

THE REACTION OF A BENZOTRIAZOLE SUBSTITUTED
VINAMIDINIUM SALT WITH GRIGNARD REAGENTS¹

Scott A. Petrich, A. Denise Main, Robin Jaeger, Stanton Q. Smith, Fred
A. Hicks, and John T. Gupton*

Department of Chemistry, University of Central Florida, Orlando,
Florida 32816, U.S.A.

James A. Sikorski*

Monsanto Corporate Research, 700 Chesterfield Parkway North, St.
Louis, Missouri 63198, U.S.A.

Alan R. Katritzky*

Department of Chemistry, University of Florida, Gainesville, Florida
32611, U.S.A.

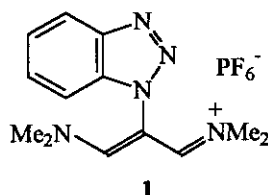
Lyle Castle

Department of Chemistry, University of South Florida, Tampa, Florida
33620, U.S.A.

Abstract- The reaction of a 2-(1-benzotriazolyl)vinamidinium salt with
Grignard reagents to yield α,β -unsaturated aldehydes with
stereochemical control is described.

Recently, the benzotriazole moiety has received much attention due to its usefulness as a synthetic
auxiliary.² It has also been shown to be a pharmacophore³ and can potentially serve as a ligand

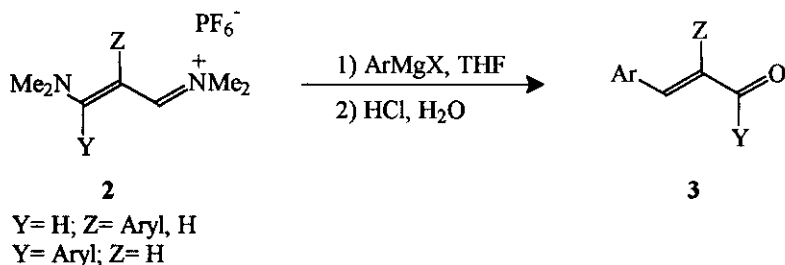
for coordination which could be useful in directing metalation reactions. In a recent article, we reported the synthesis of a novel 2-(1-benzotriazolyl)vinamidinium salt (**1**)^{4a} and its conversion



into a series of benzotriazole substituted heterocyclic systems (e.g. pyrimidines, pyrazoles and pyrroles). A focus of our research group has been to study the reactions of uniquely functionalized vinamidinium salts with a variety of reagents. This paper will describe the reaction of the novel 2-(1-benzotriazolyl)vinamidinium salt with a variety of Grignard reagents.

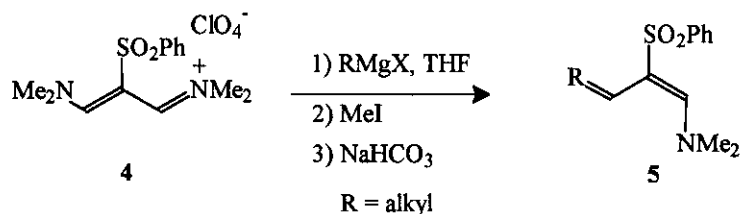
The reaction of aryl Grignard reagents with simple aryl vinamidinium salts (**2**) has been reported to yield α,β -unsaturated carbonyl compounds (**3**) (Scheme 1).⁵ However, when the substituent is a

Scheme 1



phenylsulfonyl group, the aminodiene (**5**) is reported as the only isolated product (Scheme 2).⁶

Scheme 2



The Grignard reagents must be alkyl in order for elimination to occur as depicted. The substituent on the vinamidinium backbone must therefore play an important role as to which product is formed and which Grignard reagent is used.

With the benzotriazole group as the substituent, pre-coordination with the Grignard reagent may occur which could alter the reaction and yield a different product(s) than previously observed. Additionally, if the normal pathway is followed, some interesting and useful benzotriazole appended α,β -unsaturated carbonyl compounds would be available.

The reaction of vinamidinium salt (**1**) with Grignard reagents was performed at 0 °C in THF, and after acid hydrolysis, α,β -unsaturated aldehydes (**6**) were the only products observed (Scheme 3). The reaction is general for alkyl and aryl Grignard reagents. The isolated yield for these reactions are shown in Table 1.

