# Synthesis of Bisbicyclo[1.1.1]pentyldiazene. The Smallest Bridgehead Diazene

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Bisbicyclo[1.1.1]pentyldiazene, the smallest bicyclic azo compound, has been synthesized from the precursor [1.1.1]propellane via synthesis of *N*,*N*′-bis(bicyclo[1.1.1]pentyl)sulfamide and azoxybicyclo-[1.1.1]pentane. The UV absorption of this diazene at 382 nm indicates that the compound is the trans isomer. Conversion to the cis isomer by irradiation was not possible because of attainment of a photostationary state. However, on the basis of the photochemical studies, the absorption of the cis-[1.1.1] isomer is estimated to be 384 nm.

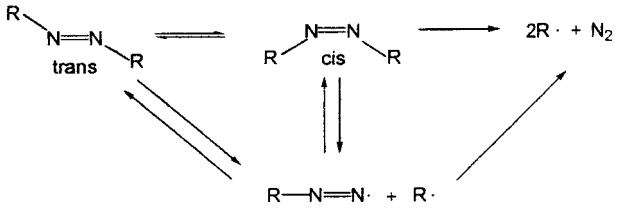
## Introduction

Diazenes have been studied since the end of the 19th century.[1] They are often highly colored being intense orange, yellow, red, blue, or green depending on their molecular structure and have been used in the dying, printing, and textile industries. Other uses include sources of free radicals[2] in industrial processes such as polymerization, cracking, and oxidations, as well as in biological systems of photosynthesis and biosynthesis.[3,4]

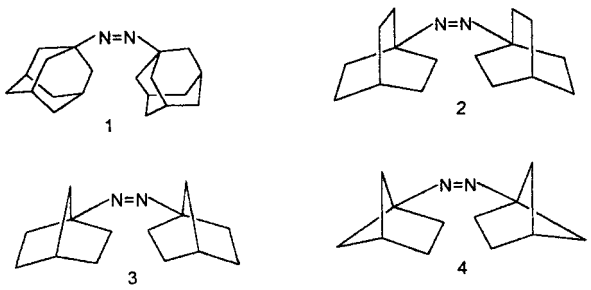
Diazenes exist in two isomeric forms, the trans and the less-stable cis isomer. Trans isomers normally are converted to the thermodynamically less-stable cis forms photochemically, and when heated, cis isomers can revert to trans isomers with the release of excess stored energy.[5] Thus, light energy is converted into heat energy, and diazenes can be considered as a source of solar energy. The cis isomer generally absorbs at a higher wavelength in the UV spectrum than the corresponding trans isomer. The highest known absorption for a cis isomer is *cis*-azoadamantane at 455 nm.[6]

The thermal and photochemical behaviors of diazenes have been studied since their very early discovery.[7] Although, historically, considerable controversy existed over the decomposition mechanism, whether it is concerted or stepwise,[8,9] the decomposition is now well-understood.[10] The recent study of the decomposition of azo methane by Zewail using femtosecond spectroscopy clearly shows the decomposition to be stepwise.[10] The general mechanisms for decomposition and isomerization are depicted in Scheme 1. Diazenes having α-hydrogens

**Scheme 1**




on carbons attached to nitrogen have a tendency to tautomerism.[11] Bridgehead diazenes with no α-hydrogen undergo trans−cis isomerization and are more stable than their acyclic counterparts. An extensive study of bridgehead diazenes such as azo-1-adamantane, azo-1-bicyclo[2.2.2]octane, azo-1-bicyclo[2.2.1]heptane, and azo-1-bicyclo[2.1.1]hexane was reported in 1982.[12] The bulkiness of the bridgehead group plays an important role in the isomerization and decomposition.[13] The smaller groups favor isomerization, whereas larger groups as in **1** and **2** undergo isomerization and decomposition to radicals and nitrogen. The probability of formation of radical decreases with the smaller R groups.[12] According to Rüchardt, the measured rate for formation of radical is $k_{rel}$(trans,300 °C): cis-ada (1.0), cis-[2.2.2] (0.13), cis-[2.2.1] (0.008).[13]




The smallest bridgehead diazene, bisbicyclo[1.1.1]-pentyldiazene, is not known, although several attempts to synthesize this diazene[12] failed from complexity in

