J. prakt. Chem. 335 (1993) 23 – 34

Journal für praktische Chemie
Chemiker-Zeitung

Aziridines. 59 [1]

Regioselectivity in Nucleophilic Ring Opening of 2-Methylaziridines. Lag of Bond Making as Model for the Abnormal Opening

Pen-Yuan Lin, Gunther Bentz and Helmut Stamm

Heidelberg, Faculty of Pharmacy, Institute of Pharmaceutical Chemistry of the University

Received April 29th, 1992 respectively August 6th, 1992

Abstract. The regioselectivity ratio RS = normal : abnormal opening of activated 2-methylaziridines **2** by nucleophiles is found to range from 0.10 to unmeasurable large (only normal opening = substitution at CH_2 by strongly basic carbanions). RS is assumed to result from S_N2 variants differing in the degree to which bond breaking is ahead of bond making including perhaps synchronous S_N2. Bond breaking will be more ahead for the N-CMe bond. High nucleophilic power pushes bond making toward a synchronous process resulting in great RS. The decrease in RS with acyl activation relative to sulfonyl activation is in accord with a flattening of the nitrogen pyramid (planarization effect). The planarization effect is retained in acidic medium by O-protonation: Rs 0.10 – 0.14 for methanolysis as compared to RS 0.43 for N-protonated sulfonylaziridine **2h**. AM1 calculations support the planarization hypothesis. – No indication for SET with trityl anion was found.

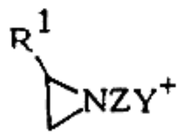
Introduction

Nucleophilic and solvolytic ring opening of aziridines are not yet well understood in some details despite many papers on mechanistic questions. Differentiation between S_N2 and S_N1 was often the aim, usually for aziridines with unsymmetrical substitution [2 – 5]. Kinetic studies [2, 3] on acid catalyzed hydrolysis provided a rate increase in the sequence (only substituents given) 2-ethyl < trans-2,3-dimethyl < no ≈ cis-2,3-dimethyl ≈ 2-methyl ≪ 2,2-dimethyl showing that steric effects are modulated or even outplayed by other effects.

The intermediacy of a carbenium ion appears questionable without extra evidence and has been disproved in some cases [4 – 6, 7a]. An S_N1-like behaviour with Walden inversion may occur in a borderline S_N2 in which breaking and making of bonds proceed neither strictly synchronously nor in steps separated by an intermediate [6, 7a]. A real S_N1 intermediate either requires a good charge stabilization [5] or has in another way to compete successfully with borderline mechanisms that require a suitable nucleophile [6, 7a] and can be suppressed by steric hindrance.

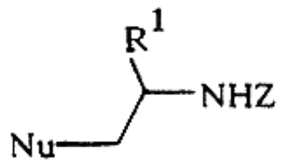
Previous work on mechanistic aspects from this laboratory concerned mostly 2,2-dimethylaziridines **8**. Solvolyses with double activation (N with positive charge plus an electron withdrawing substituent) cleave only the N-CMe_2 bond (abnormal opening), in alcohols [6] predominantly via a borderline S_N2, in the poorly nucleophilic benzene [8] via S_N1. With monoactivation (no acid) the regioselectivity depends strongly on the kind of the nitrogen substituent [9]: sulfonyl activation gives the "normal product" while acyl activation gives the "abnormal product" either exclusively by a single electron transfer (SET) mechanism with homolytic ring opening [10] or nearly exclusively by a particular type of borderline mechanism (see below) [1b]. How is this remarkable behaviour retained or modified when one of the two methyl groups is omitted (giving **2**)?

A review of previous work on **2** should reasonably include 2-ethylaziridines **1**. For both substrates the regioselectivity ratio RS = "normal" : "abnormal" ring opening increases with the nucleophilicity of the reagent [3, 7a]. This points to a competition between "pure" S_N2 and S_N2 variants whose bond breaking is ahead of bond making. The nucleophilicity effect is most simply seen in the reactions of **2n** with con-

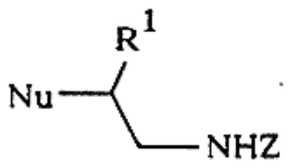


1 R^1 = Et **1n**-H^+ Y=H

2 R^1 = Me **2n**-H^+ Y=H etc.

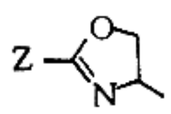


normal



abnormal

opening



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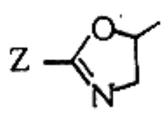

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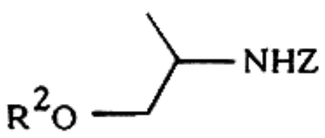

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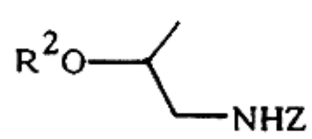
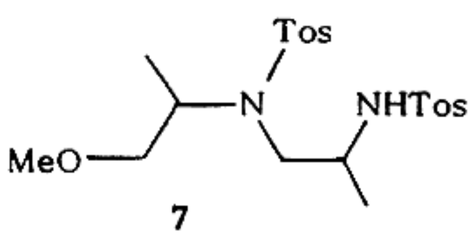


6

capitel M, E, B, H indicate

R^2= Me, Et, tBu, H



7

8

throughout this paper	Z
a	CONHPh
b	$COC_6H_4NO_2(4)$
c	$COC_6H_4Ph(4)$
d	COPh
e	$COCMe_3$
f	$COCH{=}CMe_2$
g	COCH=CHPh
h	Tos
i	SO_2Ph
j	CHO
k	$COCH{=}CH_2$
l	NHPh
m	Ph
n	H

centrated hydrohalic acids [5]: RS increases in the sequence HCl, HBr, HI from 4 to 19 in water without interference by solvolyses. Many other ring opening reactions of **1** and **2** can be found in ref. [6, 7] and are not discussed here. Acidic isomerization [11] of **2a** in aprotic solvents yields **3l** and **4l** in ratios of 0.075 – 0.18. Formation of **4l** is explained by a borderline mechanism with retention of configuration by two inversions (**2n**-H^+) or by front-side attack (**2n**-BF_3). Different protonation sites for **2a** (aziridine nitrogen) and its thio analogue (sulfur) were believed to account for different results. Since thiourea is less basic than urea [12] (protonation at C=X) one would rather expect the reverse change in protonation site if there is any.

Results and Discussion

Results of solvolyses, i.e. ring openings by poor nucleophiles, are listed in Table 1. RS was determined from the ^{1}H NMR spectra of the product mixtures. No base catalyzed reactions of **2a – g** are included since alkoxides attack the carbonyl group of acylaziridines and produce the respective esters and the aziridine base. Even the bulky acyl group of **2e** was attacked as shown by the absence of any workup residue due to the volatility of the products **2n** and methyl pivalate.

Ethoxide in run 1 attacks exclusively (within the limits of precision) the less shielded carbon atom of **2h** while methoxide in run 3 gives RS 16. These results are compatible with steric hindrance of abnormal opening and are in a qualitative manner similar to the findings for **8h** [6]. However, methanolysis of **8h** had given RS (defined analogously to RS for **2**) 1.6 leading to the paradox, that one methyl group in position 2 hinders attack in this position more than two methyl groups if relative rates are considered, i.e. rates relative to attack on the methylene carbon. A possible explanation may be developed from the hypothesis [6] that ring opening of aziridines with a trivalent nitrogen is favoured by a flat nitrogen pyramid and should therefore profit from bending of the nitrogen bonds that in the maximum results in nitrogen inversion. This hypothesis found experimental support from sulfonyl activated stilbene imines [13]: the faster inverting trans isomer reacts faster than the cis isomer quite in contrast to stilbene oxides and to protonated cis-trans isomeric 2,3-dimethylaziridine bases [2, 3] (see introduction). For steric reasons (comp. the general discussion in ref. [14a]) **8h** will invert more rapidly than **2h** which has a less stable syn and a more stable anti invertomer (comp. the X ray data for **2h** with an angle of 121° between the N-S bond and the aziridine plane [10b]). Thus, **8h** experiences more often and stronger than **2h** the increased ring strain of a flat pyramid.

Table 1 Regioselectivity in solvolyses[a] of **2 d – h**

run		**2**	mmol of catalyst	ml R^2OH	yields of products[b]	RS[c]
1	20	**2 h**	20 EtONa	50 EtOH	95 % **5 h E**	v. gr.
2	20	**2 h**	20 H_2SO_4	50 EtOH	78 % (**5 h E** + **6 h E**)	0.52
3	3	**2 h**	6 MeONa	25 MeOH	92 % (**5 h M** + **6 h M**), (4 %) **7**	16
4	5	**2 h**	–	35 MeOH	(19 %) (**5 h M** + **6 h M**), (79 %) **2 h**	1.4
5	20	**2 h**	20 H_2SO_4	50 MeOH	89 % (**5 h M** + **6 h M**)	0.43
6	2	**2 d**	–	15 MeOH	(40 %) (**5 d M** + **6 d M**), (58 %) **2 d**	0.10
7	20	**2 d**	20 H_2SO_4	50 MeOH	86 % (**5 d M** + **6 d M**)	0.10
8	20	**2 e**	20 H_2SO_4	50 MeOH	69 % (**5 e M** + **6 e M**)	0.10
9	20	**2 f**	20 H_2SO_4	50 MeOH	76 % (**5 f M** + **6 f M**)	0.14
10	20	**2 g**	20 H_2SO_4	50 MeOH	78 % (**5 g M** + **6 g M**)	0.12
11	10	**2 d**	35 $HClO_4$[d]	40 tBuOH	5 % **5 d B**, (6 %) **6 d B**,	0.8
					(0.1 %) **3 m**, (7 %) **4 m**,	0.014
					51 % **6 d H**	v. sm.

[a] 24 h (0.8 h in run 11) at room temp.; 6.5 h reflux in runs 4 and 6.
[b] Yields in parentheses are from ^{1}H-NMR.
[c] v. gr., v. sm.: very great and very small. In run 11 also RS = **3 m** : **4 m** is given.
[d] Aqueous, 70 %.

