Synthesis of Annulated γ-Lactams via Intramolecular 1,3-Dipolar Cycloadditions of Functionalized *N*-Allyl α-Diazo Amides

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N-Allyldiazoacetamides containing a phosphinyl group at the α-position underwent the intramolecular 1,3-cycloaddition, followed by 1,3-hydrogen shift to afford 6a-diethoxyphosphinyl-3a,4,5,6a-tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-ones in 74—78% yields, while the corresponding α-phenylthio amide produced 1-phenylthio-3-azabicyclo[3.1.0]hexan-2-one in 74% yield via extrusion of N_2 from the intramolecular 1,3-cycloadduct. In the application of these compounds to the conversion of functionality, the former gave a fused tricyclic heterocycle and the latter gave deallylated compounds.

Development of convenient synthetic routes to γ-lactams has been an important theme to synthetic chemists,[1] since functionalized monocyclic and bicyclic γ-lactams have been shown to have interesting biological activities[2] and to act as key intermediates for the syntheses of antibiotics,[3] naturally occurring compounds,[4] etc. While intramolecular cycloaddition reactions of diazoalkenes[5] and olefinic α-diazo ketones[6] giving fused carbocyclic and heterocyclic compounds have been extensively investigated, the related studies on the corresponding α-diazo amides have, to our knowledge, been limited in spite of their utility for the construction of a γ-lactam ring.[7]

We report here that α-phosphinyl or α-phenylthio *N*-substituted *N*-2-alkenyldiazoacetamides readily undergo intramolecular 1,3-dipolar cycloadditions to form fused γ-lactams with functionality, of which chemical reactivities and synthetic applications have been investigated.

Results and Discussion

1,3-Dipolar Cycloaddition of *N*-Allyldiazoacetamides. It is known that α-diazo β-keto phosphonates containing olefinic moieties undergo decomposition to lead to intramolecular cyclopropanation products in the presence of the catalysts such as copper and [CuI{P(OMe)$_3$}], but no reaction took place without such a catalyst.[8] For comparison with α-diazo β-keto phosphonates, we have investigated the reaction of several *N*-allyl-α-diazo-α-(diethoxyphosphinyl)acetamides. *N*,*N*-diallyl-α-diazo-α-(diethoxyphosphinyl)acetamide (**4a**), generated from *N*,*N*-diallyl-α-(diethoxyphosphinyl)acetamide (**3a**) by diazotransfer with tosyl azide, readily underwent intramolecular 1,3-dipolar cycloaddition in tetrahydrofuran (THF) at room temperature with no catalysts to give the intermediate pyrazoline **5a**, followed by 1,3-hydrogen shift leading to 5-allyl-6a-diethoxyphosphinyl-3a,4,5,6a-tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (**6a**) in 78% yield. *N*-substituted *N*-allyl-α-diazo-α-(diethoxyphosphinyl)acetamides (**4b**,**c**) similarly afforded the corresponding 6a-(diethoxyphosphinyl)tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-ones **6b**,**c** in good yields (Table 1). Since it is of interest to examine whether or not *N*-allyl-substituted diazoacetamide containing the sulfenyl group undergo intramolecular 1,3-dipolar cycloadditions similar to *N*-allyl-α-diazo-α-(diethoxyphosphinyl)acetamides **4a**—**c**, we have investigated the reaction of *N*,*N*-diallyl-α-diazo-α-(phenylthio)acetamide (**4d**). Interestingly, when *N*,*N*-diallyl-α-(phenylthio)acetamide (**3d**) was treated with tosyl azide under similar conditions, 3-allyl-1-phenylthio-3-azabicyclo[3.1.0]hexan-2-one (**8d**) was obtained in 74% yield instead of the corresponding pyrazole. The formation of **8d** can be easily rationalized in terms of the intramolecular ring closure of a zwitterion (or a diradical) intermediate **7d**, which is produced by loss of N_2 from the initially formed intramolecular 1,3-dipolar cycloadduct **5d** (Scheme 1).

