product was purified via recrystallization from ethyl acetate. Pure **18** was thereby obtained as a colorless microcrystalline solid: mp 195–196 °C; IR (KBr) 1710 (s), 1600 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 1.71 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.0 (*AB*, J_{AB} = 10.5 Hz, 1 H), 2.05 (s, 1 H), 2.24 (s, 1 H), 3.0 (br s, 4 H), 3.36–3.57 (m, 1 H), 4.12 (br s, 1 H), 7.15–8.1 (m, 5 H); ^{13}C NMR ($CDCl_3$) δ 37.91 (d), 38.30 (d), 38.89 (d), 39.21 (t), 40.97 (d), 45.52 (d), 48.97 (d), 50.07 (d), 55.93 (d), 125.90 (d), 127.13 (d), 127.59 (s), 128.76 (2 C, d), 131.82 (s), 134.29 (d), 147.03 (s), 158.61 (s), 216.62 (s). Anal. Calcd for $C_{19}H_{15}NO$: C, 83.52; H, 5.49. Found: C, 83.21; H, 5.64.

X-ray Crystallographic Analyses of 5, 6, 10, 15, and 18. All X-ray data were collected on a Nicolet R3m/μ update of a $P2_1$ diffractometer with use of the Wyckoff mode (2θ fixed, ω varied), with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). A ψ-scan empirical absorption correction was applied to all data. The structures were solved by direct methods and refined by block-cascade anisotropic least-squares techniques. Hydrogen atom positional parameters were refined, except for the ethyl hydrogen atoms in the CO_2Et group of **5**, by using a single refined isotropic thermal parameter. All computer programs were used as supplied by Nicolet for Desktop 30 Microeclipse and Nova 4/C configurations. Atomic scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography.

Acknowledgment. Financial support of this study by the Air Force Office of Scientific Research (Grant AFOSR-88-0132), the Robert A. Welch Foundation (Grant P-074 to W.H.W., Grant B-963 to A.P.M.), and the University of North Texas Faculty Research Committee is gratefully acknowledged. We thank Dr. V. Vidyasagar for his kind assistance in the preparation and characterization of **19**.

Supplementary Material Available: Tables of atomic coordinates and isotropic thermal parameters, bond lengths, bond angles, anisotropic thermal parameters, H-atom coordinates, and isotropic thermal parameters for **5, 6, 10, 15,** and **18**; selected bond distances and valence angles for **5, 6,** and **10**; structure drawings for compounds **5, 6, 10, 15,** and **18** (37 pages); observed and calculated structure factors for **5, 6, 10, 15,** and **18** (63 pages). Ordering information is given on any current masthead page.

Reactions with Aziridines. 48.[1] Friedel–Crafts Reactions with N-Sulfonated Aziridines and with Open-Chain Sulfonamides. Sulfonamides as Leaving Groups in Open-Chain Structures

Helmut Stamm,* Andreas Onistschenko, Berthold Buchholz, and Thomas Mall

Pharmazeutisch-Chemisches Institut der Universität Heidelberg, Im Neuenheimer Feld 364, D-6900 Heidelberg, Federal Republic of Germany

Received May 10, 1988

$AlCl_3$-catalyzed reactions of *N*-sulfonylaziridines (C substituents given) **1a** (no substituent), **4b** (2-phenyl), **8b** (2,3-diphenyl), and **11a–c** (2,2-dimethyl) with neat benzene, toluene, or anisole proceeded rapidly without heating. The expected *N*-sulfonyl(arylethyl)amines **2, 5, 9,** and **12** were obtained in yields of 0–84%. Apart from **1a**, the main byproducts (or the main products) **6, 10, 13,** and **14** had incorporated two molecules of arene under elimination of the corresponding isolable sulfonamides **7**. The two arene molecules were attached to both carbon atoms of the original aziridine ring, except in the reaction with **11**, where 2,3-diarylation (forming **13**) was accompanied or even replaced by 3,3-diarylation (forming **14**). Open-chain sulfonamides behave analogously provided their structure allows easy formation of a carbenium ion intermediate. Mechanisms for the formation of the non-sulfonamide products **6, 10, 13,** and **14** are proposed. Some results point to an equilibrium between a benzyl and a tertiary alkyl cation.

The high reactivity of activated aziridines[2] toward nucleophiles can be enormously increased by acid catalysis (double activation[3]) as is well known for oxiranes from the classic work of Brønsted, Kilpatrick, and Kilpatrick.[4]

When the two ring carbons of an activated aziridine carry different substituents, the regioselectivity of ring opening usually depends on the absence or presence of a catalytically effective acid. It usually changes then in a manner that is compatible with a change from S_N2 to S_N1.[2,3,5] It was shown, however, that in alcoholyses[3,6] and in reactions with Grignard reagents[5] (halide attack following a coordination of a Mg^{2+} species to the activated aziridine) a borderline mechanism without occurrence of a carbenium ion prevails.

Only few Friedel–Crafts reactions with activated aziridines have been reported so far.[7,8] A carbenium intermediate has been postulated that in one case has been proven through a rearrangement.[7] The reason for the very limited number[9] of reported reactions may be related to the low yields of isolated material, which only once (guaiazulene, BF_3 as catalyst)[8] exceeded 50%. Reasons for low yields of the desired products (derivatives of (2-arylethyl)amines) as well as further evidence for carbenium

(1) Part 47: Stamm, H.; Speth, D. *Arch. Pharm. (Weinheim)* in the press. Part 46: Mall, T.; Stamm, H. *Chem. Ber.* **1988**, *121*, 1353–1355.
(2) Ham, G. E. *J. Org. Chem.* **1964**, *29*, 3052–3055.
(3) Buchholz, B.; Stamm, H. *Isr. J. Chem.* **1986**, *27*, 17–23.
(4) Cited together with more recent papers in the following: Biggs, J.; Chapman, N. B.; Finch, A. F.; Wray, V. *J. Chem. Soc. B* **1971**, 55–63.
(5) Onistschenko, A.; Buchholz, B.; Stamm, H. *Tetrahedron* **1987**, *43*, 565–576.
(6) Compare also: Takeuchi, H.; Koyama, K. *J. Chem. Soc., Perkin Trans. 2* **1981**, 121–126. However, some results are difficult to explain by the proposed mechanism, and the kinetic evidence (second order in $MeCO_2H$) can perhaps be related with a dimerization of $MeCO_2H$ in cyclohexane. Activation by the weak acid $MeCO_2H$ needs further corroboration.
(7) Genssler, W. J.; Rockett, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 3262–3264. Genssler, W. J.; Kohler, W. R. *J. Org. Chem.* **1962**, *27*, 2754–2762. Genssler, W. J.; Dheer, S. K. *J. Org. Chem.* **1981**, *46*, 4051–4057.
(8) Kurokawa, S.; Anderson, A. G., Jr. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2059–2064.
(9) It is noteworthy that in a recent chapter[10] on Friedel–Crafts alkylation the usefulness of ethylene oxide and cyclopropane is stated without mentioning the aziridines.