This strain loosens the bond to the substituted carbon more than the N-CH_2 bond. To loosen a bond or an atom means to make them more susceptible to any kind of heterolysis in the S_N2-S_N1 spectrum. The respective difference in loosening of the two ring bonds must be smaller with **2 h**. Besides, attack on the loosened tertiary carbon of **8 h** is more easy than one may expect. This attack is much less sterically hindered than attack on a tertiary butyl substrate. The C_4 skeleton of the latter forms a steeper pyramid than the respective C_4 fragment of **8**. Flattened exocyclic pyramids are inherent properties of three-membered rings and may be illustrated by the three exocyclic bond angles around methylated carbon of **2 h** (123°, 118°, 115°) [10 b]. – A sulfonamide anion is not much inferior to methoxide ion in nucleophilicity [15]. Thus, part of the main product **5 h M** (as persisting N⁻ anion) is able to react with **2 h** in the normal manner forming some **7** (1 : 1 mixture of diastereomers). The structure of **7** follows from the NH doublet and the unusual upfield chemical shift for both CMe groups. The ether moiety of **7** is included in the RS value of run 3.

A similar monomethyl-dimethyl paradox is observed for the much slower methanolysis without catalysis: RS is 1.4 for **2 h** (run 4, 19 % conversion) and (near?) zero [6] for **8 h** (complete conversion under comparable conditions). The respective influence of nitrogen conformation is even more pronounced for acyl activation: uncatalyzed methanolysis of **2 d** (run 6) gives RS 0.10 and a conversion of 40 % as compared to 1.4 and 19 % with sulfonyl activation (**2 h** in run 4, identical conditions). The special case of acyl activation and conformation is discussed below. Again, RS for the dimethyl analogue **8 d** is (near?) zero in uncatalyzed methanolysis [1b].

Acid catalysis changes RS for **2 h** to 0.52 (run 2, ethanol) and 0.43 (run 5, methanol). This change results from the mentioned borderline mechanism with **2 h** – H^+ and the difference between both runs is compatible with the steric demands of the alcohol. No N-allyltosylamide was detected in contrast to the respective reactions with the dimethyl analogue **8 h** that yields small amounts of tosyl methallylamide [6] indicating some aziridine conversion to the carbenium ion (a tertiary one with **8 h**). A similar difference in by-products between monomethyl and dimethyl aziridines is observed with acyl activation: no oxazoline (type **3** or **4**) was detected in runs 7 – 10 in contrast to 18 % of the respective oxazoline [6] from acidic methanolysis of **8 d**. This confirms the proposed carbenium pathway to oxazolines in alcoholic solution. More interesting is the increased preference for abnormal opening of acyl activated **2** (small RS in runs 7 – 10) as compared to the sulfonyl activated **2** in run 5. Olah [16] has shown that at –60 °C N-acylaziridines are protonated on the oxygen leading to a planar N-hydroxymethyleneaziridinium structure. The sulfonylaziridine **2 h** has no possibility to form an O-protonated species that transfers much charge to the nitrogen. Even non-aziridine sulfonamides are protonated on nitrogen [17]. This difference in the likely reactive intermediate can explain the difference in RS for protonated **2 d – g** and **2 h** – H^+. It is not only the

charge that counts. O-protonated **2d–g** must have a significantly increased ring strain[1)] and the electronegativity of their nitrogen will be increased due to the change in hybridization required for the planar structure. As compared to **2h** – H^+, the N-CMe bond in protonated **2d–g** will more easily undergo heterolysis giving rise to the observed change in RS. This O-protonation can even explain the RS differences in runs 7–10 sinced **2f** – H^+ and **2g** – H^+ in runs 9 and 10 are azabutadienes $^+N=C-C=C$. This will influence charge and bond order at the nitrogen (resonance contribution from $N-C=C-C^+$) and thereby weaken the activation. All this reasoning increases the doubts about the explanation given in ref. [11] for the difference between **2a** and its thio analogue.

The identical RS for **2d** without and with acid (runs 5 and 6) makes one suspect that in the "uncatalyzed" reaction the solvent acts as acid (comp. ref. [1b]). The reaction of the probably less basic **2h** in run 4 may really be uncatalyzed. The RS change from run 3 to run 4 should reflect the change in nucleophile (MeO^- to MeOH).

Run 11 was mainly performed in order to differentiate between the isomeric oxazolines **3m** and **4m** which were unknown at that time. **4m** is assumed to arise in this medium via the respective secondary carbenium ion (comp. ref. [6]); only a trace of the isomeric **3m** could be detected. Solvolytic ring opening was much faster with a water molecule (RS very small) than with a sterically demanding tert-butanol molecule (RS = 0.8) as expected from a participation of the reacting solvent molecule in the transition state.

[1)] An additional strain of ca. 13 kcal/mol is estimated for the planar structure of an (lithiated) oxidomethylene cyclopropane anion [18].

Since the fast carbonyl reaction prevents ring opening of **2d–g** by methoxide, we turned to the reaction of **2d** with iodide ion which reacts with methyl iodide an order of ten faster than methoxide does [15]. I^- converts N-acylaziridines into N-(2-iodoalkyl) carboxamide anions which recyclize to give oxazolines. 1-Aroyl-2-alkylaziridines are said [19] to react exclusively under normal cleavage. This is supported by the text of ref. [20] which states that **2d** by reaction with LiI in THF exclusively isomerizes to **3m**. The respective experimental, however, reports for this reaction both **3m** and **4m** in yields of 63 % and 20 % corresponding to RS 3.2. This discrepancy is the more confusing since the reported ^1H NMR data for the minor isomer **4m** disagree with our findings. In two reactions of **2d** with KI in boiling THF we found RS 6.5 (65 % yield of **3m** + **4m**, 20 % of **2d** not converted) and RS 7.5 (95 % yield of oxazolines). In spite of the higher nucleophilicity of I^-, RS is lower than that one for **2h**/MeO^- in run 3 of Table 1. A part of the strong tendency of acylated 2,2-dimethylaziridines (e. g. **8d**) to undergo abnormal ring opening [9] is obviously retained in the monomethyl analogues. The leaving group of an acylaziridine is a poor one in the ground state of nitrogen inversion [1b], but its quality enormously improves in (or even near) the planar inversional transition state (barrier of inversion < 6 kcal/mol [14a, b]) leading to effects which approach those of O-protonated acylaziridines. This planarization induced borderline mechanism [1b] can account for much of the abnormal opening of **2d** thus explaning the lowering of RS on going from **2h**/MeO^- to **2d**/I^- as well as on going from **2n** – H^+/I^- (RS 19 [5]) to **2d**/I^-.

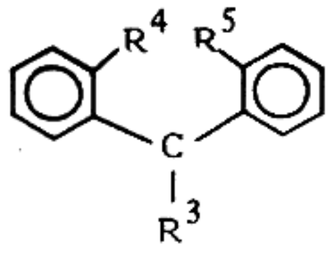
The S_N1-like partial heterolysis must be most pronounced in the strictly planar inversional transition state. Some calculations (Table 2) on planarized acylaziridines without and with O-protonation revealed the

Table 2 Bond lengths (Å) and atomic charges of aziridines obtained from AM1 calculations[a)]. Site of protonation: oxygen.

	bond lengths			atomic charges		
	N – C2	N – C3	N – exo	C2	C3	N
2j planar	1.425	1.413	1.351	−0.013	−0.062	−0.404
2j – H^+ planar	1.451	1.434	1.293	+0.033	−0.041	−0.247
2k – H^+ planar	1.447	1.431	1.307	+0.039	−0.042	−0.256
8j planar	1.434	1.411	1.351	+0.047	−0.068	−0.398
8j – H^+ planar	1.468	1.432	1.291	+0.095	−0.045	−0.244
Az – CHO planar	1.415	1.415	1.351	−0.059	−0.067	−0.404
Az – CHO pyramid	1.460	1.460	1.422	−0.145	−0.156	−0.279
Az – Me planar	1.404	1.404	1.385	−0.052	−0.052	−0.458
Az – Me pyramid	1.454	1.454	1.429	−0.181	−0.182	−0.195
2h pyramid	1.459	1.444	1.713	−0.083	−0.166	−0.350
2h pyramid (X ray)[b)]	1.487	1.485	1.656			

[a)] Planarized structures with s-cis conformation (carbonyl oxygen and C2 cis).
[b)] X Ray data: ref. [10b].

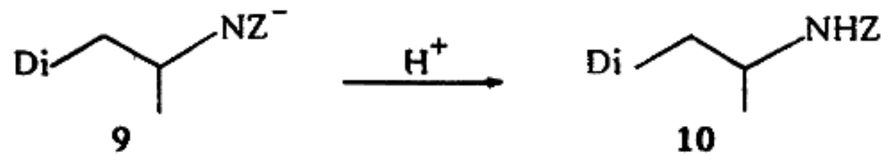
expected tendency in the differences of charges and bond lengths. For the parent compound, formylaziridine Az–CHO, also the inversional ground state was included, which shows a shortening of the ring N–C bonds in the planarized structure and a decrease of negative charge on ring carbons. The latter is immediately in accord with an increased reactivity and the shortening is in fact rather a masked lengthening since regardless of the N-substituent an aziridine ring must shorten the N-C bonds on planarization due to the change in nitrogen hybridization. In terms of the Walsh model, nitrogen contributes an sp^2 lobe to the lowest Walsh orbital in the pyramidal aziridine but an sp lobe in the planar aziridine. This general shortening is confirmed by pyramidal and planar N-methylaziridine Az-Me with a difference of 0.050 Å as compared to 0.045 Å for Az-CHO. For planarized **2j** and **8j** the difference between C2 and C3 (CH_2) is in accord with the hypothesis; charge of C3 and bond length N-C3 remain constant without an influence of the methylation of C2. As assumed, the effect of O-protonation on the N-C bonds is a general increase and greater differences: 1.451/1.434 Å (**2j**) and 1.468/1.432 Å (**8j**). The influence of conjugation (**2k** – H^+) is small and may be questionable, but the experimental difference in RS between **2f, g** and **2d, e** was also small. For the sulfonylaziridine **2h** (pyramid) the X ray bond lengths seem to better match RS 1.4 of run 4 than the calculated lengths.