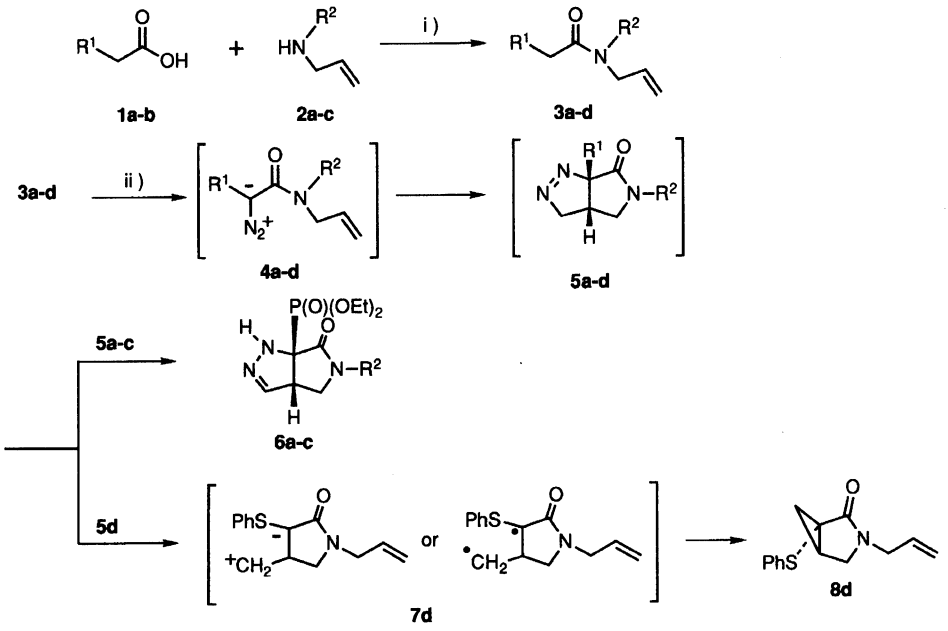
Thus, the reaction products are strongly dependent upon the substituents on the α-carbon of *N*-allyldiazoacetamides **4a**—**d**.

Synthetic Application of Fused γ-Lactams. If the substituents on the bicyclic γ-lactams prepared above are easily removed or replaced by other functional groups, the α-substituents of *N*-allyldiazoacetamides act not only as a means for introduction of functionality into fused γ-lactams but also as an useful tool for the syntheses of a variety of bicyclic and tricyclic γ-lactams which are not easily attainable by existing methods. For instance, treatment of the compound **6b** with 1.2 equiv of butyllithium in THF–hexamethylphosphoric triamide (HMPA) at −78 °C, followed by the addition of excess amounts of paraformaldehyde at room temperature afforded 10-phenyl-3-oxa-5,6,10-triazatricyclo[6.3.0.0^{1,5}]undec-6-en-11-one (**11**) in 62% yield. As outlined in Scheme 2, the formation of the compound **11** can be explained by a sequence of nucleophilic attack of the nitrogen anion of pyrazole ring to paraformaldehyde, further attack of the resulting alcoholate anion on the second molecule of paraformaldehyde, and the subsequent ring closure accompanying the elimination of sodium diethylphosphate. On the other hand, similar treatment of **6a**,**c** afforded a complicated mixture of several uncharacterizable products. The difference in reactivities between **6a**,**c** and **6b** seems to be due to acidic protons on the allylic or the benzylic position in **6a** or **6c**.

Table 1. Cycloaddition Reaction of *N*-Allyl-α-diazoacetamides **4a**—**d**[a)]

Entry	4	Substituents		Time/h	Products (yield/%)	
		R^1	R^2		**6**	**8**
1	**4a**	$P(O)(OEt)_2$	$CH_2CH{=}CH_2$	18	**6a** (78)	
2	**4b**	$P(O)(OEt)_2$	Ph	160	**6b** (74)	
3	**4c**	$P(O)(OEt)_2$	CH_2Ph	18	**6c** (74)	
4	**4d**[b)]	SPh	$CH_2H{=}CH_2$	8		**8d** (74)

a) All reactions were carried out in the presence of ^{t}BuOK at room temperature, unless otherwise noted. b) The reaction was carried out in the presence of LiN^iPr_2.



