Pergamon

Tetrahedron Vol. 50, No. 44, pp. 12571-12578, 1994

0040-4020/94 $7.00+0.00

0040-4020(94)00811-6

Benzotriazolylmethylaminosilanes: Novel Azomethine Ylide Equivalents

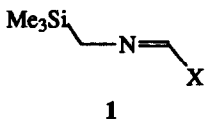
Alan R. Katritzky,* Jens Köditz and Hengyuan Lang

Center for Heterocyclic Compounds, Department of Chemistry,
University of Florida, FL 32611-7200

Abstract: *Benzotriazolylmethylaminosilanes, readily accessible from the reaction of benzotriazole, an aldehyde and an (aminomethyl)silane in water at 20 °C, are azomethine ylide equivalents which undergo stereospecific cycloadditions with dipolarophiles to give substituted pyrrolidines or 2,5-dihydropyrroles in good yields.*

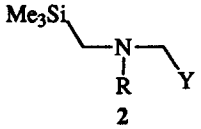
In the last decade, 1,3-dipolar cycloaddition reactions of azomethine ylides, extremely useful for the preparation of various nitrogen-containing heterocyclic systems,[1-2] have been intensively investigated. As previously pointed out,[3-4] the ease of the cycloaddition, the rapid accumulation of polyfunctionality in a relatively small molecular framework, the high stereochemical control of the cycloaddition, and the predictability of regiochemistry have all contributed to the popularity of this reaction in organic synthesis. Consequently, the development of new and convenient methods to generate 1,3-dipoles remains of considerable interest to synthetic organic chemists.

Nonstabilized azomethine ylides can be generated from several precursors including: (i) N-(silylmethyl)imines (**1**)[5-14], (ii) N-(silylmethyl)amines with suitable leaving groups (**2**)[15-21], (iii) other appropriately substituted amines (**3**)[22-24], (iv) analogous imines (**4**)[25-31], and (v) imidates or thioimidates.[32] The recently reported catalytically (CsF, AgF and F_3CCO_2H etc.) induced desilylations of N-(trimethylsilylmethyl)aminomethyl ethers (**2**, Y = OR) and N-(trimethylsilylmethyl)-N-(cyanomethyl)amines (**2**, Y = CN) show perhaps the most promise for future development in this field due to their convenient accessibility. Although the thermal induced desilylation of compounds of type **1** was observed in some cases,[11,13-14,33] there are no reports of the cycloaddition reaction of **2** solely under thermally induced conditions.



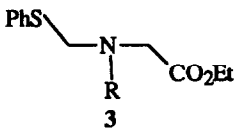
1

X = OR', SR', alkyl



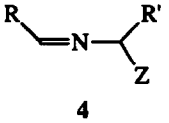
2

Y = OR', CN
R = alkyl, aryl



3

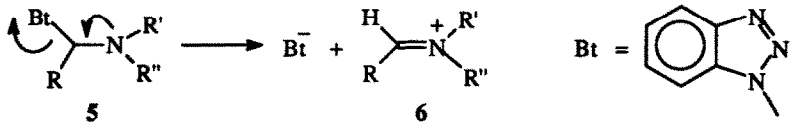
R, R' = alkyl, aryl



4

Z = CO_2R, C(O)R, CN
R, R' = aryl, alkyl

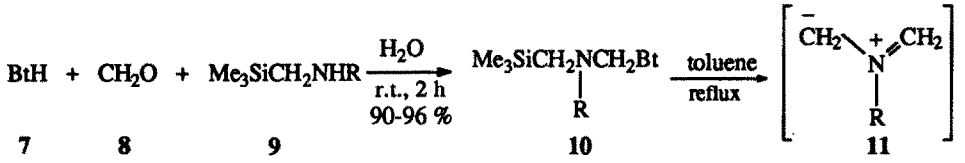
The use of benzotriazole as a synthetic auxiliary in the preparation of many classes of organic compounds, such as amines, amides, ethers, and substituted aromatic and heteroaromatic compounds, has been previously reported in our group.[34] Generally, such methods have relied on the dissociation of benzotriazole derivatives, Bt-C-X, where X is an electron-donor group or a conjugated moiety, to the benzotriazolate anion and a cation containing a double bond. When X is a nitrogen-linked substituent, an iminium intermediate is formed (see Scheme 1). Subsequent reactions with other species have led to addition, displacement, and elimination products.[34] In particular, bis(benzotriazol-1-ylmethyl)hydroxylamine (**5**, R = CH_2Bt, R' = OH)[35] has been shown to be a synthetic equivalent for nitrone 1,3-dipoles (**6**, R' = O^-).