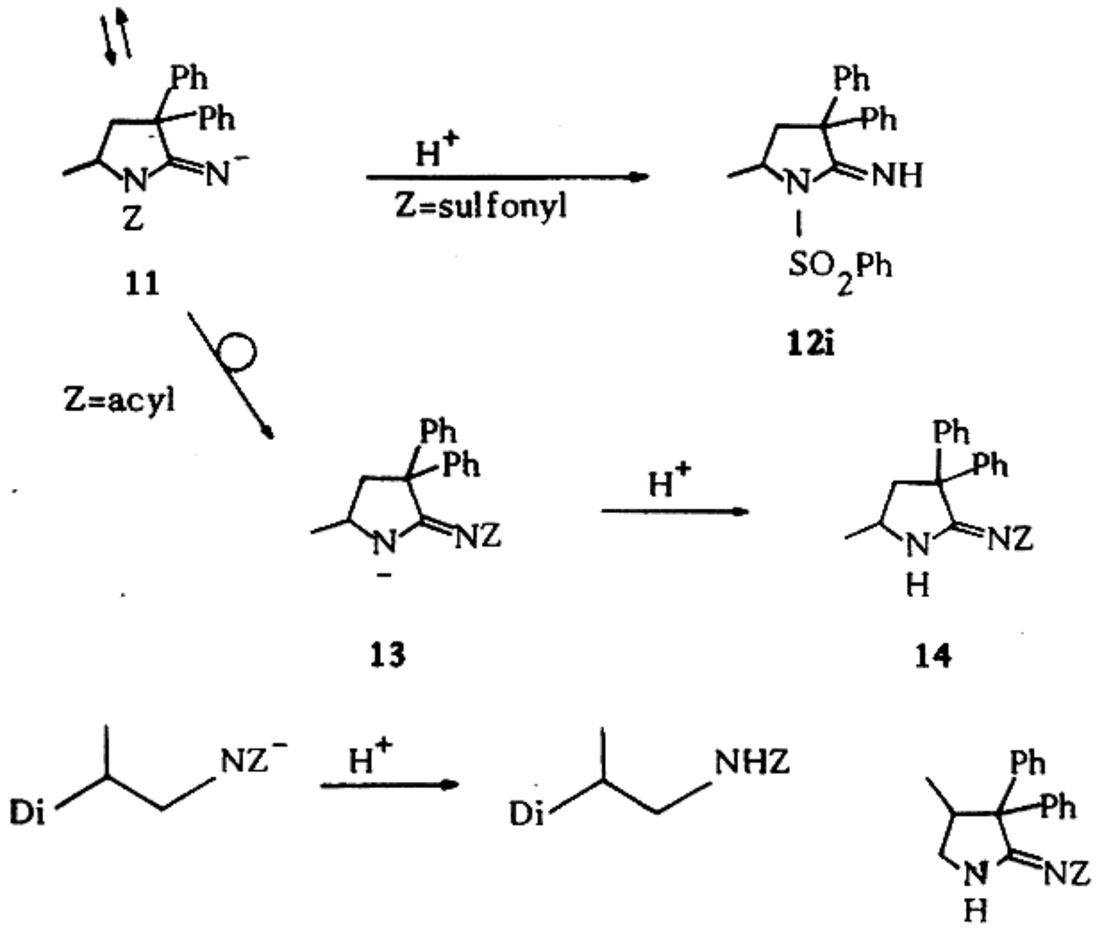
	R^3	R^4	R^5
Di	CN	H	H
AH	H	$-CH_2-$	
X	H	—O—	
Tr	Ph	H	H

Di⁻, AH⁻, X⁻, Tr⁻ = corresponding carbanions

DiH, AH_2, XH, TrH = conjugate CH-acids



9 **10**



11 **12i** **13** **14**

15 **16** **17**

Table 3 Regioselectivity in ring opening of **2b–e, h–i** by carbanions at room temperature in THF.

run	mmol of reagents[a]				THF ml	time h	products[b]	RS[c]
12	11	DiH 11	TrNA 10	**2b**	200	72 h	(49 %) **14b**, (37 %) **17b**	1.3
13	16	DiH 16	TrNA 15.2	**2c**	250	48 h	36 % **10c**, 15 % **14c**, 32 % **16c**, 14 % **17c**	1.2
14	11	DiH 11	TrNa 9.8	**2d**	250	48 h	31 % **10d**, 16 % **14d**, 24 % **16d**, 16 % **17d**	1.2
15	16.5	DiH 16.5	TrNa 15	**2e**	250	72 h	(55 %) **10e**, (38 %) **16e**	1.4
16	11	DiH 11	TrNa 10	**2i**	250	72 h	(38 %) **10i**, (48 %) **12i**, (10 %) **16i**	9
17	7.2	DiH 7.2[d]	TrNa 7.2	**2i**	115	72 h	54 % **10i**, 13 % **12i**, 6 % **16i**	11
18	7	DiH 10	BuLi 5	**2i**	100	24 h	46 % **10i**, 40 % **12i**, 1.5 % **16i**	57
19	15	AH_2 11	BuLi 10	**2i**	200	4 h	88 % **18i**, 2 % **19i**, 3 % **20i**, 0.2 % **21i**	v. gr.
20	20	AH_2 18	BuLi 10	**2e**	200	4 h	86 % **18e**, (3 %) **19e**, (3 %) **23e**, (0.5 %) **22e**, (0.6 %) **24e**	35
21	15	XH 12	BuLi 10	**2d**	200	24 h	82 % **25**, 14 % **26d**, (0.5 %) **27d**	28
22	10	TrH 10	NNa 10	**2c**	200	48 h	81 % **28c**	v. gr.
23	10	TrH 10	NNa 10	**2d**	200	48 h	90 % **28d**	v. gr.
24	25	TrH 20	BuLi 10	**2e**	120	96 h	83 % **28e**	v. gr.
25	12.5	TrH 10	BuLi 5	**2h**	120	42 h	95 % **28h**	v. gr.
26	25	TrH 10	BuLi 10	**2i**	120	72 h	97 % **28i**	v. gr.

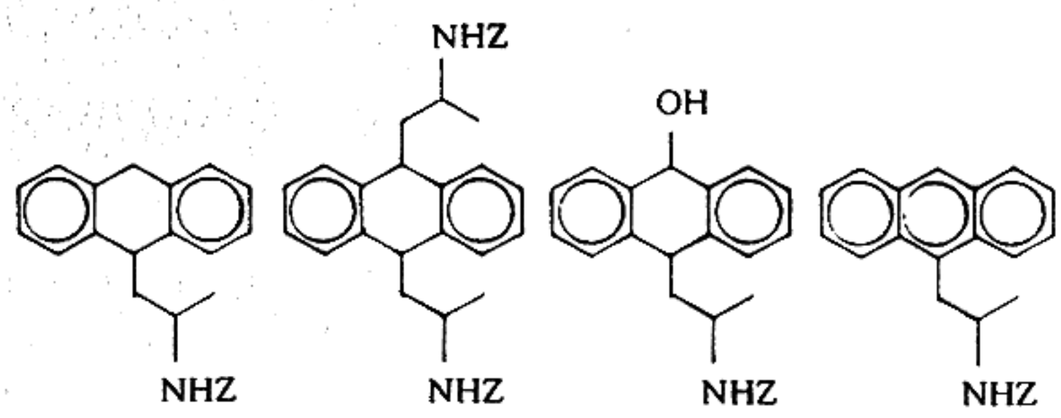
[a] NNa = sodium naphthalenide.
[b] Yields in parentheses from ^{1}H-NMR.
[c] v. gr. = very great.
[d] Excess of NNa, 7.2 mmol of TrH.

Since **8d** shows a very high preference for abnormal opening by several carbanions, e.g. diphenylacetonitrile anion Di^-, we turned to respective reactions of **2** (Table 3). The nucleophilicity of Di^- has about the same order of magnitude as methoxide ion[2]. In reactions of Di^- with activated aziridines the primary products can cyclize with (Z = acyl) [22] or without (Z = sulfonyl) [23] migration of Z. Thus, four isomeric products are possible in each reaction of Di^- with each **2**, two pairs of positional isomers, the open-chain pair and the iminopyrrolidine pair: **10/16** and **14/17** from **2b–e** or **10/16** and **12/** (isomer not detected) from **2g**.

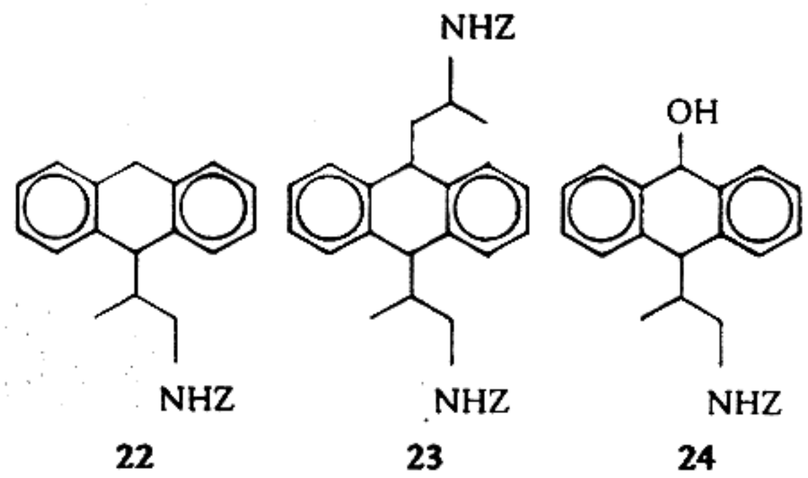
Runs 12–26 present our results. The acyl migration **11** → **13** (or their positional isomers) via attack of the anionic imino nitrogen on Z should depend on the carbonyl reactivity of Z. This is born out by run 12 and 15. With Z = nitrobenzoyl (run 12) no open-chain product was found, with Z = pivaloyl (run 15) no iminopyrrolidine. Comparison of structure **11** with structure **13** (Z = acyl) can leave no doubt that **13** is thermodynamically favoured making the migration practically irreversible in contrast to the cyclization which is most likely reversible. The variations in the cyclization of **9i** to **11i** and finally to **12i** in runs 16–18 (and in further runs not listed in Table 3) may be caused by accidental differences in the actual protonation during work-up.

RS with **2b–e**/Di^- (runs 12–15) was smaller than for **2d**/I^- and did not reveal a dependence on the kind of the acyl group. In order to avoid a complication by Michael addition no reactions with **2f, g** were run. The constancy of RS in runs 12–15 makes any SET contribution very unlikely. Reducibility decreases in the sequence **2b** > **2c** > **2d** > **2e** with a rather pronounced difference (> 1 V) at least between **2b** and **2e** which should be observable both in RS and further products. RS of runs 12–15 may result from counteracting effects of planarization and nucleophilicity. Sulfonyl activation (**2i**, runs 16–17) significantly increases RS. Some electrophilic assistance seems to operate here with Di^-Na^+ since RS increases further with Di^-Li^+ (run 18 and more runs not listed in Table 3). An assistence much weaker than protonation may come from the CH-acids present (TrH and dihydronaphthalene) or from a cation that is less firmly bound to Di^- and/or to the product anions.

