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HOMOLYTIC AZIRIDINE OPENING (AZA VARIANT OF CYCLOPROPYLCARBINYL-HOMOALLYL REARRANGEMENT) BY ADDITION OF TRIBUTYLTIN RADICAL TO N-ACYLAZIRIDINES. FACTORS CONTRIBUTING TO THE REGIOSELECTIVITY [1]

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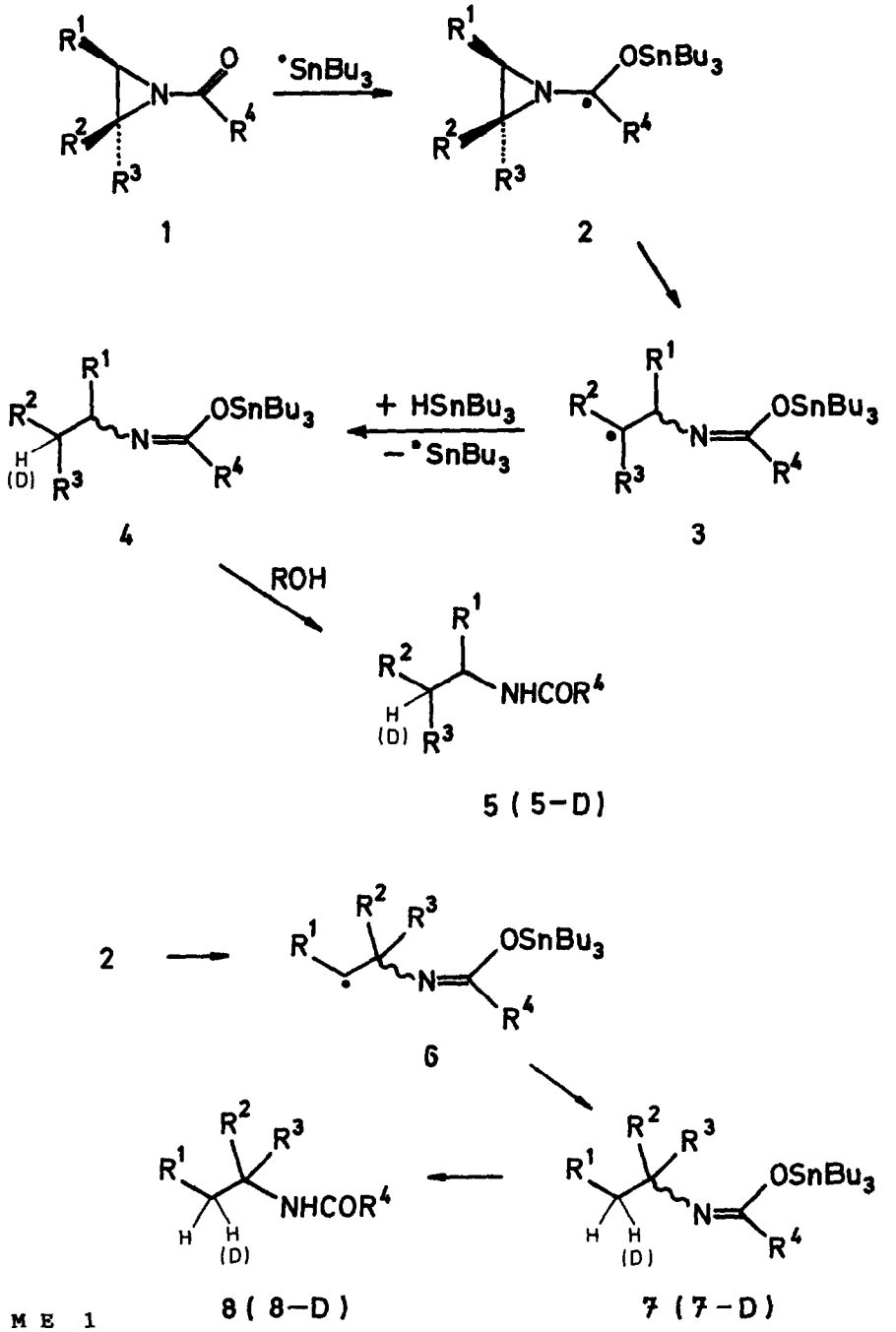
Abstract - AIBN initiated reaction of N-acylaziridines **1** with Bu_3SnH in refluxing benzene provided products **5** and **8** of reductive ring opening. Yields (practically quantitative in most cases) fell drastically with steric hindrance of the addition of $Bu_3Sn^{\bullet}$ to the acyl oxygen of **1**. They depended to some extent on the experimental conditions for hydrogen capturing when aziridine homolysis provided a primary radical **3** or **6**. The regioselectivity of (probably reversible) ring homolysis can be understood in terms of the stability of the arising radical (**3**, **6**), of stereoelectronic control (e.g. **1i** as compared to **1h**) and of frontier orbital interactions (**1j**). A possible difference in bond lengths as explanation for the formation of the primary radical from **1j** did not find support from an X-ray structure analysis of N-tosyl-2-methyl-aziridine **11**. Isomeric products were obtained only twice (**1i**, **1j**) with a dependence of the ratio **5j**:**8j** on concentration and hydrogen isotope of Bu_3SnH. No such dependence was found for the ratio **5**:**14** (reduction without and with an intervening cyclization of **3** leading to a pyrrolidone) obtained from the N-cinnamoylaziridine **11**. This ratio (1:9 for **11** and 1:3 for **1n**) must reflect the E-Z isomers in **3**. The observed preference for the formation of **E-3** from **2** can be explained by stereoelectronic and steric effects. A cinnamoyl double bond in **5** was saturated depending on experimental conditions.

