Reactions of a Tertiary Carbon Carrying a *tert*-Butyl Group: Acid-Catalyzed Alcoholyses of Activated Aziridines without and with Solvent Assistance†,[1]

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Acid-catalyzed ring opening of tosylated and acylated 2-*tert*-butylaziridines **1** (2-phenyl) and **2** (2-benzyl) generates carbenium ions **18** (from **1**) and **19** (from **2**) which rearrange by a neopentyl rearrangement to carbenium ions **20** (**18** → **20**) and **21** (**19** → **21**). Reactions of **18**–**21** form the final products: (1) deprotonation yields allylamides, homoallylamides, and enamides; (2) external trapping of **18** or **19** by a solvent molecule yields ethers; (3) internal trapping (only acylated **1** and **2**) yields oxazolines and dihydrooxazines. The amount of external trapping with **1a,b** depends on the activation: **1a** (tosyl activation) yields more methyl ether (75% vs 51%) than **1b** (benzoyl), but **1a** yields less isopropyl ether (0% vs 25%) than **1b**. The latter finding is in accord with an intramolecular interaction of the carbenium center of **18a** with one of the tosyl oxygen atoms provided that this interaction distorts the carbenium plane to a pyramid which sterically retards external trapping. The former finding is not observed with **2a** and **2b**. This points to at least some methanol-assisted ring opening of **1a**-H$^+$ that must be supported by a benzylic effect. The required conformation of the phenyl ring is fixed in **1a**-H$^+$ (N-protonation and bulky SO_2 cis to phenyl) but not in **1b**-H$^+$ (O-protonation and planar nitrogen conformation).

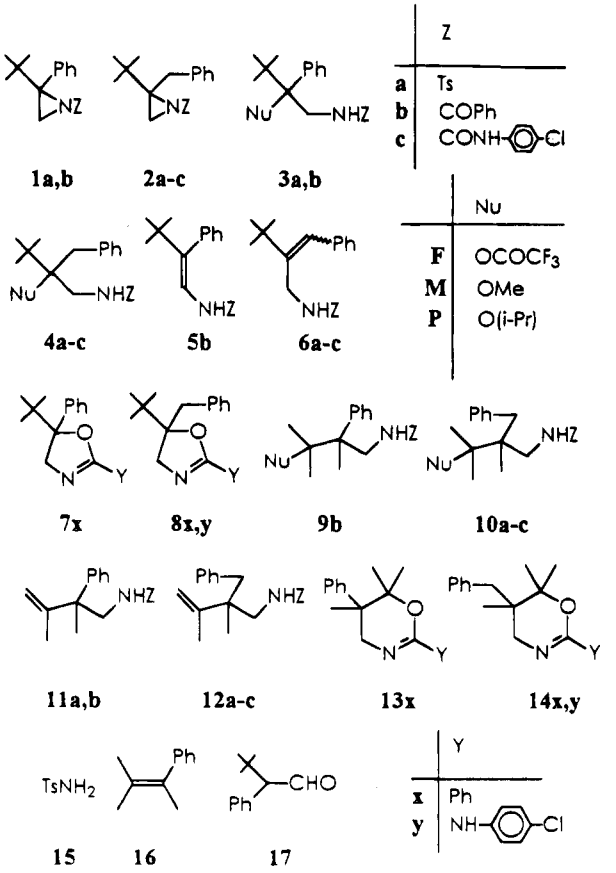
Introduction

Two preceding papers[2,3] dealt with the reactivity of the activated aziridines **1a,b** and **2a,b** whose special feature is a very crowded substitution at position 2. Steric hindrance prevented nucleophilic attack on this tertiary carbon and effectively slowed down attack on the neighboring primary carbon. We now extend this investigation to acid-catalyzed alcoholyses in order to compare the effects of high and moderate steric shielding. In several previous cases, the behavior of activated 2,2-dimethylaziridines (moderate shielding) had not been predictable based on usual considerations.

Acid-catalyzed alcoholyses of these aziridines proceed exclusively by rapid cleavage of the bond to the substituted carbon, but this cleavage is assisted by the solvent.[4] Activated 2-phenylaziridines behave quite similar and yield less than 10% racemization in the products of solvolytic ring opening.[4,5] Some kind of a benzylic effect, not necessarily the one described by King,[6] operates in acid-catalyzed alcoholyses of 2-benzyl-3-phenyl-1-(phenylsulfonyl)aziridine, since ring opening occurred exclusively at the phenylated carbon with only a small amount of racemization.[5]

Results and Discussion

Acid-catalyzed alcoholyses of activated 2-*tert*-butylaziridines **1a,b** and **2a–c** at room temperature are listed in Table 1. Complete conversion of **1** and **2** was indicated by ^{1}H NMR spectra of the crude reaction mixtures. Only products of ring opening were detected. They can be classified in two groups. One group arises via neopentyl rearrangement of an intermediate carbenium ion **18** or **19**. The other group arises without any rearrangement of the original carbon skeleton. This latter group comprises the products **3**–**8**. The final step of the reaction in both groups or the sole step in the second group may be a combination with an external nucleophile (usually



† Dedicated to my dear colleague Gerhard Schwenker on the occasion of his 70th birthday.

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Table 1. Acid[a]-Catalyzed Alcoholyses[b] of Aziridines 1 and 2

				% products[c] (yields in parentheses from ^{1}H NMR analyses)						
				without rearrangement			with rearrangement			
run	aziridine	mL of solvent	time	substit amides	alkenyl amides	cyclic imides	substit amides	alkenyl amides	cyclic imides	other products
1	**1a**	50 MeOH	20 h	(75) **3aM**				(19) **11a**		
2	**1a**	30 iPrOH	2 d					69 **11a**		19 **15**, **16**, **17**
3	**1b**	50 MeOH	1 d	(51) **3bM**	(0.2) **5b**	(23) **7x**		(9) **11b**	**13x**	
4	**1b**	50 iPrOH	1 d	25 **3bP** 4 **3bF**	3 **5b**	38 **7x**	0.6 **9bP**	11 **11b**	0.9 **13x**	
5	**2a**	50 MeOH	1 d	(8) **4aM**	(19) **6a**		(23) **10aM**	(46) **12a**		
6	**2b**	50 MeOH	1 d	(13) **4bM**	22 **6b**	(21) **8x**	(18) **10bM**	(11) **12b**	(13) **14x**	
7	**2b**	50 iPrOH	1 d	(4) **4bP**	22 **6b**	(29) **8x**	(7) **10bP**	(26) **12b**	(7) **14x**	
8	**2c**	50 MeOH	1 d	(21) **4cM**	(13) **6c**	(21) **8y**	15 **10cM**	(11) **12c**	(13) **14y**	