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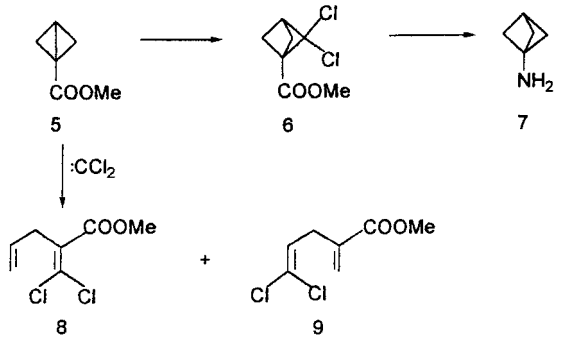
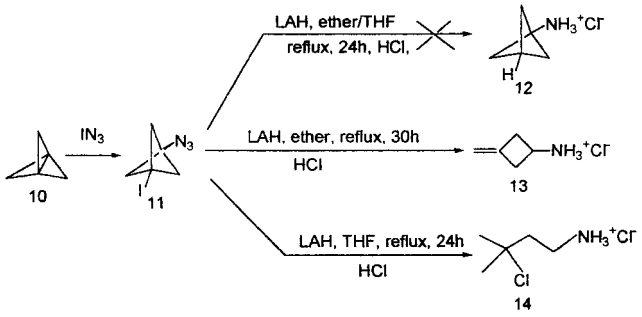
**Scheme 2**




**Scheme 3**



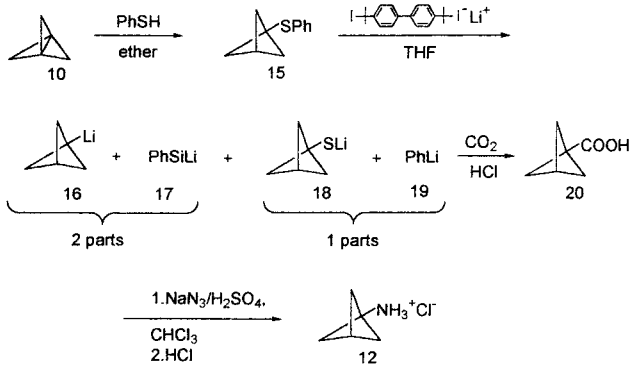

synthesis of the precursor amine **7** from ester **5** and resulted in the formation of olefins **8** and **9** (Scheme 2). This paper reports the synthesis of this diazene from [1.1.1]propellane.

## Results and Discussion

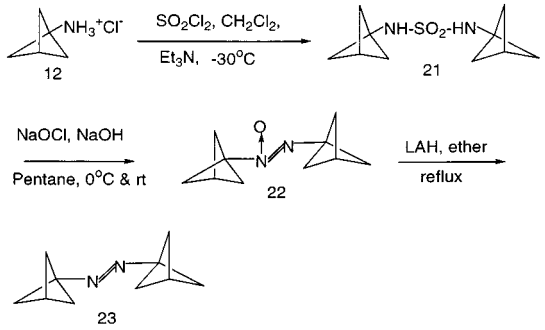
[1.1.1]Propellane (**10**) has been known since 1982[14] and undergoes 1,3 additions at its bridgehead to afford 1,3-adducts. Pseudohalogens[15,16] are probable candidates for addition to **10**, and iodine azide adds to give 3-iodobicyclo-[1.1.1]pentyl azide (**11**) in 92% yield.[17] Further reduction of 3-iodobicyclo[1.1.1]propyl azide would provide 1-bicyclo-[1.1.1]pentylamine because both the iodine and the azide are reducible. However, with a variety of reducing agents, the [1.1.1]propellane group fragments. Lithium aluminium hydride reduction of **11** in THF affords 3-methylenecyclobutylamine hydrochloride (**13**) and reduction in ether gives 3-chloro-3-methylbutylamine hydrochloride (**14**) (Scheme 3).[17]

The addition of thiophenol to **10** afforded 1-bicyclo-[1.1.1]pentylphenylsulfide (**15**) which by lithiation with lithium di-*tert*-butylbiphenyl (LDBB) followed by carboxylation provided 1-bicyclo[1.1.1]pentyl carboxylic acid (**20**) in up to 45% yield (Scheme 4).[18] While working on a larger scale, we have produced up to 55% yield of **20**. Lithiation of **15** yielded the major product 1-bicyclo-[1.1.1]pentyllithium (**16**) along with **17**, **18**, and **19**. In situ carboxylation of the mixture followed by aqueous workup removed most of the side products, and 1-bicyclo-[1.1.1]carboxylic acid (**20**) can be purified by flash chromatography. The Schmidt reaction of **20** provides 1-bicyclo-[1.1.1]pentylamine hydrochloride[19] (**12**) in up to 87% yield.