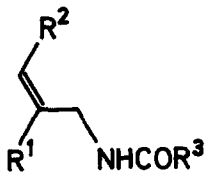
A mechanism starting with single electron transfer (SET) has been proposed[2] for the nucleophilic ring opening of certain N-acylaziridines **1**. The generated ketyl (ionic analogue of **2**, Na or Li in place of $SnBu_3$) was assumed to undergo homolytic cleavage of the aziridine ring. Indirect evidence[3] for this homolytic cleavage was based on a method that has certain drawbacks.[4] The homolytic behaviour of aziridines with tervalent nitrogen can be better studied by the method described below. A first direct proof of a C-N homolysis in an aziridine profited from charge annihilation and was triggered off by a boryl

radical on a tetravalent aziridine nitrogen[5]. A C-N homolysis of an N-sulfonylaziridine was initiated by a radical in position 2 of the aziridine ring[6]. We now report on the first homolyses initiated by generation of a ketyl-like intermediate 2 through addition of $Bu_3Sn^{\bullet}$ to N-acylaziridines 1.

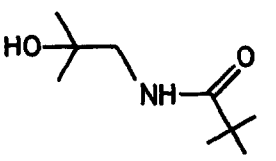


SCHEME 1

Reaction of N-acylaziridines **1** with an excess of tributyltin hydride and 0.1 equivalent of azobisisobutyronitrile (AIBN) in refluxing benzene provided the products **5** and **8** after hydrolysis or methanolysis of the reaction mixture (Table 1). Without AIBN no reaction occurred except for thermal isomerization of **1d** (16% **9b**, 81% **1d** recovered). Such isomerizations are well known for suitably substituted N-acylaziridines. The dependence of reductive opening on decomposing AIBN is evidence for a radical chain process as depicted in Scheme 1. As required by step **3** → **4** or **6** → **7** of this mechanism one deuterium atom was incorporated into the product (**5-D**, **8-D**) when the reaction was run with Bu_3SnD. Usually, reductive ring opening proceeded practically quantitatively unless the addition of $Bu_3Sn^{\bullet}$ to the acyl group of **1** was sterically hindered. Such a hindrance with N-pivaloyl aziridines (R^4 = tBu) accounts for the low yield of **5b** and for the failure of **1g** to react. Steric hindrance of this step is probably responsible for the diminished yield obtained from the N-benzoylaziridine **1d**, since in its preferred ground state of nitrogen inversion[7] (R^4CO trans to large R^3) the benzyl group (R^2) may be pushed towards the benzoyl group by the t-butyl group (R^3).



	R^1	R^2	R^3
9a	Me	H	tBu
9b	tBu	Ph	Ph



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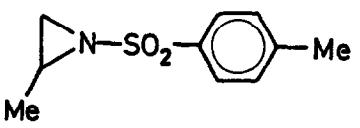


11

The stability of radical **3** (final product **5**) seems to be an important factor for the regioselectivity of ring opening, since only twice the final product **8** indicated a competing formation of the less stable radical **6**. However, in analogy to the interpretation for the behaviour of cyclopropylcarbinyl radicals derived from acyl cyclopropanes,[8,9] stereoelectronic control of ring cleavage may also often favour step **2** → **3** over step **2** → **6**. The

Table 1. Reactions of **1a-k** in refluxing benzene with an excess of Bu_3SnH or Bu_3SnD and 0.1 equivalent of AIBN.[a]

1-8	R^1	R^2	R^3	R^4	equivalent of Sn cpd.	% yield of products 5	8	1	9	10
a	H	Me	Me	Ph	1.6 Bu_3SnH	98				
a	H	Me	Me	Ph	1.6 Bu_3SnD	97				
b	H	Me	Me	tBu	1.6 Bu_3SnH	9[b]		63[b]	12[b]	16[b]
c	H	Ph	H	Ph	1.6 Bu_3SnH	99				
d	H	CH_2Ph	tBu	Ph	1.6 Bu_3SnH	50		38	12	
e	H	Ph	tBu	Ph	1.6 Bu_3SnH	99				
f	CH_2Ph	Ph	H	Ph	1.6 Bu_3SnH	99				
g	CH_2Ph	Ph	H	tBu	1.6 Bu_3SnH			99		
h	Me	Ph	H	Ph	1.6 Bu_3SnH	94				
i	Me	H	Ph	Ph	1.6 Bu_3SnH	41	49			
j	H	H	Me	Ph	1.6 Bu_3SnH	61	30			
j	H	H	Me	Ph	4 Bu_3SnH	52[c]	34[c]			
j	H	H	Me	Ph	1.6 Bu_3SnD	58	15			
k	H	H	H	Ph	1.6 Bu_3SnH	73[d]		0		
k	H	H	H	Ph	4 Bu_3SnH	87		0		
k	H	H	H	Ph	1.6 Bu_3SnD	58		0		

[a] Typically 5 mmol (1-2.5 mmol) of 1, 0.5 mmol (or less) AIBN and the given amount of tin compound were refluxed in 100 ml (50 ml) of benzene for 2 hours (0.5 hours for the cis-trans pair **1h,i**).
[b] In order to avoid loss of **5b** this run was analyzed from the H-NMR spectrum (internal calibration of the integral) of the product mixture. **9a** and **10** are artifacts of **1b** arising by solvolysis of the reaction mixture.
[c] A repetition of this run gave 54% **5j** and 32% **8j**.
[d] A repetition of this run gave 70% **5k**.

N-acylaziridines differ from the acyl cyclopropanes due to the possibility of nitrogen inversion. In principle, the former can change cis and trans relations of the acyl group by going to another inversional ground state. Unsymmetrical substitution in **1** makes the two ground states unequal. The preferred ground state of **1i** as well as of **2i** has the large groups in trans

position (Figure 1, top) and the small methyl group in cis position relative to the N-substituent. Steric repulsion as shown in the lower part (right) of Figure 1 disfavours the stereoelectronic arrangement required for the cleavage of the N-CPh bond. Thus, the less stable radical **6i** is formed together with the more stable **3i**: both products **5i** and **8i** are obtained. With the isomeric cis aziridine **1h** (as well as with **1c** and **1f**) there is no stereoelectronic difference for the two N-C bonds of **2** in the preferred inversional ground state; here the stability of the benzylic radical **3** seems to control the regioselectivity of ring cleavage providing exclusively **5h** (=**5i**) from **1h**. With **1a,b,d,e** both thermodynamic and kinetic (stereoelectronic) control would lead to the observed regioselectivity of ring opening.