0022-3263/89/1954-0193$01.50/0

Table I. $AlCl_3$-Catalyzed Reactions of *N*-Sulfonylaziridines in Neat Arenes ArH[a]

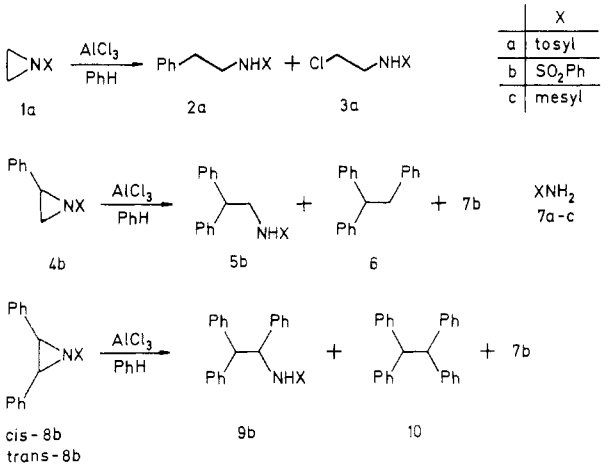
run	aziridine	ArH[b]	time,[c] min	% products[d]
1	**1a**	PH	3	(67) **2a**, (29) **3a**
2	**1a**	PH	20	(51) **2a**, (30)[e] **3a**
3	**4b**	PH	1	84 **5b**, 12 **6**, 10 **7b**
4	*cis*-**8b**	PH	5	28 **9b**, 70 **10**, 32 **7b**
5	*trans*-**8b**	PH	5	(0) **9b**, (100) **10**, (54) **7b**
6	**11b**	PH	2	51 **12bP**, (24) **13P**, (12) **14P**, 34 **7b**
7	**11c**	PH	3–4	58 **12cP**, (30) **13P**, (11) **14P**, 38 **7c**
8	**11a**	AH	3–4	(20) **12aA**, (0) **13A**, 43 **14A**, 55 **7a**, (18) **15a**, (8) **16a**
9	**11a**	AH	3–4	27 **12aA**, (0) **13A**, (56) **14A**, 56 **7a**, 13 **15a**
10	**11c**	AH	3–4	0 **12cA**, (50) **13A**, (46) **14A**
11	**11c**	AH	3–4	33 **12cA**, (11) **13A**, (43) **14A**, 9 **15c**
12	**11a**	TH	3–4	(22) **12aT**, (4) **18aT**, (34) **13T**, (34) **14T**, 66 **7a**
13	**11c**	TH	3–4	50 **12cT**, (31) **13T**, (19) **14T**, 36 **7c**

[a] A solution of 10 mmol of the aziridine in 10 mL of ArH (2 mmol of crystalline **8b** in runs 4 and 5) was at once added to the mixture of 10 mmol (12 mmol in run 1; 5 mmol in runs 4 and 5) of $AlCl_3$ and 10 mL (40 mL in run 1; 70 mL in runs 4 and 5; 30 mL in run 6) of ArH. [b] PH = benzene, AH = anisole, TH = toluene. [c] The reactions were quenched with ice under rapid stirring. [d] Yields in parentheses are from ^1H NMR analysis. [e] Material loss due to emulsification during workup.

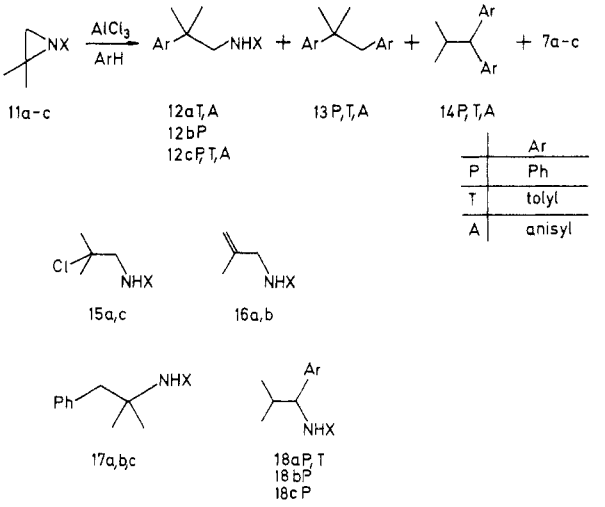
intermediates, if these are stabilized, are presented in this paper.

Results

The reactions of Table I were started at or near room temperature. Many of them developed heat on addition of the substrate with instantaneous dissolution of $AlCl_3$. The exothermicity was most pronounced with anisole, probably due to the sclubility of $AlCl_3$ in anisole prior to the addition of the aziridines.



Runs 1–5 show reactions of benzene with N-sulfonated aziridines whose ring carbons carry 0–2 phenyl groups. Good yields of the expected products **2a** and **5b** were obtained from **1a** and **4b** (runs 1–3). Since the yield of byproduct **3a** in run 1 did not decrease with increase of concentration (4-fold) and time (run 2), **3a** is likely to arise prior to quenching. With **4b** in run 3, the byproducts **6** and **7b** clearly demonstrated that the reaction can lead to an incorporation of two benzene molecules into the aziridine skeleton under elimination of the sulfonamide **7b**. This process was favored with **8b** (runs 4 and 5). The yield of the expected product **9b** was small from *cis*-**8b** and zero from *trans*-**8b**. This difference may be insignificant although a reactivity difference may exist for stereoelectronic or other reasons. The main product in runs 4 and 5 was tetraphenylethane **10**. The eliminated sulfonamide **7b** was found in less yield than **10** probably due to losses during workup.



With the 2,2-dimethylaziridines **11b,c** more sulfonamide was eliminated (runs 6 and 7) than in run 3 but less than in runs 4 and 5. This displacement provided two isomeric diphenylisobutanes **13P** and **14P**. The main products from **11b,c** and benzene were the expected products **12bP** and **12cP**.

Anisole/**11a,c** displayed some special features. Reaction of the tosylaziridine **11a** was well reproducible (runs 8 and 9) and gave only one (**14A**) of the two isomeric dianisylisobutanes besides the expected **12aA**. The mesylaziridine **11c** (runs 10 and 11) yielded both dianisyl isobutanes **13A** and **14A** but only once (run 11) the expected product **12cA**. While the yields of **14A** were comparable in runs 10 and 11, those of **13A** differred largely. From the yields of **12cA** and **13A** in these two runs it appears as if **13A** may have arisen from **12cA** or its $AlCl_3$ adduct, respectively. The byproducts **15a,c** and **16a** were found with anisole only. A methallylamide **16** was observed in that run only (run 8) which gave more sulfonamide **7** than non-sulfonamide products.

Toluene (runs 12 and 13) gave results (products **12**, **13**, and **14**) comparable to those with benzene in runs 6 and 7 except for a new product type: **12aT** was substantially contaminated with its isomer **18aT** that was identified by comparison of its characteristic ^1H NMR spectrum with that of the known[5] analogue **18aP**.

The isomers **13** and **14** could not be separated. They were identified by elementary analysis of the mixture, by absence of functional groups (IR), by ^1H NMR spectra, and, in the case of **13P/14P**, by the mass spectrum of the mixture. An authentic sample of **14P** was kindly provided by Professor Rüchardt.[10] The absence of **13A** in runs 8 and 9 allowed isolation of pure **14A**.

The anisole- and toluene-derived products can consist of positional (ortho, meta, para) isomers (compare, e.g., Olah et al.[11]). Apart from a careful inspection of ^1H NMR spectra, this detail was not investigated. It seems that

(10) Beckhaus, H.-D.; Schaetzer, J.; Rüchardt, C. *Tetrahedron Lett.* **1983**, *24*, 3307–3310. We thank Professor Christoph Rüchardt, Freiburg, for providing us with an authentic sample of **14P**.

(11) Olah, G. A.; Olah, J. A.; Okyama, T. *J. Am. Chem. Soc.* **1984**, *106*, 5284–5290.

Table II. $AlCl_3$-Catalyzed Reactions of Open-Chain Sulfonamides in Neat Arenes ArH[a]

run	mmol sulfonamide	mmol $AlCl_3$	mL ArH	time, min	% products[b]
1	1 **17a**	1	20 PH	5	(63) **13P**, (32) **14P**, 82 **7a**
2	2 **12bP**	2	20 PH	60	100 **12bP**
3	0.67 **12cA**[b] + 0.15 **15c**	10	50 AH	10	(95) **12cA**,[c] (95) **15c**
4	0.64 **12cA**[b] + 0.14 **15c**	10	50 AH	10	95 **12cA**,[c,d] 0 **15c**
5	5 **16a**	10	20 PH	10	(41) **12aP**, (4) **18aP**, (9) **13P**, (5) **14P**, (32) **7a**
6	2 **16b**	4.6	20 PH	2	(65) **12bP**, (4) **18bP**, (10) **13P**, (5) **14P**, (22) **7b**

[a] Run 4 was conducted at 70 °C (internal temperature), the other runs at room temperature. Starting sulfonamide in runs 3 and 4 was a mixture obtained from workup of runs of Table I. All runs were quenched with ice. [b] Yields in parentheses are from ^1H NMR analysis. [c] Ortho–para mixture, 49:51. [d] Yield calculated under the assumption that **15c** was converted to **12cA**.