**Scheme 4**




**Scheme 5**




A single-step synthesis of bisbicyclo[1.1.1]pentyldiazene (**23**) by oxidative coupling of 1-bicyclo[1.1.1]pentylamine with iodine pentafluoride[20] failed, and only a trace amount of **23** could be isolated. An alternative approach was successful. The conversion of 1-bicyclo[1.1.1]pentylamine to *N*,*N*′-bis(bicyclo[1.1.1]pentyl)sulfamide (**21**) was easily achieved with sulfuryl chloride and triethylamine in up to 78% yield.[21] The hypochlorite oxidation of sulfamides in the presence of a strong base affords diazenes.[22] However, our repeated attempts always provided azoxybicyclo[1.1.1]pentane (**22**) (Scheme 5) along with a very small quantity of **23**. This is the only case of which we are aware in which an azoxy compound results. The reduction of **22** with lithium aluminum hydride (LAH) in ether under mild reaction conditions provides **23** in 87% yield. The UV absorption maximum of **23** is at 382 nm, and **23** has a molar absorptivity of 22, thus establishing it as the trans isomer.

In an attempt to synthesize the cis isomer directly by chemical means using the Engel method,[23] we obtained a mixture of three compounds, **21**, **22**, and **23**. The preparation of *cis*-**23** by irradiation of the trans isomer was also unsuccessful. The comparison of **23** with a series of other bridgehead bicyclic diazenes reveals an interesting correlation (Table 1). The absorption maximum for *trans*-**23** is 382 nm and is the highest absorption maximum among the trans bicyclic diazenes. The UV absorption maxima in the cis series are 444 nm for *cis*-**2**, 423

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**Table 1. Comparison of UV Absorption for Bridgehead Diazenes**

| compounds | cis, $\lambda_{max}$ (nm) | cis, $\epsilon$ (L mol$^{-1}$ cm$^{-1}$) | trans, $\lambda_{max}$ (nm) | trans, $\epsilon$ (L mol$^{-1}$ cm$^{-1}$) | reference |
|---|---|---|---|---|---|
| **2** | 444 | | 369 | 14.7 | 13, 27 |
| **3** | 423 | 123 | 365 | 15.1 | 13, 27 |
| **4** | 404 | 118 | 371 | 21 | 13, 27 |
| **23** | (404 − 20) = 384 (calcd) | | 382 | 22 | present work |

nm for *cis*-**3**, and 404 nm for *cis*-**4**. The average difference in absorption of these cis diazenes from one to the next is about 20 nm. Thus, the estimated $\lambda_{max}$ for *cis*-**23** would be near 384 nm (404 − 20) which is almost the same as that of the trans isomer. The isolated yield of a cis isomer from irradiation of the trans isomer decreases as the bulkiness of the bridgehead group decreases.[12] The isolation of *cis*-**2** was not possible because of its lability, and its formation was indicated only by UV absorption. The yield of *cis*-**3** was not reported, and *cis*-**4** was isolated in 33% yield.[12] As bulkiness of the bridgehead diazene decreases, the difference in absorption maxima between cis and trans isomers decreases significantly and the maxima become almost the same (382 and 384 nm) for both the cis and trans bisbicyclo[1.1.1]pentyldiazene isomers. Furthermore, because the molar absorptivity of *cis*-**23** is expected to be larger than that of *trans*-**23**, the photostationary state that is established would greatly favor the trans isomer over the cis isomer.

## Conclusion

Bisbicylo[1.1.1]pentyldiazene has been synthesized by a multistep process from [1.1.1]propellane. The UV spectrum indicates that the compound is trans. The isolation of the cis isomer by irradiation was not possible. However, on the basis of the study of a series of bridgehead diazenes, the UV absorption maximum of the cis [1.1.1]diazene is estimated to be 384 nm. These two factors, the close proximity of $\lambda_{max}$ between the cis and trans isomers and the greater molar absorptivity of the cis isomer over the trans isomer, resulted in no observation of any photochemical conversion of the trans isomer to the cis one in the UV spectrum.