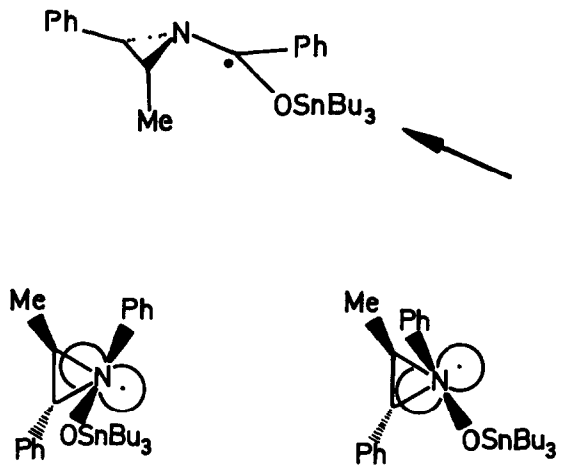


Figure 1. Preferred invertomer of **2i** (top) and line of vision (arrow) used for drawing the conformations (bottom) that give ring cleavage due to SOMO overlap. The conformation for homolysis of the N-CPh bond (right) is sterically disfavoured. Ph and $OSnBu_3$ of the radical moiety may be interchanged.

A stereoelectronic effect cannot account for the formation of **8j** in addition to the expected **5j**. The product ratio **5j**:**8j** varies from 2:1 (low concentration of Bu_3SnH) to 3:2 (high concentration of Bu_3SnH) to 4:1 (low concentration of Bu_3SnD). This variation shows that, similar to the cyclopropane analogues (e.g. N in **2j** replaced by CH, trans isomer),[8] the radicals **3j**

and **6j** rapidly[10] equilibrate via **2j** with a kinetic preference for the primary radical **6j** and a thermodynamic preference for the secondary radical **3j**. The rate of step **6j** → **7j** depends on the concentration of the hydrogen source and on the isotope of the latter. The faster this step is, the higher is the yield of **8j** relative to that of **5j**. With 2-methylcyclopropylcarbinyl radicals the kinetic preference for the formation of the primary homoallyl radical has been explained by frontier orbital control.[9,11] Our results with **1j** may be explained in the same manner. However, the following alternative explanation has obviously not yet been discussed and tested in the cyclopropane case. According to a recent theoretical determination of the molecular structure of methylcyclopropane its CH_2-CH_2 bond should be longer than its CHMe-CH_2 bond.[12] We considered therefore the possibility of a length difference for the N-CH_2 bond and the N-CHMe bond in **1j**. Since **1j** is not crystalline we selected 2-methyl-1-tosylaziridine (**11**) for an X-ray structure analysis. The essential results of this analysis are discussed by means of Figure 2. The plane through N-S-O2 nearly bisects the aziridine ring as shown by the torsional angles O2-S-N-C1 (43.8(2)°) and O2-S-N-C2 (-23.1(2)°). The bonds N-CHMe and N-CH_2 are longer than the average aziridine value 1.474 Å given by Allen[13] while the C-C bond of the aziridine ring is shorter than the average[13] aziridine value 1.484 Å. Such an influence of an electron withdrawing substituent on vicinal and distal bonds of three-membered rings can be expected.[14] An assumption of different lengths of N-C bonds in **1j** or **2j**, respectively, does not find support from the structure of **11**.

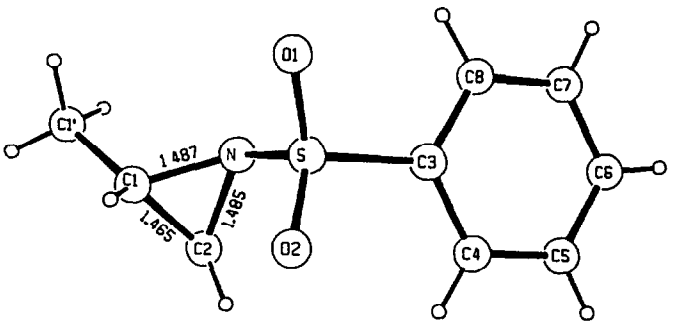


Figure 2. Structure of **11**. Standard deviation of bond lengths is 0.003 Å.

For experimental details and atomic coordinates see Experimental Part.

