143. Reaction of Diphenyl Phosphorochloridate with Amide Enolates: A New and Convenient Synthesis of 2-Monosubstituted 3-(*N*-Methyl-*N*-phenylamino)-2*H*-azirines

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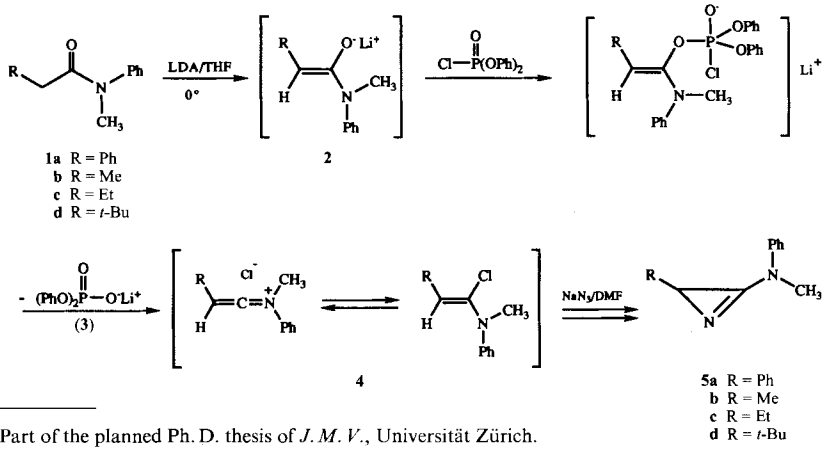
Reaction of diphenyl phosphorochloridate with amide enolates and subsequent treatment with NaN_3 leads to 2-monosubstituted 3-amino-2*H*-azirines **5** in moderate yields. The reactivity of these azirines is briefly explored.

The most general synthesis of 3-amino-2*H*-azirines bearing two substituents at C(2) is based on the procedure described by *Rens* and *Ghosez* [1] (*cf.* also [2]) in which α-chloroenamines are allowed to react with NaN_3. These aminoazirines proved to be very useful in organic synthesis [3–5]. The less stable 2-monosubstituted 3-amino-2*H*-azirines prepared *via* the β-monosubstituted α-chloroenamines are only available by a modified synthesis [6]. However, the experimental conditions needed for this reaction render the preparation of these compounds not an easy task.

We wish now to describe a new and simple method for the synthesis of 2-monosubstituted 3-(*N*-methyl-*N*-phenyl)-2*H*-azirines **5** based on the reaction of the corresponding amide enolates **2** with diphenyl phosphorochloridate ($P(O)Cl(OPh)_2$).

Thus, reaction of amides of type **1** with 1.1 equiv. of lithium diisopropylamide (LDA) in dry THF at 0°, under dry Ar leads to the amide enolate **2**, which then is treated with 1.1 equiv. of $P(O)Cl(OPh)_2$ at 0° for 24 h. We propose that under these conditions, the lithium phosphate **3** and the keteniminium salt **4** are formed in THF solution, which, after

Scheme 1



1a R = Ph
b R = Me
c R = Et
d R = *t*-Bu

2

4

5a R = Ph
b R = Me
c R = Et
d R = *t*-Bu

[1]) Part of the planned Ph. D. thesis of *J. M. V.*, Universität Zürich.

Table 1. *Prepared 2-Monosubstituted 3-Amino-2*H*-azirines* **5**

Number	Reaction time	Yield [%]	M.p. [°] or b.p. [°/Torr]
5a	3d	50	95–96
5b	3d	50	$75/8 \cdot 10^{-4}$
5c	4d	62	$130/2 \cdot 10^{-2}$
5d	5d	60	$125/2 \cdot 10^{-2}$

filtration under Ar is dropped into a suspension of NaN_3 in dry DMF and further reacted at room temperature for 3–5 d, leading to 3-amino-2*H*-azirines **5** in 50–62% yield (*Scheme 1*, *Table 1*).

The azirines **5a–d** were characterized by IR, ^{1}H- and ^{13}C-NMR, and mass spectroscopy. In the IR, they all show a strong (C=N) absorption at 1760–1780 cm^{-1} and two strong bands at 1600 and 1500 cm^{-1}. Surprisingly, neither H–C(2) nor C(2) can be detected in the NMR spectra in $CDCl_3$ solution at *ca.* 30°, but in (D_6)DMSO at 85°, the corresponding absorptions for **5a** appear at 3.56 (*s*) and 38.5 (*d*) ppm. An X-ray diffraction analysis was effected on **5a**, which did confirm the structure (*Fig.*).