[a] 2 mmol of CF_3CO_2H and 2 mmol of **1** or **2** in runs 4 and 8; 3 mmol of $HClO_4$ (70%) and 3 mmol of **1** or **2** in all other runs. [b] At room temperature. [c] A trace of a product is indicated by lack of a yield preceding the product number.

a solvent molecule), a combination with an internal nucleophile (oxygen of an acylaziridine), or loss of a proton from a carbon bound to a carbenium center. Only once (run 2) were products detected beyond this classification. Traces of **16** and **17** in this run were identified by ^{1}H NMR signals in the crude product mixture but were not rediscovered in chromatographic fractions. In run 5, the isomeric ethers **4aM** and **10aM** were obtained as a mixture only and identified by the combination of elementary analysis with ^{1}H NMR. The external combination in the unrearranged group may or may not proceed via a carbenium ion.

External combination formed the products **3** and **4**, respectively, in yields ranging from 0 to 75%. Most surprisingly, the highest (**3aM**) and the lowest yield (**3aP**) were obtained from the same aziridine (tosylaziridine **1a**) and methanol (run 1) or 2-propanol (run 2), respectively, indicating a pronounced steric hindrance. This points to a solvent-assisted path for **3aM** in run 1 although in both runs all other products clearly come from a rearrangement of **18a** or from a deprotonation of **18a** (**15** and **17**, see below). This mechanistic problem is analyzed later. Methanolysis of the second tosylaziridine (**2a**, run 5) provided 8% of ether **4aM** together with 19% of allylamide **6a** (**19a** → H^+ + **6a**) and 69% of rearranged products admitting at best a possible noncarbenium mechanism for 8% in a total of 96% of products. Thus, protonated **1a** and **2a** can and do form a carbenium ion. It is clear that the benzyl cations **18** generated from **1** are more stable than the nonconjugated cations **19** generated from **2**. The transition states for these ring openings are expected to resemble the cations in accord with results of a recent study on 2-aryl-1,1-dimethylaziridinium ions by Crist.[7] Thus, the cations **19** will form more slowly and should rearrange faster than **18**. This could explain the different yields of unrearranged products (75% vs 27%) in the two methanol runs 1 and 5. It may be noted that intervention of an ethylenephenonium ion in reactions of **2a**–**c** is not necessitated by the results of Table 1. Moreover, cation **19** is closely related to the benzyldimethylcarbinyl cation in this respect. Generation of the latter from the respective chloride and its reactions have never been complicated by a phenyl participation or by a phenonium intermediate.[8,9] Moreover, we assume that the cyclization of **19** or a respective anchimeric assistance of its formation would suffer from steric crowding. The phenonium ion resembles an 1-amido-2,2-di-*tert*-butylpropane in this respect.

Two aspects should be mentioned here before the acylaziridines are considered. Protonation occurs on oxygen of acylaziridines[10] and, most likely, on nitrogen of sulfonylaziridines. Second, carboxamides are stronger bases than sulfonamides. The following figures for pK_{BH^+} or equivalents thereof have been reported: sulfonamides,[11] near −6; benzamide,[12] −1.21; *N*-methylbenzamide,[12] −1.13; *N*-ethylbenzamide,[13] −1.92; *N*-arylureas,[14] ca. −1. Ignoring a possible influence of different nitrogen hybridizations and conformations one may conclude from these figures that a protonated sulfonylaziridine contains a distinctly better leaving group than a protonated acylaziridine.

In run 4 the expected isopropyl ether **3bP** (25%) was isolated together with the trifluoroacetate **3bF** (4%). From these yields and from the concentrations one can calculate that trifluoroacetate ion reacted 52 times faster than 2-propanol with the (probably) same electrophile. Available rate data of other substrates for acetate ion and methanol or water, respectively, are compatible with a carbenium intermediate for **3bP** and **3bF** but cannot rule out nucleophilic assistance of ring opening.[15] More noteworthy, **1b** did not show the extreme sensitivity of **1a** toward solvent change: substituting ring opening amounted to 51% in methanol (run 3) and 25% or 29%, respectively, in 2-propanol (run 4). The respective figures for **2b** were 13% vs 4%. The total yields in the mentioned

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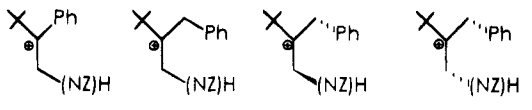
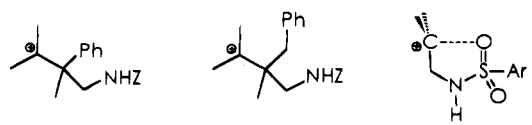
two groups of rearranged/not rearranged products are as follows: **1b** provided 9–12.5% vs 70–80% and **2b,c** provided 40–42% vs 55–56%. These yield sums are fairly constant for each aziridine type and rather independent of the solvent quite in contrast to the tosylaziridines: **1a**/methanol provided 19% vs 75%, **1a**/2-propanol 69–88% vs 0%, **2a**/methanol 69% vs 27%. On the whole, these figures suggest that a carbenium mechanism for the substituting ring opening is at least a good working hypothesis.