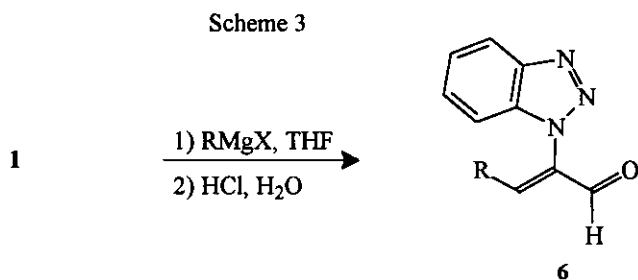
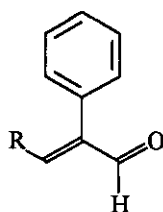


Table 1

Compound	R	% Yield (Isolated purified)
6a	Me	92
6b	Et	58
6c	<i>i</i> -Pr	48
6d	Bu	61
6e	<i>i</i> -Bu	88
6f	Pentyl	62
6g	Ph	43
6h	4-Cl-Ph	66
6i	4-F-Ph	63
6j	4- <i>t</i> -Bu-Ph	40

The stereochemistry of the α,β -unsaturated aldehydes (**6**) was not clearly defined, and the literature gave conflicting information⁷ on the stereochemistry of related systems. In our previous paper,^{5a} we reported the vinyl hydrogen of aldehydes (**8b**) and (**8c**) as being *cis* to the aldehyde.

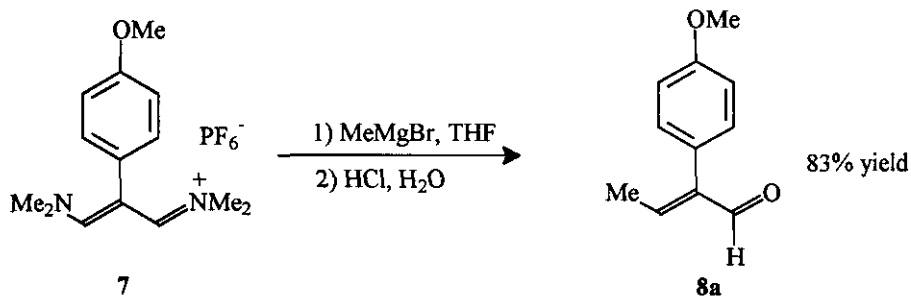


8b, R = *n*-Bu

8c, R = *n*-Hex

This was determined by additivity rules and information gathered from an nmr shift reagent study. The conditions were slightly different than those reported in this paper so a subsequent reaction was performed with the *p*-methoxyphenyl substituted vinamidinium salt (**7**) (Scheme 4).

Scheme 4

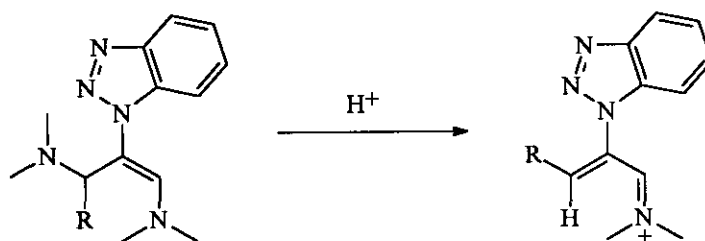


The (*E*)- α,β -unsaturated aldehyde (**8a**) was the only product observed in 83% yield. The stereochemistry of the double bond was determined by nmr NOEDIF experiments. Aldehydes (**8a**) and (**6a**) showed enhancement of the vinyl hydrogen when the aldehyde hydrogen was irradiated verifying the aldehyde as being *cis* to the vinyl hydrogen. Correspondingly, the samples of aldehydes (**8b**) and (**8c**) which were prepared in the previous paper^{5a} also showed enhancement between the vinyl hydrogen and the aldehyde hydrogen. Attempts were made to isomerize the aldehydes to the "*Z*" isomer under acidic and basic conditions, but they resulted in

recovery of the starting material. From the results obtained, we can determine that pre-coordination is not a controlling factor since the same product and stereochemistry is observed whether the substituent on the vinamidinium salt is a benzotriazole or a simple aryl group.

