Two-Step 1,2-Shifts by β-Cleavage of Carbenium Ions and Recombination in Friedel−Crafts Reactions of 2-*tert*-Butyl-1-tosylaziridines[1]

Konstantinos Bellos and Helmut Stamm*

Faculty of Pharmacy, University of Heidelberg, Neuenheimer Feld 346, D-69120 Heidelberg, Germany

Received April 24, 1998

$AlCl_3$-induced ring cleavage of two 2-*tert*-butyl-1-tosylaziridines in benzene (PhH) or anisole (AnH) generates carbenium ions (CIs). Subsequent neopentyl rearrangement forms CIs **3a**,**b**, whose β-cleavage generates $^+CH_2NTsAlCl_3^-$ (**14**) and an alkene. The intermediate **14** can recombine with the alkene at either C=C carbon, resulting in a reversal of the cleavage (**3a**,**b**) or in a formal 1,2-shift (CIs **12a**,**b**). AnH rapidly removes **14** from these interconverting systems by formation of a methoxybenzylamide species that undergoes fragmentation into $TsNHAlCl_3^-$ and methoxybenzyl cation, which gives dianisylmethane (main product). PhH reacts slowly with **14**, leaving CIs **3a**,**b** and **12a**,**b** more time for other reactions. Unreacted **14** can even be trapped by AnH at the end of a PhH run. Protonation of each alkene forms N-free CIs that react with PhH and AnH. Replacing tosyl in one of the aziridines by benzoyl makes the β-cleavage markedly slower than both the classic phenyl shift and the internal trapping of CIs.

Friedel−Crafts (FC) reactions with activated aziridines often take complicated courses and rarely lead to structures Ar−C−C−N.[2−6] Classic 1,2-shifts and other reactions typical of carbenium ions were found with *N*-sulfonylaziridines.[4−6] The intramolecular nature of 1,2-shifts in carbenium ions is well established. A two-step 1,2-shift by β-cleavage and subsequent recombination is now described, and the structural prerequisite for other examples is given.

Results and Discussion

FC reactions of aziridines **1a**,**b** are listed in Table 1. First, carbenium ions **2a**,**b** are generated, as can be deduced from the product structures depicted in Schemes 1 and 2. Incorporation of a solvent molecule (**6**, **9**−**11**, and **18**) was mainly found in fragments of **2a**,**b**. This incorporation is indicated by Ar in the formula and by the addition of **P** (phenyl) or **A** (anisyl) to the product number. Structure **A** was nearly always para; only **10A** and **11bA** were isolated as a mixture (^{1}H NMR) with a small amount of one or two additional isomers.

The sole reaction of **2a**,**b**, apart from the formation of very little **4** in runs 1 and 2, was the neopentyl rearrangement **2a**,**b** → **3a**,**b**. The only classic reactions of the new carbenium ions **3a**,**b** were deprotonation **3b** →→ **5b** in runs 2−4, a little electrophilic substitution of benzene (PhH) in run 1 (**3a** →→ **6aP**), and a 1,2-phenyl shift in **3b** (see below). Steric shielding by the benzyl group seems to slow down deprotonation of **3a**. The essential topic of this report, a two-step 1,2-shift, is demonstrated by products **7** and **8** in runs 1 and 2 because they require precursor **12a** or **13** (Scheme 2), respectively, which are interconnected by a simple hydride shift. Formation of **12a** by one or more classic 1,2-shifts is not compatible with the observed strong influence of the solvent: the yield of **7** and also that of **8** was much higher in PhH than in anisole AnH. One might expect the opposite for the deprotonation of **12a**. A two-step 1,2-shift (Scheme 2, top left) can easily explain this finding by competing reactions of intermediates **14**, and **15a**, whose formation is already proven by other products. In fact, benzylamide **9P** can only have come from the reaction of PhH with methylenimonium zwitterion **14**. This is clear evidence for the β-cleavage **3a** → **14** + **15a**, despite its very uncommon feature. The arising iminium ion is destabilized by electron withdrawal, in contrast to the product of the well-known[7] common β-cleavage. Only one similar cleavage seems to be known[8] so far, that of the proton analogue ($AlCl_3^-$ replaced by H) of **3b**. This peculiarity may be considered to be responsible for an atypical 1,2-shift and will be a prerequisite for further examples. It is this peculiar electron withdrawal that makes **14** more reactive than, for example, Eschenmoser's salt and similar reagents. This electron withdrawal enables **14** to attack both the solvent (→→ **9P**) and the alkene (**15a** → **12a**) entering the path to **7** and **8** by attack on the latter. Attack on a solvent molecule produced the $AlCl_3$ adducts **9**→$AlCl_3$ with AnH much faster than with PhH, but only **9P**→$AlCl_3$ survived until hydrolysis (→ **9P**). The AnH-derived **9A**→$AlCl_3$ fragmented (cf. ref 6) into $TsNHAlCl_3^-$ and methoxybenzyl cation, whose reaction with AnH gave dianisylmethane **10A**, the main product of run 2. The