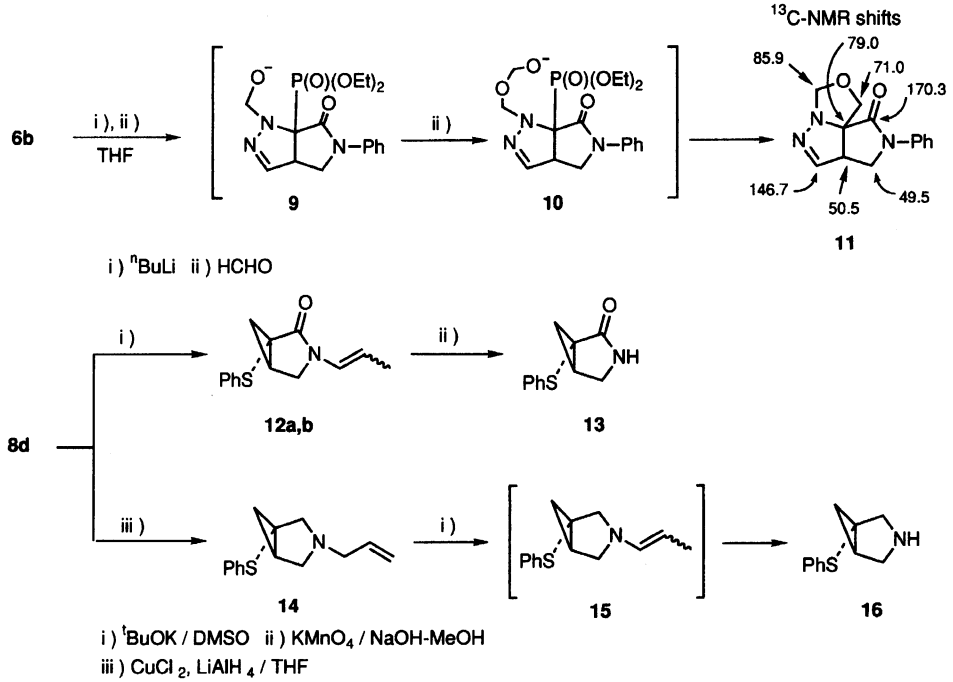
Scheme 1.

The compound **8d** was treated with potassium *t*-butoxide in dimethyl sulfoxide (DMSO) to undergo the allyl-propenyl rearrangement to produce a 4.4:1 mixture of 1-pheynlthio-3-[(*E*)-1-propenyl]- and 1-phenylthio-3-[(*Z*)-1-propenyl]-3-azabicyclo[3.1.0]hexan-2-ones (**12a,b**) in 65% yield.[9)] Oxidation of the mixture with potassium permanganate in methanol resulted in depropenylation to give 1-phenylthio-3-azabicyclo[3.1.0]-hexan-2-one (**13**) in 93% yield as a sole product.

We have also attempted to remove the phenylthio group from the compound **8d**. According to the reported desulfurization procedure, reduction of **8d** with a $LiAlH_4$–$CuCl_2$ reagent[10)] was examined to afford 3-allyl-1-phenylthio-3-azabicyclo[3.1.0]hexane (**14**) in 60% yield, but no expected desulfurization product was observed.[11)] In contrast with **8d**, treatment of **14** with potassium *t*-butoxide in DMSO afforded the deallylated product, 1-phenylthio-3-azabicyclo[3.1.0]hexane (**16**) in 76% yield in one-pot operation (Scheme 2). The formation of **16** can be explained by ready hydrolysis of the initially formed allyl-propenyl rearrange product **15**. In conclusion, (i) *N*-allyl α-diazo amides containing a functional group such as phosphinyl and sulfenyl groups at the α-position undergo intramolecular 1, 3-dipolar cycloaddition to give tetrahydropyrrolo[3,4-*c*]pyrazol-6(3*H*)-ones followed by either 1,3-hydrogen shift to give tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-ones or loss of N_2 to afford 2-azabicyclo[3.1.0]hexan-1-one. (ii) Removal and synthetic utilization of the functional groups in the products have been successfully achieved in some cases to give fused heteroatom-containing bicyclic and tricyclic compounds.