5 **6**

Scheme 1 Dissociation of (α-Benzotriazolylalkyl)amines

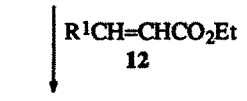
Stimulated by the convenient methods reported for 1,3-dipole generation from organosilicon compounds, and as part of our ongoing interest in the synthetic application of the benzotriazole auxiliary method, we now report that the thermally induced desilylation of benzotriazolylmethylaminosilanes serves as a novel route to azomethine ylide equivalents. Benzotriazolylmethylaminosilanes **10a-d** are readily formed from the condensation of benzotriazole, formaldehyde and (trimethylsilylmethyl)amine **9**[18,21,36] in water at room temperature in excellent yields according to the general procedure for the preparation of aminoalkylbenzotriazoles developed in this laboratory,[37] as shown in Scheme 2. An alternative method for the



7 **8** **9** **10** **11**

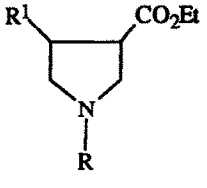
9, 10, 11 **a** R = $(CH_2)_5CH$; **b** R = n-hexyl; **c** R = allyl; **d** R = s-Bu.

12 **a** $R^1 = CO_2Et$ (Z); **b** $R^1 = CO_2Et$ (E); **c** R^1 = Ph (Z).



12

13	R	R^1	Yield	React. time (h)
a	$(CH_2)_5CH$	CO_2Et(Z)	84	20
b	$(CH_2)_5CH$	Ph(Z)	71	24
c	n-hexyl	CO_2Et(E)	87	24
d	n-hexyl	CO_2Et(Z)	89	24
e	allyl	Ph(Z)	90	72
f	s-Bu	CO_2Et(Z)	88	30



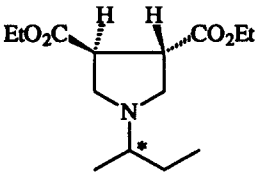
13

Scheme 2 Benzotriazole Mediated Preparation of Pyrrolidines

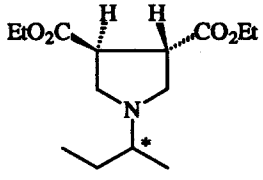
preparation of compounds **10** involves refluxing a mixture of (trimethylsilylmethyl)amines **9** and 1-hydroxymethylbenzotriazole in benzene under Dean-Stark conditions.[38]

Reaction of **10a-d** with electron-deficient alkenes **12a-c** in refluxing toluene under nitrogen afforded the novel pyrrolidine derivatives **13a-f** in good yields (Scheme 2). The reactions were monitored by GC until consumption of the starting material was complete. Separation of the products was achieved via column chromatography on silica gel. The cycloaddition reactions proceeded stereospecifically and normally gave only one isomer with retention of the olefinic dipolarophile configuration. The structures of the products and intermediates were confirmed by ^{1}H NMR, ^{13}C NMR and HR MS spectra.

Since a chiral center exists in the *sec*-butyl group, two diastereomers (*ca* 1:1) were observed in the NMR spectra of **13f**. The ^{13}C NMR spectrum shows two sets of peaks with very small chemical shift differences between all carbons except for those of the ester groups. Overlapped signals were observed for all protons in the ^{1}H NMR spectrum.