(1) (a) Aziridines, part 74. (b) For part 73, see: Lin, P. Y.; Stamm, H. *J. Chem. Res.*, in press. (c) For part 72, see: Mall, T.; Stamm, H. *J. Chem. Soc., Perkin Trans. 2* **1997**, 2135−2140.

(2) Heine, H. W.; Proctor, Z. *J. Org. Chem.* **1958**, *23*, 1554−1556.

(3) Mall, T.; Buchholz, B.; Stamm, H. *Arch. Pharm. (Weinheim, Ger.)* **1994**, *327*, 377−380 and references therein.

(4) (a) Genssler, W. J.; Rockett, J. C. *J. Am. Chem. Soc.* **1955**, *77*, 3262−3264. (b) Genssler, W. J.; Dheer, S. K., Jr. *J. Org. Chem.* **1981**, *46*, 4051−4057.

(5) Kurokawa, S.; Anderson, A. G., Jr. *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2059−2064.

(6) Stamm, H.; Onistschenko, A.; Buchholz, B.; Mall, T. *J. Org. Chem.* **1989**, *54*, 193−199.

(7) (a) Bethell, D. Carbocations and Carbanions. Stoddart, J. F., Ed. In *Comprehensive Organic Chemistry*; Baron, D., Ollis, W. D., Eds. Pergamon Press: Oxford, 1979; Vol. 1, Chapter 2.7, p 434. (b) Grob, C. A. *Angew. Chem.* **1969**, *81*, 543−554; *Angew. Chem., Int. Ed. Engl.* **1969**, *81*, 535−546.

(8) Bellos, K.; Stamm, H. *J. Org. Chem.* **1995**, *60*, 5661−5666.

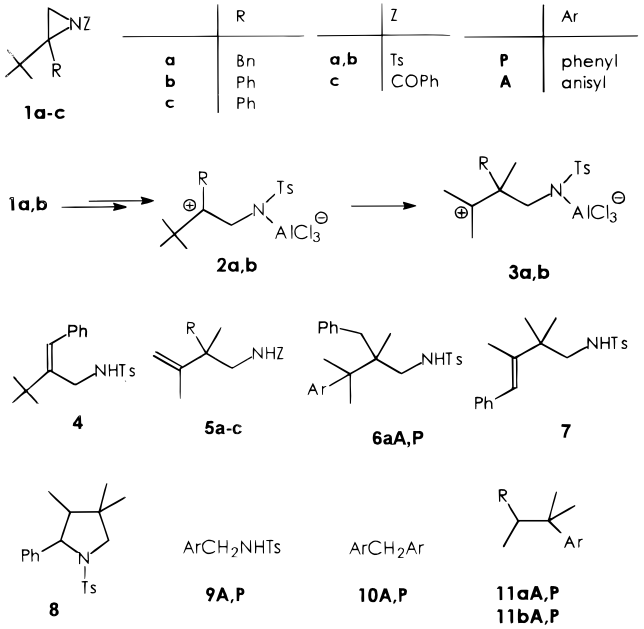
10.1021/jo980774m CCC: $15.00
Published on Web 10/02/1998

Table 1. Reactions of 1a,b with $AlCl_3$ in Benzene (PhH) or Anisole (AnH)[a]