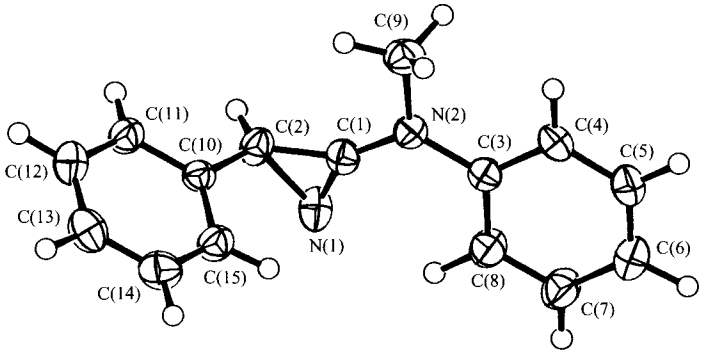
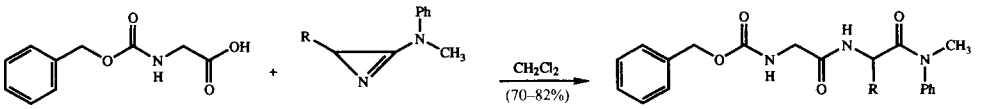


Figure. *ORTEP plot with 50% probability ellipsoids of the crystal structure of 3-(*N*-Methyl-*N*-phenylamino)-2-phenyl-2*H*-azirine* (**5a**)[2])

Furthermore, the reactivity of these 2-substituted aminoazirines toward carboxylic and thiocarboxylic acids was tested, showing no significant differences to their 2,2-disubstituted analogs [7]. When aminoazirines **5a–d** were added to a solution of Z-glycine (**6**) in CH_2Cl_2 at room temperature and stirred for 6–8 h, the dipeptides **7** were isolated in good yields (*Scheme 2*).

Scheme 2



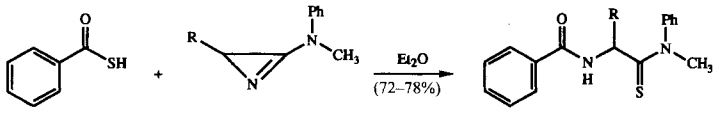
6 **5 a–c**

7a R = Ph
b R = Me
c R = Et
d R = *t*-Bu

[2]) All crystallographic data are deposited with the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, England.

In the same way, thiobenzoic acid (**8**) was allowed to react with azirines **5** in Et_2O at room temperature. After 5–6 h stirring, the corresponding thioamides **9** were obtained in good yields too (*Scheme 3*). Apparently, these reactions follow the same mechanism as formulated for the disubstituted analogs (*cf.* [5]): protonation of the amidine ring-N-atom, followed by nucleophilic attack of the carboxylate or thiocarboxylate onto C(3) of the monosubstituted aminoazirine and rearrangement to a five-membered cyclic zwitterion lead to compounds of type **7** and **9**, respectively. All compounds gave satisfactory analysis and were characterized by IR, ^{1}H- and ^{13}C-NMR, and MS.

Scheme 3



8 **5 a–c**

9a R = Ph
b R = Me
c R = Et
d R = *t*-Bu

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Experimental Part

General. Cf. [3]. Unless otherwise stated, IR spectra in $CHCl_3$ and NMR spectra in $CDCl_3$ (^{1}H at 300 MHz; ^{13}C at 50.4 MHz). MS at 70 eV, CI-MS with 2-methylpropane or NH_3.

1. *2-Monosubstituted 3-(*N*-Methyl-*N*-phenylamino)-2*H*-azirines* **5**. 1.1. *General Procedure.* To a soln. of *ca.* 24 mmol of amide **1** in 120 ml of dry THF at 0° and under Ar, 1.10–1.15 equiv. of LDA (1.5M in cyclohexane, *Aldrich* or *Fluka*) were added slowly through a septum *via* a syringe. After stirring for 1 h at 0°, 1.05 equiv. of $P(O)Cl(OPh)_2$ were added dropwise. The mixture was well stirred for 24 h, raising the temp. from 0° to r.t. The soln. was filtered under Ar and the mother liquor dropped into a suspension containing 60 mmol of NaN_3 in 25 ml of dry DMF and stirred 4–5 d at r.t. Then Et_2O was added, the mixture filtered over a *Celite* pad, the solvent evaporated, Et_2O added, and the soln. washed twice with sat. $NaHCO_3$ soln. The org. layer was dried ($MgSO_4$) and evaporated and the residue distilled or crystallized.