Allylamides **6a–c** (13–22%) arise as mixtures of geometric isomers in reactions of aziridines **2a–c**. The *Z* isomers (NOE: *t*-Bu and =CH are cis) prevailed. They could be obtained in the pure state. **6a–c** clearly arose by loss of a proton from the benzylic position of an intermediate carbenium ion **19**. A model shows that the necessary eclipsed conformations with the vacant p orbital can be achieved by both CH bonds, most easily by that CH bond whose deprotonation generates the *Z* isomer. The solvent molecule that abstracts one of the protons is nearly in a geometric position that admits addition to the carbenium center. A discussion of steric or conformational effects with **19** should therefore put the products **4** and **6** into one group. A proton detachment from carbenium ion **18** can only form an enamide **5**. But a space-filling model reveals that in this case the respective ecliptic conformations suffer from conformational restrictions due to the steric demands of both the *tert*-butyl group and the rigid phenyl ring when coplanarity for carbenium triangle (the center with the three atoms bound to it) and phenyl ring is maintained. Indeed, the observed loss of a proton from **18** was not important (maximum 3%). No **5** was obtained from the tosylaziridine **1a** but the trace of aldehyde **17** detected in run 2 may have formed during workup either from **5a** or from the isomeric Schiff base. **5a** may be hydrolyzed faster than **5b**. So, we cannot exclude that up to 19% (yield of tosylamide **15**) of **5a** had existed in run 2 prior to workup. No enamide was found in reactions of aziridines **2**. Proton detachment from the benzylic position in **19** is obviously faster than from the NCH_2 group. The reason for this difference is not quite clear. Formation of an enamide from **18** or **19** may even be independent from an external base when this step is an internal proton transfer within $CH_2N{=}CPhOH$ or within CH_2-$NHCPh{=}O$. The analogous transfer within CH_2NHSO_2-Ar might then suffer from the low basicity of the acceptor moiety providing a second explanation for the lack of **5a** in runs 1 and 2.



18a,b **19a-c** **anti-19** **syn-19**



20a,b **21a-c** **22**

The third type of products without rearrangement is represented by the oxazolines **7** and **8** which were obtained from acylaziridines in yields of 21–38%. Formation of oxazolines from acylaziridines under acid conditions is well known.[16] This isomerization has been shown to be consistent with a carbenium intermediate even when it is just a secondary one.[17] When the carbenium ions **18** and **19** can be trapped internally yielding protonated oxazolines, one expects that they are also trapped externally yielding protonated **3** or **4**. A retardation of the external trapping by a sterically demanding nucleophile (2-propanol) should then be compensated by an increase of internal trapping. This is indeed shown by comparisons of yields in runs 3 and 4 as well as in 6 and 7. A decrease of 22% for ether (and ester) **3** is coupled with a 15% increase for phenyloxazoline **7x** plus a 3% increase for enamide **5b**, while a 9% decrease for ether **4** is coupled with an 8% increase for benzyloxazoline **8x**, the yield of allylamide **6b** remaining constant. The latter fact obviates combining the yields of **4** and **6** when discussing steric or conformational effects as suggested above. The small deficit (4%) in the first comparison may be related to the low product balance (83%) in both runs. The observed interdependence of external and internal substitution is good evidence for a common intermediate, i.e., **18** and **19**, respectively.

Conformational effects have already been discussed for intermediate **18** but not for **19**. The cationic center of **19** is accessible to a nucleophile only when the respective face of the carbenium triangle is least shielded by the phenyl ring of the benzyl group. Two conformations of C^+CH_2N would therefore admit nonrearrangement reactions of **19**. The anti conformation (relative to benzyl) *anti*-**19** can lead to cyclization (internal trapping) and perhaps to internal proton abstraction by the oxygen of Z. The syn conformation *syn*-**19** makes one face of the carbenium triangle wide open to an attack. This face admits both external trapping and external proton abstraction, but the total conformational requirements for the latter are stricter than for the former and perhaps more influenced by the nature of Z. This may be the reason for the 8–9% change in yields of **4cM** and **6c** in run 8 (Z = arylcarbamoyl) relative to the yields of **4bM** and **6b** in run 6 (Z = benzoyl). The sum of **4** + **6** as well as the yield of **8** remains constant.

Reactions subsequent to the neopentyl rearrangement **18** → **20** and **19** → **21** follow expected paths (products **9–16**) and provide clear evidence for the intermediacy of **18** and **19** at least in a part of the chemical processes. Observed reactions of **20** and **21** are external trapping (**9** and **10**), internal trapping (**13** and **14**), deprotonation (**11** and **12**), and β-cleavage **20** → **16** + $TsNHCH_2^+$. The last cation forms tosylamide **15** by hydrolytic cleavage during workup.

The reactions of **2a–c** show a much higher uniformity than those of **1a,b**. Classic S_N1 cannot explain the marked difference between run 2 (no **3aP**) and run 4 (25% **3bP**). We assume that the carbenium character of **18a** and **19a** is modified by some kind of intramolecular interaction of the carbenium center with one of the sulfonyl oxygen atoms as depicted in **22**. Formation of **22** would resemble the familiar ion pair return. Similar interactions with the acyl oxygen of **18b** and **19b,c** can be transition states for the practically irreversible formation of protonated oxazolines **7**-H^+ and **8**-H^+. The analogous ring closure with **18a** and **19a** would yield

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protonated 2-oxo-1,2,3-oxathiazolines. Corresponding products have not been detected. They may be rather unstable, if they are formed at all. Their protonated form should easily and rapidly reestablish the carbenium ion. Perhaps more probable than formation of a C–O bond is a fairly strong electrostatic interaction. It may be noted that the two oxygen atoms of a tosylaziridine are in a position that, nearly without conformational changes, admits an interaction with the carbenium center as soon as the carbenium is formed (cf. X-ray structure of 2-methyl-1-tosylaziridine).[18] Protonation of the aziridine nitrogen will have no influence on the described aziridine conformation.