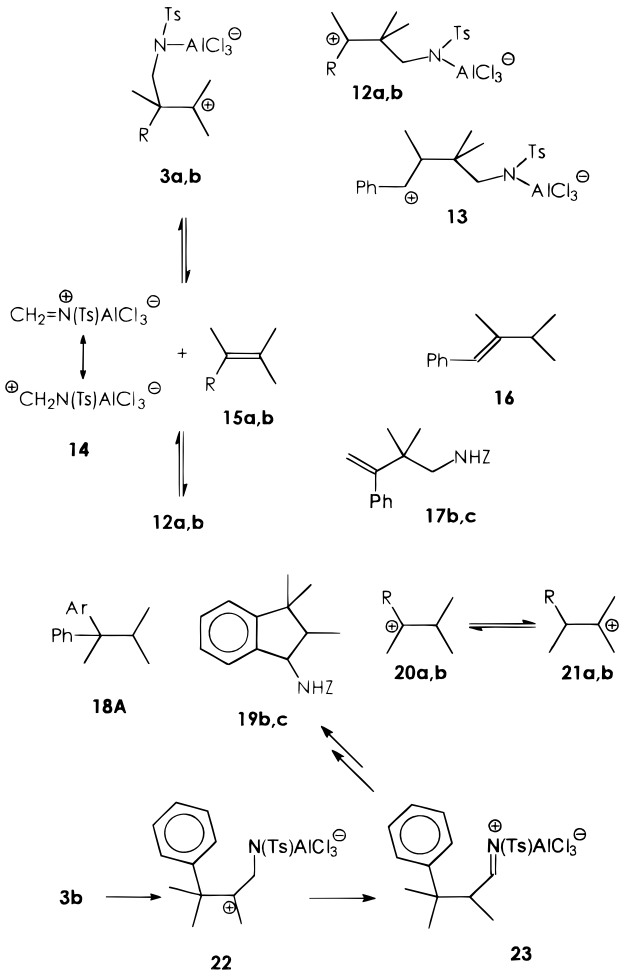
		yields (%) of products[e]											
run		**4**	**5**[b]	**6aP**	**7**	**8**	**9**[c]	**10A**	$TsNH_2$	**11**[d]	**15b**	**17b**	**18A**	**19b**
1	**1a**/PhH	2		7	56	3	5		22					
2	**1a**/AnH	tr	tr		16	tr	tr	75	75	37				
3	**1b**/PhH		9				6		75	46		5		3
4	**1b**/PhH		7				5		66	50	1.5	10		9
5	**1b**/AnH							86	100	12	tr		62	

[a] Reaction conditions: 20 min under cooling with ice; 4 mmol of **1a**,**b**; 6 mmol of $AlCl_3$; 40 mL of PhH or AnH. [b] **5a** in run 2; **5b** in runs 3 and 4. [c] **9P** in runs 1, 3, and 4; **9A** in run 2. [d] **11aA** in run 2; **11bP** in runs 3 and 4; **11bA** in run 5. [e] tr = trace.

Scheme 1



Scheme 2



eliminated $TsNHAlCl_3^-$ was hydrolyzed to $TsNH_2$ in the same yield.

There is no reason why **14** and alkene **15a** (Scheme 2) should form only **12a** and no **3a**. Extending this line of reasoning suggests reversibility for both reactions of **14** with **15a**, whereas the reaction of **14** with the solvent is (almost) irreversible under the experimental conditions. Thus, the slow reaction of **14** with PhH gave sufficient time for other reactions both of **3a** (→ **6aP**) and **12a** (products **7** and **8**), whereas the fast trapping of **14** by AnH prevented the formation of **6aA** and nearly that of **7** and **8**. Part of **14** seemed even to remain intact in run 1 (see below) until the run was quenched with ice, thus providing 22% of $TsNH_2$. The possible intermediate $TsN{=}CH_2$ is known to be labile.[9]