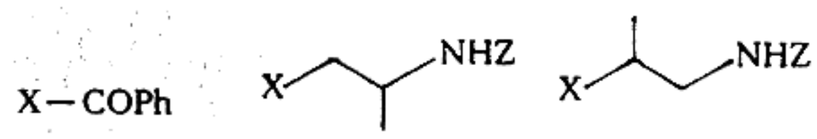
The ^1H NMR spectrum of the iminipyrrolidine **12i** caused many confusions by E-Z-isomerism of the C = NH group. In E-**12i** rotation of the phenylsulfonyl group is not much hindered, while Z-**12i** can form a hydrogen bond to one of the sulfonyl oxygens, preferring that one which avoids an ecliptic position of phenyl and methyl. There is no other reasonable explanation for the findings, especially for the downfield shift of methyl and the upfield shifts of 5-H and trans-4-H in Z-**12i**. At 25–30 °C the signals of 5-H and trans-4-H (same face of the pyrrolidine ring) in **12i** are very broad. At −10 °C they go a little downfield (change of equilibrium). At −60 °C two species are clearly recognizable, E-**12i** predominating more than at +25 °C. The isomerization is slowed down (25–30 °C) by pyridine-d_5: all signals are broadened save those with a small shift difference. A trace of trifluoroacetic acid sharpens all signals (except NH) at average positions. Attempts to completely suppress the obviously catalyzed isomerization were in vain. By chance we obtained a spectrum from a crude product mixture (run 18 prior to chromatography) showing no isomerization.



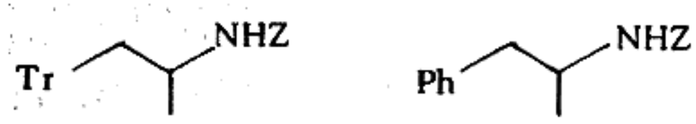
18 **19** **20** **21**



22 **23** **24**



25 **26** **27**



28 **29**

More nucleophilic carbanions increase RS so much that their reaction with activated mono alkyl (or aralkyl) aziridines should be usable as general synthetic method. Reaction of **2i** with anthracene hydride AH^- provided (run 19) only products of normal opening, the expected **18i** and the product **19i** of twofold substitution (after in situ deprotonation of the N-anion of **18i**). Two further minor products, **20i** and **21i**, are artefacts of **18i**. Oxidative hydroxylation of substituted dihydroanthracenes is known. Dehydration of **20i** results in **21i**.

Reactions of AH^- with aroylaziridines take another mechanistic route [24] and are not considered here. No mechanistic complication was found with the pivaloylaziridine **2e**. Its reaction (run 20) gave practically the

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[2] S_N2 reactivity and acidity of Di^- are compared with those of phenolates [21]. S_N2 nucleophilicities of phenolate and methoxide are compared in ref. [15].

same yield of **18** and **19** as **2i** (run 19) did, but it provided also some abnormal product **22e** (obtained in mixture with **18e**). Part of **22e** underwent secondary reactions to form **23e** and **24e**, the latter possibly during workup. **19e** and **23e** formed the last chromatographic fraction. Their structures were deduced from the elementary analysis of the mixture (1 : 1) and from ^{1}H-NMR data: four tert-butyl singlets (two for **23e**, one each for two isomers of **19e**), four methyl doublets, one doublet at 3.55 ppm that only can be assigned to a meso proton of a dihydroanthracene moiety indicating a quarter of the material to carry a $CHMeCH_2N$ chain. **24e** was obtained in mixture with **18e**. Its structure follows from a CHO singlet at 5.89 ppm, a 9-H doublet, a broad NH triplet and a very upfield shifted methyl indicating a trans structure. These results allow a rough quantification of RS. Including the second amidoethylations this is 33 showing again the common RS difference between sulfonyl and acyl activation due to the planarization effect. Practically the same RS (28) was found in the reaction of the xanthenyl anion X^- with **2d** (run 21) where, as expected [24], mainly carbonyl attack occurred providing **25**.

The only nucleophile for which outer-sphere SET to dimethylaziridines (**8c–e**) was proven [10 a] is trityl anion Tr^-. Reaction of Tr^- with **2c–e, h, i** (runs 22–26) gave only **28c–e, h, i** without any indication of SET. SET to **2h, i** would have cleaved the N-S bond [25].

The observed rearrangement [26] via a borderline attack by bromide on **8h** in its reaction with Grignard reagents prompted a reaction of **2h** with phenylmagnesium bromide in boiling THF. Only **29h** (82 %) was obtained without any isomers. Reactions outside the S_N2-S_N1 range seem to occur with **8** only but not with **2**.

Support by the Fonds der Chemischen Industrie is gratefully acknowledged. We thank Dr. Peter Bischof, Institute of Organic Chemistry, Heidelberg, for the AM1 calculations (program from ISKA, Bensheim, Germany) and for his interest in the problem.

Experimental

^{1}H-NMR: $CDCl_3$, Bruker W 250 (250 MHz) spectrometer. IR: KBr (oily compounds: film) Perkin-Elmer 283 spectrometer. Column chromatography (column dimensions in cm): silica gel Merck, 0.063–0.2 mm. Analyses of mixtures by ^{1}H-NMR unless otherwise stated. Abbreviations: chr. (chromatography), dichl. (CH_2Cl_2), mixt. (mixture). General workup: evaporation at low bath temp. provided a residue that was taken up in dichl., washed with water and evaporated. Further work-up or analysis is given.

Unknown aziridines **2c, e–g, i** were prepared analogously to **2d** [1b].

2-Methyl-1-(4-phenylbenzoyl)aziridine (**2c**)

92 %; mp. 57–59 °C. IR (cm^{-1}): 1671. ^{1}H-NMR δ: 1.42 (d, J = 5.3, Me), 2.17 (d, J = 3.4, 3-H_{tr}), 2.56–2.65 (m, 2-H/3-H_{cis}), 7.36–7.51 (m, m-H/p-H of Ph), 7.60–7.69 (m, o-H of Ph/m-H of COAr), 8.07–8.12 (m, o-H of COAr).

$C_{16}H_{15}NO$	Calcd.	C 81.04	H 6.38	N 5.91
(237.1)	Found	C 80.98	H 6.35	N 5.89

2-Methyl-1-pivaloylaziridine (**2e**)

81 %; oil. IR (cm^{-1}): 1689. ^{1}H-NMR δ: 1.25 (s, tBu), 1.34 (d, J = 5.4, Me), 1.85 (d, J = 3.1, 3-H_{tr}) 2.38–2.47 (m, 2-H/3-H_{cis}).

$C_8H_{15}NO$	Calcd.	C 68.04	H 10.71	N 9.92
(141.2)	Found	C 67.82	H 10.76	N 9.98

1-(3,3-Dimethylacryloyl)-2-methylaziridine (**2f**)

58 %; oil. IR (cm^{-1}): 1668, 1637. ^{1}H-NMR δ: 1.30 (d, J = 5.5, NCMe), 1.85 (d, J = 1.3, C = CMe_{cis}), 1.94 (d, J = 4.0, 3-H_{tr}), 2.17 (d, J = 1.1, C = CMe_{tr}), 2.57 (d, J = 6.7, 3-H_{cis}), 2.72 (qdd, J = 5.5/6.7/4.0, 2-H), 5.93 (qq, J = 1.3/1.1, C = CH).

$C_8H_{13}NO$	Calcd.	C 69.03	H 9.41	N 10.06
(139.2)	Found	C 69.07	H 9.67	N 10.30

1-Cinnamoyl-2-methylaziridine (**2g**)

88 %; oil. IR (cm^{-1}): 1680, 1627. ^{1}H-NMR δ: 1.38 (d, J = 5.4, Me), 2.05 (d, J = 3.5, 3-H_{tr}), 2.44 (d, J = 5.8, 3-H_{cis}), 2.58 (qdd, J = 5.4/5.8/3.5, 2-H), 6.64 (d, J = 16.0, COC = CH), 7.36–7.40 (m, m-H/ p-H of Ph), 7.52–7.55 (m, o-H of Ph) 7.68 (d, J = 16.0, COCH = C).

$C_{12}H_{13}NO$	Calcd.	C 76.98	H 7.00	N 7.48
(187.2)	Found	C 76.73	H 6.96	N 7.42

2-Methyl-1-phenylsulfonylaziridine (**2i**)

92 %; mp. 57–59 °C. IR (cm^{-1}): 1317, 1157. ^{1}H-NMR δ: 1.27 (d, J = 5.6, Me), 2.05 (d, J = 4.7, 3-H_{tr}), 2.65 (d, J = 7.0, 3-H_{cis}); 2.88 (qdd, J = 5.6/7.0/4.7, 2-H), 7.53–7.69 (m, m-H/p-H), 7.94–7.99 (m, o-H).

$C_9H_{11}NO_2S$				
(197.3)				
Calcd.	C 54.80	H 5.52	N 7.10	S 16.26
Found	C 54.97	H 5.58	N 7.17	S 16.22

General Procedure Alcoholyses for Runs of Table 1:

The residue was chromatographed (45 × 3.5, dichl.) or analyzed with ^{1}H-NMR.

Run 1. Chr. provided 4.89 g (94 %) of **5hE**.

N-(2-Ethoxy-1-methylethyl)-4-toluenesulfonamide (**5hE**)

Oil. IR (cm^{-1}): 3280, 1330, 1155, 1090. ^{1}H-NMR δ: 1.10 (t, J = 7.2, OCMe), 1.11 (d, J = 6.9 Hz, NCMe), 2.42 (s, Me of Tos), 3.23 (d, J = 5.4, $NCCH_2O$), 3.36 (m_c, NCH/CH_2 of Et), 4.97 (d br, J = 7, NH), 7.31 (d, J = 8, m-H), 7.78 (d, J = 8, o-H).

$C_{12}H_{19}NO_3S$	Calcd.	C 56.01	H 7.44	N 5.44
(257.4)	Found	C 56.19	H 7.31	N 5.61

Run 2. 4.89 g (95 %, chr.) of a 34 : 66 mixt. of **5hE** and **6hE**. Oil.

N-(2-Ethoxypropyl)-4-toluenesulfonamide (**6 h E**, in mixt. with **5 h E**).