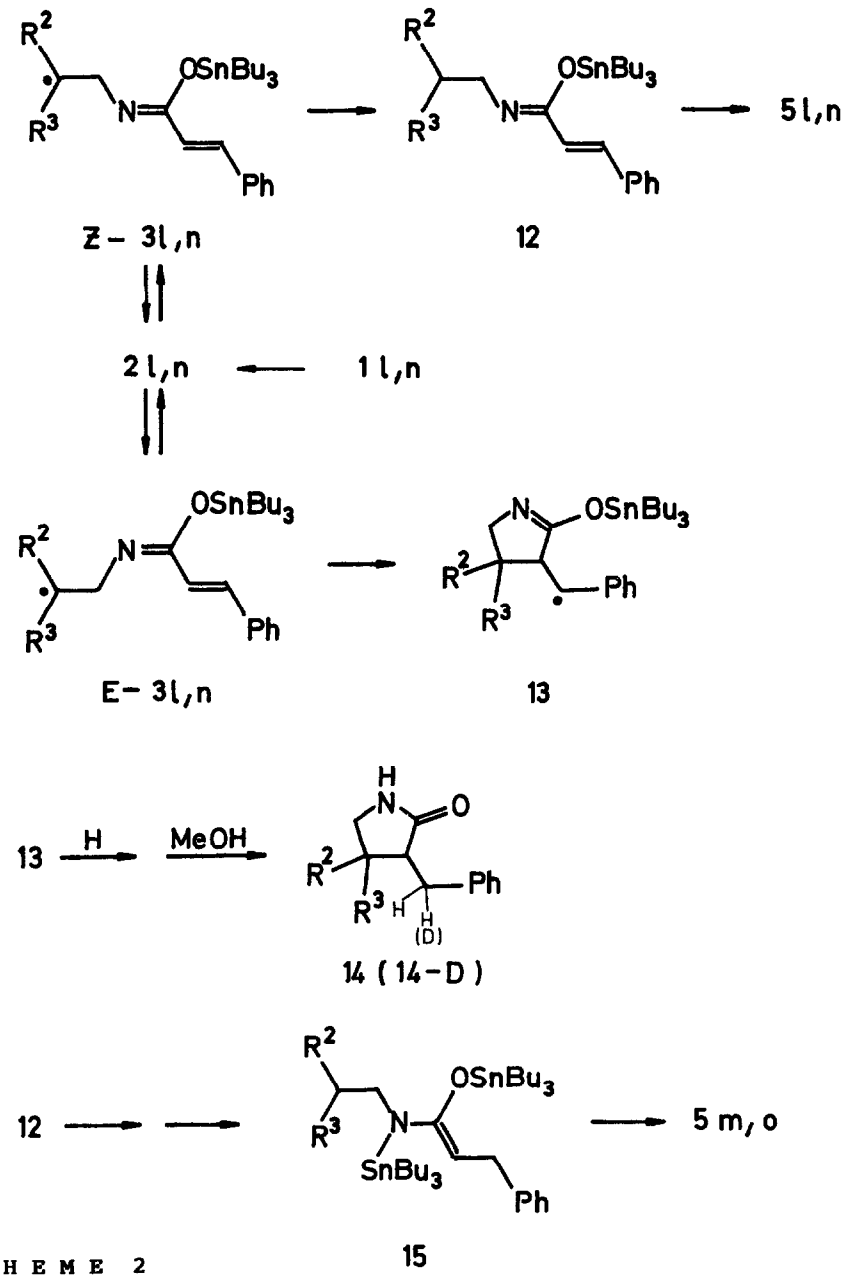
The yields of **5**, **8-10** and recovered **1** obtained from **1a-i** sum up to ca. 100%. For **1j** these joint yields are smaller than 100% and decrease significantly with Bu_3SnD. We have no explanation at present for this small deficit which is more pronounced in the reactions of **1k**. Despite complete conversion of **1k** we could identify only the product **5k** whose yield (never exceeding 87%) increased with the concentration of Bu_3SnH and decreased when Bu_3SnD was substituted for Bu_3SnH as may be expected from an isotope effect. Thus, it appears that primary radicals **3** or **6** may find another reaction path which competes with hydrogen abstraction. In chromatographic fractions consisting mainly of Bu_3SnOH or $(Bu_3Sn)_2O$ the ^{1}H-NMR spectrum revealed benzoyl groups of unidentified minor components. Since in the reactions of benzoyl cyclopropane with Bu_3SnH/AIBN in toluene some carbonyl reduction to an alcohol occurred[15] besides the expected ring opening analogously to step **2k** → **3k**, we considered the possibility of this side reaction with **1k**. The respective product can formally be derived from an addition of aziridine to the carbonyl group of benzaldehyde and should produce benzaldehyde during workup. We were not able to detect benzaldehyde by thin layer chromatography in the runs with **1k** or in other runs.

It is noteworthy that N-phenylsulfonylaziridine (**11** devoid of the two methyl groups) did not react with Bu_3SnH/AIBN under the experimental conditions of Table 1. This sulfonylaziridine was quantitatively recovered in contrast to **1k** and the other N-benzoylaziridines in Table 1.

While focussing our interest on the process of ring opening and its regioselectivity, we had a special reason[15] to further look into the possibility of an intramolecular trapping of the radical **3** under the experimental conditions of Table 1. With the N-cinnamoylaziridines **11,n** (Scheme 2, Table 2) this trapping could be realized by providing the pyrrolidones **14l,n** as main products in good yields. These yields lie remarkably close to the yields (86% **14l**, 78% **14n**) obtained from **11,n** and the lithium salt of 9,10-dihydroanthracene in THF.[16]

A minor part of radicals **31,n** did not cyclize as shown by the formation of **51-o**. This part was greater with the tertiary radical **3n** than

with the primary radical 31 and this part was practically constant in all reactions of 11 unaffected by the concentration of Bu_3SnH or by the isotope effect with Bu_3SnD. The simultaneous formation of cyclized (14) and non-cyclized (5) products and its independence of the hydrogen donor can be rationalized by the formation of syn-anti isomers of 31,n. The direct



SCHEME 2

Table 2. Reactions of aziridines **11,n** in refluxing benzene with an excess of Bu_3SnH or Bu_3SnD and 0.1 equivalent AIBN.[a]

1-5 12-14	R^1	R^2=R^3	R^4	equivalents of Sn cpd.	yield (%) of products
l	H	H	CH=CHPh	1.6 Bu_3SnH	(9) **51** (1) **5m** (88) **141**
l	H	H	CH=CHPh	3.9 Bu_3SnH	(4) **51** (4) **5m** (91) **141**
l	H	H	CH=CHPh	5 Bu_3SnH	(0) **51** (12) **5m** (88) **141**
l	H	H	CH=CHPh	1.6 $Bu_3Sn\underline{D}$	(9) **51** (1) **5m** (86) **141**
m	H	H	CH_2CH_2Ph		
n	H	Me	CH=CHPh	1.6 Bu_3SnH	(17) **5n** (6) **5o** (73) **14n**
o	H	Me	CH_2CH_2Ph		

[a] Experimental conditions as in Table 1.