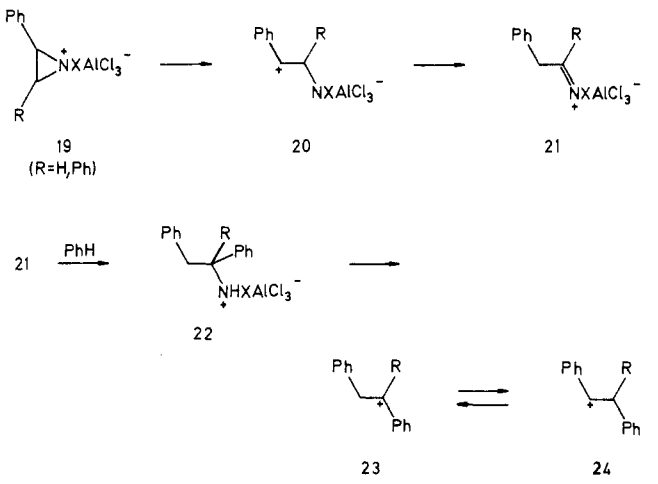
toluene formed mainly para and meta but much less ortho products and that anisole formed mainly or even exclusively two isomers: para and probably ortho. As shown by the aromatic AA'BB' ^1H NMR spectra, **13A** and **14A** consist at least mainly of para isomers while the products **12** were made up of the para isomer and a substantial amount of a second isomer, assumedly ortho since the ^1H NMR spectrum did not show an 1 H (approximate) singlet upfield from 7 ppm for the meta isomer. The para:ortho ratio was 40:60 for **12cA**, 52:48 for **12aA** in run 9, and 70:30 in run 8. Some *p*-**12aA** and a sample of *o*-**12cA** were obtained pure.

Some open-chain sulfonamides were studied (Table II). Short reaction (run 1) of benzene with **17a** yielded quantitatively **13P** and **14P** in the same ratio (2:1) as obtained from **11b** in run 6 of Table I. Part of the eliminated sulfonamide (**7a**) was lost. In contrast, **12bP** and **12cA** were not affected by $AlCl_3$/benzene (run 2) or $AlCl_3$/anisole (run 3) at room temperature or even at 70 °C (run 4). Compound **12cA** was used as an ortho–para mixture containing some **15c**. The ^1H NMR spectra did not reveal a change of the ortho–para ratio, but at 70 °C the accompanying **15c** disappeared in favor of more **12cA**. The two *N*-methallylsulfonamides **16a,b** and benzene (runs 5 and 6) provided the same (**13P** and **14P**) or the analogous (**7a** and **12aP**) products to those from benzene and **11b** (run 6, Table I), but in addition they provided **18aP**[5] and **18bP**; **18bP** and **12aP** were identified by ^1H NMR comparison with **18aP** and **12bP**. With **16a,b** the eliminated sulfonamide (**7a,b**) was in excess of the sum of **13P** + **14P**.

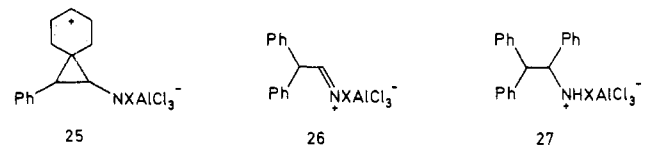
Discussion

The first event in all reactions of Table I is a rapid coordination of $AlCl_3$ with the aziridine nitrogen or a sulfonyl oxygen as indicated by the instant dissolution of $AlCl_3$ in benzene or toluene. The fate of the coordination species depends mainly on the C-substituents of the aziridine. Compound **1a**, as primary alkylating agent (compare ref 12), reacts in an S_N2 manner, including a competition between the two nucleophiles benzene and chloride, which is already known from methyloxirane.[13] However, the $AlCl_3$ adducts of **4b**, **8b**, and **11a–c** can form stabilized carbenium ions on spontaneous opening and obviously do react in this manner as shown by the regioselectivity in ring opening and by rearrangements typical of carbenium ions. The reactivity difference between a primary *N*-alkyl and a carbenium ion forming tertiary *N*-alkylsulfonamide is more pronounced in the absence of ring strain as is well demonstrated by the stability of **12bP** under conditions where the isomeric analogue **17a** completely eliminated the sulfonamide group (runs 1 and 2, Table II). Near room temperature, the novel[14] sulfonamide type of alkylating agents (**12**, **16**, **17**) seems to be insufficiently reactive for transferring a primary alkyl group to an aromatic nucleus. At elevated temperatures, however, a sulfonamide group may be displaced even from a primary alkyl residue (preliminary experiment). Heating **12aP** (10:1 mixture[5] with **18a**) in benzene to 75 °C for 10 min gave an isolated yield of 84% tosylamide **7a** while the hexane extract of the reaction products showed ^1H NMR signals that were compatible with **13P** and **14P**. Both starting materials had disappeared.

Scheme I



The products obtained from **4b** are assumed to arise via **19** → **20** (R = H, Scheme I) with subsequent branching of the reaction. Attack of **20** (R = H) on benzene gives the main product **5b**. A 1,2-hydride shift in **20** (R = H) leads to **21** (R = H) and hence to **22** (R = H). $PhSO_2NHAlCl_3^-$, isolated as **7b**, is smoothly eliminated from **22**, generating another benzylic cation (**23** = **24**, R = H) whose reaction with benzene produces **6**. Hydride shifts or other reaction paths from a first-formed carbenium to an iminium intermediate of type **21** will be favored by the migration of the positive charge from carbon to nitrogen.

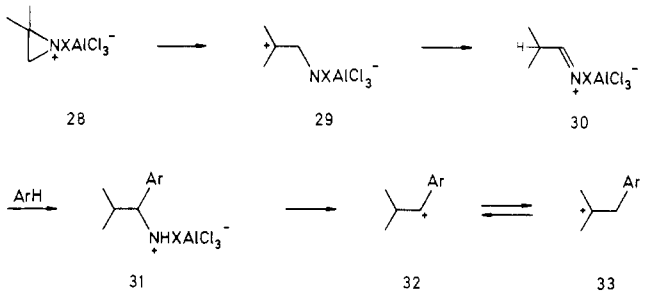


(12) Heaney, H. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. D., Stoddard, J. F., Eds.; Pergamon Press: Oxford, 1979; Vol. 1, p 268–274.

(13) Nakajima, T.; Suga, S.; Sugita, T.; Ichikawa, K. *Tetrahedron* **1969**, *25*, 1807–1816.

(14) C–N bond cleavage of N-substituted sulfonamides by boiling half-concentrated aqueous hydrochloric acid has been found (without alkyl transfer) for the N-substituents cinnamyl, 1-phenylallyl, 1-phenylpropyl, and *tert*-butyl but not for benzyl or allyl: Briscoe, P. A.; Challenger, F.; Duckworth, P. S. *J. Chem. Soc.* **1956**, 1755–1768.