## Experimental Section

**General.** THF and ether were distilled from sodium and benzophenone. Pentane was distilled from sodium. Acetonitrile and triethylamine were distilled from phosphorus pentoxide, pyridine was distilled from potassium hydroxide, and dichloromethane was distilled from calcium sulfate. Thiophenol was first dried over calcium chloride and then distilled under reduced pressure with a positive flow of nitrogen. Methanol was distilled from magnesium. Biphenyl was recrystallized from methanol. All the solvents after distillation were preserved under either 4 Å molecular sieves or potassium hydroxide and used with a positive pressure of nitrogen.

The syntheses of [1.1.1]propellane[24] (**10**), 3-iodobicyclo-[1.1.1]pentyl azide (**11**), 3-methylenecyclobutylamine hydrochloride (**13**), and 3-chloro-3-methylbutylamine hydrochloride (**14**) have been described in a previous paper.[17]

**4,4′-Di-*tert*-butylbiphenyl.**[25] To 75 mL of nitromethane in a 250 mL dry three-neck flask equipped with a condenser, an addition funnel, a magnetic stirrer, and a stopper was added 13.15 g (0.085 mol) of biphenyl. The mixture was stirred, and 3.0 g of anhydrous aluminum chloride was added. The color of the solution changed to deep violet. A solution of 17.36 g (0.19 mol) of 2-chloro-2-methylpropane (*tert*-butyl chloride) in 20 mL of nitromethane was added dropwise to the stirred mixture over 30 min. At the end of the addition, the reaction started vigorously as was evidenced by the evolution of hydrogen chloride gas through the condenser. The reaction mixture was stirred overnight and poured onto crushed ice in a 500 mL beaker. The ice was allowed to melt, and the solution was warmed to room temperature. The organic layer was extracted with a mixture of nitromethane/pentane (1:1, 3 × 50 mL), dried over anhydrous magnesium sulfate, and then filtered. The light yellow color filtrate was treated with silica gel (100 g) to provide a colorless solution. Evaporation of the solvent afforded a white powder which was purified by crystallization from nitromethane to give white needlelike crystals of 4,4′-di-*tert*-butylbiphenyl: 21.0 g, 92%, mp 127.5−129° C (lit.[25] 128.6−129 °C). $^1$H NMR ($CDCl_3$): $\delta$ 7.53−7.44 (m, 8H), 1.35 (s, 18H). $^{13}$C NMR ($CDCl_3$): $\delta$ 127.1, 126.0, 31.6, 0.2.

**Bicyclo[1.1.1]pentylphenylsulfide (15).**[18] To a solution of 4.63 mmol of [1.1.1]propellane in ether at 0 °C was added 0.51 g (4.63 mmol) of thiophenol in 15 mL of ether dropwise, and the mixture was stirred at room temperature for 30 min. Evaporation of ether under vacuum gave a colorless oil, which was dissolved in 5 mL of pentane and purified by passing through a short column of silica gel with pentane. Evaporation of pentane yielded **15** as a colorless oil: 0.75 g, 92%. $^1$H NMR ($CDCl_3$): $\delta$ 7.45−7.32 (m, 5H), 2.72 (s, 1H), 1.95 (s, 6H) [lit.[18] $\delta$ 7.50−7.44 (m, 2H), 7.35−7.25 (m, 4H), 7.23 (s, 1H), 1.96 (s, 6H)].