IR (cm^{-1}): 3395, 1330, 1167, 1094. ^{1}H-NMR δ: 1.1 (NCCMe, overlap), 1.13 (t, J = 7.1, Me of Et), 2.42 (s, Me of Tos), 2.78 (ddd, J = 13.0/7.9/4.0, 1 H of NCH_2), 3.08 (ddd, J = 13.0/3.5/7.9, 1 H of NCH_2), ca. 3.3 – 3.4 (NCCH, hidden), 3.52 (m_c, OCH_2), 5.06 (m_c, NH, overlap), 7.32 (d, J = 8.4, m-H), 7.75 (d, J = 8.4, o-H).

$C_{12}H_{19}NO_3S$
(257.4) (**6 h E** + **5 h E**)

Calcd.	C 56.01	H 7.44	N 5.44	S 12.46
Found	C 56.11	H 7.66	N 5.38	S 12.51

Run 3. 698 mg of a mixt. consist. of 26 mg (4 %) of **7** and 672 mg (92 %) of a 15 : 1 mixt. of **5 h M** and **6 h M**. Oil. For **6 h M** see run 5.

N-(2-Methoxy-1-methylethyl)-4-toluenesulfonamide (**5 h M**, contamin. with **6 h M**/**7**): IR (cm^{-1}): 3245, 1331, 1152, 1090. ^{1}H-NMR δ: 1.09 (d, J = 6.7, CMe), 2.42 (s, Me of Tos), 3.19 (m_c, OCH_2), 3.21 (s, OMe), 3.40 (m_c, NCH), 4.86 (d br, J = 6 – 7, NH), 7.31 (d, J = 8.4, m-H), 7.78 (d, J = 8.4, o-H).

$C_{11}H_{17}NO_3S$
(243.3)

Calcd.	C 54.37	H 7.05	N 5.76	S 13.20
Found	C 54.34	H 7.05	N 5.79	S 13.23

N-(2-Methoxy-1-methylethyl)-N-[2-(4-tolylsulfonamido) propyl]-4-toluenesulfonamide (**7**, diastereomers), mixt. with **5 h M**/**6 h M**: ^{1}H-NMR δ: 0.70 (d, J = 6.8, $Me_{centr.}$), 0.76 (d, J = 6.8, $Me_{centr.}$), 1.14 (d, J = 6 – 7, $Me_{periph.}$), 1.19 (d, J = 6 – 7, $Me_{periph.}$), 3.10 (s, OMe), 3.31 (s, OMe), 6.00 (d br, J = 6, NH), 6.22 (d br, J = 3, NH).

Run 4. ^{1}H-NMR (300 MHz) analysis.

Run 5. 4.33 g (89 %, chr.) of a 27 : 62 mixt. of **5 h M** and **6 h M**. Oil.

N-(2-Methoxypropyl)-4-toluenesulfonamide (**6 h M**), contamin. with **5 h M**: IR (cm^{-1}): 3260, 1331, 1162, 1090. ^{1}H-NMR δ: 1.07 (d, J = 6.3, CMe), 2.42 (s, Me of Tos), 2.77 (ddd, J = 13.0/7.8/3.8, 1 H of NCH_2), 3.08 (ddd, J = 13.0/4.0/8.0, 1 H of NCH_2), 3.24 (s, OMe), 3.40 (m_c, OCH), 5.13 (s br, NH), 7.32 (d, J = 8.5, m-H, 7.74 (d, J = 8.5, o-H).

$C_{11}H_{17}NO_3S$
(243.3)

Calcd.	C 54.37	H 7.05	N 5.76	S 13.20
Found	C 54.19	H 7.27	N 5.84	S 13.43

Run 6. Analogous to run 4.

Run 7. 3.32 g (86 %. chr.) of a 8 : 78 mixt. of **5 d M** and **6 d M**. Oil.

N-(2-Methoxy-1-methylethyl)benzamide (**5 d M**), in mixt. with **6 d M**. ^{1}H-NMR δ: 1.26 (d, J = 6.8, CMe), 3.34 (s, OMe), 3.40 – 3.46 (m, $NCHCH_2O$), other signals hidden (**6 d M**).

N-(2-Methoxypropyl)benzamide (**6 d M**), contamin. with **5 h M**. Oil. IR (cm^{-1}): 3330, 1644, 1540, 1150. ^{1}H-NMR δ: 1.14 (d, J = 6.5. CMe), 3.24 – 3.33 (m, 1 H of NCH_2), 3.32 (s, OMe), 3.47 – 3.58 (m, OCH), 3.61 – 3.71 (m, 1 H of NCH_2), 7.05 (t br, J = 7, NH), 7.37 – 7.53 (m, m-H/o-H), 7.83 (d, J = 8.5, o-H).

$C_{11}H_{15}NO_2$	Calcd.	C 68.37	H 7.82	N 7.25
(193.2)	Found	C 68.27	H 8.14	N 7.26

Run 8. 2.39 g (69 %, chr.) of a 9 : 91 mixt. of **5 e M** and **6 e M**. Oil.

N-(2-Methoxy-1-methylethyl)pivaloylamide (**5 e M**), in mixt. with **6 e M**. ^{1}H-NMR δ: 1.19 (s, tBu), 1.21 (d, J = 6, CMe), 3.36 (s, OMe), other signals hidden (**6 e M**).

N-(2-Methoxypropyl)pivalamide (**6 e M**), contamin. with **5 e M**. Oil. IR (cm^{-1}): 3265, 1643, 1537, 1102. ^{1}H-NMR δ: 1.13 (d, J = 6.6, CMe), 1.21 (s, tBu), 3.03 – 3.13 (m, 1 H of NCH_2), 3.35 (s, OMe), 3.40 – 3.57 (m, OCH/1 H of NCH_2), 6.09 (s br, NH).

$C_9H_{19}NO_2$	Calcd.	C 62.39	H 11.05	N 8.08
(173.3)	Found	C 62.11	H 11.35	N 7.78

Run 9. 2.60 g (76 %, chr.) of a 12 : 88 mixt. of **5 f M** and **6 f M**. Oil.

N-(2-Methoxy-1-methylethyl)-3,3-dimethylacrylamide (**5 f M**), in mixt. with **6 f M**. ^{1}H-NMR δ: 1.19 (d, J = 6.9, CMe), 1.89 (s, $C=CMe_{cis}$), 2.09 (s, $C=CMe_{tr}$), 3.35 (s, OMe), 5.60 (s br, C = CH), other signals hidden (**6 f M**).

N-(2-Methoxypropyl)-3,3-dimethylacrylamide (**6 f M**), contamin. with **5 f M**. Oil. IR (cm^{-1}): 3310, 1669, 1638, 1531, 1095. ^{1}H-NMR δ: 1.15 (d, J = 6.4, CMe), 1.83 (d, J = 1.1, $C=CMe_{cis}$), 2.17 (d, J = 1.1, $C=CMe_{tr}$), 3.07 – 3.20 (m, 1 H of NCH_2), 3.34 (s, OMe), 3.36 – 3.57 (m, OCH/1 H of NCH_2), 5.63 (m_c, C = CH), 6.19 (t br, J = 7, NH).

$C_9H_{17}NO_2$	Calcd.	C 63.13	H 10.01	N 8.18
(171.2)	Found	C 63.09	H 10.02	N 8.23

Run 10. 3.55 g (81 %, chr.) of a 9 : 72 mixt. of **5 g M** and **6 g M**. Oil.

N-(2-Methoxy-1-methylethyl)cinnamamide (**5 g M**), in mixt. with **6 g M**. ^{1}H-NMR δ: 1.27 (d, J = 6.8, CMe) 3.33 (s, OMe), 6.63 (d, J = 17.4, COC = CH), other signals hidden (**6 g M**).

N-(2-Methoxypropyl)cinnamamide (**6 g M**), contamin. with **5 g M**. Oil. IR (cm^{-1}): 3300, 1659, 1622, 1550, 1100. ^{1}H-NMR δ: 1.16 (d, J = 6.2, CMe), 3.33 (s, OMe), 3.27 – 3.39 (m, 1 H of NCH_2), 3.48 – 3.67 (m, OCH/1 H of NCH_2), 6.66 (d, J = 17.3, COC = CH), 7.22 (t, J = 7, NH), 7.25 – 7.33 (m, m-H/p-H), 7.43 – 7.49 (m, o-H), 7.68 (d, J = 17.3, COCH).

$C_{13}H_{17}NO_2$	Calcd.	C 71.30	H 7.82	N 6.40
(219.3)	Found	C 71.10	H 7.91	N 6.59

Run 11. Chr. (30 × 3, dichl./EtOAc/MeOH 50 : 10 : 1) gave 112 mg (5 %) of **5 d B**, 262 mg of a mixt. and 833 mg (51 %) of **6 d H**. The mixt. consist. of 110 mg (7 %) of **4 m**, 150 mg (6 %) of **6 d E** and 2 mg (0.1 %) of **3 m**.

N-(1-Methyl-2-tert-butoxyethyl)benzamide (**5 d B**). Oil. IR (cm^{-1}): 3280, 1641, 1538, 1100. ^{1}H-NMR δ: 1.19 (s, tBu), 1.28 (d, J = 6.8, Me), 3.44 (m_c, NCH/1 H of OCH_2), 4.30 (m_c, 1 H of OCH_2), 6.48 (s br, NH), 7.34 – 7.48 (m, m-H/p-H), 7.71 – 7.81 (o-H).

$C_{14}H_{21}NO_2$	Calcd.	C 76.66	H 9.65	N 6.39
(219.3)	Found	C 76.36	H 9.54	N 6.21

N-(2-tert-Butoxypropyl)benzamide (**6 d B**), in mixt. with **4 m** and **3 m**. Oil. ^{1}H-NMR δ: 1.16 (d, J = 6.8, Me), 1.19 (s, tBu), 3.25 (m_c, 1 H of NCH_2), 3.51 (m_c, 1 H of NCH_2), 3.91 (m_c, OCH), 6.95 (t br, J = 5, NH), 7.33 – 7.41 (m, m-H/p-H), 7.80 (m_c, o-H).

N-(2-Hydroxypropyl)benzamide (**6 d H**). Mp. 89 – 92 °C (lit. [25] 92 – 93 °C). ^{1}H-NMR δ: 1.21 (d, J = 6.4, Me), 3.28 (ddd, J = 13.8/7.6/5.2, 1 NCH), 3.63 (ddd, J = 13.8/3.2/6.3, 1 NCH), 3.81 (s, OH), 4.01 (m_c, OCH), 7.02 (t, J = 5, NH), 7.33 – 7.51 (m, m-H/p-H), 7.77 (m_c, o-H).