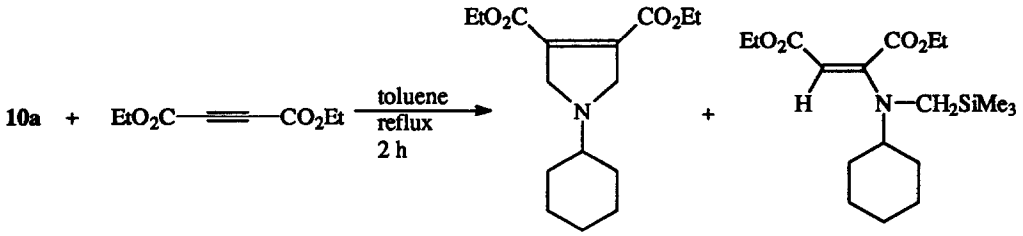


13f(I)



13f(II)

When the acetylenic dipolarophile diethyl acetylenedicarboxylate **14** was used, compound **15** was obtained as the major product (48%) in addition to a by-product, enamine **16** (25%). We believed that under the reaction conditions used the starting compound **10a** partly decomposes to **9a**. Subsequent addition of **9a** to the strongly activated acetylene results in formation of the enamine. In the case of the less reactive alkenes **12** discussed previously, the decomposed species could recombine to form **10a** which undergoes subsequent



14 **15** **16**

Scheme 3 Benzotriazole Mediated Preparation of Dihydropyrrole

1,3-dipolar cycloaddition reactions. The structure of compound **16** was determined by ^{1}H, and ^{13}C NMR including APT (attached proton test) experiments. The ethylenic proton appears at relatively high field (4.42 ppm) in the ^{1}H spectrum. This is typical for a structure in which ethoxycarbonyl is *trans* to the amino group,

and in accordance with literature reports[39-41] in which a secondary amine or lithium amide reacted with an activated acetylene compound to give compounds similar to **16**. Further conformation of the structure was obtained by demonstrating that direct reaction of **9a** with diethyl acetylenedicarboxylate gave the same compound. Attempts to increase the ratio of **15:16** by performing the reaction in refluxing THF failed. Similarly, no improvement was achieved after increasing the reaction time to 10 h.

In summary, this work demonstrates that benzotriazolylmethylaminosilanes are novel and convenient precursors of azomethine ylides. The present methodology gives pyrrolidine or 2,5-dihydropyrrole derivatives under thermal equilibrium conditions without the use of catalysts (AgF, CsF etc.) required by other methods in good yields which compare favorably with those previously obtained. This method, with readily accessible starting materials, represents a new approach to the 1,3-dipolar cycloaddition reactions of organosilicon compounds and is an alternative to the existing procedures.[15-21]

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Varian 300 MHz spectrometer with TMS as an internal reference for ^1H spectra and solvent $CDCl_3$ for ^{13}C spectra. High resolution mass measurements were performed on an AEL MS-30 mass spectrometer. Column chromatography was carried out on MCB silica gel (230-400 mesh).

(Trimethylsilylmethyl)amine **9a** was prepared according to the literature method.[18,21,36] The novel compounds **9b-d** were also prepared by an adaptation of a literature procedure.[18,21,36] The benzotriazole adducts **10a-d** were prepared according to a previously described procedure.[37]

N-(Trimethylsilylmethyl)cyclohexylamine (9a): Obtained as an oil. Yield: 90%. ^1H NMR δ 0.00 (s, 9 H), 0.92-1.30 (m, 5 H), 1.50-1.90 (m, 5 H), 2.02 (s, 2 H), 2.22-2.27 (m, 1 H). ^{13}C NMR δ -2.7, 25.0, 26.2, 33.0, 36.9, 60.6.

N-(Trimethylsilylmethyl)hexylamine (9b): Obtained as an oil. Yield: 95%. (HR MS found: M + 1 = 188.1816; $C_{10}H_{25}NSi$ requires M + 1 = 188.1914). ^1H NMR δ -0.02 (s, 9 H), 0.82 (t, 3 H, J = 7.1 Hz), 1.18-1.26 (m, 6 H), 1.38-1.43 (m, 2 H), 2.00 (s, 2 H), 2.53 (t, 2 H, J = 7.1 Hz). ^{13}C NMR δ -2.7, 13.8, 22.5, 26.9, 29.6, 31.8, 40.2, 54.6.

N-(Trimethylsilylmethyl)allylamine (9c): Obtained as an oil. Yield: 91%. (Lit.[42-43]) ^1H NMR δ -0.22 (s, 9 H), 0.72 (br s, 1 H), 1.79 (s, 2 H), 3.00 (dd, 2 H, J = 6.0, 1.4 Hz), 4.79-4.92 (m, 2 H), 5.60-5.68 (m, 1 H). ^{13}C NMR δ -2.75, 39.6, 56.7, 115.6, 137.0.