1.2. *3-(*N*-Methyl-*N*-phenylamino)-2-phenyl-2*H*-azirine* (**5a**; *cf.* [6] [8]). From 3.5 g (15.55 mmol) of *N*-methyl-*N*,*2-diphenylacetamide* (**1a**), after flash chromatography [9] (FC; hexane/AcOEt 9:1), 1.726 g (50%) of **5a**. Colorless crystals. M.p. 95–96° (hexane/AcOEt). IR: 3060*w*, 3000*s*, 2920*w*, 2820*w*, 1770*s*, 1600*s*, 1500*s*, 1455*s*, 1420*w*, 1385*s*, 1355*s*, 1315*m*, 1280*m*, 1255*m*, 1170*m*, 1110*s*, 1090*s*, 1070*m*, 1030*m*, 1010*m*, 995*w*, 935*s*, 890*w*, 820*w*, 695*s*, 660*m*, 630*m*. ^{1}H-NMR ((D$_6$)DMSO, 85°): 7.45–7.05 (*m*, 10 arom. H); 3.56 (*s*, H–C(2)); 3,44 (*s*, MeN). ^{13}C-NMR ((D$_6$)DMSO, 85°): 154.9 (*s*, C=N); 142.7, 140.7 (2*s*, 2 arom. C); 128.8, 127.8, 126.5, 125.6, 123.0, 117.0 (6*d*, 10 arom. CH); 38.5 (*d*, C(2)); 35.3 (*q*, MeN). EI-MS: 222 (27, M^+), 221 (100, $[M-1]^+$), 207 (52), 206 (12), 194 (11), 180 (11), 118 (21), 117 (17), 107 (16), 106 (16), 104 (13), 91 (17), 89 (23), 77 (75), 63 (12), 51 (28), 39 (15).

1.3. *2-Methyl-3-(*N*-methyl-*N*-phenylamino)-2*H*-azirine* (**5b**). From 4.0 g (24 mmol) of *N*-methyl-*N*-phenylpropanamide (**1b**). Distillation (bulb-to-bulb; $75°/8.5 \cdot 10^{-4}$ Torr) gave 1.92 g (50%) of **5b**. Pale yellow oil. IR: 2980*m*, 1758*s*, 1600*s*, 1500*s*, 1452*w*, 1379*w*, 1351*m*, 1315*w*, 1195*w*, 1110*m*, 1054*w*, 1032*w*, 982*w*, 693*m*, 661*w*. ^{1}H-NMR: 7.4–7.05 (*m*, 5 arom, H); 3.45 (*s*, MeN); 1.37 (*d*, Me); H–C(2) could not be detected. ^{13}C-NMR: 142.3 (*s*, 1 arom. C); 129.1, 122.9, 116.4 (3*d*, 5 arom. CH); 36.4 (*q*, MeN); 19.5 (*q*, Me); C=N and C(2) could not be detected. CI-MS: 161 (100, $[M+1]^+$).

1.4. *2-Ethyl-3-(*N*-methyl-*N*-phenylamino)-2*H*-azirine* (**5c**). From 4.0 g of (22 mmol) *N*-methyl-*N*-phenylbutanamide (**1c**). Distillation (bulb-to-bulb; $130°/2 \cdot 10^{-2}$ Torr) gave 2.37 g (62%) of **5c**. Pale yellow oil. IR: 2970*s*,

2220*m*, 1760*s*, 1600*s*, 1500*s*, 1460*w*, 1425*w*, 1410*w*, 1380*w*, 1365*w*, 1320*w*, 1260*w*, 1190*w*, 1115*m*, 1080*w*, 1035*w*, 1010*w*, 1000*w*, 940*w*, 695*s*, 660*w*. ^{1}H-NMR: 7.45–7.05 (*m*, 5 arom. H); 3.47 (*s*, MeN); 1.65–1.5 (*m*, CH_2); 0.95–0.9 (*m*, Me); H–C(2) was not detected. CI-MS: 349 (100, $[2M + 1]^+$).