Independent of the precise nature of the interaction in **22**, this interacting face of the carbenium triangle is completely shielded against external attack. But this interaction may even slow down reactions with the rear side in case the interaction is strong enough to destroy the ideal carbenium planarity in favor of a flat pyramid. Such a distorted carbenium triangle in **22**, and even more so an intermediate with a C–O bond, must suffer from steric hindrance of nucleophilic attack on the rear side, and this hindrance should be much more pronounced with 2-propanol than with methanol. Considering only products **3**, this could explain the difference between runs 2 and 1 or runs 2 and 4. But such a distorted carbenium **18** is not capable of explaining the yields of **3aM** and **3bM** relative to one another. When one face of **18a** is completely shielded and the other face has an increased steric demand relative to a fully planar ion in **18b**, the yield of methyl ether **3aM** cannot be higher than the yield of methyl ether **3bM**. This discrepancy is resolved when a part of both ethers or at least of sulfonamide ether **3aM** is formed with nucleophilic assistance by the solvent. The better leaving group in the protonated sulfonylaziridine may favor such a borderline mechanism in run 1 more than in run 3. A more fundamental reactivity difference between **1a** and **1b** is expected from the geometry of their protonated forms. O-Protonated **1b** has a planarized nitrogen conformation that does not restrict rotations of the phenyl ring in position 2. In **1a** and its conjugated acid, the *tert*-butyl group forces the tosyl group into anti or trans conformation (syn or cis relative to phenyl). It is easy to imagine, even without having a space-filling model at hand, that the two tosyl oxygen atoms hinder a rotation of phenyl and enforce a conformation that is suited for an orbital dependent[6] benzylic effect. This should accelerate formation of **18** but it should accelerate even more an assisted ring opening of **1a**-H^+. Thus, we propose that **3aM** arises both with and without solvent assistance. A similar contribution by a borderline S_N2 is expected to be absent with **2a–c** and, at the most, negligible with **1b**. The steric hindrance of solvent assistance can be overcome to a recognizable extent only with the help of a conformationally favored benzylic effect (**1a**/methanol).

Experimental Section

General Methods and Materials. ^1H NMR spectra were recorded from $CDCl_3$ solutions containing TMS. IR spectra were recorded from KBr tablets unless otherwise stated. Chr (column chromatography) was performed with 0.063–0.2 mm silica gel (Merck); column dimensions (thickness × length, cm) are given for the specific workup. PLC (preparative layer chromatography) was performed with silica gel 60 F 254 (Merck, 5717), 20 cm × 20 cm, 2 mm thick; zones are given from top to bottom, they were extracted with warm EtOAc (ethyl acetate).

Starting Materials. The activated aziridines **1a,b** and **2a,b** are known.[3,18]

2-Benzyl-1-[(4-chlorophenyl)carbamoyl]-2-*tert*-butylaziridine (2c). A solution of 8.45 g (55 mmol) of 4-chlorophenyl isocyanate in 40 mL of diethyl ether was dropwise added to a stirred solution of 10.4 g (55 mmol) of 2-benzyl-2-(1,1-dimethylethyl)aziridine[18] in 100 mL of diethyl ether. Evaporation provided a residue that was recrystallized from petroleum ether: yield 74%; mp 187–189 °C; IR 3290, 1650 cm^{-1}; ^1H NMR δ 1.03 (s, 9H), 2.07 (s, 1H), 2.25 (s, 1H), 3.06 (d, J = 14.9 Hz, 1H), 3.29 (d, J = 14.9 Hz, 1H), 6.57 (s br, 1H), 7.07–7.21 (m, 5H), 7.24–7.30 (m, 2H), 7.33–7.39 (m, 2H). Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 70.03; H, 6.78; N, 8.25.

General Method of Alcoholyses. All reactions were conducted with continuous stirring. The aziridine was added to the solution of the acid in the alcohol. Acid (70% $HClO_4$ or 99% CF_3CO_2H), alcohol, and other details of each run are given in Table 1. Evaporation provided a residue that was taken up in CH_2Cl_2 and twice washed with water. Evaporation of the dried organic layer yielded a residue whose further treatment is given below for each run.

Run 1. Chr (3 × 60, toluene/EtOAc 1:1) provided 795 mg of a mixture and 21 mg of **3aM**. The mixture consisted (^1H NMR) of 190 mg (19%) of **11a** and 605 mg (total 815 mg corresponding to 75%) of **3aM**. For **11a** see run 2.

***N*-(3,3-Dimethyl-2-methoxy-2-phenylbutyl)toluene-4-sulfonamide (3aM):** mp 142–145 °C; IR 3320, 1335, 1166, 1118, 1095 cm^{-1}; ^1H NMR δ 0.83 (s, 9H), 2.44 (s, 3H), 3.13 (s, 3H), 3.38 (dd, J = 2.3/8.2 Hz, 1H), 3.76 (dd, J = 8.2/12.6 Hz, 1H), 4.43 (m_c, 1H), 7.01–7.08 (m, 2H), 7.20–7.33 (m, 3H), 7.34 (d br, J = 8.2 Hz, 2H), 7.77 (d, J = 8.2 Hz, 2H). Anal. Calcd for $C_{20}H_{27}NO_3S$: C, 66.45; H, 7.53; N, 3.87. Found: C, 66.51; H, 7.38; N, 3.98.

Run 2. ^1H NMR of the residue showed the presence of **16** and **17**. The structure of the latter was recognized from the aldehydic doublet (10.10) and its J = 3.3 Hz (3 Hz is typical for CHCHO)[19] in combination with a *tert*-butyl singlet (1.05, the only tBu in run 2) and a reasonable chemical shift (3.30) for the aliphatic CH. The chemical shifts of the methyl singlets of **16** are (lit.[20]) as follows: 1.58 (1.57), 1.80 (1.80), 1.94 (1.94). Chr (3 × 60) provided (CH_2Cl_2) 680 mg (69%) of **11a** and (EtOAc) 100 mg (19%) of **15** identified by mp and TLC.

***N*-(2,3-Dimethyl-2-phenyl-3-butenyl)toluene-4-sulfonamide (11a):** mp 89–91 °C; IR 3280, 1645, 1333, 1165 cm^{-1}; ^1H NMR δ 1.40 (s br, 3H), 1.41 (s, 3H), 2.42 (s, 3H), 3.27 (d, J = 6.1 Hz, 2H), 4.10 (t br, J = 6.1 Hz, 1H), 4.90 (s, 1H), 5.03 (s, 1H), 7.11–7.36 (m, 7H), 7.69 (d, J = 8.2 Hz, 2H). Anal. Calcd for $C_{19}H_{23}NO_2S$: C, 69.27; H, 7.04; N, 4.25. Found: C, 69.24; H, 6.96; N, 4.11.