isomerization **Z-3** ⇄ **E-3** will be slow[17] as compared to the subsequent steps[18] **Z-3** → **12** and **E-3** → **13**. The only mechanism for an equilibrium between **Z-3** and **E-3** under the experimental conditions would be the reversibility of ring opening **2** → **3** with an intervening internal rotation in **2** (C-N bond). Considering stereoelectronic prerequisites for ring opening in **2** there would be two rotamers each that could provide **E-3** and **Z-3**. The rotameric population in **21** must depend on the relative steric demands of CH=CHPh and $OSnBu_3$. The latter is more sterically demanding and thus favours rotamers yielding **E-3** which cyclizes. With **2n** only the N-CMe_2 bond is split. This implies that only one rotamer each gives **E-3** and **Z-3**. Both these rotamers have one of the methyl groups on the side of $OSnBu_3$ in **2n**. It seems that therefore the difference in rotameric populations is not so marked as with **21** which gives a cyclization/non-cyclization ratio of 9:1 as compared to the ratio of 3:1 with **2n**. There is no reason to assume a significant slowing down of the cyclization step due to the greater stability of the tertiary radical **E-3n** as compared to **E-31**.[19]

Reduction of the C=C double bond in the non-cyclized products (**5m,o**)

occurs obviously subsequent to the formation of **12** since this reduction increases with the concentration of Bu_3SnH (first three entries in Table 2). We therefore propose the sequence **12** → **15** → **5m,o**. Reduction of Schiff bases with trialkyltin hydride and AIBN in refluxing cyclohexane has been described previously.[20] In our run with Bu_3SnD, deuterium was incorporated into **5m-D** in both positions that follow from the above reaction sequence: one deuterium in position 2 of the ethyl group and one deuterium in the benzylic position of the dihydrocinnamoyl group.

EXPERIMENTAL

IR spectra (KBr tablets unless otherwise stated) were recorded on a Perkin-Elmer 283 spectrometer. ^{1}H-NMR spectra (250 MHz, $CDCl_3$) were recorded on a Bruker WM 250 spectrometer. Chemical shifts are given in ppm, coupling constants in Hz. Multiplicity abbreviations: s, d, t, m, mc (multiplet centred at). Mass spectra were obtained from a Varian MAT 311-A spectrometer. Column chromatography (column dimensions given in cm) was performed with silica gel Merck 0.063-0.2 mm. TLC was performed on aluminium sheets silica gel 60 F_{254} pre-coated Merck using CH_2Cl_2/ethyl acetate 25:1 for the detection of benzaldehyde.

Starting Materials.

N-Acylaziridines **1a-c,f,k** are known.[21] **1d,e,g-i,l,n** were prepared from the respective aziridine base (no substituent on N) and the respective acyl chloride (benzoic anhydride for **1h** and **1i**) according to a proven method.[22] Ref. is given below for these bases except for the base required for **1d** whose synthesis follows.

2-Benzyl-2-tert-butylaziridine. (Method of ref.[23])
A Grignard preparation from 48.6 g (2 mol) of magnesium turnings and 253.2 g (2 mol) of benzyl chloride in 700 ml of diethyl ether was mixed with 700 ml of toluene and heated until internal temperature reached 110°C. A solution of 46.1 g of the oxime of 3,3-dimethyl-2-butanone (pinacolone oxime) in 100 ml of toluene was added dropwise while stirring. The mixture was refluxed another 3 h, cooled and mixed with 500 g of ice. The precipitate was dissolved by addition of ammonium chloride. The organic layer was separated and combined with three ethereal washings of the aqueous layer and evaporated. The residue was chromatographed (70 × 3). After removing by-products with CH_2Cl_2, elution with ethyl acetate provided the base which was distilled in vacuo. Yield 76%. Oil; b.p. 75°C (0.1 Torr); IR (film) ν 3300/cm; H-NMR δ 1.01 (s, 10H, tBu and 1H of N-CH_2), 1.48 (s, 1H of NCH_2), 2.94 (d, 13.7 Hz, 1H of N-C-CH_2), 3.10 (d, 13.7 Hz, 1H of N-C-CH_2), 7.04-7.13 (m, 2 o-H of Ph), 7.22-7.39 (m, 2H, m-H and p-H of Ph). Anal. Calcd. for $C_{13}H_{19}N$: C, 82.48; H, 10.12; N, 7.40. Found: C, 82.29; H, 10.18; N, 7.64.

2-Benzyl-1-benzoyl-2-tert-butylaziridine (**1d**). Yield 96%. M.p. 117-118°C (ligroin); IR ν 1655/cm; H-NMR δ 1.08 (s, 9H, tBu), 2.00 (s, 1H of N-CH_2), 2.44 (s, 1H of N-CH_2), 3.15 (d, 15.0 Hz, 1H of N-C-CH_2), 3.18 (d, 15.0 Hz, 1H of N-C-CH_2), 7.02-7.21 (m, 5H, Ph of benzyl), 7.34-7.52 (m, 3 H, m-H + p-H of COPh), 7.83-7.90 (m, 2 o-H of COPh). Anal. Calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.63; H, 7.84; N, 4.64.

1-Benzoyl-2-tert-butyl-2-phenylazırıdıne (**1e**). Yıeld 89% (Requıred azırıdıne base: ref.[23]). M.p. 137-139°C (lıgroın); IR ν 1646/cm; H-NMR δ 1.06 (s, 9H, tBu), 2.69 (s, 1H of CH_2), 2.87 (s, 1H of CH_2), 7.01-7.61 (m, 8H, Ph and m-H + p-H of COPh), 7.93-8.00 (m, 2 o-H of COPh). Anal. Calcd. for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.88; H, 7.62; N, 5.01.