1.5. *2-(*tert*-Butyl)-3-(*N*-methyl-*N*-phenylamino)-2*H*-azirine* (**5d**). From 2.5 g (12 mmol) of *N*,3,3-trimethyl-*N*-phenylbutanamide (**1d**). FC (hexane/AcOEt 9:1) gave 1.48 g (60%) of **5d**. Yellow oil. IR: 2960*s*, 2870*m*, 1760*s*, 1600*s*, 1500*s*, 1480*m*, 1465*w*, 1390*w*, 1365*m*, 1350*w*, 1320*w*, 1270*m*, 1250*w*, 1185*w*, 1120*m*, 1100*w*, 1035*w*, 1010*w*, 960*w*, 895*w*, 880*w*, 695*s*, 660*w*. ^{1}H-NMR: 7.4–7.1 (*m*, 5 arom. H); 3.76 (*s*, MeN); 0.93 (*s*, 9 H); H–C(2) was not observed. ^{13}C-NMR ((D_6)DMSO): 164.0 (*s*, C=N); 145.0 (*s*, 1 arom. C); 128.9, 119.3, 113.1 (3 *d*, 5 arom. CH); 38.9 (*q*, MeN); 31.6 (*q*, Me_3C); C(2) and Me_3C could not be detected. CI-MS: 203 (13, $[M + 1]^+$), 188 (100, $[(M - 15) + 1]^+$).

2. *Reaction of* **5** *with Z-Glycine* (**6**). 2.1. *General Procedure.* To a well stirred soln. of 313 mg (1.5 mmol) of **6**, in 4 ml of dry CH_2Cl_2 at r.t., a soln. of 1.5 mmol of the corresponding aminoazirine **5** in 0.5 ml of CH_2Cl_2 was added. After stirring overnight, the solvent was evaporated, the residue partitioned between Et_2O and sat. $NaHCO_3$ soln., the org. phase dried ($MgSO_4$) and evaporated, and the resulting residue filtered over a short column of SiO_2 (hexane/AcOEt 4:1).

2.2. N^2-*[*N^2-*(Benzyloxycarbonyl)glycyl]-*N^1-*methyl-*N^1*,2-diphenylglycine-amide* (*Z-Gly-(2Ph)Gly-N(Ph)-Me*; **7a**). Colorless plates (530 mg, 82%). M.p. 135–136°. IR: 3430*m*, 3320*w*, 3010*m*, 2940*w*, 1725*s*, 1685*s*, 1650*s*, 1600*m*, 1495*s*, 1455*m*, 1430*w*, 1395*s*, 1250*s*, 1170*w*, 1130*w*, 1110*w*, 1075*w*, 1050*m*, 1030*w*, 970*w*, 910*w*, 700*s*, 660*w*. ^{1}H-NMR: 7.5–7.15 (*m*, 13 H); 6.95–6.9 (*m*, 3 H); 5.55–5.5 (*m*, 2 H); 5.09 (*s*, PhCH_2O); 3.95–3.8 (*m*, 2 H); 3.24 (*s*, MeN). ^{13}C-NMR: 169.6, 168.0, 156.3 (3*s*, 3 C=O); 141.7, 137.6, 136.6 (3*s*, 3 arom. C); 136.1, 129.4, 128.4, 128.3, 128.2, 127.9, 127.8, 127.7, 127.6 (9*d*, 15 arom. CH); 66.7 (*t*, PhCH_2O); 54.4 (*q*, MeN); 43.9 (*d*, C(2)); 37.8 (*t*, CH_2). CI-MS: 432 (100, $[M + 1]^+$). Anal. calc. for $C_{25}H_{25}N_3O_4$ (431.48): C 69.59, H 5.83, N 9.73; found: C 69.52, H 5.90, N 9.87.