Run 3. Chr (3 × 60, CH_2Cl_2) provided 5 mg of a mixture consisting (^1H NMR) of 2 mg (0.2%) of **5b** and 3 mg of **3bM**. Further elution yielded 90 mg of **3bM**. Elution with EtOAc provided 651 mg of a mixture consisting (^1H NMR) of 379 mg (total 742 mg corresponding to 51%) of **3bM**, 194 mg (23%) of **7x**, 78 mg (9%) of **11b**, and a trace of **13x**. Products **5b**, **7x**, **11x**, and **13x** are characterized under run 4.

***N*-(3,3-Dimethyl-2-methoxy-2-phenylbutyl)benzamide (3bM):** mp 121–123 °C; IR 3420, 1670, 1664, 1653, 1650, 1540, 1535, 1530, 1120, 1073 cm^{-1}; ^1H NMR δ 0.96 (s, 9H), 3.26 (s, 3H), 3.93 (dd, J = 3.1/14.9 Hz, 1H), 4.45 (dd, J = 6.1/14.9 Hz, 1H), 6.41 (s br, 1H), 7.27–7.53 (m, 8H), 7.64–7.70 (m, 2H). Anal. Calcd for $C_{20}H_{25}NO_2$: C, 77.14; H, 8.09; N, 4.50. Found: C, 76.93; H, 8.09; N, 4.47.

Run 4. Chr (2.5 × 90, CH_2Cl_2) yielded 16 mg (3%) of **5b**, 31 mg (4%) of **3bF**), and 171 mg (25%) of **3bP**. Elution with EtOAc provided 287 mg of mixture I and 13 mg of mixture II.

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Chr (3 × 60, CH_2Cl_2) of mixture I yielded 59 mg (11%) of **11b** and (EtOAc) 210 mg (38%) of **7x**. PLC (toluene/EtOAc 10:1) of mixture II provided 5 mg (0.9%) of **13x** and 4 mg (0.6%) of **9bP**.

***N*-(3,3-Dimethyl-2-isopropoxy-2-phenylbutyl)benzamide (3bP):** mp 96–99 °C; IR 3455, 1670, 1527, 1522, 1518, 1117, 1080, 1065, 1032 cm^{-1}; ^1H NMR δ 0.94 (s, 9H), 1.21 (d, J = 6.0 Hz, 6H), 3.87 (sept, J = 6.0 Hz, 1H), 4.07 (dd, J = 3.0/15.1 Hz, 1H), 4.36 (dd, J = 6.7/15.1 Hz, 1H), 6.22 (s br, 1H), 7.27–7.60 (m, 10H). Anal. Calcd for $C_{22}H_{29}NO_2$: C, 77.84; H, 8.61; N, 4.13. Found: C, 77.71; H, 8.80; N, 4.18.

***N*-[3,3-Dimethyl-2-phenyl-2-(trifluoroacetoxy)butyl]-benzamide (3bF):** oil; IR 3450, 1788, 1780, 1660, 1652, 1533, 1524, 1239 cm^{-1}; ^1H NMR δ 1.08 (s, 9H), 3.60 (dd, J = 1.6/16.3 Hz, 1H), 5.27 (dd, J = 9.9/16.3 Hz, 1H), 7.03–7.10 (m, 2H), 7.24–7.57 (m, 9H). Molecular mass calcd for M^+ of $C_{21}H_{22}F_3NO_3$ *m/e* 393.1553, found *m/e* 393.1554.

***N*-(3,3-Dimethyl-2-phenyl-1-butenyl)benzamide (5b):** mp 119–121 °C; IR 3440, 1674, 1660, 1502 cm^{-1}; ^1H NMR δ 1.16 (s, 9H), 6.99–7.52 (m, 12H). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.55; H, 7.46; N, 5.02.

5-*tert*-Butyl-5-phenyl-4,5-dihydrooxazole (7x): mp 73–75 °C; IR 1661, 1273, 1087, 1029 cm^{-1}; ^1H NMR δ 0.96 (s, 9H), 4.23 (d, J = 15.0 Hz, 1H), 4.48 (d, J = 15.0 Hz, 1H), 7.21–7.54 (m, 8H), 8.00–8.08 (m, 2H). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.54; H, 7.46; N, 5.10.

***N*-(3-Isopropoxy-2-phenyl-2,3,3-trimethylbutyl)benzamide (9bP):** oil; IR (film) 3410, 3390, 1660, 1523, 1115 cm^{-1}; ^1H NMR δ 1.06 (s, 6H), 1.07 (d, J = 6.1 Hz, 3H), 1.16 (d, J = 6.1 Hz, 13H), 1.48 (s, 3H), 3.84 (sept, J = 6.1 Hz, 1H), 4.00 (dd, J = 5.4/13.7 Hz, 1H), 4.15 (dd, J = 5.4/13.7 Hz, 1H), 6.88 (s br, 1H), 7.20–7.56 (m, 8H), 7.59–7.68 (m, 2H); molecular mass calcd for M^+ of $C_{22}H_{29}NO_2$ *m/e* 339.2200, found *m/e* 339.2202.

***N*-(2,3-Dimethyl-2-phenyl-3-butenyl)benzamide (11b):** mp 90–92 °C; IR 3360, 1643, 1554, 1550 cm^{-1}; ^1H NMR δ 1.48 (s, 3H), 1.59 (s br, 3H), 3.90 (d, J = 5.6 Hz, 2H), 5.11 (s, 1H), 5.15 (s br, 1H), 5.92 (s br, 1H), 7.21–7.55 (m, 8H), 7.62–7.70 (m, 2H). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.75; H, 7.36; N, 5.07.

5,6,6-Trimethyl-5-phenyl-3,4-dihydro-6*H*-oxazine (13x): mp 74–76 °C; IR 1662, 1247, 1073, 1032 cm^{-1}; ^1H NMR δ 1.22 (s, 3H), 1.42 (s, 3H), 1.44 (s, 3H), 3.57 (d, J = 17.5 Hz, 1H), 4.25 (d, J = 17.5 Hz, 1H), 7.21–7.51 (m, 8H), 7.94–8.01 (m, 2H). Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.79; H, 7.83; N, 4.94.