Experimental

General. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ on a JEOL JNM-FX-60 or JEOL JNM-EX-270 spectrometer, operating ^{1}H NMR at 60 or 270 MHz, and ^{13}C NMR at 15.04 or 67.80 MHz, respectively, with Me_4Si as an internal standard. DEPT and 2D proton–proton and proton–carbon correlations were used when necessary, to as-



Scheme 2.

sign ^{1}H and ^{13}C NMR spectra. IR spectra were recorded with a Shimadzu IR-408 instrument. Mass spectra were taken with a JEOL DX-300 spectrometer. Melting points were measured in open capillary tubes and are uncorrected.

Preparation of *N*-Allylacetamide 3a—d.[12] *N*-Allylacetamides **3a—d** were prepared from acids **1a,b** (5.00 mmol), and allylamines **2a—c** (5.00 mmol) by the published procedure.[13]

***N*,*N*-Diallyl-α-(diethoxyphosphinyl)acetamide (3a):** Yield 1.27 g, (92%).

***N*-Allyl-*N*-phenyl-α-(diethoxyphosphinyl)acetamide (3b):** Yield 1.34 g, (86%).

***N*-Allyl-*N*-benzyl-α-(diethoxyphosphinyl)acetamide (3c):** Yield 1.38 g, (85%).

***N*,*N*-Diallyl-α-(phenylthio)acetamide (3d):** Yield 1.04 g, (84%).

Intramolecular 1,3-Dipolar Cycloaddition of *N*-Allyl α-Diazo Amides 4a—d. General Procedure: To a solution of an *N*-allylacetamide **3a—d** (10.0 mmol) in THF (20 ml) was added potassium *t*-butoxide (1.12 g, 10.0 mmol) or lithium diisopropylamide (10.0 mmol). After the solution was stirred for 0.5 h, a solution of *p*-toluenesulfonyl azide (1.97 g, 10.0 mmol) in THF (30 ml) was added and the mixture was stirred at room temperature under a nitrogen atmosphere until disappearance of *N*-allyldiazoacetamides (observed by monitoring the diazo IR absorptionband at 2100 cm^{-1}). After the reaction mixture was filtered through a celite pad, the filtrate was concentrated in vacuo. The residue was chromatographed on silica gel to afford **6a—c** or **8d**. The yields of the products and the reaction conditions were summarized in Table 1. The compound **6a—c** or **8d** had the following properties (Tables 2 and 3).

5-Allyl-6a-diethoxyphosphinyl-3a,4,5,6a-tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (6a): Yield 2.35 g (7.80 mmol); oil; R_F 0.32 [AcOEt–hexane (4 : 1)]; IR (neat) 1680 cm^{-1}; ^{1}H NMR δ=1.34 (6H, t, J=7.0 Hz, Me), 3.16—4.52 (9H, m, NCH_2, OCH_2, and CH), 4.96—5.38 (2H, m, $CH{=}C\underline{H}_2$), 5.38—5.98 (1H, m, $C\underline{H}{=}CH_2$), 6.44 (1H, br, NH), 6.72 (1H, s, N=CH); MS m/z 301 (M^+). Found: C, 47.76; H, 6.99; N, 13.48%. Calcd for $C_{12}H_{20}N_3O_4P$: C, 47.84; H, 6.69; N, 13.95%.

6a-Diethoxyphosphinyl-5-phenyl-3a,4,5,6a-tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (6b): Yield 2.50 g (7.41 mmol); mp 89—90 °C; IR (KBr) 1690 cm^{-1}; ^{1}H NMR δ=1.33 (6H, t, J=7.0 Hz, Me), 3.76—4.50 (7H, m, NCH_2, OCH_2, and CH), 6.56 (1H, br, NH), 6.79 (1H, s, N=CH), 7.00—7.68 (5H, m, phenyl H); MS m/z 337 (M^+). Found: C, 53.34; H, 5.99; N, 12.24%. Calcd for $C_{15}H_{20}N_3O_4P$: C, 53.41; H, 5.98; N, 12.46%.