2.3. N^2-*[*N^2-*(Benzyloxycarbonyl)glycyl]-*N^1-*methyl-*N^1*-phenylalanine-amide* (*Z-Gly-Ala-N(Ph)Me*; **7b**). Colorless microcrystals (398 mg, 72%). M.p. 98.3°. IR: 3420*m*, 3095*m*, 1744*s*, 1680*s*, 1598*m*, 1498*s*, 1452*s*, 1430*w*, 1399*m*, 1371*w*, 1245*m*, 1195*w*, 1120*m*, 1050*m*, 1005*w*, 985*w*, 965*w*, 912*w*, 700*s*, 662*w*. ^{1}H-NMR: 7.4–7.15 (*m*, 10 H); 6.80 (*d*, *J* = 7, 1 H); 5.45–5.15 (*m*, 1 H); 5.05 (*s*, PhCH_2O); 4.55–4.45 (*m*, 1 H); 3.80 (*t*, *J* = 5, 2 H); 3.19 (*s*, MeN); 1.07 (*d*, *J* = 7, 3 H). ^{13}C-NMR: 172.6, 168.2, 158.4, (3*s*, 3 C=O); 142.4, 136.2 (2*s*, 2 arom. C); 129.9, 128.3, 127.9, 127.8, 127.2 (5*d*, 10 arom. CH); 66.8 (*t*, PhCH_2O); 45.8 (*q*, MeN); 37.7 (*d*, C(2)); 18.3 (*q*, Me). CI-MS: 370 (100, $[M + 1]^+$). Anal. calc. for $C_{20}H_{23}N_3O_4$ (369.41): C 65.03, H 6.28, N 11.38; found: C 65.05, H 6.42, N 11.31.

2.4. N^2-*[*N^2-*(Benzyloxycarbonyl)glycyl]-2-ethyl-*N^1-*methyl-*N^1*-phenylglycine-amide* (*Z-Gly-(2Et)Gly-N(Ph)Me*; **7c**). Colorless flakes (437 mg, 76%). M.p. 82–83°. IR: 3660*w*, 3420*m*, 3300*w*, 3002*m*, 2987*w*, 2940*w*, 2880*w*, 1720*s*, 1680*s*, 1650*s*, 1598*m*, 1500*s*, 1455*m*, 1400*m*, 1345*w*, 1245*m*, 1200*w*, 1148*w*, 1120*m*, 1050*m*, 985*w*, 822*w*, 700*s*, 662*w*. ^{1}H-NMR: 7.45–7.2 (*m*, 10 H); 6.76 (*d*, *J* = 8.1, 1 H); 5.50 (*t*, *J* = 5.1, 1 H); 5.10 (*s*, PhCH_2O); 4.6–4.5 (*m*, 1 H); 3.87 (*t*, *J* = 4.3, 2 H); 3.25 (*s*, MeN); 1.77 (*s*, 1 H); 1.6–1.55 (*m*, 1 H); 1.45–1.4 (*m*, 1 H); 0.70 (*t*, *J* = 7.3, Me). ^{13}C-NMR: 173.8, 170.0, 158.0 (3*s*, 3 C=O); 142.5, 136.2 (2*s*, 2 arom. C); 129.9, 128.4, 128.3, 128.1, 128.0, 127.3 (6*d*, 10 arom. CH); 67.0 (*t*, PhCH_2O); 50.9 (*q*, MeN); 44.2 (*t*, CH_2); 37.8 (*d*, C(2)); 25,8 (*t*, CH_2); 9.5 (*q*, Me). CI-MS: 384 (100, $[M + 1]^+$).

2.5. N^2-*[*N^2-*(Benzyloxycarbonyl)glycyl]-2-(*tert*-butyl)-*N^1-*methyl-*N^1*-phenylglycine-amide* (*Z-Gly-(2^{t}Bu)-Gly-N(Ph)Me*; **7d**). Colorless microcrystals (431 mg, 70%). M.p. 105.5–106.5°. IR: 3420*m*, 3320*w*, 3000*s*, 2970*s*, 1720*s*, 1680*s*, 1640*s*, 1595*s*, 1525*s*, 1500*s*, 1470*m*, 1455*m*, 1430*m*, 1395*s*, 1370*m*, 1315*w*, 1265*s*, 1240*s*, 1195*w*, 1170*w*, 1150*w*, 1130*w*, 1100*w*, 1050*w*, 1030*w*, 990*w*, 910*w*, 700*s*, 665*w*. ^{1}H-NMR: 7.45–7.2 (*m*, 10 H); 6.55 (*d*, *J* = 9, 1 H); 5.42 (br. *s*, 1 H); 5.15 (*d*, *J* = 2, PhCH_2O); 4.73 (*d*, *J* = 9, 1 H); 4.0–3.85 (*m*, 2 H); 3.29 (*s*, MeN); 0.80 (*s*, 9 H). ^{13}C-NMR: 171.0, 167.9, 156.4 (3*s*, 3 C=O); 143.0, 136.2 (2*s*, 2 arom. C); 129.5, 128.4, 128.2, 128.0, 127.8, 127.5 (6*d*, 10 arom. CH); 67.0 (*t*, PhCH_2O); 55.5 (*q*, MeN); 44.4 (*t*, CH_2); 37.8 (*d*, C(2)); 35.5 (*s*, Me_3C); 25.4 (*q*, Me_3C). CI-MS: 412 (100, $[M + 1]^+$). Anal. calc. for $C_{23}H_{29}N_3O_4$ (411.49): C 67.13, H 7.10, N 10.21; found: C 66.93, H 7.05, N 10.41.

