-29-6; 8d, 98943-75-0; 8g, 98943-76-1; 8h, 98943-77-2; 8i, 98943-78-3; 9a, 614-17-5; 9b, 70772-75-7; 9c, 5705-57-7; 9c-D, 98943-95-4; 9d, 98943-79-4; 9e, 3278-14-6; 9f, 77414-34-7; 10a, 98943-80-7; 10b, 98943-81-8; 10c, 98943-82-9; 11b, 98943-83-0; 11c, 33561-46-5; 11d, 98943-84-1; 11h, 36556-72-6; 12c, 33561-48-7; 12d, 98943-85-2; 13d, 98943-86-3; 18a, 10302-15-5; 19a, 5048-63-5; 19b, 5048-64-6; 21a, 98943-87-4; 22a, 98943-88-5; 22b, 98943-89-6; 23a, 19871-46-6; 24, 98943-90-9; 25, 70686-42-9; 26a, 70650-93-0; 26b, 98943-91-0; 28, 98943-92-1; 29, 98943-93-2; 30, 98943-94-3; AH^-, 14314-91-1; AH_2, 120-12-7; XH, 92-83-1; A^{2-}, 23013-59-4.

(Phosphine)carbonylnitrosylacylcobaltate Complexes as Acyl Transfer Reagents. Acylation of Allylic Halides, Conjugated Enones, and Quinones

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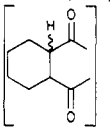
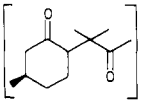
The complex $Co(NO)(CO)_2(PPh_3)$ is an air stable, easily handled crystalline solid, prepared from $Co_2(CO)_8$, sodium nitrite, and triphenylphosphine without isolation of the volatile intermediate $Co(NO)(CO)_3$. Treatment of this complex with organolithium reagents at −40 °C generated unstable acylate complexes $[RCOCo(NO)(CO)(PPh_3)]^-$ which readily transferred the acyl group to allylic halides to produce β,γ-unsaturated ketones, to conjugated ketones to produce 1,4-dicarbonyl compounds, and to quinones to form 4-acylcyclohexadienones.

Reduction of transition-metal carbonyl complexes generates anionic metal carbonyl species that are often potent nucleophiles. Reaction of these "carbonylate" complexes with organic halides or tosylates produces acylmetal complexes many of which are useful acyl transfer reagents in organic synthesis. Thus "Collman's reagent", $Na_2Fe(CO)_4$, reacts with organic halides to give the acylate complex $[RCOFe(CO)_4]^-$ which converts reactive organic halides and tosylates to ketones and which can also be converted to aldehydes and carboxylic acid derivatives.[1,2] Similarly $NaCo(CO)_4$ acylates reactive organic halides and epoxides to give carboxylic acid derivatives.[3,4]

Alternatively, reaction of iron pentacarbonyl with organolithium reagents generates the same acylate complex as that from $Na_2Fe(CO)_4$ and organic halides, $[RCOFe(CO)_4]^-$. This complex has been converted to ketones, conjugated enones,[5] amides,[6] and other carbonyl-containing products[7] by reaction with electrophiles such as organic halides, epoxides, or imines. In contrast, reaction of these acylate iron complexes with electrophiles prone to reaction at oxygen, such as ethyl fluorosulfonate results in O-alkylation of the acyl group, resulting in carbene complex formation.[8]

Nickel carbonyl also forms reactive acylate complexes upon treatment with organolithium reagents. These complexes, generated and used in situ, convert conjugated enones to 1,4-diketones,[9] allylic halides to β,γ-unsaturated ketones,[10] and alkynes to 1,4-diketones,[11] as well as undergo coupling to form α-diketones when treated with acid.[12] In spite of the useful transformations effected by these nickel acylate complexes, they have found little use in synthetic organic chemistry in the 15–20 years of their existence.[13] This is undoubtedly due to the extreme volatility and toxicity of nickel carbonyl and the resulting problems in handling this material. Cobalt nitrosyl tricarbonyl, $Co(NO)(CO)_3$, is isoelectronic with nickel carbonyl and is also a volatile, toxic liquid. However, it readily forms an air-

Table I. Acylation of Conjugated Enones by Cobalt Acylate Complexes 2 (Eq 1)

3	R	R′	R″	yield,[a] %
a	Me	Ph	Me	87
b	*n*-Bu	Ph	Me	78
c	Me	Ph	Ph	58
d	Me	$(Me)_2$	Me	39
e	*n*-Bu	$(Me)_2$	Me	75
f	Me	Me	Me	60
g	*n*-Bu	Me	Me	69
h	Me	$(Me)_2$	$CH{=}CMe_2$ [b]	91
i	Me	$-(CH_2)_4-$		0[c]
j				73[d]
k				47

[a] Reported yields are for isolated, purified products. [b] This species only underwent *mono*acylation. [c] Cyclohexenone was recovered unchanged. [d] Mixture of stereoisomers.

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