The observed stereochemistry is probably the result of coplanarity factors which arise during the elimination step in the formation of the carbon-carbon double bond (Scheme 5). The transition state leading to the product shown should be lower with the R group *trans* to the iminium group. If the R group was *cis*, there would be a large steric interaction and the transition state would be higher.

Scheme 5



It is interesting to note that many of the benzotriazole substituted α,β -unsaturated aldehydes were liquids and decompose after standing at room temperature for a period of time. They can be stored in the freezer, but should be used in a relatively short period of time. This instability is observed more often when the substituent is alkyl than aryl and is accentuated when a drying agent such as magnesium sulfate is brought into contact with the enals. The yield of the aldehyde is reduced in this case which may be due to chelation of the magnesium cation and, perhaps, subsequent polymerization in a Michael type reaction.

In order to obtain complete characterization of the products, a derivative of the aldehydes was prepared. The reaction of the aldehydes (6) with 2,4-dinitrophenylhydrazine in ethanol under acid catalysis afforded the corresponding hydrazones (9) in relatively good yield (Scheme 6). The yields before recrystallization are given in Table 2. The resulting hydrazones (9) were stable and

Scheme 6

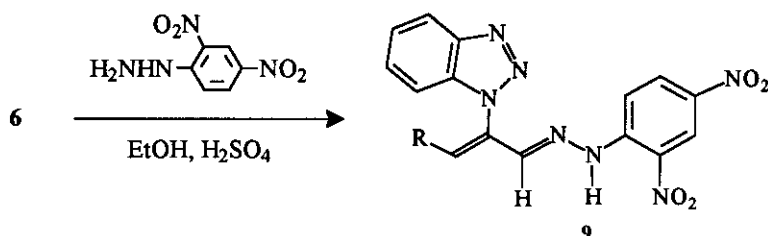


Table 2

Compound	R	% Yield (Isolated crude)
9a	Me	92
9b	Et	32
9c	<i>i</i> -Pr	87
9d	Bu	68
9e	<i>i</i> -Bu	67
9f	Pentyl	64
9g	Ph	57
9h	4-Cl-Ph	73
9i	4-F-Ph	73
9j	4- <i>t</i> -Bu-Ph	89

could be stored at room temperature indefinitely. The spectra of the hydrazones (9) had the same features as the aldehydes (6) and were characteristic of hydrazones. Subsequent exact mass determinations were accomplished for these hydrazones and the results were consistent with the proposed structures.

In summary, we have synthesized a series of benzotriazole substituted α,β -unsaturated aldehydes from the corresponding vinamidinium salt in good yields and with stereochemical control. This procedure is potentially useful as a general route to heterocyclic appended α,β -unsaturated aldehydes and further substantiates the role of vinamidinium salts as useful three carbon synthons.

EXPERIMENTAL

The following procedures are typical of the experimental conditions used for the preparation of the α,β -unsaturated aldehydes and their subsequent conversion to 2,4-dinitrophenylhydrazones.

The vinamidinium salts were synthesized in the same manner as described by Gupton, *et al.*⁴ All melting points and boiling points are uncorrected and all purified compounds gave a single spot on tlc analysis on silica gel 7GF with an ethyl acetate/hexane mixture as the eluent.

Z-2-(1-Benzotriazolyl)but-2-enal (6a): A 5.5 ml (0.0077 mol) aliquot of 1.4 M methylmagnesium bromide was added to 1.00 g (0.0026 mol) of 2-(1-benzotriazolyl)-1,1,5,5-tetramethyl-1,5-diazapentadienium hexafluorophosphate^{4a} in 40 ml of dry THF at 0 °C. The solution was stirred for an hour, allowed to warm to room temperature and stirred for another hour. After cooling down to 0 °C, 20 ml of a 50:50 mixture of acetic acid and water were added and the resulting mixture was allowed to warm to room temperature for an hour while stirring. The solution was partitioned between water and chloroform and the organic layer was neutralized by saturated sodium bicarbonate solution. The organic layer was dried over sodium sulfate and concentrated in vacuo. The residue was eluted through approximately 3 cm of 70-230 mesh silica gel with ethyl acetate. The solvent was removed in vacuo leaving a crystalline product. A purified sample was obtained by radial chromatography of the residue on a 2 mm-thick plate of silica gel on a Harrison Chromatotron. A gradient elution starting with hexanes and adding ethyl acetate afforded a major band containing the desired product (0.44 g, 92% yield). The product had the following properties: mp 87-92 °C; ¹H nmr (DMSO-d₆) δ 1.90 (d, J = 7.0 Hz, 3H), 7.45-7.65 (m, 3H), 7.74 (q, J = 7.0 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 9.78 (s, 1H); ¹³C nmr (CDCl₃) δ 16.9, 112.2, 122.2, 126.3, 130.3, 135.4, 140.1, 147.5, 152.0 and 188.1; ir (CHCl₃) 1699 cm⁻¹; Hrms for C₁₀H₉N₃O calcd 187.0746, found 187.0751.