Run 5. Chr (3 × 60, toluene/EtOAc 10:1) provided 187 mg of mixture I, 792 mg of mixture II, and 40 mg of mixture III. Mixture I consisted (^1H NMR) of 62 mg (6%) of **6a** and 125 mg (12%) of **12a**. PLC (toluene/EtOAc 10:1) of this mixture provided 32 mg of **6a**, 88 mg of a mixture (**6a** and **12a**), and 55 mg of **12a**. Mixture II consisted (^1H NMR) of 134 mg (total 196 mg corresponding to 19%) of **6a**, 349 mg (total 474 mg corresponding to 46%) of **12a**, 59 mg of **4aM**, and 250 mg of **10aM**. Mixture III consisted (^1H NMR) of 31 mg (total 90 mg corresponding to 8%) of **4aM** and 9 mg (total 259 mg corresponding to 23%) of **10aM**.

***N*-(2-Benzyl-3,3-dimethyl-2-methoxybutyl)-4-toluenesulfonamide (4aM) in mixture with *N*-(2-Benzyl-2,3-dimethyl-3-methoxybutyl)-4-toluenesulfonamide (10aM):** oil. ^1H NMR (**4aM**): δ 0.97 (s, 9H), 2.43 (s, 3H), 2.71 (d, J = 14.0 Hz, 1H), 2.99 (d, J = 14.0 Hz, 1H), 3.0–3.4 (m, 2H for both isomers), 3.36 (s, 3H), 4.35 (m_c, 1H), 7.13–7.38 (m, 7H), 7.60 (d, J = 8.3 Hz, 2H). Anal. Calcd for $C_{21}H_{29}NO_2$: C, 67.16; H, 7.78; N, 3.73. Found: C, 66.78; H, 7.38; N, 3.98.

^1H NMR (**10aM**): δ 0.63 (s, 3H), 1.02 (s, 3H), 1.09 (s, 3H), 2.43 (s, 3H), 2.62 (d, J = 13.3 Hz, 1H), 3.05 (d, J = 13.3 Hz, 1H), 3.0–3.4 (m, 2H for both isomers), 3.24 (s, 3H), NH signal not identified, 7.13–7.39 (m, 7H), 7.67–7.76 (m, 2H).

(*Z*)-*N*-(2-*tert*-Butyl-3-phenylallyl)-4-toluenesulfonamide ((*Z*)-6a): mp 145–148 °C; IR 3300, 1638, 1324, 1165, 1160 cm^{-1}; ^1H NMR ((*Z*)-**6a**) δ 1.14 (s, 9H), 2.44 (s, 3H), 3.62 (d, J = 5.7 Hz, 2H), 4.09 (t br, J = 5.7 Hz, 1H), 6.57 (s, 1H), 7.00–7.07 (m, 2H), 7.13–7.28 (m, 5H), 7.51–7.58 (m, 2H); ^1H NMR ((*E*)-**6a**, identifiable signals only) 1.12 (s, 9H), 3.68 (d, J = 6.0 Hz, 2H), 4.48 (s br, 1H), 6.30 (s br, 1H). Anal. Calcd for $C_{20}H_{25}NO_2S$: C, 69.94; H, 7.34; N, 4.08. Found: C, 69.81; H, 7.34; N, 4.20.

***N*-(2-Benzyl-2,3-dimethyl-3-butenyl)-4-toluenesulfonamide (12a):** mp 107–109 °C; IR 3290, 3270, 1644, 1333, 1165 cm^{-1}; ^1H NMR δ 0.92 (s, 3H), 1.64 (s, 3H), 2.44 (s, 3H), 2.61 (d, J = 13.4 Hz, 1H), 2.68 (d, J = 13.3 Hz, 1H), 2.73 (dd, J = 6.9/11.5 Hz, 1H), 2.93 (dd, J = 4.9/11.5 Hz, 1H), 4.16 (m_c, 1H), 4.66 (s br, 1H), 4.97 (s br, 1H), 7.00–7.07 (m, 2H), 7.17–7.37 (m, 5H), 7.70–7.77 (m, 2H). Anal. Calcd for $C_{20}H_{25}NO_2S$: C, 69.94; H, 7.34; N, 4.08. Found: C, 69.65; H, 7.31; N, 4.24.

Run 6. Chr (1.5 × 90, toluene/EtOAc 10:1) provided 193 mg (22%) of **6b**, 56 mg (6%) of **12b** and 64 mg of a mixture consisting (^1H NMR) of 41 mg (total 97 mg corresponding to 11%) of **12b** and 23 mg of **8x**. Further elution yielded 162 mg (total 185 mg corresponding to 21%) of **8x**, 105 mg of **14x**, and 13 mg of a mixture consisting (^1H NMR) of 8 mg (total 113 mg corresponding to 13%) of **14x**, 2 mg of **4bM**, and 3 mg of **10bM**. Continued elution provided 309 mg of a mixture consisting (^1H NMR) of 131 mg (total 133 mg corresponding to 13%) of **4bM** and 178 mg (total 181 mg corresponding to 18%) of **10bM**. PLC (cyclohexane/EtOAc 2:1) of 100 mg of the last mixture yielded 40 mg of **4bM** and 52 mg of **10bM**.

***N*-(2-Benzyl-3,3-dimethyl-2-methoxybutyl)benzamide (4bM):** oil; IR (film) 3460, 1671, 1663, 1530, 1523, 1519, 1100, 1080 cm^{-1}; ^1H NMR δ 1.12 (s, 9), 2.57 (d, J = 14.3 Hz, 1H), 3.24 (d, J = 14.4 Hz, 1H), 3.51 (s, 3H), 3.52 (dd, J = 4.5/14.4 Hz, 1H), 3.89 (dd, J = 5.2/14.4 Hz, 1H), 5.91 (s br, 1H), 7.08–7.44 (m, 10H). Anal. Calcd for $C_{21}H_{27}NO_2$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.37; H, 8.38; N, 4.20.