Reactions of 2 d with potassium iodide

1.943 g (12 mmol) of KI and 1.641 g (10 mmol) of **2 d** in 200 ml of THF were heated at reflux for 1 d. Usual workup. Chr. (33 × 3, dichl./EtOAc 9 : 1) provided 336 mg (20 %) of **2 d** and 1.067 g of a mixt. of 925 mg (56 %) of **3 m** and 142 mg (9 %) of **4 m**. A second run (10 mmol of **2 d**, 50 mmol of KI) provided 1.579 g of a mixt. of 1.393 g (84 %) of **3 m** and 186 mg (11 %) of **4 m**. **3 m** and **4 m** are described in ref. [20]. Our ^{1}H-NMR data deviate as follows. **3 m** δ: 1.37 (d, J = 6.8, Me), 3.94 (t, J = 7.8, 1 OCH), 4.38 (m_c, NCH), 4.50 (dd, J = 7.8/10.3, 1 OCH), 7.35 – 7.50 (m, m-H/p-H), 7.94 (d, J = 8.3, o-H). **4 m** δ: 1.43 (d, J = 6.8, Me), 3.61 (dd, J = 14.8/8.0, 1 NCH), 4.14 (dd, J = 14.8/9.1, 1 NCH), 4.85 (m_c, OCH), 7.35 – 7.50 (m, m-H/p-H), 7.94 (d, J = 8.3, o-H).

General procedure for runs of Table 3

For the carbanion technique see ref. [9 a] and ref. [22] (BuLi). In runs 12 – 17, 22 – 23 sodium, naphthalene and TrH were stirred in 100 ml of THF for 1 d. A solution of DiH in THF was dropwise added in runs 12 – 16 until colour change (red/yellow-brown) giving the amount of DiH from the residual volume; the amount of **2** was adjusted. Usual workup. Chr. (100 × 3.5, dichl.) removed hydrocarbons. Further workup is given. Carbanions in runs 18 – 21, 24 – 26 were generated by BuLi in 100 – 200 ml of THF; **2** was added in 5 – 20 ml of THF.

Run 12. Continued chr. yielded 3.40 g (85 %) of a mixt. of 1.92 g (48 %) of **14 b** and 1.48 g (37 %) of **17 b**.
Mixt. of **14 b** and **17 b**. IR (cm^{-1}): 3330, 1605, 1595.

$C_{24}H_{21}N_3O_3$	Calcd.	C 72.17	H 5.30	N 10.52
(399.5)	Found	C 72.07	H 5.35	N 10.63

3,3-Diphenyl-5-methyl-2-(4-nitrobenzoylimino)pyrrolidine (**14 b**).
^{1}H-NMR δ: 1.42 (d, J = 6.3, Me), 2.36 (dd, J = 9.4/12.9, 4-H_{cis}), 3.01 (dd, J = 5.5/12.9, 4-H_{tr}), 4.06 (m_c, 5-H), 7.23 – 7.48 (m, CPh_2), 8.15 (m, o-H), 8.29 – 8.34 (m, m-H), 10.62 (s br, NH).

3,3-Diphenyl-4-methyl-2-(4-nitrobenzoylimino)pyrrolidine (**17 b**).
^{1}H-NMR δ: 0.87 (d, J = 6.9, Me), 3.26 (dd, J = 4.5/10.6, 5-H_{cis}), 3.46 (m_c, 4-H), 3.85 (dd, J = 6.9/10.6, 5-H_{tr}), 6.98 – 7.02 (m, o-H of Ph_{cis}), 7.23 – 7.48 (m, m-H/p-H of CPh_2), 7.64 – 7.68 (m, o-H of Ph_{tr}), 8.15 – 8.21 (m, o-H of COAr), 8.29 – 8.34 (m, m-H of COAr).

Run 13. Continued chr. yielded 0.98 g (15 %) of **14 c**, 0.92 g (14 %) of **17 c**, (EtOAc) 2.09 g (32 %) of **16 c** and 2.36 g (36 %) of **10 c**.

N-(3-Cyano-3,3-diphenyl-1-methylpropyl)-4-phenylbenzamide (**10 c**).
Mp. 185 – 187 °C. IR (cm^{-1}): 3340, 2240, 1634, 1533. ^{1}H-NMR δ: 1.35 (d, J = 6.6, Me), 2.62 (dd, J = 4.6/14.4, 1 H of $NCCH_2$), 2.95 (dd, J = 8.7/14.4, 1 H of $NCCH_2$), 4.13 – 4.28 (m, NCH), 6.08 (d br, J = 8.1, NH), 7.25 – 7.49 (m, CPh_2 and m-H/p-H of COArPh), 7.57 – 7.61 (m, o-H of COArPh/m-H of COAr), 7.72 – 7.75 (m, o-H of COAr).

$C_{30}H_{26}N_2O$	Calcd.	C 83.70	H 6.08	N 6.51
(430.6)	Found	C 83.42	H 6.37	N 6.29

N-(3-Cyano-3,3-diphenyl-2-methylpropyl)-4-phenylbenzamide (**16 c**).
Mp. 196 – 197 °C. IR (cm^{-1}): 3405, 2240, 1662, 1538. ^{1}H-NMR δ: 1.25 (d, J = 6.4, Me), 3.27 – 3.39 (m, NCH_2), 3.81 – 3.88 (m, NCCH), 6.31 (s br, NH), 7.35 – 7.52 (m, m-H/p-H of CPh_2 and COArPh), 7.54 – 7.62 (m, o-H of COArPh/m – H of COAr), 7.70 – 7.75 (m, o-H of COAr/1 o-H of each Ph in CPh_2).

$C_{30}H_{26}N_2O$	Calcd.	C 83.70	H 6.08	N 6.51
(430.6)	Found	C 83.48	H 6.09	N 6.44

3,3-Diphenyl-5-methyl-2-(4-phenylbenzoylimino)pyrrolidine (**14 c**).
Mp. 214 – 215 °C. IR (cm^{-1}): 3315, 1605, 1581. ^{1}H-NMR δ: 1.39 (d, J = 6.2, Me), 2.33 (dd, J = 9.4/12.9, 4-H_{cis}), 2.97 (dd, J = 5.7/12.9, 4-H_{tr}), 3.99 (m_c, 5-H), 7.23 – 7.76 (m, 17 arom. H), 8.25 – 8.32 (m, o-H of COAr), 10.61 (s br, NH).

$C_{30}H_{26}N_2O$	Calcd.	C 83.70	H 6.08	N 6.51
(430.6)	Found	C 83.83	H 6.22	N 6.44

3,3-Diphenyl-4-methyl-2-(4-phenylbenzoylimino)pyrrolidine (**17 c**).
Mp. 157 – 159 °C. IR (cm^{-1}): 3300, 1611, 1584. ^{1}H-NMR δ: 0.83 (d, J = 7.0, Me), 3.17 (dd, J = 7.8/10.5, 5-H_{cis}), 3.38 (m_c, 4-H), 3.76 (dd, J = 4.5/10.5, 5-H_{tr}), 7.01 – 7.05 (m, o-H of Ph_{cis}), 7.19 – 7.44 (m, 11 H), 7.56 – 7.76 (m, o-H of COArPh/m-H of COAr), 8.26 – 8.30 (m, o-H of COAr), 10.74 (s br, NH).

$C_{30}H_{26}N_2O$	Calcd.	C 83.70	H 6.08	N 6.51
(430.6)	Found	C 83.57	H 6.22	N 6.55

Run 14. Continued chr. gave 0.56 g (16 %) of **14 d**, 0.56 g (16 %) of **17 d** and (EtOAc) 2.19 g of a mixt. whose chr. (60 × 3.5, EtOAc) gave 0.83 g (24 %) of **16 d** and 1.08 g (31 %) of **10 d**.

N-(3-Cyano-3,3-diphenyl-1-methylpropyl)benzamide (**10 d**).
Mp. 140 – 142 °C. IR (cm^{-1}): 3300, 2240, 1634, 1555. ^{1}H-NMR δ: 1.33 (d, J = 6.6, Me), 2.58 (dd, J = 4.7/14.4, 1 H of $NCCH_2$), 2.92 (dd, J = 8.7/14.4, 1 H of $NCCH_2$), 4.14 – 4.32 (m, NCH), 6.09 (d br, J = 8.0, NH), 7.27 – 7.48 (m, 13 arom. H), 7.63 – 7.67 (m, o-H of COPh).

$C_{24}H_{22}N_2O$	Calcd.	C 81.31	H 6.26	N 7.90
(354.5)	Found	C 81.17	H 6.36	N 7.78

N-(3-Cyano-3,3-diphenyl-2-methylpropyl)benzamide (**16 d**).
Mp. 154 – 155 °C. IR: 3420, 2245, 1668, 1535. ^{1}H-NMR δ: 1.13 (d, J = 6.4, Me), 3.22 – 3.24 (m, NCH_2), 3.79 – 3.86 (m, NCCH), 6.21 (s, NH), 7.23 – 7.52 (m, 11 H), 7.63 – 7.78 (m, o-H of COPh/1 o-H of 2 Ph in CPh_2).

$C_{24}H_{22}N_2O$	Calcd.	C 81.31	H 6.26	N 7.90
(354.5)	Found	C 81.44	H 6.24	N 7.65

3,3-Diphenyl-5-methyl-2-benzoyliminopyrrolidine (**14 d**).
Mp. 135 – 137 °C. IR (cm^{-1}): 3280, 1617, 1581. ^{1}H-NMR δ: 1.34 (d, J = 6.3, Me), 2.29 (dd, J = 9.4/12.8, 4-Hc_{is}), 2.94 (dd, J = 5.7/12.8, 4-H_{tr}), 3.95 (m_c, 5-H), 7.19 – 7.47 (m, 13 H), 8.21 – 8.23 (m, o-H of COPh), 10.58 (s br, NH).

$C_{24}H_{22}N_2O$	Calcd.	C 81.31	H 6.26	N 7.90
(354.5)	Found	C 81.25	H 6.40	N 7.93

3,3-Diphenyl-4-methyl-2-benzoyliminopyrrolidine (**17 d**).
Mp. 210 – 211 °C. IR (cm^{-1}): 3305, 1615, 1583. ^{1}H-NMR δ: 0.83 (d, J = 7.0, Me), 3.17 (dd, 4.5/10.5, 5-H_{cis}), 3.38 (m_c, 4-H), 3.76 (dd, J = 4.5/10.5, 5-H_{tr}), 7.00 – 7.03 (m, o-H of Ph_{cis}), 7.23 – 7.52 (m, 9 H), 7.61 – 7.70 (m, o-H of Ph_{tr}), 8.21 (d, J = 7.0, o-H of COPh), 10.70 (s br, NH).