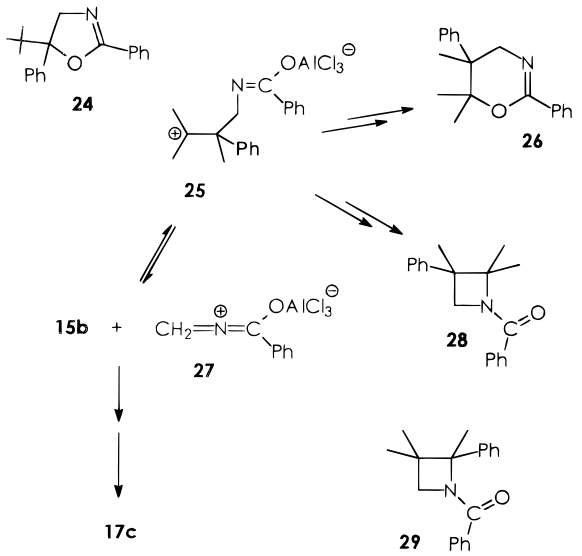
Protonation of alkene **15a** can generate carbenium ions **20a** and **21a** (Scheme 2). The nitrogen-free product **11aA** arose from arylation of the sterically less demanding isomer **21a**. The yield of this sole product derived from **15a** without participation of **14** was only half the yields of **10A** and $TsNH_2$. This fact points to a loss of **15a** or of its styrene isomer **16**, which can arise from **20a**, during workup.[10] A similar loss of **15a** or **16** in run 1 is indicated by the isolation of **9P** and $TsNH_2$ despite the absence of **11aP**. The structure of **11aA** follows from the ^1H NMR spectrum for $CH{-}CH_2$ that forms nearly an AA′X system whose decoupling shows CH_2 to be AX. Ring current effects make CH−CH nearly isochronous and shift the second CH_2 signal downfield by more than 0.7 ppm.

Apart from steps **1b** → **2b** → **3b**, only reactions of **1a** have been discussed so far. The aziridine **1b** (runs 3−5) behaved analogously, with a few variations that more or less may have been expected. One of them, the production of **19b**, is discussed below. There is also good evidence for the two-step 1,2-shift (Scheme 2, top left) **3b** → **12b**. Deprotonation of **12b** can only provide **17b**, whereas **12a** gave **7** in higher yields (runs 1 and 2). β-Cleavage **3b** → **14** + **15b** was unequivocally confirmed by detection of **15b** (runs 4−5). As discussed above, **14** reacted in runs 3−5 giving unchanged or nearly unchanged yields of **9A**,**P** and an increased yield of **10A**. The equilibrium for protonated alkene **15b** has to be on the side of benzyl cation **20b**. For steric reasons, PhH

(9) Kinoshita, H.; Inomata, K.; Hayashi, M.; Kondon, I.; Kotake, H. *Chem. Lett.* **1986**, 1033−1036.

(10) The volatility of 1-*tert*-butylstyrene (isomer of **15a** and **16**) is known (see Experimental Section of ref 11). The lower (C_{11}) homologue **15b** has been lost in another reaction of **1b**[8]. **15b** is known,[12] and the data given[12a] suggest a coevaporation with solvent during workup. Formation of **11aP** (not detected) from **21a** may suffer not only from the low FC reactivity of PhH but also from the conversion **15a** → **16**.

Scheme 3



was exclusively attacked by the minor equilibrium component **21b** (→ **11bP**), whereas AnH reacted mainly with the major component **21b**, giving more **18A** than **11bA**. Indan **19b** is assumed to arise from consecutive 1,2-shifts **3b** → **22** → **23**, followed by an intramolecular electrophilic substitution in the ortho position.

Survival of some **14** in PhH was unequivocally proven in an exact repetition of run 3. Unreacted **14** was trapped by AnH (30 mL) that was added prior to quenching. After the reaction was continued for 10 min, 27% of **10A** was found. The incomplete conversion of **14** can be ascribed to the short reaction time and the low temperature of the runs shown in Table 1 and also to a more moderate FC reactivity compared to that of **21b** when one considers the low concentration and the apparently higher steric demands of the latter. This points to a pronounced iminium character of **14** with negligible mesomerism, although other reasons for a moderate FC reactivity are conceivable. The reactivity of **14** may gain practical value when it can be generated from $TsN{=}CH_2$.

The electron withdrawal power which is essential for the two-step 1,2-shift can also be provided by a benzoyl group, as could be shown by a single run with **1c** in PhH despite the strong tendency[2,3] to internally trap the carbenium ions derived from *N*-acylaziridines. The *N*-acylaziridines coordinate a Lewis acid to the oxygen.[3,8,13] Thus, for this run with **1c** (Sheme 3), benzoyl counterparts (BCP) of intermediates shown already in Schemes 1 and 2 have $N(Ts)AlCl_3^-$ replaced by $N{=}CPh{-}OAlCl_3^-$ (cf. ref 8).