5-Benzyl-6a-diethoxyphosphinyl-3a,4,5,6a-tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-one (6c): Yield 2.60 g (7.40 mmol); mp 118—119 °C; IR (KBr) 1680 cm^{-1}; ^{1}H NMR δ=1.32 (6H, t, J=7.0 Hz, Me), 3.08—3.78 (2H, m, NCH_2), 3.92—4.56 (7H, m, OCH_2, $PhCH_2$, and CH), 5.40—6.28 (1H, br, NH), 6.64 (1H, s, N=CH), 7.26 (5H, s, phenyl H); MS m/z 351 (M^+). Found: C, 54.35; H, 6.33; N, 11.86%. Calcd for $C_{16}H_{22}N_3O_4P$: C, 54.70; H, 6.31; N, 11.96%.

3-Allyl-1-phenylthio-3-azabicyclo[3.1.0]hexan-2-one (8d): Yield 1.82 g (7.42 mmol); oil; R_F 0.44 [AcOEt–hexane (1 : 2)]; IR (neat) 1680 cm^{-1}; ^{1}H NMR δ=1.28 (1H, dd, J_{cis}=17.7 Hz, J_{gem}=5.0 Hz, cyclopropane CH_2), 1.39 (1H, dd, J_{trans}=20.7 Hz, J_{gem}=5.0 Hz, cyclopropane CH_2), 1.94—2.36 (1H, m, CH), 3.08—3.92 (4H, m, NCH_2), 4.80—5.32 (2H, m, $CH{=}C\underline{H}_2$), 5.32—6.04 (1H, m, $C\underline{H}{=}CH_2$), 7.00—7.36 (5H, m, phenyl H); MS m/z 245 (M^+). Found: C, 68.50; H, 6.31; N, 5.67%. Calcd for $C_{14}H_{15}NOS$: C, 68.54; H, 6.16; N, 5.71%.

The Reaction of 6b and Paraformaldehyde. To a mixture of **6b** (0.67 g, 2.00 mmol) and paraformaldehyde

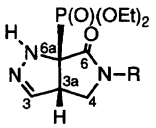


Table 2. ^{13}C NMR Assignment of 3a,4,5,6a-Tetrahydropyrrolo[3,4-*c*]pyrazol-6(1*H*)-ones[a)]

Compounds	Substituents R	^{13}C NMR ($CDCl_3$) δ, (^{31}P-^{13}C coupling const/Hz) 3	3a	4	6	6a
6a	$CH_2CH{=}CH_2$	143.8	47.8	45.3	169.4	69.1
		(12.0)	(3.4)		(6.9)	(176.2)
6b	Ph	143.7	47.2	49.1	169.6	69.7
		(12.0)			(7.7)	(176.2)
6c	CH_2Ph	143.8	47.5	46.6	169.6	68.9
		(11.2)	(3.5)		(6.9)	(176.2)

a) All chemical shifts relative to Me_4Si (δ=0.0).

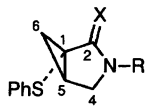


Table 3. ^{13}C NMR Data of 3-Azabicyclo[3.1.0]hexanes[a)]

Compds	R	X	^{13}C NMR, Chemical shifts δ 1	2	4	5	6	R		
8d	$CH_2CH{=}CH_2$	O	33.4	172.1	45.5	23.0	22.5	46.9	118.1	132.1
12a	(*E*)-$CH{=}CH_2CH_3$	O	33.7	169.9	45.7	23.2	23.0	14.9	106.0	124.4
12b	(*Z*)-$CH{=}CH_2CH_3$	O	33.0	171.7	48.8	22.4	22.4	12.6	111.6	123.4
13	H	O	32.4	176.4	42.8	25.6	22.1	—	—	—
14	$CH_2CH{=}CH_2$	H_2	29.0	57.6	54.3	25.7	17.7	60.0	116.8	135.5
16	H	H_2	30.8	54.4	48.5	27.2	15.9	—	—	—

a) Chemical shifts for $CDCl_3$ solutions relative to Me_4Si (δ=0.0).

(0.60 g, 20.0 mmol) in 60 ml of THF–HMPA (5:1) was added butyllithium (2.40 mmol) at −78 °C. After the reaction mixture was stirred at room temperature for 5 h, the reaction was quenched with the addition of water. The mixture was extracted with $CHCl_3$, dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane(2:1) affording **11**.