cıs-2-Benzyl-3-phenyl-1-trımethylacetylazırıdıne (**1g**). Yıeld 48% (Requıred azırıdıne base: ref.[24]). M.p. 73-74°C (CCl_4); IR ν 1681/cm; H-NMR δ 1.26 (s, 9H, tBu), 2.48 (dd, 14.7 Hz, 8.2 Hz, 1H of CH_2), 2.91 (dd, 14.7 Hz, 4.9 Hz, 1H of CH_2), 3.05 (mc, 1H, 2-H), 3.69 (d, 6.2 Hz, 1H, 3-H), 6.89-7.00 (m, 2 aromatıc H), 7.10-7.24 (m, 3 aromatıc H), 7.29-7.48 (m, 5 aromatıc H). Anal. Calcd. for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.60; H, 7.97; N, 4.76.

cıs-1-Benzoyl-2-methyl-3-phenylazırıdıne (**1h**). Yıeld 95% (Requıred azırıdıne base: ref.[25]). M.p. 41-43°C (lıgroın); IR ν 1675/cm; H-NMR δ 1.16 (d, 5.7 Hz, 3H, Me), 2.81-3.16 (m, 1H, 2-H), 3.76 (d, 6.7 Hz, 1H, 3-H), 7.30-7.48 (m, 8H, Ph and m-H + p-H of COPh), 7.97-8.08 (m, 2 o-H of COPh). Anal. Cald. for $C_{16}H_{15}NO$: C, 80.97; H, 6.37; N, 5.91. Found: C, 80.93; H, 6.39; N, 5.90.

trans-1-Benzoyl-2-methyl-3-phenylazırıdıne (**1ı**). Yıeld 93% (Requıred azırıdıne base: ref.[26]). Oıl; IR (fılm) ν 1670/cm; H-NMR δ 1.27 (d, 5.7 Hz, 3H, Me), 2.76-2.97 (m, 1H, 2-H), 3.40 (d, 2.9 Hz, 1H, 3-H), 7.23-7.48 (m, 8H, Ph and m-H + p-H of COPh), 7.93-8.04 (m, 2 o-H of COPh). Anal. Calcd. for $C_{16}H_{15}NO$: C, 80.97; H, 6.37; N, 5.91. Found: C, 80.80; H, 6.43; N, 5.89.

1-Benzoyl-2-methylazırıdıne (**1j**). Yıeld 89%. Oıl; IR(fılm) ν 1679/cm; H-NMR δ 1.33 (d, 5.3 Hz, 3H, Me), 2.08 (d, 3.4 Hz, 1H, trans 3-H), 2.47-2.56 (m, 2H, 2-H and cıs-3-H), 7.37-7.54 (m, 3H, m-H + p-H of Ph), 7.99-8.04 (m, 2 o-H of Ph). Anal. Calcd. for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.50; H, 6.83; N, 8.67.

1-Cınnamoylazırıdıne (**1ı**). Yıeld 92%. M.p. 52-54°C; IR ν 1672/cm; H-NMR δ 2.26 (s, 4H, CH_2CH_2), 6.66 (d, 16.0 Hz, 1H, COCH=), 7.27-7.40 (m, 3H, m-H + p-H of Ph), 7.52-7.57 (m, 2 o-H of Ph), 7.70 (d, 16.0 Hz, 1H, COC=CH). Anal. Calcd. for $C_{11}H_{11}NO$: C, 76.28; H, 6.40; N, 8.09. Found: C, 76.06; H, 6.35; N, 8.10.

1-Cınnamoyl-2,2-dımethylazırıdıne (**1n**). Yıeld 81%. Oıl; IR (fılm) ν 1662/cm; H-NMR δ 1.37 (s, 6H, 2 Me), 2.25 (s, 2H, CH_2), 6.61 (d, 16.0 Hz, 1H, COCH=), 7.37-7.40 (m, 3H, m-H + p-H of Ph), 7.53-7.70 (m, 2 o-H of Ph), 7.73 (d, 16.0 Hz, 1H, COC=CH). Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.78; H, 7.42; N, 6.89.

2-Methyl-1-(4-toluylsulfonyl)azırıdıne (**1ı**). Yıeld 90%. M.p. 64°C; IR ν 1325, 1162/cm; H-NMR δ 1.25 (d, 5.6 Hz, 3H, Me), 2.03 (d, 4.6 Hz, 1H, trans 3-H), 2.44 (s, 3H, Me of Ts), 2.61 (d, 7.0 Hz, 1H, cıs 3-H), 2.83 (qdd, 5.6 Hz, 7.0 Hz, 4.6 Hz, 1H, 2-H), 7.29-7.36 (m, 2 m-H of Ts), 7.80-7.85 (m, 2 o-H of Ts). Anal. Calcd. for $C_{10}H_{13}NO_2S$: C, 56.85; H, 6.20; N, 6.63; S, 15.18. Found: C, 56.88; H, 6.25; N, 6.60; S, 15.38.

Reactıons of **1** wıth Bu_3SnH/AIBN; typıcal procedure. Under nıtrogen, a solutıon of **1**, AIBN and Bu_3SnH ın dry benzene was heated to reflux for 2 h. Cf. Table 1 for further detaıls. 1-2 ml of water or methanol were added to the warm (ca. 40-60°C) mıxture. The resıdue obtaıned by evaporatıon was chromatographed (sılıca gel, 3 cm × 30 cm). CH_2Cl_2 or toluene removed excess of Bu_3SnH. Products were then eluted with CH_2Cl_2 and/or ethyl acetate. Products **5a,c,f,j-l,n**, **8j** and **9a**[27] are known. New products are descrıbed below. Deuterated products (**5-D**, **8-D**, **14-D**) are descrıbed only by those H-NMR data that changed on deuteratıon; the degree of deuteratıon was 95-100% (H-NMR).

N-Isobutyl-trımethylacetamıde (**5b**). M.p. 85°C; IR ν 3365, 1645, 1545/cm; H-NMR δ 0.91 (d, 6.8 Hz, 6H, CMe_2), 1.21 (s, 9H, tBu), 1.78 (mc, N-C-CH), 3.07 (mc, NCH_2), 5.70 (s, 1H, NH). Anal. Calcd. for $C_9H_{19}NO$: C, 68.74; H, 12.18; N, 8.91. Found: C, 69.09; H, 12.27; N, 9.16.