Z-2-(1-Benzotriazolyl)pent-2-enal (6b): This compound was prepared in 58% yield in a manner identical to the preparation of compound (6a) with the exception that ethylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: bp 110 °C at 0.5 torr; ¹H nmr (DMSO-d₆) δ 1.07 (t, J = 7.5 Hz, 3H), 2.19 (pentet, J = 7.5 Hz, 2H), 7.45-7.71 (m, 3H), 7.67 (t, J = 7.5 Hz, 1H), 8.16 (d, J = 8 Hz, 1H), 9.78 (s,

1H); ^{13}C nmr (DMSO- d_6) δ 14.2, 23.6, 112.5, 121.2, 126.2, 130.1, 135.1, 137.4, 146.4, 159.7 and 190.0; ir (neat) 1697 cm^{-1} ; mass spectrum m/z 201 (M^+).

Z-2-(1-Benzotriazolyl)-4-methylpent-2-enal (6c): This compound was prepared in 48% yield in a manner identical to the preparation of compound (6a) with the exception that isopropylmagnesium bromide was used as one of the starting materials and the residue was purified by bulb-to-bulb distillation. The purified product of this reaction exhibited the following properties: bp 88°C at 1.0 torr; ^1H nmr (CDCl_3) δ 1.15 (d, $J = 6.6\text{ Hz}$, 6H), 2.60 (m, 1H), 7.03 (d, $J = 10.4\text{ Hz}$, 1H), 7.25-7.55 (m, 3H), 8.11 (d, $J = 8\text{ Hz}$, 1H), 9.67 (s, 1H); ^{13}C nmr (CDCl_3) δ 23.9, 30.4, 112.1, 122.1, 126.3, 130.3, 135.6, 136.8, 147.6, 163.0 and 188.5; ir (neat) 1698 cm^{-1} ; mass spectrum m/z 215 (M^+).

Z-2-(1-Benzotriazolyl)hept-2-enal (6d): This compound was prepared in 61% yield in a manner identical to the preparation of compound (6a) with the exception that *n*-butylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: bp 118°C at 0.9 torr; ^1H nmr (CDCl_3) δ 0.85 (t, $J = 7.5\text{ Hz}$, 3H), 1.31 (sextet, $J = 7.5\text{ Hz}$, 2H), 1.55 (pentet, $J = 7.5\text{ Hz}$, 2H), 2.33 (q, $J = 7.5\text{ Hz}$, 2H), 7.22 (t, $J = 7.5\text{ Hz}$, 1H), 7.37-7.56 (m, 3H), 8.15 (d, $J = 8.1\text{ Hz}$, 1H), 9.69 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 15.2, 23.4, 29.6, 31.2, 112.5, 121.2, 126.2, 130.1, 135.2, 138.0, 146.4, 159.7 and 190.0; ir (neat) 1702 cm^{-1} ; mass spectrum m/z 229 (M^+).

Z-2-(1-Benzotriazolyl)-5-methylhex-2-enal (6e): This compound was prepared in 88% yield in a manner identical to the preparation of compound (6a) with the exception that isobutylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: bp 98°C at 0.5 torr; ^1H nmr (CDCl_3) δ 0.92 (d, $J = 6.6\text{ Hz}$, 6H), 1.91 (septet, $J = 6.8\text{ Hz}$, 1H), 2.24 (t, $J = 7.0\text{ Hz}$, 2H), 7.23-7.56 (m, 4H), 8.13 (d, $J = 8.2\text{ Hz}$, 1H), 9.72 (s,

1H); ^{13}C nmr (CDCl_3) δ 24.4, 30.1, 39.4, 112.1, 122.2, 126.3, 130.3, 135.6, 139.4, 147.5, 156.2 and 188.2; ir (neat) 1700 cm^{-1} ; mass spectrum m/z 229 (M^+).