3. *Reaction of* **5** *with Thiobenzoic Acid* (**8**). 3.1. *N-[α-(*N*-Methyl-*N*-phenylthiocarbamoyl)benzyl]benzamide* (**9a**). To a stirred soln. of 1 mmol (0.12 ml) of **8** in 2.5 ml of dry Et_2O at 0°, 222 mg (1 mmol) of **5a** in 0.5 ml of Et_2O were added. The mixture was then stirred for 5 h, the solvent removed, and the residue purified by flash chromatography (SiO_2, hexane/AcOEt 9:1): 280 mg (78%) of **9a**. Colorless oil: IR: 3320*w*, 3000*m*, 2920*w*, 1655*s*, 1600*w*, 1580*w*, 1510*s*, 1495*s*, 1480*s*, 1390*s*, 1270*m*, 1160*m*, 1115*m*, 1075*w*, 1030*w*, 1000*w*, 920*w*, 700*s*, 660*w*. ^{1}H-NMR: 8.24 (*d*, *J* = 8, 1 H); 8.0–7.15 (*m*, 16 H); 6.49 (br. *s*, 1 H); 6.08 (*d*, *J* = 8, 1 H); 3.75 (*s*, MeN). ^{13}C-NMR: > 200 (*s*, C=S); 165.2 (*s*, C=O); 144.1, 138.4, 134.0 (3 *s*, 3 arom. C); 134.7, 132.3, 130.4, 130.3, 130.2, 130.1, 130.0, 128.8, 128.0 (9 *d*, 15 arom. CH); 58.0 (*q*, MeN); 46.4 (*d*, CH). CI-MS: 361 (100, $[M + 1]^+$).

3.2. N-*[1-(*N-*Methyl*-N-*phenylthiocarbamoyl)ethyl]benzamide* (**9b**). To a stirred soln. of 1 mmol (0.12 ml) of **8** in 2.5 ml of dry Et_2O at 0° were added 160 mg (1 mmol) of **5b** in 0.5 ml of Et_2O *via* a syringe. After 5 h raising the temp. from 0° to r.t., the resulting solid was filtered off, washed with hexane/Et_2O, and dried: 214 mg (72%) of **9b**. Colorless solid. M.p. 139°. IR (KBr): 3280*s*, 3050*m*, 3020*w*, 2990*w*, 2920*w*, 2850*w*, 1630*s*, 1600*m*, 1575*s*, 1550*s*, 1490*s*, 1470*s*, 1440*s*, 1395*s*, 1380*m*, 1355*s*, 1330*s*, 1315*s*, 1260*m*, 1195*m*, 1175*m*, 1140*m*, 1120*s*, 1070*m*, 1035*m*, 1000*m*, 990*m*, 940*w*, 925*m*, 880*w*, 810*m*, 770*m*, 725*s*, 695*s*, 665*m*, 635*m*, 615*w*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.55–7.4 (*m*, 8 arom. H); 5.10 (*q*, J = 6.5, 1 H); 3.75 (*s*, MeN); 1.32 (*d*, J = 6.5, Me). CI-MS: 299 (100, $[M+1]^+$). Anal. calc. for $C_{17}H_{18}N_2SO$ (298.40): C 68.42, H 6.07, N 9.38, S 10.89; found: C 68.57, H 6.12, N 9.14, S 10.89.