N-(2-Benzyl-3,3-dimethylbutyl)benzamide (**5d**). M.p. 79-81°C; IR ν 3300, 1633, 1555/cm; H-NMR δ 1.08 (s, 9H, tBu), 1.73 (mc, 1H, N-C-CH), 2.40 (dd, 13.7 Hz, 11.0 Hz, 1 benzylic H), 3.07 (ddd, 13.7 Hz, 9 Hz, 4 Hz, 1 NCH), 3.15 (mc, 1 benzylic H), 4.01 (mc, 1 NCH), 5.42 (s, 1H, NH), 7.13-7.44 (m, 10H, 2 Ph). Anal. Calcd. for $C_{20}H_{25}NO$: C, 81.31; N, 8.23; N, 4.74. Found: C, 81.04; H, 8.37; N, 4.72.

N-(3,3-Dimethyl-2-phenylbutyl)benzamide (**5e**). M.p. 85-87°C; IR ν 3290, 1632, 1550/cm; H-NMR δ 0.97 (s, 9H, tBu), 2.73 (dd, 12.2 Hz, 4.2 Hz, 1H, N-C-CH), 3.56 (ddd, 12.2 Hz, 13.3 Hz, 3.7 Hz, 1 NCH), 4.23 (ddd, 13.3 Hz, 4.2 Hz, 7.2 Hz, 1 NCH), 5.66 (s, 1H, NH), 7.18-7.47 (m, 10H, 2 Ph). Anal. Calcd. for $C_{19}H_{23}NO$: C, 81.10; H, 8.24; N, 4.98. Found: C, 81.23; H, 8.23; N, 4.86.

N-(1-Methyl-2-phenylethyl)benzamide (**5h=5i**). M.p. 128-129°C; IR ν 3330, 1635, 1540/cm; H-NMR δ 1.22 (d, 6.5 Hz, 3H, Me), 2.81-2.99 (m, 2H, CH_2), 4.39-4.55 (m, 1H, NCH), 5.96 (d, 5.7 Hz, 1H, NH), 7.21-7.34 (m, 5H, Ph), 7.37-7.51 (m, 3H, m-H and p-H of COPh), 7.67-7.78 (m, 2 o-H of COPh). Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.29; H, 7.16; N, 5.85. Found: C, 80.42; H, 7.21; N, 5.93.

N-([2-D_1]Propyl)benzamide (**5j-D**). H-NMR δ 0.97 (d, 7.4 Hz, 3H, Me), 1.62 (mc, 1H, CHD), 3.41 (dd, 6.8 Hz, 6.2 Hz, 2H, NCH_2), 6.31 (s, 1H, NH), 7.38-7.52 (m, 3H, m-H + p-H of Ph), 7.73-7.79 (m, 2 o-H of Ph).

N-([2-D_1]Ethyl)benzamide (**5k-D**). H-NMR δ 1.24 (tt, 7.2 Hz, 1.8 Hz, 2H, CH_2D), 3.40 (mc, 2H, NCH_2), 6.20 (s br, 1H, NH), 7.37-7.55 (m, 3H, m-H + p-H of Ph), 7.77 (mc, 2 o-H of Ph).

N-([2-D_1]Ethyl)cinnamamide (**5l-D**). H-NMR δ 1.20 (tt, 7.2 Hz, 1.9 Hz, 2H, CH_2D), 3.43 (mc, 2H, NCH_2), 5.82 (s br, 1H, NH), 6.40 (d, 15.6 Hz, 1H, COCH), 7.30-7.42 (m, 3H, m-H + p-H of Ph), 7.44-7.54 (m, 2 o-H of Ph), 7.62 (d, 15.6 Hz, 1H, COC=CH).

N-Ethyl-3-phenylpropionamide (**5m**). Oil; IR (film) ν 3310, 1647, 1556, 1552/cm; H-NMR δ 1.07 (t, 7.3 Hz, 3H, Me), 2.42-2.48 (m, 2H, $COCH_2$), 2.97 (mc, CO-C-CH_2), 3.25 (dq, 5.7 Hz, 7.3 Hz, 2H, NCH_2), 5.35 (s br, 1H, NH), 7.15-7.24 (m, 3H, m-H + p-H of Ph), 7.24-7.33 (m, 2 o-H of Ph). $C_{11}H_{15}NO$ Calcd. 177.1153. Found 177.1153 (MS). - **5m-D** (2 D incorporated): H-NMR δ 1.05 (tt, 7.2 Hz, 1.9 Hz, 2H, CH_2D), 2.45 (d, 7.7 Hz, 2H, $COCH_2$), 2.90-2.97 (m, 1H, CO-C-CH), 3.25 (mc, 2H, NCH_2).

N-Isobutyl-3-phenylpropionamide (**5o**). M.p. 59°C; IR ν 3320, 1640, 1550/cm; H-NMR δ 0.83 (d, 6.7 Hz, 6H, 2 Me), 1.68 (sept, 6.7 Hz, 1H, N-C-CH), 2.48 (mc, 2H, $COCH_2$), 2.97 (mc, 2H, CO-C-CH_2), 3.03 (dd, 6.6 Hz, 6.1 Hz, 2H, NCH_2), 5.52 (s br, 1H, NH), 7.15-7.23 (m, 3H, m-H + p-H of Ph), 7.23-7.35 (m, 2 o-H of Ph). Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.07; H, 9.33; N, 6.82. Found: C, 75.92; H, 9.22; N, 6.92.

N-(1-Phenylpropyl)benzamide (**8i**). M.p. 115-116°C; IR ν 3360, 1640, 1525/cm; H-NMR δ 0.95 (t, 7.4 Hz, 3H, Me), 1.88-2.01 (m, 2H, CH_2), 5.03 (mc, 1H, NCH), 6.46 (d, 7.3 Hz, 1H, NH), 7.23-7.39 (m, 5H, Ph), 7.40-7.50 (m, 3H, m-H + p-H of COPh), 7.75-7.78 (m, 2 o-H of COPh). Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.29; H, 7.16; N, 5.85. Found: C, 80.12; H, 7.26; N, 5.91.