10-Phenyl-3-oxa-5,6,10-triazatricyclo[6.3.0.0^{1,5}]-undec-6-en-11-one (11): Yield 0.30 g (1.23 mmol, 62%); mp 186.5—187 °C; IR (KBr) 1690 cm^{-1}; ^{1}H NMR δ=3.73 (1H, dd, J_{cis}=9.7 Hz, J_{trans}=5.4 Hz, CH), 3.85—3.93 (1H, m, one H of NCH_2), 3.91 (1H, d, J_{gem}=9.2 Hz, one H of OCH_2C), 4.08 (1H, dd, J_{cis}=9.7 Hz, J_{gem}=9.7 Hz, one H of NCH_2), 4.27 (1H, d, J_{gem}=9.2 Hz, one H of OCH_2C), 4.48 (1H, J_{gem}=7.3 Hz, one H of OCH_2N), 5.17 (1H, d, J_{gem}=7.3 Hz, one H of OCH_2N), 7.00 (1H, s, N=CH), 7.00—7.62 (5H, m, phenyl H); MS *m/z* 243 (M^+). Found: C, 63.89; H, 5.54; N, 16.93%. Calcd for $C_{13}H_{13}N_3O_2$: C, 64.19; H, 5.39; N, 17.27%.

Allylic Rearrangement of 8d. To a solution of potassium *t*-butoxide (0.22 g, 2.00 mmol) in DMSO (8 ml) was added **8d** (0.49 g, 2.00 mmol). The reaction mixture was stirred at room temperature for 10 min under a nitrogen atmosphere, diluted with water and taken to pH 8 with solid carbon dioxide. The mixture was extracted with $CHCl_3$. After drying over anhydrous sodium sulfate, the $CHCl_3$ extract was evaporated in vacuo. The residue was chromatographed on preparative thin-layer chromatography (TLC) (silica gel with AcOEt:hexane=1:6) to give allylic rearranged compounds **12a** and **12b** in 65% yield (Table 3).

1-Phenylthio-3-[(*E*)-1-propenyl]-3-azabicyclo-[3.1.0]hexan-2-one (12a): Yield 0.26 g (7.40 mmol, 53%); oil; R_F 0.53 [AcOEt–hexane (1:3)]; IR (neat) 1695 cm^{-1}; ^{1}H NMR δ=1.31 (1H, dd, J_{trans}=17.4 Hz, J_{gem}=5.0 Hz, cyclopropane CH_2), 1.42 (1H, dd, J_{cis}=20.4 Hz, J_{gem}=5.0 Hz, cyclopropane CH_2), 1.67 (3H, dd, J_{vic}=6.6 Hz, J=1.6 Hz, Me), 1.98—2.42 (1H, m, CH), 3.15—3.76 (2H, m, NCH_2), 4.91 (1H, dq, J_{trans}=14.4 Hz, J_{vic}=6.6 Hz, NCH=C<u>H</u>), 6.78 (1H, dq, J_{trans}=14.4 Hz, J=1.6 Hz, NC<u>H</u>=CH), 7.06—7.50 (5H, m, phenyl H). MS Found *m/z* 245.0868. Calcd for $C_{14}H_{15}NOS$: 245.0874 (M^+).

1-Phenylthio-3-[(*Z*)-1-propenyl]-3-azabicyclo-[3.1.0]hexan-2-one (12b): Yield 0.06 g (0.24 mmol, 12%); oil; R_F 0.48 [AcOEt–hexane (1:3)]; IR (neat) 1695 cm^{-1}; ^{1}H NMR δ=1.33 (1H, dd, J_{trans}=17.3 Hz, J_{gem}=5.0 Hz, cyclopropane CH_2), 1.44 (1H, dd, J_{cis}=20.1 Hz, J_{gem}=5.0 Hz, cyclopropane CH_2), 1.69 (3H, dd, J_{vic}=7.3 Hz, J=1.8 Hz, Me), 2.02—2.42 (1H, m, CH), 3.48—4.06 (2H, m, NCH_2), 4.95 (1H, dq, J_{cis}=9.5 Hz, J_{vic}=7.3 Hz, NCH=C<u>H</u>), 6.78 (1H, dq, J_{cis}=9.5 Hz, J=1.8 Hz, NC<u>H</u>=CH), 7.12—7.82 (5H, m, phenyl H). MS Found *m/z* 245.0870. Calcd for $C_{14}H_{15}NOS$: 245.0874 (M^+).