N-(Trimethylsilylmethyl)-sec-butylamine (9d): Obtained as an oil. Yield: 86%. (HR MS found: M + 1 = 160.1525; $C_8H_{21}NSi$ requires M + 1 = 160.1601). ^1H NMR δ -0.04 (s, 9 H), 0.81 (t, 3 H, J = 7.4 Hz), 0.95 (d, 3 H, J = 6.3 Hz), 1.19-1.28 (m, 1 H), 1.38-1.46 (m, 1 H), 1.93 (d, 1 H, J = 13.5 Hz), 2.00 (d, 1 H, J = 13.5), 2.38 (sexet, 1 H, J = 6.3 Hz). ^{13}C NMR δ -2.6, 10.3, 19.3, 28.8, 36.9, 58.3.

N-Benzotriazolylmethyl-N-(trimethylsilylmethyl)cyclohexylamine (10a): Obtained as a solid. Yield: 90%. M.p.= 65 °C (HR MS found: M - 1 = 315.1969; $C_{17}H_{28}N_4Si$ requires M - 1 = 315.1925). ^1H NMR δ -0.06 (s, 9 H), 1.00-1.41 (m, 5 H), 1.50-1.90 (m, 5 H), 2.21 (s, 2 H), 2.50-2.70 (m, 1 H), 5.42 (s, 2 H), 7.30-7.50 (m, 2 H), 7.72 (d, 1 H, J = 7.1 Hz), 8.05 (d, 1 H, J = 7.1 Hz). ^{13}C NMR δ -1.8, 25.8, 26.0, 29.7, 39.7, 61.5, 67.3, 110.7, 119.6, 123.6, 126.8, 133.1, 146.2).

N-Benzotriazolylmethyl-N-(trimethylsilylmethyl)hexylamine (10b): A mixture of two isomers (1-benzotriazole and 2-benzotriazole, ratio, ca. 5:1 from NMR) was obtained as an oil. Yield: 94%. (HR MS found: M - 1 = 317.2128; $C_{17}H_{30}N_4Si$ requires M - 1 = 317.2081). ^1H NMR δ -0.06 (s, 9 H), 0.77 (t, 3 H, J = 7.0 Hz), 1.17 (br s, 6 H), 1.40-1.51 (m, 2 H), 2.00 and 2.09 (s, s, total 2 H), 2.37-2.42 (m, 2 H), 5.30 (1-isomer) and 5.44 (2-isomer) (s, s, total 2 H), 7.20-7.28 (1-isomer and 2-isomer) (m, 5/4 H), 7.36 (1-isomer) (t, 3/4 H, J = 7.3 Hz), 7.52 (1-isomer) (d, 3/4 H, J = 7.3 Hz), 7.80 (2-isomer) (dd, 1/2 H, J = 7.3, 1.3 Hz), 7.95 (1-isomer) (d, 3/4 H, J = 7.3 Hz). ^{13}C NMR δ -1.5, 13.9, 22.6, 26.8, 27.3, 31.7, 43.8, 54.8, 69.1, 110.2, 118.3 (2-isomer), 119.3, 123.6, 125.9 (2-isomer) 127.0, 128.2 (2-isomer), 133.9, 145.9.

N-Benzotriazolylmethyl-N-(trimethylsilylmethyl)allylamine (10c): A mixture of two isomers (1-benzotriazole and 2-benzotriazole, ratio, ca 5:1 from NMR) was obtained as an oil. Yield: 93%. (HR MS found: M = 274.1549; $C_{14}H_{22}N_4Si$ requires M = 274.1613). ^1H NMR δ -0.08 (s, 9 H), 2.04 (1-isomer) and 2.08 (2-isomer) (s, s, total 2 H), 3.06 (1-isomer) and 3.17 (2-isomer) (d, d, total 2 H, J = 6.1, 6.1 Hz), 5.05-5.18 (m, 2 H), 5.30 (1-isomer) and 5.44 (2-isomer) (s, s, total 2 H), 5.70-5.82 (m, 1 H), 7.22-7.28 (1-isomer and 2-isomer) (m, 5/4 H), 7.37 (1-isomer) (t, 3/4 H, J = 7.1 Hz), 7.52 (1-isomer) (d, 3/4 H, J = 7.1 Hz), 7.78-7.82 (2-isomer) (m, 1/2 H), 7.96 (1-isomer) (d, 3/4 H, J = 7.1 Hz). ^{13}C NMR δ -1.6, 43.3, 57.3, 68.3, 110.2, 118.4 (2-isomer), 118.5, 119.6, 123.6, 126.0 (2-isomer), 127.1, 133.8, 134.9, 135.1, 145.6.