Z-2-(1-Benzotriazolyl)oct-2-enal (6f): This compound was prepared in 62% yield in a manner identical to the preparation of compound (6a) with the exception that *n*-pentylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: bp $118\text{ }^\circ\text{C}$ at 0.2 torr; ^1H nmr (DMSO-d_6) δ 0.78 (t, $J = 6.6\text{ Hz}$, 3H), 1.09-1.53 (m, 6H), 2.18 (q, $J = 7.0\text{ Hz}$, 2H), 7.45-7.60 (m, 3H), 7.70 (t, $J = 7.7\text{ Hz}$, 1H), 8.17 (d, $J = 8.2\text{ Hz}$, 1H), 9.79 (s, 1H); ^{13}C nmr (DMSO-d_6) δ 15.4, 23.3, 28.7, 29.7, 32.3, 112.5, 121.1, 126.1, 130.1, 135.1, 138.0, 146.4, 158.7 and 189.9; ir (neat) 1699 cm^{-1} ; mass spectrum m/z 243 (M^+).

Z-2-(1-Benzotriazolyl)-3-phenylprop-2-enal (6g): This compound was prepared in 43% yield in a manner identical to the preparation of compound (6a) with the exception that phenylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: bp $110\text{ }^\circ\text{C}$ at 0.1 torr; ^1H nmr (DMSO-d_6) δ 6.93 (d, $J = 7.7\text{ Hz}$, 2H), 7.28-7.58 (m, 6H), 8.21 (d, $J = 8.8\text{ Hz}$, 1H), 8.44 (s, 1H), 9.91 (s, 1H); ^{13}C nmr (CDCl_3) δ 112.0, 122.3, 126.5, 130.5, 131.2, 132.7, 132.8, 134.4, 134.6, 134.9, 147.9, 149.3 and 189.1; ir (neat) 1697 cm^{-1} ; mass spectrum m/z 249 (M^+).

Z-2-(1-Benzotriazolyl)-3-(4-chlorophenyl)prop-2-enal (6h): This compound was prepared in 66% yield in a manner identical to the preparation of compound (6a) with the exception that 4-chlorophenylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: bp $122\text{ }^\circ\text{C}$ at 0.1 torr; ^1H nmr (DMSO-d_6) δ 6.97 (d, $J = 8.4\text{ Hz}$, 2H), 7.42 (d, $J = 8.4\text{ Hz}$, 2H), 7.45-7.63 (m, 3H), 8.22 (d, $J = 7.7\text{ Hz}$, 1H), 8.45 (s, 1H), 9.91 (s, 1H); ^{13}C nmr (DMSO-d_6) δ 112.4, 121.4, 126.5, 130.5, 131.2, 131.7, 133.7, 134.5, 134.6, 138.7, 146.8, 149.6 and 190.6; ir (neat) 1697 cm^{-1} ; mass spectrum m/z 283 (M^+).

Z-2-(1-Benzotriazolyl)-3-(4-fluorophenyl)prop-2-enal (6i): This compound was prepared in 63% yield in a manner identical to the preparation of compound (6a) with the exception that 4-fluorophenylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 93-94 °C; ^1H nmr (CDCl_3) δ 6.91-6.95 (m, 4H), 7.17-7.22 (m, 1H), 7.40-7.52 (m, 2H), 7.82 (s, 1H), 8.15-8.19 (m, 1H), 9.82 (s, 1H); ^{13}C nmr (CDCl_3) δ 112.0, 118.6 (d, $J = 21.9$ Hz), 122.3, 126.7, 129.0 (d, $J = 3.4$ Hz), 130.7, 134.3, 134.9, 135.2 (d, $J = 9.1$ Hz), 147.8, 148.5, 166.6 (d, $J = 255$ Hz) and 189.2; ir (neat) 1684 cm^{-1} ; mass spectrum m/z 267 (M^+).