$C_{24}H_{22}N_2O$	Calcd.	C 81.31	H 6.26	N 7.90
(354.5)	Found	C 81.27	H 6.28	N 7.61

Run 15. Continued chr. provided a mixt. of 2.76 g (55 %) of **10 e** and 1.91 g (38 %) of **16 e**.

Mixt. of **10 e** and **16 e**. IR (cm^{-1}): 3340, 2240, 1635, 1532.

$C_{22}H_{26}N_2O$	Calcd.	C 79.00	H 7.34	N 8.38
(334.5)	Found	C 79.02	H 7.88	N 8.50

N-(3-Cyano-3,3-diphenyl-1-methylpropyl)pivalamide (**10 e**).
^{1}H-NMR δ: 1.15 (s, tBu), 1.21 (d, J = 6.6, Me), 2.47 (dd, J = 4.9/14.4, 1 H of $NCCH_2$), 2.80 (dd, J = 8.5/14.4, 1 H of $NCCH_2$), 3.96 (m_c, NCH), 5.62 (d br, J = 7.8, NH), 7.23 – 7.69 (m, CPh_2).

N-(3-Cyano-3,3-diphenyl-2-methylpropyl)pivalamide (**16 e**).
^{1}H-NMR δ: 1.03 (d, J = 6.7, Me), 1.12 (s, tBu), 2.98 (ddd, J = 8.7/13.5/6.1, 1 H of NCH_2), 3.15 – 3.28 (m, NCCH), 3.65 (ddd, J = 5.9/13.5/4.5, 1 H of NCH_2), 5.93 (s br, NH), 7.23 – 7.69 (m, CPh_2).

Run 16. Continued chr. (EtOAc) gave 3.79 g of a mixt. consist. of 1.50 g (38 %) of **10 i**, 0.39 g (10 %) of **16 i** and 1.89 g (48 %) of **12 i**.

Run 17. Chr. (33 × 3, toluene) gave hydrocarbons, DiH, (toluene/EtOAc 10 : 1) 1.01 g of mixt. **a**, 880 mg of **10 i** and 241 mg of mixt. **b** Mixt. **a** consist. of 484 mg of **10 i**, 159 mg (6 %) of **16 i** and 366 mg (13 %) of **12 i**. Mixt. **b** contained (int. stand.) 158 mg (total 1.522 g corresp. to 54 %) of **10 i**.

Run 18. Chr. (35 × 4, toluene) gave 128 mg of DiH, 107 mg of benzophenone, (toluene/EtOAc 4 : 1) 589 mg of **12 i**, 947 mg of mixt. **a** and 152 mg of mixt. **b**. Mixt. **a** was 189 mg (total 778 mg corresp. to 40 %) of **12 i** and 758 mg of **10 i**. Mixt. **b** was 134 mg (total 895 mg corresp. to 46 %) of **10 i** and 15 mg (1.5 %) of **16 i**.

N-(3-Cyano-3,3-diphenyl-1-methylpropyl)benzenesulfonamide (**10 i**).
Mp. 85 – 88 °C. IR (cm^{-1}): 3270, 2245, 1340, 1169. ^{1}H-NMR δ: 1.15 (d, J = 6.4, Me), 2.48 (dd, J = 7.6/14.3, 1 H of $NCCH_2$), 2.86 (dd, J = 5.4/14.3, 1 H of $NCCH_2$), 3.30 (m_c, NCH), 4.45 (d, J = 7.2, NH), 7.16 – 7.40 (m, CPh_2), 7.47 (m_c, m-H of SO_2Ph), 7.54 (m_c, p-H of SO_2Ph), 7.70 (m_c, o-H of SO_2Ph).

$C_{23}H_{22}N_2O_2S$	Calcd.	C 70.74	H 5.68	N 7.17
(390.5)	Found	C 70.70	H 5.80	N 7.22

3,3-Diphenyl-2-imino-5-methyl-1-phenylsulfonylpyrrolidine (**12 i**).
Mp. 143 – 145 °C. IR (cm^{-1}): 3320, 1665, 1350, 1175. ^{1}H-NMR ($CDCl_3$ + drop of CF_3CO_2H) δ: 1.51 (d, J = 6.1, Me), 2.35 (dd, J = 13.1/6.4, 4-H_{tr}), 2.94 (dd, J = 13.1/6.2, 4-H_{cis}), 4.03 (m_c, 5-H), 5.83 (s vbr, NH), 7.02 (m_c, m-H of CPh_2), 7.15 (m_c, p-H of CPh_2), 7.25 (d, J = 8.4, o-H of CPh_2), 7.39 (m_c, m-H of SO_2Ph), 7.56 (m_c, p-H of SO_2Ph), 7.83 (d, J = 8.4, o-H of SO_2Ph). ^{1}H-NMR of E – 12 i δ: 1.48 (d, Me), 2.45 (dd, 4-H_{tr}), 2.94 (dd, 4-H_{cis}), 4.20 (m_c, 5-H), 7.56 (d, o-H of SO_2Ph), NH not recognizable. ^{1}H-NMR of Z-**12 i** δ: 1.56 (d, Me), 2.21 (dd, 4-H_{tr}), 2.94 (dd, 4-H_{cis}), 3.82 (m_c, 5-H), 8.03 (m_c, o-H of SO_2Ph), 9.38 (s, NH).

$C_{23}H_{22}N_2O_2S$	Calcd.	C 70.74	H 5.68	N 7.17
(390.5)	Found	C 70.36	H 5.71	N 7.15

N-(3-Cyano-3,3-diphenyl-2-methylpropyl)benzenesulfonamide (**16 i**).
In mixt. with **10 i**. ^{1}H-NMR δ: 1.13 (d, J = 7.6, Me), 2.75 – 2.90 (m, NCCH), 3.03 – 3.18 (m, NCH_2), 4.48 (t br, J = 6.6, NH), 7.68 (m_c, o-H of SO_2Ph), other signals hidden (**10 i**).

Run 19. Chr. (43 × 4, toluene) yielded hydrocarbons, 3.89 g of mixt. **a** and 219 mg of mixt. **b**. 2.906 g of **18 i** were isolated from mixt. **a** by suction and subsequent washing with methanol/ether (1 : 1). Mother liquor and washings yielded (second chr. 15 × 3, toluene/ EtOAc 9 : 1) some anthraquinone and 418 mg (total 3.324 g corresp. to 88 %) of **18 i**. Mixt. **b** yielded (same technique of chr.) 9 mg (0.2 %) of **21 i** and 164 mg of a mixt. consist. of 57 mg (2 %) of **19 i** and 107 mg (3 %) of **20 i**. A crystal of **19 i** was manually picked out.

N-[2-(9, 10-Dihydro-9-anthryl)-1-methylethyl]benzenesulfonamide (**18 i**).
Mp. 136 – 139 °C. IR (cm^{-1}): 3370, 1330, 1160. ^{1}H-NMR δ: 1.01 (d, J = 6.4, Me), 1.54 (m_c, $NCCH_2$), 3.33 (m_c, NCH), 3.74 (d, J = 18.3, 10-$H_{pseudo\ eq}$), 3.84 (d, J = 18.3, 10-$H_{pseudo\ ax}$), 5.26 (s br, NH), 7.11 – 7.56 (m, 11 H), 7.72 – 7.77 (m, o-H).

$C_{23}H_{23}NO_2S$	Calcd.	C 73.18	H 6.14	N 3.71
(377.5)	Found	C 73.16	H 6.22	N 3.71

9,10-Bis-(2-phenylsulfonamidopropyl)-9, 10-dihydroanthracene (**19 i**).

Mp. 85 – 88 °C. IR (cm^{-1}): 3290, 1330, 1165. ^{1}H-NMR δ: 1.00 (d, J = 7.6, Me), 1.55 – 1.77 (m, $NCCH_2$), 3.54 (m_c, NCH), 3.99 (t, J = 7.0, 9-H/10-H), 4.64 (s, NH), 7.12 – 7.61 (m, 14 H), 7.78 – 7.82 (m, o-H).

$C_{32}H_{34}N_2O_4S_2$ Calcd. 574.1958 Found 574.1956 (MS)

N-[2-(9,10-Dihydro-10-hydroxy-9-anthryl)-1-methylethyl] benzenesulfonamide (**20 i**).

In mixt. with **19 i**. ^{1}H-NMR δ: 0.97 (d, J = 6.5, Me), 1.82 – 1.93 (m, 1 NCCH), 2.04 – 2.13 (m, 1 NCCH), 3.39 (m_c, NCH), 4.02 (t, J = 7.5, 9-H), 4.66 (d br, J = 8.8, NH), 5.87 (s, 10-H), 7.16 – 7.60 (m, 11 H), 7.69 – 7.73 (m, o-H), 8.37 (s, OH).

N-2-(9-Anthryl)-1-methylethyl benzenesulfonamide (**21 i**).

Impure. ^{1}H-NMR δ: 1.22 (d, J = 6.2, Me), 3.59 – 3.88 (m, $NCHCH_2$), 4.65 (d br, J = 6.8, NH), 7.07 – 7.59 (m, 7 arom. H), 7.86 – 7.97 (m, 4-H/5-H/o-H), 8.08 – 8.12 (m, 1-H/8-H), 8.28 (s, 10-H).

Run 20. Chr. (40 × 4, toluene/EtOAc 10 : 1) gave fore-runs of AH_2 and anthraquinone, 2.398 g of **18 e**, 172 mg of mixt. **a**, 84 mg of mixt. **b** and 144 mg of an 1 : 1 mixt. of **19 e** and **23 e** (3 % each). Mixt. **a** consisted of 155 mg of **18 e** and 17 mg (0.5 %) of **22 e**, mixt. **b** of 64 mg (total 2.772 g corresp. to 86 %) of **18 e** and 20 mg (0.6 %) of **24 e**.

N-2-(9,10-Dihydro-9-anthryl)-1-methylethyl pivalamide (**18 e**).