Scheme II

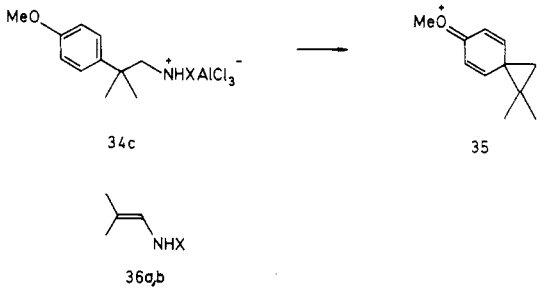


A reaction sequence similar to that of **4b** ought to be considered for R = Ph in Scheme I, i.e. for reactions of *cis*-**8b** and *trans*-**8b**, ending up in the equilibrium **23** ⇄ **24** and in the formation of **10** from **24** (R = Ph). However, formation of phenonium zwitterion **25** from **20** is an attractive alternative; **25** could isomerize to the iminium zwitterion **26** and then form **27** and **24** (R = Ph), or **25** and benzene could produce **27** directly and independently of the reacting position in **25**. Since **27** can also arise immediately from **20** (R = Ph), there are at least three reasonable paths from **20** to **27**. Including the hydride shift, there are available at least four paths to **24** (R = Ph) and finally to **10**. It may well be that more than one is followed simultaneously. Presence and absence of the minor product **9b** from *cis*-**8b** and *trans*-**8b** may have the trivial reason of a less vigorous reaction with *cis*-**8b** due to an assumed slower solution of *cis*-**8b** in the reaction mixture. However, an inherent reactivity difference cannot be excluded.

Compounds **11a–c** first form **28** and **29** (Scheme II). Reaction of **29** with a solvent molecule leads to **12**. Possibly except for X = mesyl (**12cP,T,A**), **12** seems not to be the precursor of other products (compare run 2 of Table II). At least **14** requires the 1,2-hydride shift **29** → **30**. Attack of **30** on a solvent molecule yields **31**, which also can be derived from structure **18** by addition of $AlCl_3$; **18aP** and **18bP** were obtained from **16a,b** but not from **11a,b**. Compound **18aT** was detected in run 12 of Table I. In the vigorous reactions of Table I, **31** usually eliminates $XNHAlCl_3^-$, producing **32** that equilibrates with **33**; **32** and **33** give **14** and **13**, respectively, on reaction with the solvent. Establishment of the equilibrium **32** ⇄ **33** at least for Ar = Ph is proven by a remarkable constant yield ratio **13P**:**14P** = 2:1 from four different starting materials (**11b**, **16a,b**, and **17a**), one of them (17a) implicating the necessicity to enter this equilibrium from the right side. The fifth starting material (**11c**) gave a small deviation in favor of **13P** (vide infra).

For Ar = tolyl the ratio of **13**:**14** was found to be 1:1, indicating a corresponding shift of the equilibrium **32** ⇄ **33** by the electron-releasing methyl group. The benzylic cation **32** must be favored much more with Ar = anisyl. Indeed, no **13A**, only **14A**, was obtained from **11a**. So, for **11a,b** the results are fully compatible with a formation of the diarylisobutanes from the equilibrating carbenium ions **32** and **33**.

It is difficult to explain findings in which **11c** deviates from **11a,b**, above all in the reactions with anisole. With **11c**, it seems as if **32** and **33** are not the only source of **13** and **14**. The two runs with **11c** in anisole show a rather constant yield of **14A** and a rather constant joint yield of **12cA** + **13A** while the yield of **13A** changes from 0 to 33%. Therefore we assume tentatively that **13A** arises from **34c** via **35**. With benzene or toluene a part of **13P,T** may analogously arise from the $AlCl_3$ adducts of **12cP,T** by intramolecular displacement of $MsNHAlCl_3^-$. A second path to **13** that avoids the equilibrium **32** ⇄ **33** could explain the changes in the ratio **13**:**14** on going from **11a,b** to **11c**.



The failure to separately transform **12cA** into **13A** could be due to a different coordination of $AlCl_3$ with the sulfonamide functions of **11c** and **12cA**. Likewise, a change in the initial coordination to **11** could influence the tendency to form the phenonium intermediate when the sulfonamide **7** to be displaced bears the $AlCl_3$ once on oxygen and in the other case on nitrogen. Coordination to nitrogen may be sterically hindered with X = $ArSO_2$ (**11a,b**). Steric hindrance in the coordination of a Lewis acid (Mg^{2+} species) to a sulfonylaziridine of type **11** has recently been proposed to explain a difference in reactivity.[5]

Obviously, some details of the novel sulfonamide displacement are not easy to reconcile with one another. The discussion of a change in coordination served to point to an aspect of possible importance. Another aspect should be considered too. The basicity toward protons (pK_a) is –6.54 for anisole,[15] –6.64 for **7b**,[16] and –6.0 for the *N*-methyl derivative of **7c**.[16] The similarity of these numbers suggests that sulfonamide groups and anisole structures possibly may compete for Lewis acids or protons. So, as an alternative to the above discussion, coordination of $AlCl_3$ to the anisole moiety of **12cA** could have prevented the conversion of **12cA** into **13A**. As for the idea of $AlCl_3$ coordination to a sulfonyl oxygen, arguments have been presented[16] in favor of N-protonation. On the other side, X-ray data[17] seem to place sulfonamides closer to a planar carboxamide, that is protonated on oxygen, than to an amine.

Scheme II may be modified in such a way as to generate the tertiary carbenium ion **33** from the arene and methallyl cation derived by elimination of $XNHAlCl_3^-$ from a respective precursor. This precursor would be an $AlCl_3$ adduct of **16** and may have arisen by proton transfer within **29**. This modified interpretation, however, would again encounter the difficulty in explaining the experimental results with X = mesyl. On the other hand, the proposed reaction sequence in Scheme II finds support from the reactions of **16a,b**. Coordination of $AlCl_3$ to the sulfonamide group of **16a,b** followed by proton transfer should generate the carbenium zwitterion **29** less exothermically than in the reactions of **17a** or of **11a–c**. Thus, some of the postulated intermediate **31** survived and was obtained as **18aP** and **18bP** together with **12aP**, **12bP**, **13P**, and **14P**. The reason for the survival of some **31** (isolated as **18aT**) in run 12 is not clear.

Since the yields of eliminated **7a,b** exceeded the joint yields of **13P** and **14P** in runs 5 and 6 of Table II, a side

(15) Arnett, E. W.; Wu, C. Y. *J. Am. Chem. Soc.* **1962**, *84*, 1680–1684.
(16) Virtanen, P. O. I.; Maikkula, M. *Tetrahedron Lett.* **1968**, 4855–4858 and references cited therein.
(17) We thank Professor Hermann Irngartinger for a search in the Cambridge Crystallographic Database. The sum of the bond angles on nitrogen of *N,N*-dialkyl sulfonamides was 351.7°. This figure is closer to planarity (360°) than to a regular tetrahedron (328.5°). Sulfonylaziridines give a sum near 290°.

reaction is outside Scheme II or its modification. Most probably part of **16a,b** was isomerized by $AlCl_3$ to the enamides **36a,b**, which provided **7a,b** and isobutyraldehyde by hydrolysis (compare ref 5). An analogous formation of **36a** from **29** (possibly via **16a** that was also found) may explain the excess of isolated **7a** over the yield of **13A** + **14A** in run 8 of Table I.

Experimental Section

General Method and Materials. ^1H NMR spectra ($CDCl_3$) were recorded on Bruker W 250 or HX-90E spectrometers. Chemical shifts are reported in δ (ppm) downfield from internal Me_4Si followed in parentheses by peak multiplicity (s, d, t, q, m; m_c = multiplet centered at), coupling constants J, number of protons if necessary for clarity, and assignment. IR spectra (KBr tablets unless otherwise stated) were recorded on a Perkin-Elmer 283 spectrometer. Mass spectra and exact m/e of molecular ions (M^+) were obtained from a Varian MAT 311 spectrometer.

Silica gel (Merck; 0.063–0.2 mm for columns whose dimensions in centimeters are given; TLC plates F_{254}; 2-mm PLC plates 60 F_{254}) was used for chromatography. Benzene, toluene, and anisole were refluxed over potassium metal and distilled prior to use.