The BCP of **2b** either was internally trapped (oxazoline **24**, 11%) or generated **25** (BCP of **3b**). The latter cyclized expectedly (**26**, 17%) and unexpectedly (azetidine **28**), or it underwent reactions as described for **3b**, resulting in the products shown in Scheme 1 (**5c**, 6%) or Scheme 2 (**17c**, 3% and **19c**, 23%). Product **17c** is derived from the two-step 1,2-shift outlined in Scheme 3. Only two products (**17c** and **29**, see below) requiring β-cleavage of **25** were found (about 9% taken together). Products arising from **25** without cleavage totalled about 63%. Cleavages of **25** and of its analogue **3b** have to compete with 1,2-shifts of phenyl (indans **19b** and **c**, 3−9% and 23%, respectively). Although the cleavage of **25** had to furthermore compete with cyclizations (**26** and **28**), the amount of phenyl shifts occurring in **25** was greater than in **3b**. Clearly, β-cleavage of **25** is slower than that of **3b**.

The structure of **28** followed from the spectra. A geminal proton coupling of 8.4 Hz is in accord with an azetidine.[14] The ^{1}H NMR spectrum of **28** revealed a contamination (about one-fifth) that is assumed to be **29** because the signals, especially the aliphatic ones, were very similar or identical to the signals for **28**. Only the chemical shift of one methyl group changed from 1.80 ppm (**28**) to 0.89 ppm. The total yield of **28** and **29** was 29%.

Experimental Section

General Methods and Materials. ^{1}H NMR spectra were recorded from $CDCl_3$ solutions containing TMS. IR spectra were recorded from KBr tablets unless otherwise stated. Column chromatography (chr) (column dimensions 3 × 60 cm) was performed with 0.063−0.2 mm silica gel (Merck). Preparative layer chromatography (PLC) was performed with silica gel 60 F254 (Merck 5717), 20 × 20 cm, 2 mm thick; zones were extracted with hot ethyl acetate.

Starting Materials and Known Products. The aziridines **1a**,**b**[15] and **1c**[16] are known. The products **4**, **5a**−**c**, **15b**, **24**, and **26** are already described.[8]

General Method of Reactions. For details, see Table 1. The reaction mixtures were continuously stirred. Reactant **1a**,**b** was added at once to a stirred mixture of PhH or AnH and $AlCl_3$. The reactions were quenched by the addition of ice. This mixture was taken up in 300 mL of ethyl acetate and washed with water three times. The residue obtained by evaporation was subjected to chr; details are given with each run.

Run 1. Chr with CH_2Cl_2 provided 50 mg of a mixture consisting (^{1}H NMR) of 28 mg (2%) of **4** and 22 mg of **7**. Further elution yielded 720 mg of **7**, 120 mg of mixture I, 90 mg of **6aP**, and 50 mg (5%) of **9P**. Elution with ethyl acetate gave 152 mg (11%) of $TsNH_2$. PLC (toluene−ethyl acetate, 20:1) of mixture I provided (from bottom to top) 36 mg (total 126 mg, corresponding to 7%) of **6aP**, 34 mg (total 776 mg, corresponding to 56%) of **7**, and 44 mg (3%) of **8**.

***N*-(2-Benzyl-3-phenyl-2,3,3-trimethylbutyl)toluene-4-sulfonamide (6aP):** mp 158−160 °C; IR 3265, 1328, 1162 cm^{-1}; ^{1}H NMR δ 0.97 (s, 3H), 1.06 (s, 3H), 1.13 (s, 3H), 2.43 (s, 3H), 2.59 (d, J = 15.8 Hz, 1H), 2.75 (d, J = 15.8 Hz, 1H), 2.85 (dd, J = 12.4/6.6 Hz, 1H), 2.95 (dd, J = 12.4/6.9 Hz, 1H), 4.36 (t, J = 6.6 Hz, 1H), 7.03−7.35 (m, 12H), 7.67−7.74 (m, 2H). Anal. Calcd for $C_{26}H_{31}NO_2S$: C, 74.07; H, 7.41; N, 3.32. Found: C, 74.05; H, 7.23; N, 3.20.

***N*-(4-Phenyl-2,2,3-trimethyl-3-butenyl)toluene-4-sulfonamide (7):** mp 106−108 °C; IR 3270, 1658, 1331, 1166 cm^{-1}; ^{1}H NMR δ 1.12 (s, 6H), 1.63 (d, J = 1.1 Hz, 3H), 2.40 (s, 3H), 2.89 (d, J = 6.1 Hz, 2H), 4.45 (t, J = 6.0 Hz, 1H), 6.30 (s br, 1H), 7.13−7.37 (m, 7H), 7.70−7.78 (m, 2H). Anal. Calcd for $C_{20}H_{25}NO_2S$: C, 69.94; H, 7.34; N, 4.08. Found: C, 69.86; H, 7.41; N, 4.00.