Mp. 169 – 170 °C. IR (cm^{-1}): 3330, 1635, 1535. ^{1}H-NMR δ: 1.10 (d, J = 6.5, Me), 1.17 (s, tBu), 1.72 (m_c, $NCCH_2$), 3.85 (d, J = 18.2, 10-$H_{pseudo\ eq}$), 4.00 (m_c, 9-H/NCH), 4.09 (d, J = 18.2, 10-$H_{pseudo\ ax}$), 5.33 (d br, J = 7.1, NH), 7.15 – 7.33 (m, 8 H).

$C_{22}H_{27}NO$	Calcd.	C 82.20	H 8.47	N 4.36
(321.5)	Found	C 82.42	H 6.47	N 4.42

N-[2-(9,10-Dihydro-9-anthryl)propyl]pivalamide (**22 e**).

In mixt. with **18 e**. ^{1}H-NMR δ: 0.88 (d, J = 7.5, Me), 1.01 (s, tBu), ca. 1.7 (m_c, NCCH), 3.13 (m_c, 1 H of NCH_2), 3.26 (m_c, 1 H of NCH_2), 3.83 (d, J = 18.2, 10-$H_{pseudo\ eq}$), ca 4.0 (9-H), 4.09 (d, J = 18.2, 10-$H_{pseudo\ ax}$), 7.40 (d, J = 8.0, 1-H), other signals hidden (**22 e**).

trans-N-[2-(9,10-Dihydro-10-hydroxy-9-anthryl)propyl] pivalamide (**24 e**).

Mixt. with **18 e**. ^{1}H-NMR δ: 0.49 (d, J = 6.9, Me), 0.98 (s, tBu), 4.29 (d, J = 2.7, 9-H), 5.80 (t, J = 7, NH), 5.89 (s, 10-H).

9,10-Bis-(2-pivalamidopropyl)-9,10-dihydroanthracene (**19 e**) *and 9-(2-pivalamidopropyl)-10-(1-methyl-2-pivalamidoethyl)-9,10-dihydroanthracene* (**23 e**).

^{1}H-NMR δ: 4 s (tBu) 1.07, 1.08, 1.10, 1.24; 4 d (J = 6.5 – 6.6) 1.03, 1.15, 1.21, 1.24; 1 d (J = 10.0) 3.55; 3 d (br, J = 8 – 9) 5.42, 5.71, 5.95; 1 t (br, J = 6, NH) 5.82.

$C_{30}H_{42}N_2O_2$	Calcd.	C 77.91	H 9.15	N 6.06
(462.7)	Found	C 77.70	H 8.87	N 6.11

Run 21. Chr. (40 × 4, toluene) provided 551 mg of XH and 2.362 g (82 %) of **25** [38]. Toluene/EtOAc gave 42 mg of **2 d**, 14 mg of a 1 : 1 mixt. of **2 d** and **26 d**, 455 mg of **26 d**, 33 mg of mixt. **a** and 28 mg of mixt. **b**. Mixt. **a** consisted of 23 mg (total 485 mg corresp. to 14 %) of **26 d** and 10 mg of **27 d**. Mixt. **b** contained (int. stand.) 8 mg (total 18 mg corresp. to 0.5 %) of **27 d** besides unknown products.

N-[2-(9-Xanthyl)-1-methylethyl]benzamide (**26 d**).

Mp. 181 – 182 °C. IR (cm^{-1}): 3315, 1670, 1525. ^{1}H-NMR δ: 1.16 (d, J = 6.5, Me), 1.92 (m_c, $NCCH_2$, 4.10 (t br, J = 5.7, 9-H), 4.27 (m_c, NCH), 5.79 (d br, J = 8.5, NH), 7.03 – 7.54 (m, 13 H), 7.64 (m_c, o-H).

$C_{33}H_{21}NO_2$	Calcd.	C 80.44	H 6.16	N 4.08
(343.4)	Found	C 80.52	H 6.35	N 3.98

N-[2-(9-Xanthyl)propyl]benzamide (**27 d**), in mixt. with **26 d**. ^{1}H-NMR δ: 0.87 (d, J = 7.0, Me), 2.16 (m_c, NCCH), 3.22 (m_c, 1 H of NCH_2), 3.35 (m_c, 1 H of NCH_2), 4.06 (d, J ca. 3.9, 9-H), 5.93 (t br, J = 6, NH), 7.56 (m_c, o-H of COPh), other signals hidden (**26 d**).

Run 22. Chr. (15 × 7, petr. ether) gave hydrocarbons and (EtOAc) 3.91 g of a mixt. whose chr. (105 3.5, dichl.) gave 3.56 g (81 %) of **28 c**.

N-(1-Methyl-3,3,3-triphenylpropyl)-4-phenylbenzamide (**28 c**).

Mp. 251 – 254 °C. IR (cm^{-1}): 3305, 1627, 1543. ^{1}H-NMR δ: 1.29 (d, J = 6.4, Me), 2.82 – 2.97 (m, $NCCH_2$), 3.92 – 4.09 (m, NCH), 5.58 (d br, J = 6.9, NH), 7.09 – 7.60 (m, 24 H).

$C_{35}H_{31}NO$	Calcd.	C 87.31	H 6.49	N 2.91
(485.6)	Found	C 87.43	H 6.70	N 3.08

Run 23. Twofold chr. as in run 22 yielded 3.65 g (90 %) of **28 d**.

N-(1-Methyl-3,3,3-triphenylpropyl)benzamide (**28 d**).

Mp. 200 – 202 °C. IR (cm^{-1}): 3280, 1626, 1537. ^{1}H-NMR δ: 1.27 (d, 6.4, Me), 2.83 (dd, J = 8.4/14.8, 1 NCCH), 2.94 (dd, J = 3.4/14.8, 1 NCCH), 3.92 – 4.13 (m, NCH), 5.51 (d br, J = 6.9, NH), 7.07 – 7.38 (m, 20 H).

$C_{29}H_{27}NO$	Calcd.	C 86.01	H 6.71	N 3.41
(405.5)	Found	C 86.08	H 6.92	N 3.47

Run 24. Chr. (15 × 3, petroleum ether) gave 2.942 g TrH and (EtOAc) a mixt. whose chr. (45 × 3.5, dichl.) yielded 725 mg of TrH. Elution with dichl./EtOAc (10 : 1) provided 3.195 g (83 %) of **28 e**.

N-(1-Methyl-3,3,3-triphenylpropyl)pivalamide (**28 e**).

Mp. 176 – 177 °C. IR (cm^{-1}): 3330, 1628, 1533. ^{1}H-NMR δ: 0.86 (s, tBu), 1.08 (d, J = 6.4, Me), 2.73 (dd, J = 3.8/14.7, 1 NCCH), 2.84 (dd, J = 8.3/14.7, 1 NCCH), 3.68 – 3.85 (m, NCH), 5.19 (d, J = 6.6, NH), 7.13 – 7.38 (m, CPh_3).

$C_{27}H_{31}NO$	Calcd.	C 84.11	H 8.10	N 3.63
(385.6)	Found	C 84.26	H 8.19	N 3.61

Run 25. Chr. (45 × 3.5, dichl.) gave TrH and 2.170 g (95 %) of **28 h**.

N-(1-Methyl-3,3,3-triphenylpropyl)-4-toluenesulfonamide (**28 h**).

Mp. 152 – 154 °C. IR (cm^{-1}): 3250, 1332, 1162. ^{1}H-NMR δ: 0.71 (d, J = 6.4, Me), 2.42 (s, Me of Tos), 2.61 (ss, J = 6.2/14.4, 1 H of $NCCH_2$), 2.94 (dd, J = 5.0/14.4, 1 H of $NCCH_2$), 3.21 (m_c, NCH), 4.24 (d br, J = 6.3, NH), 7.10 – 7.33 (m, CPh_3/m-H), 7.51 (m_c, o-H).

$C_{29}H_{29}NO_2S$	Calcd.	C 76.45	H 6.42	N 3.07
(455.6)	Found	C 76.41	H 6.51	N 3.21

Run 26. Chr. (15 × 3, petroleum ether) removed 3.260 g of TrH. Elution with EtOAc provided a mixt. whose chr. (45 × 3.5, dichl.) yielded 70 mg of TrH and 4.280 g (97 %) of **28 i**.

N-(1-Methyl-3,3,3-triphenylpropyl)benzenesulfonamide (**28 i**).

Mp. 113 – 115 °C. IR (cm^{-1}): 3240, 1330, 1165, 1159. ^{1}H-NMR δ: 0.75 (d, J = 6.4, Me), 2.63 (dd, J = 5.3/14.4, 1 H of $NCCH_2$), 2.94 (dd, J = 5.3/14.4, 1 H of $NCCH_2$), 3.23 (m_c, NCH), 4.21 (d br, J = 6.2, NH), 7.13 – 7.33 (m, CPh_3), 7.38 – 7.48 (m, m-H of SO_2Ph), 7.48 – 7.57 (m, p-H of SO_2Ph), 7.59 – 7.66 (m, o-H of SO_2Ph).

$C_{28}H_{27}NO_2S$	Calcd.	C 76.16	H 6.16	N 3.17
(441.6)	Found	C 76.21	H 6.23	N 3.30

Reaction of 2 h with phenylmagnesium bromide

A solution of 2.11 g (10 mmol) of **2 h** in 100 ml of THF was added dropwise (30 min) to a boiling solution prepared from 1.20 g (50 mmol) of magnesium turnings and 1.57 g (10 mmol) of bromobenzene in 100 ml of THF. Heating at reflux was continued for 5 h. After cooling to room temp. the mixt. was poured onto ice. Five extractions with 50 ml of dichl. each yielded 2.46 g (82 %) of **29 h**.

N-(1-Methyl-2-phenylethyl)-4-toluenesulfonamide (**29 h**).

Oil. IR (cm^{-1}): 3290, 1330, 1165. ^{1}H-NMR δ: 1.06 (d, J = 6.6, Me), 2.39 (s, Me of Tos), 2.61 (dd, J = 6.3/13.5, 1 H of $NCCH_2$),h 2.71 (dd, J = 7.1/13.5, 1 H of $NCCH_2$), 3.41 – 3.58 (m, NCH), 4.93 (d br, J = 7.5, NH), 6.98 – 7.40 (m, 7 H), 7.61 – 7.84 (m, o-H of Tos).

$C_{16}H_{19}NO_2S$	Calcd.	C 66.41	H 6.62	N 4.84
(289.4)	Found	C 66.24	H 6.61	N 4.94

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Address for correspondence:

Prof. Dr. H. Stamm
Universität Heidelberg, Pharmazeutisch-Chemisches Institut
Im Neuenheimer Feld 346
W-6900 Heidelberg, Bundesrepublik Deutschland