The activated aziridines were prepared by the proved two-phase method[18] from the respective aziridine base and the respective sulfonyl chloride. Compounds **1a**, **4b**,[4] both **8b**,[19] **11a**,[20] and **11b**[21] are known; **1c** is described below.

2,2-Dimethyl-1-(methylsulfonyl)aziridine (11c): yield 85% (without purification); oil; IR (film) 1300, 1150 (both SO_2N) cm^{-1}; NMR (90 MHz) δ 1.45 (s, 2 Me), 2.33 (s, CH_2), 2.97 (s, SO_2Me). Anal. Calcd for $C_5H_{11}NO_2S$: C, 40.25; H, 7.43; N, 9.39. Found: C, 40.01; H, 7.48; N, 9.53.

General Method. To the stirred arene were added in turn $AlCl_3$ and a solution (except entries 4 and 5 in Table I) of the reactant. Both isomeric forms of **8b** were added in crystalline form, i.e. undissolved (runs 4 and 5 in Table I). The reaction was quenched with ice with stirring. CH_2Cl_2 or ethyl acetate (EtOAc) was added, and the organic layer was washed with water and evaporated in a rotatory evaporator. Further treatment (column chromatography or ^1H NMR analysis) of the residue is given below for each entry. The quantitative composition of mixtures (residues or chromatographic fractions) was determined from weight and ^1H NMR spectrum of the mixture.

Table I, Entry 1. NMR analysis of the residue (2.52 g) indicated 1.84 g (67%) of **2a** and 0.68 g (29%) of **3a**.

Table I, Entry 2. NMR analysis of the residue (2.10 g) indicated 1.40 g (51%) of **2a** and 0.70 g (30%) of **3a**. The material deficit was caused by emulsification during workup.

Table I, Entry 3. The residue was taken up in a small quantity of CH_2Cl_2. Insoluble material was filtered off and washed with CH_2Cl_2, thus yielding 0.15 g (10%) of **7b**. The combined CH_2Cl_2 solutions were chromatographed (3 × 30, CH_2Cl_2), yielding 0.31 g (12%) of **6** and then 2.84 g (84%) of **5b**.

***N*-(2,2-Diphenylethyl)benzenesulfonamide (5b)**: mp 103 °C; IR 3305 (NH), 1330, 1162 (both SO_2N) cm^{-1}; NMR (90 MHz) δ 3.52 (d, J = 7.7 Hz, NCH_2), 4.04 (t, J = 7.8 Hz, NCCH), 4.67 (s br, NH), 6.99–7.24 (m, CPh_2), 7.25–7.51 (m, meta and para H of SO_2Ph), 7.69–7.79 (m, ortho H of SO_2Ph). Anal. Calcd for $C_{20}H_{19}NO_2S$: C, 71.19; H, 5.68; N, 4.15. Found: C, 70.89; H, 5.66; N, 4.19.

1,1,2-Triphenylethane (6): mp 49 °C (lit.[22] mp 54 °C).

Table I, Entry 4. Chromatography (1.5 × 90, CH_2Cl_2) yielded in turn 470 mg (70%) of **10**, 230 mg (28%) of **9b**, and (CH_2Cl_2/EtOAc, 1:1) 100 mg (32%) of **7b**.

***N*-(1,2,2-Triphenylethyl)benzenesulfonamide (9b)**: mp 229–230 °C; IR 3300 (NH), 1320, 1162 (both SO_2N) cm^{-1}; NMR (250 MHz) δ 4.09 (d, J = 10.1 Hz, NCCH), 4.79 (d, J = 4.4 Hz, NH), 5.06 (dd, J = 10.2 Hz, J = 4.6 Hz, NCH), 6.84–7.11 (m, 10 aromatic H), 7.16–7.47 (m, 10 aromatic H). Anal. Calcd for $C_{26}H_{23}NO_2S$: C, 75.51; H, 5.61; N, 3.39. Found: C, 75.35; H, 5.40; N, 3.32.

1,1,2,2-Tetraphenylethane: mp 211–212 °C (lit.[22] mp 211 °C).

Table I, Entry 5. NMR analysis of the residue (840 mg) indicated 670 mg (100%) of **10** and 170 mg (54%) of **7b**.

Table I, Entry 6. The residue was taken up in a small quantity of CH_2Cl_2. Insoluble material was filtered off and washed with CH_2Cl_2 thus yielding 470 mg of **7b**. The combined CH_2Cl_2 solutions provided on chromatography (3 × 27, CH_2Cl_2) in turn 760 mg of a mixture, 1.49 g (51%) of **12bP**, and 64 mg (total 534 mg = 34%) of **7b**. The mixture consisted of 502 mg (24%) of **13P** and 258 mg (12%) of **14P**.

***N*-(2-Methyl-2-phenylpropyl)benzenesulfonamide (12bP)**: mp 88 °C; IR 3280 (NH), 1320, 1165 (both SO_2N) cm^{-1}; NMR (90 MHz) δ 1.27 (s, CMe_2), 3.02 (d, J = 6.6 Hz, NCH_2), 4.82 (t br, J = 6.6 Hz, NH), 7.20 (s, CPh), 7.25–7.53 (m, meta and para H of SO_2Ph), 7.69–7.80 (m, ortho H of SO_2Ph). Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.41; H, 6.62; N, 4.84. Found: C, 66.69; H, 6.53; N, 5.00.

1,2-Diphenyl-2-methylpropane (13P),[23] obtained as liquid mixture with **14P**: mass spectrum, m/e 210 (M^+), 119 (M – Ph), 91.

1,1-Diphenyl-2-methylpropane (14P),[24] obtained as liquid mixture with **13P**: the ^1H NMR spectrum was identical with that of an authentic sample;[10] mass spectrum, m/e 210 (M^+), 167 (Ph_2CH), 165 (fluorenyl), 152 (*o*-biphenylene).

Mixture of 13P and 14P: mass spectrum (100 eV, 25 °C), m/e (relative intensity) 210 (13), 168 (11), 167 (64), 166 (7), 165 (16), 119 (100), 91 (63). Anal. Calcd for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.49; H, 8.66.

Table I, Entry 7. Chromatography (3 × 60) provided (CH_2Cl_2) 860 mg of a mixture consisting of 620 mg (30%) of **13P** and 240 mg (11%) of **14P**, (CH_2Cl_2/EtOAc, 3:2) 1.32 g (58%) of **12cP**, and (EtOAc) 360 mg (38%) of **7c**.

***N*-(2-Methyl-2-phenylpropyl)methanesulfonamide (12cP)**: mp 62 °C; IR 3300 (NH), 1315, 1155 (both SO_2N) cm^{-1}; NMR (60 MHz) δ 1.33 (s, CMe_2), 2.57 (s, SO_2Me), 3.17 (d, J = 8.0 Hz, NCH_2), 4.67 (s br, NH), 7.23 (s, Ph). Anal. Calcd for $C_{11}H_{17}NO_2S$: C, 58.12; H, 7.54; N, 6.16. Found: C, 58.16; H, 7.55; N, 6.13.

Table I, Entry 8. Chromatography (3 × 60) provided (CH_2Cl_2) 1.16 g (43%) of **14A**, (CH_2Cl_2/EtOAc, 3:2) 1.32 g of a mixture, and (EtOAc) 940 mg (55%) of **7a**. The mixture consisted of 470 mg (14%) of *p*-**12aA**, 200 mg (6%) of *o*-**12aA**, 470 mg (18%) of **15a**, and 180 mg (8%) of **16a**;[5] **12aA** and **15a** are characterized under entry 9.

1,1-Bis(4-methoxyphenyl)-2-methylpropane (14A): oil;[25] NMR (90 MHz) δ 0.86 (d, J = 6.4 Hz, CMe_2), 2.13–2.53 (m, CH of iPr), 3.30 (d, J = 10.6 Hz, CH of benzhydryl type), 3.64 (s, 2 OMe), 6.71–6.81 (m, ortho H of anisyl), 7.10–7.20 (m, meta H of anisyl).