**1-Bicyclo[1.1.1]pentane Carboxylic Acid (20).**[18] An oven-dried 250 mL three-neck flask, equipped with a glass coated magnetic stirrer, a condenser, and a rubber septum, was put under positive pressure of argon. The flask was heated with a flame by occasional release of the argon from the septum. When the flask was cool, 16.32 g (61.26 mmol) of 4,4′-di-*tert*-butylbiphenyl and 50 mL of dry THF were introduced, and a positive pressure of argon was maintained throughout the reaction. Lithium wire was cleaned with a sharp knife in petroleum ether (bp 40−60 °C) and dried with filter paper, and 0.42 g (60.52 mmol) was cut, while held in the stream of argon, into very small pieces with a pair of scissors. The pieces fell into the flask by gravitation. The funnel was replaced with a rubber septum, and the mixture was magnetically stirred. The surface of the lithium wire became shiny, and within 7 min, the solution became dark green. The solution was stirred at 0 °C under a positive pressure of argon for 4 h, during which time all of the lithium reacted, and lithium di-*tert*-butylbiphenyl (LDBB) was formed. Into another 250 mL three-neck flask, which was dried as above, under a positive pressure of argon were added 5.28 g (29.97 mmol) of 1-bicyclo[1.1.1]-pentylphenylsulfide (**18**) and 30 mL of dry THF. The mixture was stirred and cooled to −78 °C. The freshly prepared lithium di-*tert*-butylbiphenyl (LDBB) was cannulated dropwise over a 30 min period. When the addition was completed, the reaction mixture was stirred between −65 and −55° C for 1 h and cooled to −78 °C. A stream of carbon dioxide was bubbled into the solution using a long needle, and an exit needle vented the carbon dioxide stream. The solution became colorless within 5 min, and the carbon dioxide stream was continued until the solution became milky white and was allowed to warm to room temperature. The solution became colorless after evaporation of excess carbon dioxide. A saturated solution of 50 mL of sodium bicarbonate and 50 mL of ether was added to the stirred solution. The aqueous layer was separated, acidified with excess hydrochloric acid, and extracted with ether (3 × 30 mL). The combined organic layers were dried over anhydrous magnesium sulfate and evaporated to a colorless oil of two components (TLC). Separation by silica gel flash chromatography with dichloromethane afforded **20** as a white solid: 1.9 g (57%). IR (KBr): 1704 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.43 (s, 1H), 2.11 (s, 6H) [lit.[22] $\delta$ 2.45 (s, 1H), 2.13 (s, 6H)]. $^{13}$C NMR ($CDCl_3$): $\delta$ 175.7, 51.5, 42.3, 27.8.

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**1-Bicyclo[1.1.1]pentylamine Hydrochloride (12).**[26] 1-Bicyclo[1.1.1]pentane carboxylic acid (**23**) (1.84 g, 16.41 mmol), 30 mL of chloroform, and 6 mL of concentrated sulfuric acid were added to a three-neck 100 mL flask equipped with a reflux condenser, a magnetic stirrer, and a stopper. The mixture was stirred and heated to 35−40 °C in an oil bath. Sodium azide (2.17 g, 33.37 mmol) was added to the slowly stirred solution over 1 h. The solution was cooled to room temperature and made basic with 33% sodium hydroxide solution. The basic solution was then steam distilled into an ice−water receiver. Evaporation of the chloroform and water afforded a light orange amine salt, which was purified by crystallization from ethyl acetate−ethanol to give 1-bicyclo[1.1.1]pentylamine hydrochloride (**12**): 1.70 g, (87%); mp 242−244 °C. $^1$H NMR ($D_2O$): $\delta$ 2.50 (s, 1H), 1.94 (s, 6H) [lit.[19] $\delta$ 2.61 (1H), 2.06 (6H)]. $^{13}$C NMR ($D_2O$): $\delta$ 50.9, 44.9, 23.2.

***N,N′*-Bis(1-bicyclo[1.1.1]pentyl)sulfamide (21).** 1-Bicyclo[1.1.1]pentylamine hydrochloride (**12**) (1.0 g, 8.35 mmol) was taken up in 5 mL of 10% NaOH solution, and the free amine was extracted with dichloromethane (5 × 5 mL). The combined dichloromethane was dried over KOH for 4 h. An oven-dried 100 mL three-necked flask equipped with a condenser, addition funnel, and magnetic stirring bar under a positive pressure of argon was charged with 0.84 g (8.30 mmol) of triethylamine. Dichloromethane-containing free amine was decanted to the reaction flask and cooled to −30 to −35 °C in a dry ice−acetone bath. A solution of 4.18 mL (1 M, 4.18 mmol) of sulfuryl chloride in dichloromethane was added from the addition funnel slowly over 30 min, and then the mixture was stirred for 2 h at the same temperature. It was allowed to warm to room temperature and stirred overnight. The mixture was poured into a separatory funnel, washed with 5% HCl (3 × 20 mL), dried over anhydrous magnesium sulfate, and filtered. Evaporation of the filtrate under vacuum provided a light gray solid, which was purified by crystallization from ethyl acetate−water to give *N*,*N*′-bis(1-bicyclo[1.1.1]pentyl)sulfamide (**21**) as white crystals: 0.74 g (78%); mp 201−203 °C. IR (KBr): 3298, 2985, 2921, 2865, 1498, 1424, 1323, 1267, 1157, 973, 922, 885 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 4.84 (s, 1H), 2.44 (s, 1H), 2.03 (s, 6H). $^{13}$C NMR ($CDCl_3$): $\delta$ 52.6, 48.5, 23.9. Anal. Calcd for $C_{10}H_{16}N_2O_2S$: C, 52.60; H, 7.08; N, 12.27. Found: C, 52.72; H, 7.07; N, 12.22.