(*Z*)-*N*-(2-*tert*-Butyl-3-phenylallyl)benzamide ((*Z*)-6b): mp 114–115 °C; IR 3300, 1628, 1515 cm^{-1}; ^1H NMR ((*Z*)-**6b**) δ 1.23 (s, 9H), 4.28 (d, J = 4.8 Hz, 2H), 5.86 (s br, 1H), 6.66 (s, 1H), 7.19–7.54 (m, 10H); ^1H NMR ((*E*)-**6b**, identifiable signals only) δ 1.06 (s, 9H), 4.22 (dd, J = 5.7/1.2 Hz, 2H), 6.38 (s br, 1H), 6.59 (s, 1H). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 82.05; H, 7.99; N, 4.57.

5-Benzyl-5-*tert*-butyl-4,5-dihydrooxazole (8x): mp 53–54 °C; IR 1662, 1656, 1280, 1070, 1029 cm^{-1}; ^1H NMR δ 1.03 (s, 9H), 2.69 (d, J = 13.9 Hz, 1H), 3.34 (d, J = 13.9 Hz, 1H), 3.71 (d, J = 15.3 Hz, 1H), 3.93 (d, J = 15.3 Hz, 1H), 7.08–7.23 (m, 5H), 7.32–7.49 (m, 3H), 7.78–7.85 (m, 2H). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.89; H, 7.86; N, 4.91.

***N*-(2-Benzyl-2,3-dimethyl-3-methoxybutyl)benzamide (10bM):** oil; IR (film) 3390, 1670, 1664, 1528, 1521, 1144, 1132, 1066 cm^{-1}; ^1H NMR δ 0.83 (s, 3H), 1.30 (s, 6H), 2.61 (d, J = 13.5 Hz, 1H), 3.12 (d, J = 1H), 3.15 (dd, J = 2.0/14.3 Hz, 1H), 3.37 (s, 3H), 3.39 (dd, J = 5.6/14.3 Hz, 1), 7.10–7.17 (m, 2H), 7.19–7.31 (m, 3H), 7.40–7.54 (m, 3H), 7.76–7.83 (m, 2H), 8.23 (s br, 1H). Anal. Calcd for $C_{21}H_{27}NO$: C, 77.50; H, 8.36; N, 4.30. Found: C, 77.73; H, 8.56; N, 4.40.

***N*-(2-Benzyl-2,3-dimethyl-3-butenyl)benzamide (12b):** mp 51–52 °C; IR 3370, 1645, 1638, 1540, 1533 cm^{-1}; ^1H NMR δ 1.06 (s, 3H), 1.91 (s, 3H), 2.73 (d, J = 13.4 Hz, 1H), 2.86 (d, J = 13.4 Hz, 1H), 3.41–3.58 (m, 2H), 4.80 (s, 1H), 5.07 (s, 1H), 5.98 (s br, 1H), 7.09–7.17 (m, 2H), 7.19–7.33 (m, 3H), 7.37–7.54 (m, 3H), 7.65–7.73 (m, 2H). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.89; H, 7.88; N, 4.93.

5-Benzyl-5,6,6-trimethyl-4,5-dihydro-6*H*-oxazine (14x): mp 96–99 °C; IR 1653, 1262, 1073, 1031 cm^{-1}; ^1H NMR δ 0.91 (s, 9H), 1.42 (s, 3H), 1.48 (s, 3H), 2.60 (d, J = 13.0 Hz, 1H), 2.75 (d, J = 13.0 Hz, 1H), 3.10 (d, J = 17.5 Hz, 1H), 3.34 (d, J = 17.5 Hz, 1H), 7.11–7.46 (m, 8H), 7.94–8.01 (m, 2H). Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.67; H, 7.72; N, 4.85.

Run 7. Chr (1.5 × 90, toluene/EtOAc 10:1) provided 129 mg (22%) of **6b**, 315 mg of mixture I, 52 mg of mixture II, and 78 mg of mixture III consisting (^1H NMR) of 26 mg of **14x** and 52 mg (7%) of **10bP**. Mixture I consisted (^1H NMR) of 137 mg of **8x**, 152 mg (26%) of **12b**, and 26 mg (4%) of **4bP**. Mixture II consisted (^1H NMR) of 36 mg (total 173 mg corresponding to 29%) of **8x** and 16 mg (total 42 mg corresponding to 7%) of **14x**. PLC (toluene/EtOAc 6:1) of 100 mg of mixture I provided 39 mg of **8x**, 41 mg of **6b**, and 14 mg of **4bP**. PLC (cyclohexane/EtOAc 2:1) of mixture II provided 23 mg of **14x** and 45 mg of **10bP**.

***N*-(2-Benzyl-3,3-dimethyl-2-isopropoxybutyl)benzamide (4bP):** oil; IR (film) 3450, 1672, 1664, 1522, 1134, 1098 cm^{-1}; ^1H NMR δ 1.04 (s, 9H), 1.18 (d, J = 6.0 Hz, 6H), 3.09 (d, J = 14.0 Hz, 1H), 3.15 (d, J = 14.0 Hz, 1H), 3.78 (dd, J = 4.9/14.4 Hz, 1H), 3.85 (dd, J = 5.3/14.4 Hz, 1H), 4.21 (sept, J = 6.0 Hz, 1H), 6.40 (s br, 1H), 7.21–7.59 (m, 10H). Anal. Calcd for $C_{23}H_{31}NO_2$: C, 78.15; H, 8.84; N, 3.96. Found: C, 78.04; H, 8.77; N, 3.97.

***N*-(2-Benzyl-2,3-dimethyl-3-isopropoxybutyl)benzamide (10bP):** oil; IR (film) 3380, 1661, 1523, 1518, 1131, 1110 cm^{-1}; ^1H NMR δ 0.80 (s, 3H), 1.13 (s, J = 6.0 Hz, 3H), 1.20 (s, 3H), 1.29 (s, 3H), 1.31 (s, 3H), 2.60 (d, J = 13.3 Hz, 1H), 3.16 (d, J = 13.3 Hz, 1H), 3.19 (dd, J = 2.8/14.4 Hz, 1H), 3.37 (dd, J = 5.7/14.4 Hz, 1H), 7.08–7.53 (m, 8H), 7.77–7.86 (m, 2H). Anal. Calcd for $C_{23}H_{31}NO_2$: C, 78.15; H, 8.84; N, 3.96. Found: C, 78.23; H, 8.86; N, 3.86.