3.3. N-*[1-(*N-*Methyl*-N-*phenylthiocarbamoyl)propyl]benzamide* (**9c**). In analogy to *Exper. 3.2*, 1 mmol (0.12 ml) of **8** was reacted with 174 mg (1 mmol) of **5c**. Filtration of the formed solid and washing with hexane/Et_2O yielded 237 mg (76%) of **9c**. Colorless powder. M.p. 109–110°. IR (KBr): 3300*s*, 3059*m*, 2970*m*, 2924*m*, 2880*w*, 1670*s*, 1600*m*, 1579*m*, 1538*s*, 1493*s*, 1470*s*, 1370*s*, 1350*m*, 1335*m*, 1308*s*, 1270*m*, 1170*m*, 1155*m*, 1112*m*, 1098*m*, 1070*m*, 1048*m*, 1022*m*, 991*w*, 932*w*, 860*w*, 811*w*, 780*s*, 738*m*, 700*s*, 672*m*, 650*m*, 630*m*, 615*m*. ^{1}H-NMR: 7.85–7.8 (*m*, 2 arom. H); 7.55–7.05 (*m*, 8 arom. H); 5.05–5.0 (*m*, 1 H); 1.8–1.65 (*m*, 2 H); 3.76 (*s*, MeN); 0.77 (*t*, J = 7.4, Me). ^{13}C-NMR: > 200 (*s*, C=S); 166.2 (*s*, C=O); 144.4, 134.3, (2 *s*, 2 arom, C); 131.4, 130.1, 128.9, 128.4, 127.0, 126.4 (6 *d*, 10 arom. CH); 55.9 (*q*, MeN); 45.8 (*d*, CH); 30.2 (*t*, CH_2); 10.2 (*q*, Me). CI-MS: 313 (100, $[M+1]^+$). Anal. calc. for $C_{18}H_{20}N_2SO$ (312.42): C 69.20, H 6.45, N 8.96, S 10.26; found: C 69.37, H 6.64, N 8.88, S 10.08.

4. *X-Ray Crystal Structure Determination of* **5a**[2]). Crystals of **5a** were obtained from MeCN. All measurements were made on a *Nicolet-R3* diffractometer in the *Wyckoff* ω-scan mode using graphite-monochromated CuK_α radiation (λ = 1.54059 Å) at −60°. Data collection and refinement parameters are listed in *Table 2*[3]). The

Table 2. *Crystallographic Data of 2-Phenyl-3-(*N-*methyl*-N-*phenylamino)*-2H-*azirine* (**5a**)

Empirical formula	$C_{15}H_{14}N_2$
Formula weight	222.29
Crystal color, habit	colorless prism
Crystal dimensions [mm]	0.39 × 0.40 × 0.42
Crystal system	triclinic
No. of reflections used for unit cell determination (2θ range)	25 (95–100°)
Lattice parameters	a = 8.002(1) Å b = 8.4797(9) Å c = 10.212(1) Å α = 102.76 (1)° β = 104.58(1)° γ = 107.353(9)° V = 606.3 (1) Å^3
Space group	$P\bar{1}$
Z value	2
D_{calc}	1.218 g cm^{-3}
$F(000)$	236
μ(CuK_α)	5.289 cm^{-1}
$2\theta_{(max)}$	116°
No. of reflections measured	total: 1781; unique: 1640 (R_{int} = 0.019)
Function minimized	$\Sigma w(\|F_o\| - \|F_c\|)^2$
Least-squares weights	$[\sigma^2(F_o)]^{-1}$
Reflections used in refinement ($I > 3\sigma(I)$)	1583
Variables	211
Final R; R_w	0.0452; 0.0409
Goodness of fit indicator	13.95
Max. shift/error in final cycle	0.001
Max. and min. peak in final diff.	0.17, −0.15 e Å^{-3}

[3]) The intensities were corrected for *Lorentz* and polarisation effects, and absorption corrections were applied using DIFABS [10].

structure was solved by direct methods using SHELXS86 [11] which revealed the positions of all non-H-atoms[4]). The non-H-atoms were refined anisotropically. All of the H-atoms were located in a difference *Fourier* map, and their positions were allowed to refine together with individual isotropic temperature factors. A secondary extinction coefficent was included in the refinement.

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[4]) Full-matrix least-squares refinement on *F* was performed with SHELX76 [12].