N-Benzotriazolylmethyl-N-(trimethylsilylmethyl)-sec-butylamine (10d): A mixture of two isomers (1-benzotriazole and 2-benzotriazole, ratio, ca 5:1 from NMR) was obtained as an oil. Yield: 95%. (HR MS found: M - 1 = 289.1845; $C_{15}H_{26}N_4Si$ requires M - 1 = 289.1780).1613 . ^1H NMR δ -0.89 (s, 9 H), 0.60-0.80 (m, 6 H), 1.10-1.18 (m, 1 H), 1.20-1.35 (m, 1 H), 2.18 (1-isomer) and 2.41 (2-isomer) (s, s, total 2 H), 2.51-2.72 (m, 1 H), 5.25 (2-isomer) and 5.30 (1-isomer) (s, s, total 2 H), 7.16-7.28 (1-isomer and 2-isomer) (m, 7/4 H), 7.50 (1-isomer) (d, 3/4 H, J = 7.3 Hz), 7.74-7.82 (2-isomer) (m, 1/2 H), 7.88 (1-isomer) (d, 3/4 H, J = 7.3 Hz). ^{13}C NMR δ -1.8, 10.9, 14.8, 26.6, 33.9, 58.0, 68.5, 110.2, 119.4, 123.5, 126.8, 132.9, 145.8.

*1,3-Dipolar Cycloaddition Reaction of Benzotriazolylmethylaminosilanes **10** with Dipolarophiles **12**, General Procedure:* Benzotriazolylmethylaminosilane **10** (5 mmol) and the dipolarophile **12** or **14** (6 mmol) were refluxed in toluene (15 ml) under N_2 for the appropriate time as shown in Scheme 2. The solvent was then removed and the residue chromatographed on silica gel using hexane and ethyl acetate (30:1) as the eluent to furnish the substituted pyrrolidines **13** or substituted 2,5-dihydropyrrole **15**.

N-Cyclohexyl-3,4-diethoxycarbonylpyrrolidine (13a): Obtained as an oil. Yield: 84%. (Found: M + 1 = 298.2060; $C_{16}H_{27}NO_4$ requires M + 1 = 298.2098). ^1H NMR δ 1.26 (t, 6 H, J = 7.1 Hz), 1.22-2.10 (m, 11 H),

2.83 (t, 2 H, J = 6.4 Hz), 2.96 (t, 2 H, J = 6.4 Hz), 3.38 (t, 2 H, J = 5.3 Hz), 2.15 (q, 4 H, J = 7.1 Hz). ^{13}C NMR δ 14.0, 24.5, 25.8, 31.3, 44.9, 54.1, 60.7, 62.5, 173.3.

N-Cyclohexyl-3-ethoxycarbonyl-4-phenylpyrrolidine (13b): Obtained as an oil. Yield: 71%. (HR MS found: M = 301.2023; $C_{19}H_{27}NO_2$ requires M = 301.2042). ^{1}H NMR δ 1.19 (t, 3 H, J = 7.1 Hz), 1.13-1.34 (m, 4 H), 1.58-2.00 (m, 6 H), 2.10-2.22 (m, 1 H), 2.80 (t, 2 H, J = 7.1 Hz), 3.00-3.20 (m, 3 H), 3.62 (q, 2 H, J = 7.1 Hz), 7.20-7.34 (m, 5 H). ^{13}C NMR δ 14.1, 24.7, 25.8, 31.2, 46.7, 50.9, 54.8, 59.1, 60.6, 63.1, 126.5, 127.4, 128.4, 143.1, 173.8.