***N*-(4-Methylphenylsulfonyl)-2-phenyl-3,4,4-trimethylpyrrolidine (8):** mp 113−118 °C; IR 1350, 1162 cm^{-1}; ^{1}H

(11) Bellos, K.; Werry, J.; Assithianakis, P.; Weiss, R.; Mall, T.; Bentz, G.; Stamm, H. *J. Prakt. Chem.* **1996**, *338*, 270−278.
(12) (a) Brewster, J. H.; Patterson, J.; Fidler, D. E. *J. Am. Chem. Soc.* **1954**, *76*, 6368−6371. (b) Overberger, C. G.; Gainer, H. *J. Am. Chem. Soc.* **1958**, *80*, 4561−4565.
(13) Olah, G. A.; Szilagyi, P. J. *J. Am. Chem. Soc.* **1969**, *91*, 2949−2955.
(14) Lwowski, W. Structure of Small and Large Rings. In *Comprehensive Heterocyclic Chemistry*; Katritzky, A., Rees, C. W., Eds.; Pergamon Press: Oxford, 1984: Vol. 1, p 10.
(15) Bellos, K.; Stamm, H.; Speth, D. *J. Org. Chem.* **1991**, *56*, 6846−6849.
(16) Werry, J.; Stamm, H.; Lin, P.-Y.; Falkenstein, R.; Gries, S.; Irngartinger, H. *Tetrahedron* **1989**, *45*, 5015−5028.

NMR δ 0.59 (s, 3H), 0.74 (d, J = 6.8 Hz, 3H), 0.98 (s, 3H), 1.77 (dq, J = 10.1/6.8 Hz, 1H), 2.38 (s, 3H), 3.35 (d, J = 10.7 Hz, 1H), 3.61 (d, J = 10.7 Hz, 1H), 4.09 (d, J = 10.1 Hz, 1H), 7.13−7.31 (m, 7H), 7.44−7.52 (m, 2H). Anal. Calcd for $C_{20}H_{25}NO_2S$: C, 69.94; H, 7.34; N, 4.08. Found: C, 69.72; H, 7.40; N, 4.01.

Run 2. Chr with CH_2Cl_2 provided 359 mg of **11aA** and 132 mg of a mixture consisting (^{1}H NMR) of 40 mg of **11aA** and 92 mg of **10A**. Further elution gave 592 mg (total 684 mg, corresponding to 75%) of **10A** and a small amount of a mixture containing (^{1}H NMR) traces of **4**, **5a**, and **8**. Continued elution provided 216 mg (16%) of **7** and a small amount of a mixture containing (^{1}H NMR) a trace of **9A**. Elution with ethyl acetate gave 510 mg (75%) of $TsNH_2$.

1-Phenyl-3-(4-methoxyphenyl)-2,3-dimethylbutane(11aA): oil; ^{1}H NMR δ 0.70 (d, J = 6.1 Hz, 3H), 1.30 (s, 3H), 1.33 (s, 3H), 1.94 (m_c, 1H), 1.95 (m_c, 1H), 2.69 (m_c, 1H), 3.79 (s, 3H), 6.84−6.92 (m, 2H), 6.98−7.05 (m, 2H), 7.08−7.37 (m, 5H). Anal. Calcd for $C_{19}H_{24}O$: C, 85.03; H, 9.01. Found: C, 85.01; H, 9.05.

Run 3. Chr with CH_2Cl_2 provided 413 mg (46%) of **11bP** and 187 mg of an inseparable mixture of isomers consisting (^{1}H NMR) of 125 mg (9%) of **5b** and 62 mg (5%) of **17b**. Further elution yielded 39 mg (3%) of **19b** and 58 mg (6%) of **9p**. Elution with ethyl acetate yielded 511 mg (75%) of $TsNH_2$.