Run 8. Chr (3 × 60, CH_2Cl_2/EtOAc 10:1) provided 196 mg of mixture I, 218 mg of mixture II, 67 mg of **4cM**, and 168 mg (15%) of **10cM**. Elution with acetone yielded 348 mg of mixture III. Components (^1H NMR) of mixtures were as follows. Mixture I: 115 mg of **6c** and 81 mg of **12c**. Mixture II: 18 mg (total 133 mg corresponding to 13%) of **6c**, 36 mg (total 117 mg corresponding to 11%) of **12c**, and 164 mg (total 231 mg corresponding to 21%) of **4cM**. Mixture III: 218 mg (21%) of **8y** and 130 mg (13%) of **14y**. PLC (toluene/EtOAc 4:1) of 100 mg of mixture I yielded 53 mg of **6c** and 41 mg of **12c**; PLC (toluene/EtOAc 3:1) of 100 mg of mixture III yielded 56 mg of **8y** and 37 mg of **14y**.

***N*-(4-Chloroanilino)-*N'*-(2-benzyl-3,3-dimethyl-2-methoxybutyl)urea (4cM):** mp 181–183 °C; IR 3250–3410, 1661, 1552, 1095, 1073 cm^{-1}; ^1H NMR δ 1.06 (s, 9H), 2.71 (d, J = 14.5 Hz, 1H), 3.18 (d, J = 14.6 Hz, 1H), 3.46 (m_c, 2H), 3.50 (s, 3H), 4.61 (t br, J = 6 Hz, 1H), 6.23 (s br, 1H), 7.03–7.10 (m, 2H), 7.14–7.29 (m, 7H). Anal. Calcd for $C_{21}H_{27}ClN_2O_2$: C, 67.28; H, 7.26; N, 7.47. Found: C, 67.57; H, 7.36; N, 7.49.

(*Z*)-*N*-(4-Chloroanilino)-*N'*-(2-benzylidene-3,3-dimethylbutyl)urea ((*Z*)-6c): 179–182 °C; IR 3340, 1644, 1568, 1558 cm^{-1}; ^1H NMR ((*Z*)-**6c**) δ 1.18 (s, 9H), 4.06 (d, J = 4.6 Hz, 2H), 4.51 (s br, 1H), 6.24 (s br, 1H), 6.55 (s, 1H), 7.04–7.10 (m, 2H), 7.17–7.36 (m, 7H); ((*E*)-**6c**, identifiable signals only) δ 1.03 (s, 9H), 4.02 (dd, J = 6.0/1.5 Hz, 2H), 4.8 (s br, 1H), 6.48 (s, 1H). Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 69.89; H, 6.67; N, 8.10.

5-Benzyl-2-*tert*-butyl-(4-chloroanilino)-4,5-dihydrooxazole (8y): mp 148–151 °C; IR 3460 br, 1673, 1660, 1652, 1263, 1092, 1077, 1038 cm1^{-1}; ^1H NMR δ 1.12 (s, 9H), 2.72 (d, J = 14.1 Hz, 1H), 3.32 (d, J = 14.1 Hz, 1H), 3.54 (d, J = 10.7 Hz, 1H), 3.72 (d, J = 10.7 Hz, 1H), 4.07 (s br, 1H), 7.07–7.36 (m, 9H). Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 69.95; H, 6.62; N, 8.00.

***N*-(4-Chloroanilino)-*N'*-(2-benzyl-2,3-dimethyl-3-methoxybutyl)urea (10cM):** mp 146–148 °C; IR 3400, 1672, 1558, 1552, 1540, 1132 cm^{-1}; ^1H NMR δ 0.74 (s, 3H), 1.19 (s, 3H), 1.20 (s, 1H), 2.52 (d, J = 13.3 Hz, 1H), 2.98 (d, J = 13.3 Hz, 1H), 3.06 (s, 3H), 1 H of NCH_2 is hidden under singlet at 3.06 and doublet at 2.98, 3.13 (dd, J = 5.5/13.6 Hz, 1H), 6.60 (s br, 1H), 6.78 (s br, 1H), 7.10–7.31 (m, 9H). Anal. Calcd for $C_{21}H_{27}ClN_2O_2$: C, 67.28; H, 7.26; N, 7.47. Found: C, 67.39; H, 7.27; N, 7.43.

***N*-(4-Chloroanilino)-*N'*-(2-benzyl-2,3-dimethyl-3-butenyl)urea (12c):** mp 173–175 °C; IR 3395, 1657, 1649, 1565, 1555 cm^{-1}; ^1H NMR δ 0.98 (s, 3H), 1.82 (s, 3H), 2.63 (d, J = 13.3 Hz, 1H), 2.75 (d, J = 13.4 Hz, 1H), 3.27 (m_c, 2H), 4.66 (s br, 2H), 4.95 (s, 1H), 6.56 (s br, 1H), 7.04–7.11 (m, 2H), 7.16–7.30 (m, 7H). Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 70.21; H, 6.88; N, 8.21.

5-Benzyl-2-(4-chloroanilino)-5,6,6-trimethyl-4,5-dihydro-6*H*-oxazine (14y): mp 155–158 °C; IR 2760–3300, 1677, 1256, 1109, 1086 cm^{-1}; ^1H NMR δ 0.94 (s, 3H), 1.44 (s, 3H), 1.48 (s, 3H), 2.61 (d, J = 13.1 Hz, 1H), 2.77 (d, J = 13.1 Hz, 1H), 2.93 (d, J = 14.7 Hz, 1H), 3.20 (d, J = 14.7 Hz, 1H), 4.48 (s br, 1H), 7.11–7.35 (m, 9H). Anal. Calcd for $C_{20}H_{23}ClN_2O$: C, 70.06; H, 6.76; N, 8.17. Found: C, 69.74; H, 6.58; N, 8.09.

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