N-Hexyl-3,4-E-diethoxycarbonylpyrrolidine (13c): Obtained as an oil. Yield: 87%. (HR MS found: M + 1 = 300.2219; $C_{16}H_{29}NO_4$ requires M + 1 = 300.2201). ^{1}H NMR δ 0.88 (t, 3 H, J = 6.5 Hz), 1.20-1.35 (m, 12 H), 1.42-1.51 (m, 2 H), 2.31-2.48 (m, 2 H), 2.70-2.80 (m, 2 H), 2.80-2.90 (m, 2 H), 3.41 (quintet, 2 H, J = 5.8 Hz), 4.16 (q, 4 H, J = 6.5 Hz). ^{13}C NMR δ 13.7, 13.8, 22.3, 26.8, 28.3, 31.4, 45.0, 55.3, 56.6, 60.6, 173.1.

N-Hexyl-3,4-Z-diethoxycarbonylpyrrolidine (13d): Obtained as an oil. Yield: 89%. (HR MS found: M + 1 = 300.2169; $C_{16}H_{29}NO_4$ requires M + 1 = 300.2201). ^{1}H NMR δ 0.88 (t, 3 H, J = 6.8 Hz), 1.22-1.42 (m, 12 H), 1.42-1.51 (m, 2 H), 2.30-2.45 (m, 2 H), 2.70-2.80 (m, 2 H), 2.80-2.90 (m, 2 H), 3.38-3.42 (m, 2 H), 4.14 (q, 4 H, J = 6.8 Hz). ^{13}C NMR δ 13.5, 13.6, 22.1, 26.6, 28.0, 31.2, 44.8, 55.1, 56.4, 60.3, 172.8.

N-Allyl-3,4-Z-diethoxycarbonylpyrrolidine (13e): Obtained as an oil. Yield: 90%. (HR MS found: M + 1 = 260.1205; $C_{16}H_{21}NO_2$ requires M + 1 = 260.1305). ^{1}H NMR δ 1.21 (t, 3 H, J = 7.1 Hz), 2.73(dd, 1 H, J = 9.4, 7.0 Hz), 2.90-3.22 (m, 6 H), 3.66 (q, 1 H, J = 7.1 Hz), 4.11 (q, 2 H, J = 7.1 Hz), 5.20 (dd, 2 H, J = 12.2, 7.2 Hz), 5.82-6.00 (m, 1 H), 7.20-7.35 (m, 5 H). ^{13}C NMR δ 14.1, 46.9, 51.5, 57.3, 58.7, 60.6, 61.7, 116.9, 126.4, 127.3, 128.4. 135.3, 143.7, 174.0.

N-sec-Butyl-3,4-Z-diethoxycarbonylpyrrolidine (13f): A mixture of two diastereomers (ratio, *ca* 1:1) was obtained as an oil. Yield: 88%. (HR MS found: M + 1 = 272.1868; $C_{14}H_{25}NO_4$ requires M + 1 = 272.1962). ^{1}H NMR δ 0.87 (t, 3 H, J = 7.2 Hz), 0.99 (t, 3 H, J = 7.2 Hz), 1.20-1.40 (m, 7 H), 1.50-1.65 (m, 1 H), 2.20-2.30 (m, 1 H), 2.77-2.85 (m, 2 H), 2.88-2.98 (m, 2 H), 3.32-3.42 (m, 2 H), 4.10-4.22 (q, q, total 4 H, J = 7.2 Hz). ^{13}C NMR δ 9.6 and 10.1, 14.2, 16.3 and 16.9, 27.5 and 27.7, 45.19 and 45.22, 53.7 and 54.0, 59.2 and 59.4, 60.9, 173.6.

N-Cyclohexyl-3,4-diethoxycarbonyl-2,5-dihydropyrrole (15): Obtained as an oil. Yield: 48%. (HR MS found: M + 1 = 296.1819; $C_{16}H_{25}NO_4$ requires M + 1 = 296.1942). ^{1}H NMR δ 1.20-1.86 (m, 10 H), 1.30 (t, 6 H, J = 7.2 Hz), 2.28-2.36 (m, 1 H), 3.83 (s, 4 H), 4.25 (q, 4 H, J = 7.2 Hz). ^{13}C NMR δ 13.8, 24.2, 25.7, 31.3, 58.1, 60.9, 61.5, 136.6, 163.4.