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**Azoxybicyclo[1.1.1]pentane (22).** *N*,*N*′-Bis(1-bicyclo[1.1.1]pentyl)sulfamide (**21**) (0.5 g, 2.19 mmol), 60 mL of pentane, and 20 mL of 5% NaOCl (chlorox) were added to a 250 mL three-neck flask and cooled to 0 °C in an ice bath. The reaction mixture was stirred for 2 h at 0 °C, the ice bath was removed, and the mixture was stirred overnight at room temperature. Completion of the reaction was evidenced by the disappearance of the sulfamide. The yellow organic layer was separated from the aqueous layer and washed with water (2 × 20 mL), 5% HCl (2 × 20 mL), and water (10 mL), followed by drying over anhydrous magnesium sulfate. Evaporation of the solvent under vacuum gave a yellow solid. The crude solid was purified by silica gel flash chromatography with pentane, and evaporation of the solvent under vacuum afforded a light yellow solid. Further purification was done by recrystallization from pentane to give azoxybicyclo[1.1.1]pentane (**22**): 0.23 g (59%); mp 79.5−80.5 °C. IR (KBr): 3016, 2937, 2897, 1720, 1481, 1357, 1267, 1207 cm$^{-1}$. $^1$H NMR ($CDCl_3$): $\delta$ 2.58 (s, 1H), 2.54 (s, 1H), 2.27 (s, 6H), 2.23 (s, 6H). $^{13}$C NMR ($CDCl_3$): $\delta$ 63.1, 56.3, 52.4, 52.1, 26.8, 20.4. UV (pentane) $\lambda_{max}$: 233 nm. Anal. Calcd for $C_{10}H_{14}N_2O$: C, 67.39; H, 7.92; N, 15.72. Found: C, 67.32; H, 8.03; N, 15.63.

**Bisbicyclo[1.1.1]pentyldiazene (23).** To a stirred slurry of 0.09 g (2.37 mmol) of lithium aluminum hydride in 25 mL of dry ether in a 100 mL three-neck flask under argon was added 0.29 g (1.62 mmol) of azoxybicyclo[1.1.1]pentane (**22**) slowly over a 10 min period. When the addition was completed, the reaction mixture was refluxed gently for 16 h and cooled to room temperature. The reaction mixture was cooled in an ice bath, and unreacted lithium aluminum hydride was taken up with ice cold water (10 mL). The organic layer was separated, the aqueous layer was extracted with ether (4 × 20 mL), and the combined organic layers were dried over anhydrous magnesium sulfate. Evaporation of the solvent afforded a yellow solid. The solid was purified by recrystallization from pentane and by sublimation to give bisbicyclo[1.1.1]pentyldiazene (**23**) as yellow crystals: 0.23 g (87%); mp 108−110 °C. $^1$H NMR ($CDCl_3$): $\delta$ 2.58 (s, 1H), 2.10 (s, 6H). $^{13}$C NMR ($CDCl_3$): $\delta$ 65.7, 51.5, 23.4. UV (pentane) $\lambda_{max}$: 382 nm. $\epsilon$ = 22.4 mol$^{-1}$ cm$^{-1}$. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.02; H, 8.71; N, 17.27. Found: C, 74.41; H, 8.82; N, 16.90. HRMS: calcd for $C_{10}H_{14}N_2$, 162.1157; found, 162.1150.

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