2,3-Diphenyl-2-methylbutane (11bP): oil; ^{1}H NMR δ 1.07 (d, J = 7.2 Hz, 3H), 1.19 (s, 3H), 1.27 (s, 3H), 3.00 (q, J = 7.2 Hz, 1H), 6.98−7.04 (m, 2H), 7.10−7.33 (m, 8H). Anal. Calcd for $C_{17}H_{20}O$: C, 91.01; H, 8.99. Found: C, 90.72; H, 8.91.

***N*-(2,2-Dimethyl-3-phenyl-3-butenyl)toluene-4-sulfonamide (17b):** ^{1}H NMR δ 1.07 (s, 6H), 2.43 (s, 3H), 2.81 (d, J = 6.0 Hz, 2H), 4.68 (t br, J = 6.0 Hz, 1H), 4.95 (d, J = 1.1 Hz, 1H), 5.18 (d, J = 1.1 Hz, 1H), 6.87−6.94 (m, 2H), 7.11−7.35 (m, overlapping with signals of **5b**), 7.72−7.79 (m, 2H, slightly downfield from signals of **5b**). Mixture of **17b** and **5b**: oil. Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.13; H, 7.05; N, 4.17.

3-(4-Methylphenylsulfonyl)-1,1,2-trimethylindan (19b): mp 104−109 °C; IR 3326, 3265, 1318, 1163 cm^{-1}; ^{1}H NMR δ 0.93 (s, 3H), 0.95 (d, J = 7.0 Hz, 3H), 1.36 (s, 3H), 1.76 (dq, J = 10.0/7.0 Hz, 1H), 2.46 (s, 3H), 4.40 (t, J = 9.9 Hz, 1H), 4.60 (d br, J = 9.6 Hz, 1H), 6.84−6.91 (m, 1H), 7.06−7.39 (m, 5H), 7.84−7.91 (m, 2H). Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.33; H, 7.15; N, 4.12.

Run 4. Chr with CH_2Cl_2 provided 384 mg of **11bP** and 72 mg of a mixture consisting (^{1}H NMR) of 63 mg (total 447 mg, corresponding to 50%) of **11bP** and 9 mg (1.5%) of **15b**. Further elution yielded 143 mg of a mixture consisting (^{1}H NMR) of 56 mg of **5b** and 87 mg of **17b**. Continued elution gave 183 mg of a mixture consisting (^{1}H NMR) of 40 mg (total 96 mg, corresponding to 7%) of **5b**, 45 mg (total 132 mg, corresponding to 10%) of **17b**, and 98 mg of **19b**. Further elution provided 26 mg (total 124 mg, corresponding to 9%) of **19b** and 57 mg (5%) of **9P**. Elution with ethyl acetate gave 451 mg (66%) of $TsNH_2$.

Run 5. Chr with CH_2Cl_2 provided 317 mg of a mixture consisting (^{1}H NMR) of a trace of **15b**, 118 mg (12%) of **11bA**, and 199 mg of its isomer **18A**. Further elution yielded 428 mg (total 627 mg, corresponding to 62%) of **18A** and 255 mg of **10A** (*para-para*-**10A** containing an isomer) and 510 mg of **10A** (*para-para* only, total for all isomers 765 mg, corresponding to 86%). Elution with ethyl acetate gave 683 mg (100%) of $TsNH_2$.

2-Methyl-2-methoxyphenyl-2-phenylbutane (11bA) (in mixture with **18A**) oil; ^{1}H NMR δ (*para*-isomer) 1.08 (d, J = 7.2 Hz, 3H), 1.19 (s, 3H), 1.25 (s, 3H), 2.98 (q, J = 7.2 Hz, 1H), 3.72 (s, 3H), 6.75 (m_c, 2H), 7.13 (m_c, 2H), ca. 7.21 (m_c, 5H); ^{1}H NMR δ (minor isomer, probably *ortho*) 1.46 (s, 3H), 1.47 (d, J = 7.1 Hz, 3H), 1.52 (s, 3H), 2.98 (q, J = 7.2 Hz, 1H), 3.73 (s, 3H); the aromatic signals cannot be distinguished from those of the *para* isomer and those of **18A**. Anal. Calcd for $C_{18}H_{22}O$ (mixture of **11bA** and **18A**): C, 84.99; H, 8,72. Found: C, 84.98; H, 8.47.