Diethyl (trimethylsilylmethyl)cyclohexylaminomaleate (16): Obtained as an oily by-product uring the preparation of N-cyclohexyl-3,4-diethoxycarbonyl-2,5-dihydropyrrole (**15**). Yield: 25%. (HR MS found: M + 1 = 356.2244; $C_{18}H_{33}NO_4Si$ requires M + 1 =356.2337). ^{1}H NMR δ 0.15 (s, 9 H), 1.00-1.45 (m, 5 H), 1.22

(t, 3 H, J = 7.1 Hz), 1.37 (t, 3 H, J = 7.1 Hz), 1.60-1.75 (m, 5 H), 2.60 (s, 2 H), 3.18 (t, 1 H, J = 7.1 Hz), 4.06 (q, 2 H, J = 7.1 Hz), 4.40 (q, 2 H, J = 7.1 Hz), 4.42 (s, 1 H). ^{13}C NMR δ 13.9, 14.5, 25.0, 25.5, 31.1, 35.6, 58.8, 61.4, 61.6, 84.0, 154.5, 165.8, 167.7.

ACKNOWLEDGEMENT

This work was supported by the German Academic Exchange Service (DAAD).

REFERENCES

1. Terao, Y.; Aono, M.; Achiwa, K.; *Heterocycles*, **1988**, *27*, 981.
2. Padwa, A.; "1,3-Dipolar Cycloaddition Chemistry", Vol. 1, Ed. by A. Padwa, Wiley-Interscience, 1984.
3. Padwa, A.; *Angew. Chem., Int. Ed. Engl.*, **1976**, *15*, 123.
4. Oppolzer, W.; *Angew. Chem., Int. Ed. Engl.*, **1977**, *16*, 10.
5. Alanine, A. I. D.; Fishwick, C. W. G.; *Tetrahedron Lett.*, **1989**, *30*, 4443.
6. Fishwick, C. W. G.; Jones, A. D.; Mitchell, M. B.; *Tetrahedron Lett.*, **1989**, *30*, 4447.
7 Alanine, A. I. D.; Fishwick, C. W. G.; Szantay Jr, C.; *Tetrahedron Lett.*, **1989**, *30*, 6573.
8 Achiwa, K.; Motoyama, T.; Sekiya, M.; *Chem. Pharm. Bull.*, **1983**, *31*, 3939.
9. Achiwa, K.; Sugiyama, K.; Sekiya, M.; *Chem. Pharm. Bull.*, **1985**, *33*, 1975.
10. Fishwick, C. W. G.; Jones, A. D.; Mitchell, M. B.; Szantay Jr, C.; *Tetrahedron Lett.*, **1988**, *29*, 5325.
11. Anderson, W. K.; Dabrah, T. T.; *Syn. Commun.*, **1986**, *16*, 559.
12. Tsuge, O.; Kanemasa, S.; Yamada, T.; Matsuda, K.; *J. Org. Chem.*, **1987**, *52*, 2523.
13. Achiwa, K.; Imai, n.; Inaoka, T.; Sekiya, M.; *Chem. Pharm. Bull.*, **1984**, *32*, 2878.
14. Achiwa, K.; Sekiya, M.; *Chem. Lett.*, **1981**, 1213.
15. Bégué, J.-P.; Bonnet-Delpon, D.; Lequeux, T.; *Tetrahedron Lett.*, **1993**, *34*, 3279.
16. Wee, A. G. H.; *J. Chem. Soc., Perkin Trans. 1*, **1989**, 1363.
17. Padwa, A.; Chen, Y.-Y.; *Tetrahedron Lett.*, **1983**, *24*, 3447.
18. Padwa, A.; Chen, Y.-Y.; Chiacchio, U.; Dent, W.; *Tetrahedron*, **1985**, *41*, 3529.
19. Hosomi, A.; Sakata, Y.; Sakurai, H.; *Chem. Lett.*, **1984**, 1117.
20. Terao, Y.; Kotaki, H.; Imai, N.; Achiwa, K.; *Chem. Pharm. Bull.*, **1985**, *33*, 2762.
21. Padwa, A.; Chen, Y.-Y.; Dent, W.; Nimmesgern, H.; *J. Org. Chem.*, **1985**, *50*, 4006.
22. Imai, N.; Terao, Y.; Achiwa, K.; Sekiya, M.; *Tetrahedron Lett.* **1984**, *25*, 1579.
23. Imai, N.; Nemoto, M.; Terao, Y.; Achiwa, K.; Sekiya, M.; *Chem. Pharm. Bull.*, **1986**, *34*, 1080.
24. Imai, N.; Terao, Y.; Achiwa, K.; *Heterocycles*, **1985**, *23*, 1107.
25. Grigg, R.; Montgomery, J.; Somasunderam, A.; *Tetrahedron*, **1992**, *48*, 10431.
26. Barr, D. A.; Grigg, R.; Sridharan, V.; *Tetrahedron Lett.*, **1989**, *30*, 4727.
27. Amornraksa, K.; Barr, D.; Donegan, G.; Grigg, R.; Ratananukul P.; Sridharan V.; *Tetrahedron*, **1989**, *45*, 4649.