Table I, Entry 9. Chromatography (3 × 30, CH_2Cl_2) provided in turn 1.54 g of mixture a, 760 mg of mixture b, 500 mg of mixture c, 140 mg of *p*-**12aA**, and 960 mg (56%) of **7a**. The compositions of the mixtures were as follows. Mixture a, 1325 mg of **14A** and 216 mg of anisole; mixture b, 296 mg of *o*-**12aA**, 182 mg (total 1506 mg = 56%) of **14A**, and 281 mg of **15a**; mixture c, 121 mg (total 417 mg = 13%) of *o*-**12aA**, 317 mg (total 457 mg = 14%) of *p*-**12aA**, and 63 mg (total 344 mg = 13%) of **15a**. Mixture b provided 19 mg of crystalline **15a** on crystallization from methanol.

***N*-[2-(2-Methoxyphenyl)-2-methylpropyl]toluene-4-sulfonamide (*o*-12aA)**, obtained in mixtures only: NMR (90 MHz) δ 1.32 (s, CMe_2), 2.34 (s, Me of Ts), 3.29 (d, J = 6.4 Hz, NCH_2), 3.58 (s, OMe), 4.60 (t, J = 6.4 Hz, NH), 6.71–7.79 (m, aromatic H).

***N*-[2-(4-Methoxyphenyl)-2-methylpropyl]toluene-4-sulfonamide (*p*-12aA)**: mp 54 °C; IR 3285 (NH), 1320, 1158 (both SO_2N) cm^{-1}; NMR (90 MHz) δ 1.27 (s, CMe_2), 2.40 (s, Me of Ts), 2.98 (d, J = 6.6 Hz, NCH_2), 3.75 (s, OMe), 4.44 (t, J = 6.6

(18) Woods, C. W.; Borkovec, A. B.; Hart, F. M. *J. Med. Chem.* **1964**, *7*, 371–373.
(19) Mall, T.; Stamm, H. *J. Org. Chem.* **1987**, *52*, 4812–4814.
(20) Klötzer, W. *Monatsh. Chem.* **1970**, *101*, 1841–1850.
(21) Stamm, H.; Sommer, A.; Woderer, A.; Wiesert, W.; Mall, T.; Assithianakis, P. *J. Org. Chem.* **1985**, *50*, 4946–4955.
(22) Biltz, H. *Justus Liebigs Ann. Chem.* **1897**, *296*, 219–260.
(23) Bodroux, F. *Compt. Rend. Hebd. Sceances Acad. Sci.* **1901**, *132*, 1333–1336.
(24) Hauser, C. R.; Hamrick, P. J., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 3142–3145.
(25) Rogers, E. F.; Brown, H. D.; Rasmussen, I. M.; Heal, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 2991–2999.

Hz, NH), 6.72–6.82 (m, ortho H of anisyl), 7.08–7.18 (m, meta H of anisyl), 7.18–7.28 (m, meta H of Ts), 7.57–7.68 (m, ortho H of Ts). Anal. Calcd for $C_{18}H_{23}NO_3S$: C, 64.84; H, 6.95; N, 4.20. Found: C, 64.81; H, 6.92; N, 4.49.

***N*-(2-Chloro-2-methylpropyl)toluene-4-sulfonamide (15a)**: mp 93–94 °C (lit.[26] mp 94–95 °C).

Table I, Entry 10. Chromatography (3 × 60, CH_2Cl_2) yielded 2.60 g of a mixture consisting of 1.35 g (50%) of **13A** and 1.25 g (46%) of **14A**. No **12cA** could be eluted.

Table I, Entry 11. Chromatography (3 × 30, CH_2Cl_2) gave 1.47 g of mixture a, 200 mg of mixture b, and 800 mg of mixture c. The compositions of the mixtures were as follows. Mixture a, 309 mg (11%) of **13A** and 1.61 g (43%) of **14A**; mixture b, 186 mg of *o*-**12cA** and 14 mg of **15c**; mixture c, 320 mg (total 506 mg = 20%) of *o*-**12cA**, 336 mg (13%) of *p*-**12cA**, and 144 mg (total 158 mg = 9%) of **15c**. Crystallization of mixture b from methanol yielded 20 mg of pure *o*-**12cA**.

***N*-[2-(2-Methoxyphenyl)-2-methylpropyl]methanesulfonamide (*o*-12cA)**: mp 62 °C; IR 3270 (NH), 1322, 1159 (both SO_2N) cm^{-1}; NMR (90 MHz) δ 1.39 (s, CMe_2), 2.66 (s, SO_2Me), 3.51 (d, J = 6.3 Hz, NCH_2), 3.84 (s, OMe), 4.39 (t, J = 6.3 Hz, NH), 6.77–7.29 (m, 4 aromatic H). Anal. Calcd for $C_{12}H_{19}NO_3S$: C, 56.01; H, 7.44; N, 5.44. Found: C, 56.52; H, 7.28; N, 5.40.

***N*-[2-(4-Methoxyphenyl)-2-methylpropyl]methanesulfonamide (*p*-12cA)**, obtained as mixture only: NMR (90 MHz) δ 1.34 (s, CMe_2), 2.69 (s, SO_2Me), 3.19 (d, J = 6.6 Hz, NCH_2), 3.78 (s, OMe), 4.31 (t, J = 6.6 Hz, NH), 6.81–6.91 (m, ortho H of anisyl), 7.21–7.31 (m, meta H of anisyl).

1,2-Bis(4-methoxyphenyl)-2-methylpropane (13A), obtained as mixture with **14A**: NMR (90 MHz) δ 1.25 (s, CMe_2), 2.74 (s, CH_2), 3.63 (s, OMe), 6.65–6.85 (m, ortho H of anisyl), 7.05–7.25 (m, meta H of anisyl).

***N*-(2-Chloro-2-methylpropyl)methanesulfonamide (15c)**, identified by comparison with an authentic probe that was prepared from **11c** and $AlCl_3$ in CH_2Cl_2 as described below for **3a**: mp 41 °C; IR 3305 (NH), 1330, 1160 (both SO_2N) cm^{-1}; NMR (90 MHz) δ 1.60 (s, CMe_2), 2.95 (s, SO_2Me), 3.29 (d, J = 6.9 Hz, NCH_2), 4.26 (t, J = 6.9 Hz, NH). Anal. Calcd for $C_5H_{12}ClNO_2S$: C, 32.35; H, 6.51; N, 7.54. Found: C, 32.76; H, 6.46; N, 7.32.

Table I, Entry 12. Chromatography (3 × 60, CH_2Cl_2) provided in turn 1.62 g of a mixture consisting of 0.81 g (34%) of **13T** and 0.81 g (34%) of **14T**, (CH_2Cl_2/EtOAc, 3:2) 825 mg (26%) of a mixture consisting of 695 mg (22%) of **12aT** and 130 mg (4%) of **18aT**, and (EtOAc) 1.13 g (66%) of **7a**.

***N*-(2-Methyl-2-tolylpropyl)toluene-4-sulfonamide (12aT, main component, probably the para isomer)**: mp 79 °C (recrystallized twice from methanol); IR 3275 (NH), 1305, 1160 (both SO_2N) cm^{-1}; NMR (250 MHz) δ 1.29 (s, CMe_2), 2.32 (s, Me of *C*-tolyl), 2.43 (s, Me of Ts), 3.01 (d, J = 6.5 Hz, NCH_2), 4.37 (d, J = 6.4 Hz, NH), 7.10 (s, 4 aromatic H of tolyl), 7.25–7.30 (m, meta H of Ts), 7.60–7.65 (m, ortho H of Ts). Anal. Calcd for $C_{18}H_{23}NO_2S$: C, 68.11; H, 7.30; N, 4.41. Found: C, 68.02; H, 7.29; N, 4.41.