N-([Monomethyl-D_1]isopropyl)benzamide (**8j-D**). H-NMR δ 1.26 (d, 6.4 Hz, 3H, Me), 1.33 (dd, 6.5 Hz, 14.4 Hz, 2H, CH_2D), 4.27 (mc, 1H, NCH), 6.14 (s, 1H, NH), 7.36-7.51 (m, 3H, m-H + p-H of Ph), 7.73-7.80 (m, 2 o-H pf Ph).

E-N-(2-Benzylidene-3,3-dimethylbutyl)benzamide (**9b**). M.p. 115°C; IR ν 3300, 1628, 1515/cm; H-NMR δ 1.23 (s, 9H, tBu), 4.28 (d, 4.8 Hz, 2H, NCH_2), 5.86 (s br, 1H, NH), 6.66 (s, 1H, C=CH), 7.19-7.54 (m 10H, 2 Ph). 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, 4.77.

N-(2-Hydroxy-2-methylpropyl)-trimethylacetamide (**10**). M.p. 115°C; IR ν 3375, 1629, 1552/cm; H-NMR δ 1.21 (s, 6H, $OCMe_2$), 1.23 (s, 9H, tBu), 3.15 (s, 1H, OH), 3.26 (d, 5.9 Hz, NCH_2), 6.29 (s br, 1H, NH). Anal. Calcd. for $C_9H_{19}NO_2$: C, 62.39; H, 11.05; N, 8.08. Found: C, 62.72; H, 11.11; N, 8.12.

3-Benzylpyrrolidin-2-one (**141**). M.p. 107-109°C; IR ν 3220, 1691/cm; H-NMR δ 1.75-1.92 (m, 1H, 4-H), 2.07-2.22 (m, 1H, 4-H), 2.57-2.77 (m, 2H, 3-H and 1 benzylic H), 3.16-3.34 (m, 3H, NCH_2 and 1 benzylic H), 6.43 (s br, 1H, NH), 7.14-7.38 (m, 5H, Ph). Anal. Calcd. for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found: C, 75.68; H, 7.38; N, 7.83. - **141-D**: H-NMR δ 2.57-2.77 (m, 1.5H, 3-H and 0.5 benzylic H); 3.16-3.34 (m, 2.5H, NCH_2 and 0.5 benzylic H).

3-Benzyl-4,4-dimethylpyrrolidin-2-one (**14n**). M.p. 155-156°C; IR ν 3300, 1705, 1665/cm; IR ($CDCl_3$) ν 3230, 1700/cm; H-NMR δ 0.89 (s, 3H, Me), 1.09 (s, 3H, Me), 2.51 (dd, 9.5 Hz, 5.0 Hz, 1H, 3-H), 2.58 (dd, 14.7 Hz, 9.9 Hz, 1 benzylic H), 2.93 (dd, 9.5 Hz, 1.6 Hz, 1H, NCH cis to benzyl), 3.05 (d, 9.5 Hz, 1H, NCH trans to benzyl), 3.22 (mc, 1 benzylic H), 6.96 (s br, 1H, NH), 7.17-7.26 (m, 1 o-H of Ph), 7.27-7.29 (m, 4 H of Ph). Anal. Calcd. for $C_{13}H_{17}NO$: C, 76.79; H, 8.41; N, 6.89. Found: C, 76.58; H, 8.33; N, 6.94.

X-Ray structure analysis of **11**. **11** crystallized in the monoclinic space group $P2_1/c$ with Z=4 molecules per unit cell. The cell dimensions (Å) are a=10.031(3), b=8.009(2), c=12.412(3); β=97.60(3)°. $D_{calc.}$ = 1.33 g cm^{-3}. 2371 independent reflexions in the range up to $\sin\theta/\lambda \leq 0.66$ $Å^{-1}$ were measured on a diffractometer (Enraf-Nonius CAD4, MoKα radiation, graphite monochromator, ω-2θ scan). 1546 Intensities were taken as observed ($I>2.5\sigma(I)$). The structure was solved by direct methods. The full matrix refinement of 162 variables on F^2 with anisotropic temperature factors for the heavy atoms and isotropic ones for the hydrogens converged to an R factor of 0.036. All computations were performed on a PDP-11/44 computer with the program system SDP[28].

Table 3.
Atomic coordinates of **11** and temperature factors U_{eq} of non-hydrogen atoms[29]:

$$U_{eq} = 1/3\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$$

Atom	x	y	z	$U_{eq} \times 10^4$ [Å^2]
S	0 31502(5)	0 05289(6)	-0.17455(4)	395(2)
O(1)	0 27856(16)	0 04824(20)	-0.29028(10)	566(8)
O(2)	0 44854(14)	0 00104(19)	-0 13190(12)	531(8)
N	0 28069(16)	0 24433(21)	-0 13599(13)	423(8)
C(1)	0 38733(21)	0 37188(29)	-0.14112(18)	507(11)
C(2)	0 36120(25)	0 30796(30)	-0 03535(19)	586(12)
C(3)	0 19954(19)	-0 06470(24)	-0 11168(15)	387(9)
C(4)	0 23897(22)	-0 13179(28)	-0 00931(17)	495(11)
C(5)	0 14911(27)	-0 22644(33)	0 03863(21)	658(14)
C(6)	0 02159(27)	-0 25478(33)	-0 01465(25)	723(15)
C(7)	-0 01655(23)	-0 18863(32)	-0 11590(23)	699(14)
C(8)	0 07143(21)	-0 09235(28)	-0 16581(18)	534(11)
C(1')	0 33758(29)	0 53740(30)	-0 18486(22)	696(15)

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