28. Grigg, R.; Donegan, G.; Gunaratne, H. Q. N.; Kennedy, D. A.; Malone, J. F.; Sridharan, V.; Thianpatanagul, S.; *Tetrahedron*, **1989**, *45*, 1723.
29. Barr, D. A.; Grigg, R.; Gunaratne, H. Q. N.; Kemp, J.; McMeekin, P.; Sridharan, V.; *Tetrahedron*, **1988**, *44*, 557.
30. (a) Grigg, R.; Basanagoudar, L. D.; Kennedy, D. A.; Malone, J. F.; Thianpatanagul, S.; *Tetrahedron Lett.*, **1982**, *23*, 2803. (b). Grigg, R.; Gunaratne, H. Q. N.; Kemp, J.; *Tetrahedron Lett.* **1984**, *25*, 99.
31. Tsuge, O.; Ueno, K.; *Heterocycles*, **1983**, *20*, 2133.
32. Vedejs, E.; West, F. G.; *J. Org. Chem.*, **1983**, *48*, 4774. and references cited therein.
33. Imai, N.; Achiwa, K.; *Chem. Pharm. Bull.*, **1987**, *35*, 593.
34. Katritzky, A. R.; Rachwal, S.; Hitchings, G. J.; *Tetrahedron*, **1991**, *47*, 2683.
35. Katritzky, A. R.; Hitchings, G. J.; Zhao, X.; *J. Chem. Soc. Perkin Trans. 1*, **1990**, 2371.
36. Noll, J. E.; Speier, J. L.; Daubert, B. F.; *J. Am. Chem. Soc.*, **1951**, *73*, 3867.
37. Katritzky, A. R.; Pilarski, B.; Urogdi, L.; *Org. Prep. Proc. Int.*, **1989**, *21*, 135.
38. Katritzky, A. R.; Rachwal, S.; Rachwal, B.; *J. Chem. Soc. Perkin Trans 1*, **1987**, 799.
39. Khetan, S. K.; Hiriyakkanavar, J. G.; George, M. V.; *Tetrahedron*, **1968**, *24*, 1567.
40. Khetan, S. K.; George, M. V.; *Tetrahedron*, **1969**, *25*, 527.
41. Feit, B.-A.; Dickerman, S.; Masrawe, C.; Fishman, A.; *J. Chem. Soc. Perkin Trans. 1*, **1988**, 927.
42. Mironov, V. F.; Sheludyakov, V. D.; Rodionov, E. S.; *Zh. Obshch. Khim.*, **1974**, *44*, 1502; C.A.81:91624t.
43. Sheludyakov, V. D.; Kirilina, N. I.; Paushkin, Ya. M.; Kirilin, A. D.; *Dokl. Akad. Nauk SSSR*, **1980**, *254*, 1412; C.A.94:157002r.

(*Received in USA* 10 *August* 1994; *revised* 16 *September* 1994; *accepted* 19 *September* 1994)