***N*-(2-Methyl-1-tolylpropyl)toluene-4-sulfonamide (18aT, main component, probably the para isomer)**: NMR (250 MHz, in mixture with **12aT**, compare the published[5] data for **18aP**) δ 0.72 (d, J = 6.7 Hz, 1 Me of iPr), 0.92 (d, J = 6.7 Hz, 1 Me of iPr), 1.82–1.94 (m, CH of iPr), 2.25 or 2.31 or 2.33 (s, Me of *C*-tolyl), 2.32 (s, Me of Ts), m for *N*-CH (near 4 ppm) was hidden under NH signal of **12aT**, 7.46–7.49 (m, ortho H of Ts), other aromatic signals between 6.88 and 7.25 ppm cannot be assigned.

NMR data (250 MHz) for further positional isomers. (a) Isomers of **12aT**: isomer number 2 (probably meta isomer) δ 3.02 (d, J = 6.5 Hz, NCH_2); isomer number 3 (minor component, probably ortho isomer) δ 3.21 (d, J = 6.5 Hz). (b) Isomers of **18aT**: δ 0.78 (d, J ca. 6.5 Hz, 1 Me of iPr), 1.00 (d, J ca. 6.5 Hz, 1 Me of iPr). (c) Six singlets between 2.16 and 2.33 ppm for Me of *C*-tolyl and aromatic signals between 6.88 and 7.25 ppm cannot be assigned to any particular isomer of **12aT** or **18aT**.

1,2-Ditolyl-2-methylpropane (13T), obtained as liquid mixture with **14T**: ^1H NMR (250 MHz) (a) signals common to all isomers: δ 6.91–7.24 (m, aromatic H); (b) 6 singlets (and further shoulders) not specifically assignable between 2.24 and 2.34 ppm (Me of tolyl); (c) isomer number 1 (main component) δ 1.28 (s, CMe_2), 2.81 (s, CH_2), 6.61–6.69 (m, 1 ortho H), 6.71–6.77 (m, 1 ortho H); (d) isomer number 2 δ 1.29 (s, CMe_2), 2.81 (s, CH_2), 6.61–6.69 (m, 1 ortho H), 6.71–6.77 (m, 1 ortho H); (e) isomer number 3 (minor component δ 1.37 (s, CMe_2), 2.88 (s, CH_2).

1,1-Ditolyl-2-methylpropane (14T),[25] obtained as liquid mixture with **13T**: ^1H NMR (250 MHz) (a) signals common to all isomers δ 0.86 (d, J = 6.5 Hz, CMe_2), 2.3–2.5 (m, CH of iPr), 6.91–7.24 (m, aromatic H); (b) 6 singlets (and further shoulders) not specifically assignable between 2.24 and 2.34 ppm (Me of tolyl); (c) three benzhydryl type doublets with J = 10.7 Hz at 3.30, 3.32, and 3.32 ppm, indicating two major and one minor (the last one) components. Mixture of **13T** and **14T**: Anal. Calcd for $C_{18}H_{22}$: C, 90.70; H, 9.30. Found: C, 90.79; H, 9.29.

Table I, Entry 13. Chromatography (3 × 60, CH_2Cl_2) gave in turn 1.18 g of a mixture consisting of 739 mg (31%) of **13T** and 441 mg (19%) of **14T**, (CH_2Cl_2/EtOAc, 3:2) 1.21 g (50%) of **12cT**, and (EtOAc) 340 mg (36%) of **7c**.

***N*-(2-Methyl-2-tolylpropyl)methanesulfonamide (12cT, main component, probably the para isomer)**: mp 72 °C (recrystallized twice from methanol); IR 3295 (NH), 1315, 1150 (both SO_2N) cm^{-1}; NMR (250 MHz) δ 1.36 (s, CMe_2), 2.32 (s, Me of tolyl), 2.72 (s, SO_2Me), 3.22 (d, J = 6.6 Hz, NCH_2), 4.19 (t br, J = 6.4 Hz, NH), 7.22 (m_c, 4 aromatic H). Anal. Calcd for $C_{12}H_{19}NO_2S$: C, 59.72; H, 7.93; N, 5.80. Found: C, 59.81; H, 7.87; N, 5.57. ^1H NMR (250 MHz) data for further positional isomers of **12cT**: (a) isomer number 2 (probably meta isomer) δ 2.36 (s, Me of tolyl), 3.24 (d, J = 6.6 Hz, NCH_2); (b) isomer number 3 (minor component, probably ortho isomer) δ 2.37 (s, Me of tolyl), 3.45 (d, J ca. 6.5 Hz, NCH_2); (c) aromatic signals between 7.03 and 7.30 ppm cannot be assigned.

Table II, Entry 1 (1 mmol of $AlCl_3$ dispersed in 10 mL of benzene, 1 mmol of **17a** dissolved in 10 mL of benzene). Chromatography (2 × 32, CH_2Cl_2) provided 200 mg of a mixture consisting of 139 mg (63%) of **13P** and 71 mg (32%) of **14P** followed (CH_2Cl_2/EtOAc, 1:1) by 140 mg (82%) of **7a**.

Table II, Entry 2 (2 mmol of $AlCl_3$ dispersed in 10 mL of benzene, 2 mmol of **12bP** dissolved in 10 mL of benzene). The residue consisted of 580 mg (100%) of **12bP**.

Table II, Entry 3 (10 mmol of $AlCl_3$ dispersed in 40 mL of anisole, 200 mg of a mixture obtained in run 12, Table I, and dissolved in 10 mL of anisole). This mixture was made up (NMR) of 40% *o*-**12cA**, 42% *p*-**12cA**, and 18% **15c**. After 10 min at room temperature and quenching with ice, the usual workup provided 190 mg (95%) of unchanged starting material.

Table II, Entry 4. The residue (190 mg) of entry 3 was used as starting material. The reaction was performed as in entry 3 but at 70 °C (internal temperature). The usual workup provided 190 mg of a residue that was identical with the starting material except for the disappearance of **15c**.

Table II, Entry 5 (10 mmol of $AlCl_3$ dispersed in 10 mL of benzene, 5 mmol of **16a**[5] dissolved in 10 mL of benzene). Chromatography (3 × 60, CH_2Cl_2) provided 150 mg of mixture (a) consisting of 96 mg (9%) of **13P** and 54 mg (5%) of **14P**, (CH_2Cl_2/EtOAc, 4:1) 680 mg of mixture (b) consisting of 620 mg (41%) of **12aP** and 60 mg (4%) of **18aP**,[5] and (EtOAc) 270 mg (32%) of **7a**.

***N*-(2-Methyl-2-phenylpropyl)toluene-4-sulfonamide (12aP)**, obtained as mixture only, identified by comparison with **12bP**: NMR (90 MHz) δ 1.31 (s, CMe_2), 2.42 (s, Me of Ts), 3.04 (d, J = 6.6 Hz, NCH_2), 4.82 (s br, NH), 7.24 (s, Ph), 7.24–7.31 (m, meta H of Ts), 7.58–7.69 (m, ortho H of Ts).

Table II, Entry 6 (4.6 mmol of $AlCl_3$ dispersed in 10 mL of benzene, 2 mmol of **16b** in 10 mL of benzene). Chromatography (2.5 × 35, CH_2Cl_2) provided 63 mg of a mixture consisting of 42 mg (10%) of **13P** and 21 mg (5%) of **14P**, 400 mg of a mixture consisting of 375 mg (65%) of **12P** and 25 mg (4%) of **18bP**, and (EtOAc) 69 mg (22%) of **7b**.