Depropenylation of 12a, 12b. A mixture (0.25 g, 1.00 mmol) of **12a** and **12b** in 0.5 equiv methanolic sodium hydroxide (20 ml) was treated with a 4% aqueous potassium

permanganate solution in MeOH until the reaction mixture showed no starting compound when examined by thin-layer chromatography. The mixture was filtered through the celite pad, concentrated in vacuo and extracted with $CHCl_3$. After evaporation of $CHCl_3$, the residue was chromatographed on preparative TLC (silica gel with $CHCl_3 : Et_2O = 1 : 2$) to give depropenylated compound **13**.

1-Phenylthio-3-azabicyclo[3.1.0]hexan-2-one (13): Yield 0.19 g (0.93 mmol, 93%); mp 155—155.5 °C; IR (KBr) 1685 cm^{-1}; ^1H NMR δ=1.30 (1H, dd, J_{trans}=14.0 Hz, J_{gem}= 4.8 Hz, cyclopropane CH_2), 1.40 (1H, dd, J_{cis}=17.0 Hz, J_{gem}=4.8 Hz, cyclopropane CH_2), 1.94—2.38 (1H, m, CH), 3.10—3.77 (2H, m, NCH_2), 4.00—4.68 (1H, br, NH), 7.04—7.46 (5H, m, phenyl H). MS *m/z* 205 (M^+). Found: C, 64.20; H, 5.47; N, 6.74%. Calcd for $C_{11}H_{11}NOS$: C, 64.36; H, 5.40; N, 6.82%.

Reduction of 8d. To a suspension of $LiAlH_4$ (0.76 g, 20.0 mmol) in THF (35 ml) was added $CuCl_2$ (1.34 g, 10.0 mmol) and the mixture was stirred for 1 h under a nitrogen atmosphere (black precipate appeared immediately). Then a THF solution (5 ml) of **8g** (1.23 g, 5.00 mmol) was added dropwise and the mixture was stirred at room temperature for 30 min. After hydrolysis, a precipitate was filtered through a celite pad and the filtrate was extracted with diethyl ether. The extract was dried over anhydrous sodium sulfate and evaporated in vacuo. The residue was chromatographed on silica gel with AcOEt–hexane (1 : 9) to give **14**.

3-Allyl-1-phenylthio-3-azabicyclo[3.1.0]hexane (14): Yield 0.69 g (3.00 mmol, 60%); oil; R_F 0.51 [AcOEt–hexane (1 : 9)]; IR (neat) 2750, 1475 cm^{-1}; ^1H NMR δ=0.74—1.12 (1H, m, cyclopropane CH_2), 1.44—1.80 (2H; m, cyclopropane CH_2 and CH), 2.44 (1H, d, J=8.9 Hz, one H of NCH_2), 2.50 (1H, d, J=8.9 Hz, one H of NCH_2), 2.88—3.37 (4H, m, allyl H and NCH_2CS), 4.86—5.28 (2H, m, $CH{=}C\underline{H}_2$), 5.50—6.15 (1H, m, $C\underline{H}{=}CH_2$), 7.02—7.46 (5H, m, phenyl H); MS *m/z* 231(M^+). Found: C, 72.58; H, 7.41; N, 5.86%. Calcd for $C_{14}H_{17}NS$: C, 72.68; H, 7.41; N, 6.05%.

Deallylation of 14. Deallylation of **14** was carried out according to the allylic rearrangement procedure as described above to give **16**.

1-Phenylthio-3-azabicyclo[3.1.0]hexane (16): Yield 0.29 g (1.52 mmol, 76%); mp 56—57 °C; IR (KBr) 3259, 1580 cm^{-1}; ^1H NMR δ=0.88—1.28 (2H, m, cyclopropane CH_2), 1.52—2.84 (1H, m, CH), 2.20—2.64 (1H, br, NH), 2.76—3.40 (4H, m, NCH_2), 7.00—7.46 (5H, m, phenyl H); MS *m/z* 191 (M^+). Found: C, 68.77; H, 6.99; N, 7.27%. Calcd for $C_{11}H_{13}NS$: C, 69.07; H, 6.85; N, 7.32%.

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