3-Methyl-2-(4-methoxyphenyl)-2-phenylbutane (18A): oil; ^{1}H NMR δ 0.81 (d, J = 6.7 Hz, 3H), 0.83 (d, J = 6.7 Hz, 3H), 1.57 (s, 3H), 2.65 (sept, J = 6.7 Hz, 1H), 3.75 (s, 3H), 6.75 (m_c, 2H), 7.13 (m_c, 2H), ca. 7.21 (m_c, Ph). Anal. Calcd for $C_{18}H_{22}O$: C, 84.99; H, 8,72. Found: C, 85.09; H, 8.51.

Bis(methoxyphenyl)methane (10A) (*para-para* isomer): mp 51−52 °C; ^{1}H NMR δ 3.84 (s, 2H), 3.73 (s, 6H), 6.83 (m_c, 4H), 7.09 (m_c, 4H), the presence of two or more isomers in one eluate was indicated by singlets at 3.77, 3.80, and 3.91 and by a multiplet at ca. 7.13. Anal. Calcd for $C_{15}H_{16}O_2$: C, 78.92; H, 7.06. Found: C, 78.79; H, 7.06.

Reaction of 1c in Benzene. Reaction and workup were performed as described for the runs of Table 1 but without cooling. Chr with CH_2Cl_2 provided 260 mg (23%) of **19c** and 100 mg of a mixture consisting (^{1}H NMR) of 69 mg (6%) of **5c** and 31 mg (3%) of **17c**. Continued elution yielded 133 mg of **26** and 180 mg of a mixture consisting (^{1}H NMR) of 125 mg (11%) of **24** and 55 mg (total 188 mg, corresponding to 17%) of **26**. Elution with ethyl acetate gave 327 mg (29%) of a mixture of **28** and its isomer **29** in a ratio (^{1}H NMR) of about 4:1.

***N*-(2,2-Dimethyl-3-phenyl-3-butenyl)benzamide (17c)** (in mixture with isomer **5c**): oil; ^{1}H NMR δ (**17c**) 1.19 (s, 6H), 3.43 (d, J = 5.6 Hz, 2H), 5.07 (d, J = 1.3 Hz, 1H), 5.32 (d, J = 1.3 Hz, 1H), 6.20 (s br, 1H), 7.11−7.18 (m, 2H), 7.20−7.54 (m, 6H), 7.69−7.76 (m, 2H of both isomers). Anal. Calcd for $C_{19}H_{21}NO$ (both isomers): C, 81.68; H, 7.58; N, 5.01. Found: C, 81.57; H, 7.40; N, 5.07.

3-Benzamido-1,1,2-trimethylindan (19c): mp 166−169 °C; IR 3340, 1634, 1536 cm^{-1}; ^{1}H NMR δ 1.07 (s, 3H), 1.20 (d, J = 7.0 Hz, 3H), 1.35 (s, 3H), 1.92 (dq, J = 10.0/7.0 Hz, 1H), 5.43 (t, J = 9.9 Hz, 1H), 6.22 (d br, J = 9.6 Hz, 1H), 7.17−7.34 (m, 4H), 7.42−7.58 (m, 3H), 7.81−7.88 (m, 2H). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.89; H, 7.57; N, 4.80.

1-Benzoyl-2,2,3-trimethyl-3-phenylazetidine (28) (contaminated with isomer **29**): viscous mass; IR 1656 cm^{-1}; ^{1}H NMR δ 1.28 (s, 3H), 1.62 (s, 3H), 1.80 (s, 3H), 3.88 (d, J = 8.4 Hz, 1H), 4.65 (d, J = 8.4 Hz, 1H), 7.01−7.52 (m, 8H), 7.60 (m_c, 2H); MS (**28**, 138 °C) *m/e* (relative intensity) 279 (2, M$^+$), 162 (14), 118 (100), 105 (45), 77 (26). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.68; N, 5.01. Found: C, 81.59; H, 7.98; N, 4.96. Molecular mass calcd for M$^+$ of $C_{19}H_{21}NO$: *m/e* 279.1624, found *m/e* 279.1625.

1-Benzoyl-2,3,3-trimethyl-2-phenylazetidine (29) (only in mixture with main component **28**): ^{1}H NMR δ 0.89 (s, 3H), 1.26 (s, 3H), 1.62 (s, 3H), 3.85 (m_c, 1H), 4.60 (m_c, 1H), 7.01−7.62 (m, indistinguishable from **28**).

Acknowledgment. This work was supported by the Fonds der Chemischen Industrie.

JO980774M