***N*-(2-Methyl-1-phenylpropyl)benzenesulfonamide (18bP)**, obtained as mixture with **12bP**: NMR (90 MHz) δ 0.73 (d, J = 6.6 Hz, 1 Me of iPr), 0.92 (d, J = 6.7 Hz, 1 Me of iPr), ca. 1.8–1.9 (m, CH of iPr), m for *N*-CH was hidden under NH signal of **12bP**.

***N*-(2-Phenethyl)toluene-4-sulfonamide (2a).** Authentic material was prepared from 1.72 g of Mg, 9.44 g (60 mmol) of PhBr, 1.64 g (8.3 mmol) of **1a** in 60 mL of THF using the method

(26) Markov, V. I.; Burmistrov, S. I. *J. Gen. Chem. USSR* **1965**, *35*, 153–157.

described in ref 5. The workup included chromatography (3 × 30, CH_2Cl_2) and yielded 1.87 g (82%) of **2a**: mp 59–62 °C (lit.[27] mp 65–66 °C).

***N*-(2-Chloroethyl)toluene-4-sulfonamide (3a).** Authentic probe: **1a** was added to a mixture of $AlCl_3$ and CH_2Cl_2. After 10 min the mixture was washed with water. Evaporation of the organic layer provided **3a**: mp 98 °C (lit.[28] mp 99 °C).

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and Professor Hans Suschitzky for the help in improving the English.

Registry No. **1a**, 3634-89-7; **2b**, 5450-75-9; **3a**, 6331-00-6; **4b**, 19871-46-6; **5b**, 117583-57-0; **6**, 1520-42-9; **7a**, 70-55-3; **7b**, 98-10-2; **7c**, 88-05-1; *cis*-**8b**, 110143-77-6; *trans*-**8b**, 110143-78-7; **9b**, 117583-58-1; **10**, 632-50-8; **11a**, 5048-64-6; **11b**, 5048-63-5; **11c**, 117583-63-8; **12aA**, 117583-64-9; **12aP**, 117583-61-6; **12aT**, 117583-69-4; **12bP**, 42801-56-9; **12cA**, 117583-68-3; **12cP**, 117583-59-2; **12cT**, 117583-72-9; **13A**, 117583-65-0; **13P**, 1985-96-2; **13T**, 117583-70-7; **14A**, 117583-66-1; **14P**, 1634-11-3; **14T**, 117583-71-8; **15a**, 2849-72-1; **15c**, 117583-60-5; **16a**, 1206-41-3; **16b**, 1203-15-2; **17a**, 110871-36-8; **18aP**, 110871-37-9; **18aT**, 117583-67-2; **18bP**, 117583-62-7; PH, 71-43-2; AN, 100-66-3; TH, 108-88-3.

(27) Johnson, T. B.; Guest, H. G. *Am. Chem. J.* **1909**, *42*, 340–353.
(28) Peacock, D. H.; Dutta, U. C. *J. Chem. Soc.* **1934**, 1303–1305.

Stereochemical Aspects of the "*tert*-Amino Effect". 1. Regioselectivity in the Synthesis of Pyrrolo[1,2-*a*]quinolines and Benzo[*c*]quinolizines

Walter H. N. Nijhuis,[†] Willem Verboom,[†] A. Abu El-Fadl,[‡,§] Sybolt Harkema,[‡] and David N. Reinhoudt*[,†]

Laboratories of Organic Chemistry and Chemical Physics, University of Twente, 7500 AE Enschede, The Netherlands

Received June 20, 1988

Substituted 2-vinyl-*N*,*N*-dialkylanilines cyclize in refluxing 1-butanol to give substituted pyrrolo[1,2-*a*]quinolines and benzo[*c*]quinolizines. This reaction proceeds via a 1,5-hydrogen transfer and subsequent C–C bond formation. When in the 2-vinyl-*N*,*N*-dialkylanilines **4**, R^1 = H and R^2 = H (**4a,d**), CH_3 (**4b,e**), or C_2H_5 (**4f**), the cyclization products **5a,b,d–f** are formed selectively, with the substituent R^2 at the bridgehead carbon atom. This regioselectivity is lost when R^2 = CH_2OCH_3 (**4c,g**), and a mixture of the regioisomers **5c,g**, **6c,g**, and **7c,g** is formed. Reaction of compounds **4h–n** (R^1 = CH_3) yields the pyrrolo[1,2-*a*]quinolines **5–7(h–j)** and benzo[*c*]quinolizines **5–7(k–n)** selectively, in which the substituent at the bridgehead carbon atom is at the same face of the molecule (cis) as the hydrogen atom at C-5 [**5–7(h–j)**] or at C-6 [**5–7(k–n)**]. The configuration of these compounds was determined by ^1H NOE difference spectroscopy and single-crystal X-ray analysis (**6n**). Heating of **4o–q** (R^1 = 4-$C_6H_4CH_3$) in refluxing 1-butanol gives mixtures of the cis [**5–7(o–q)**] and trans [**8–10(o–q)**] compounds. The mechanism of these cyclizations, which are further examples of the "*tert*-amino effect", and the effect of variation in substituents are discussed.

Introduction

In 1972 Meth-Cohn and Suschitzky reviewed the formation of heterocycles by ring closure of ortho-substituted tertiary anilines (the "*tert*-amino effect").[1] We have demonstrated that this type of reaction has a wider applicability, e.g. for the synthesis of pyrrolo- and pyrido-[1,2-*a*]indoles, pyrrolo[1,2-*a*]quinolines, benzo[*c*]-quinolizines, [1,4]oxazino[4,3-*a*]quinolines,[2] and pyrazinoquinolines.[3] The synthesis of benzoxazines,[4] benzothiazines, and a quinoxaline[5] can also be regarded as examples of this type of reaction. The formation of all these compounds takes place via either a 1,5- or a 1,6-hydrogen shift, depending on the structure of the reactant. The two different types of dipolar species subsequently undergo cyclization to give 6- and 5-membered rings, respectively.

In the course of our investigations of the "*tert*-amino effect" we have studied the formation of pyrrolo[1,2-*a*]-quinolines and benzo[*c*]quinolizines in more detail, in particular the regioselective aspects. When we could control the regioselectivity of the cyclization reaction this would greatly enhance the synthetic utility of the "*tert*-amino effect" in heterocyclic synthesis.

In the present paper dealing with this regioselectivity we describe the thermal isomerization of 2-vinyl-*N*,*N*-dialkylanilines **4** (X = –, CH_2) with different substituents at the α-carbon atom of the vinyl moiety (R^1 = H, CH_3, or 4-$C_6H_4CH_3$) and at one of the two carbon atoms adjacent to nitrogen of the amine moiety (R^2 = H, CH_3, CH_2CH_3, or CH_2OCH_3). Firstly, we describe the effect of the nature (size, stabilizing effect) of the substituent R^2 when R^1 = H. Secondly, the influence of both the substituents R^1 ($\neq$ H) and R^2 on the regioselectivity of the cyclization will be discussed.

Results

Synthesis of the Starting Materials 4. The starting compounds **4** for the thermal isomerization were conven-

[†] Laboratory of Organic Chemistry.
[‡] Laboratory of Chemical Physics.
[§] Present address: Physics Department, Faculty of Science, Assiut University, Assiut, Egypt.

(1) Meth-Cohn, O.; Suschitzky, H. *Adv. Heterocycl. Chem.* **1972**, *14*, 211.
(2) Verboom, W.; Reinhoudt, D. N.; Visser, R.; Harkema, S. *J. Org. Chem.* **1984**, *49*, 269.
(3) Nijhuis, W. H. N.; Verboom, W.; Reinhoudt, D. N. *Synthesis* **1987**, 641.
(4) Verboom, W.; van Dijk, B. G.; Reinhoudt, D. N. *Tetrahedron Lett.* **1983**, *24*, 3923.
(5) Verboom, W.; Hamzink, M. R. J.; Reinhoudt, D. N.; Visser, R. *Tetrahedron Lett.* **1984**, *25*, 4309.

0022-3263/89/1954-0199$01.50/0