Z-2-(1-Benzotriazolyl)-3-(4-(1,1-dimethylethyl)phenyl)prop-2-enal (6j): This compound was prepared in 40% yield in a manner identical to the preparation of compound (6a) with the exception that 4-(1,1-dimethylethyl)phenylmagnesium bromide was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 177-179 °C; ^1H nmr (CDCl_3) δ 1.23 (s, 9H), 6.86 (d, $J = 8.4$ Hz, 2H), 7.25 (m, 3H), 7.42-7.49 (m, 2H), 7.83 (s, 1H), 8.18 (m, 1H), 9.82 (s, 1H); ^{13}C nmr (CDCl_3) δ 32.9, 37.1, 112.1, 122.2, 126.5, 128.3, 129.9, 130.5, 133.0, 133.9, 135.1, 147.9, 150.1, 158.7 and 189.2; ir (KBr pellet) 1693 cm^{-1} ; Hrms for $\text{C}_{19}\text{H}_{19}\text{N}_3\text{O}$ calcd 305.1528, found 305.1514.

(2E,4Z)-4-(2-Benzotriazolyl)-5-(4-chlorophenyl)-1-(2,4-dinitrophenyl)-1,2-diazapenta-2,4-diene (9h): A 25 ml beaker was charged with 0.14 g (0.71 mol) of 2,4-dinitrophenylhydrazine. After adding 1 ml of sulfuric acid, water was slowly added until the solid dissolved followed by 1 ml of ethanol. A 25 ml flask was charged with 0.20 g (0.71 mol) of aldehyde (6h). The hydrazine solution was added and an orange solid was collected by vacuum filtration and rinsed with cold water. The solid was dried in vacuo leaving 0.24 g (73% yield) of product which was recrystallized from a 3:1 ethanol/water solution. A 55% yield was obtained after recrystallization. The solid exhibited the following properties: mp 270 °C; ^1H nmr ($\text{DMSO}-d_6$) δ 6.75 (d, $J = 9.6$ Hz, 1H), 6.83 (d, $J = 8.6$ Hz, 2H), 7.33 (d, $J = 8.6$ Hz, 2H), 7.55 (m, 3H), 7.73 (s, 1H), 8.08 (d of d, $J = 9.6$

Hz, $J = 2.6$ Hz, 1H), 8.23 (m, 1H), 8.78 (d, $J = 2.6$ Hz, 1H), 8.89 (s, 1H), 11.86 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 112.4, 117.3, 121.5, 124.6, 126.4, 130.4, 130.8, 131.4, 131.9, 132.1, 132.6, 133.2, 134.6, 136.4, 137.7, 139.3, 145.6, 146.8 and 148.0; ir (KBr pellet) 1616 and 3287 cm^{-1} ; Hrms for $\text{C}_{21}\text{H}_{14}\text{N}_7\text{O}_4\text{Cl}$ calcd 463.0796, found 463.0806.

(2E,4Z)-4-(2-Benzotriazolyl)-1-(2,4-dinitrophenyl)-1,2-diazahepta-2,4-diene (9a): This compound was prepared in 92% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6a) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 237 $^{\circ}\text{C}$; ^1H nmr (CDCl_3) δ 1.85 (d, $J = 7.3$ Hz, 3H), 6.74 (q, $J = 7.3$ Hz, 1H), 6.98 (d, $J = 9.5$ Hz, 1H), 7.36-7.55 (m, 3H), 8.01-8.06 (m, 2H), 8.21 (d, $J = 7.4$ Hz, 1H), 9.04 (d, $J = 1.6$ Hz, 1H), 11.23 (s, 1H); ir (KBr pellet) 1613 and 3295 cm^{-1} ; Hrms for $\text{C}_{16}\text{H}_{13}\text{N}_7\text{O}_4$ calcd 367.1029, found 367.1026.

(2E,4Z)-4-(2-Benzotriazolyl)-1-(2,4-dinitrophenyl)-1,2-diazahepta-2,4-diene (9b): This compound was prepared in 32% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6b) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 177 $^{\circ}\text{C}$; ^1H nmr (DMSO- d_6) δ 1.02 (t, $J = 7.6$ Hz, 3H), 1.99 (pentet, $J = 7.6$ Hz, 2H), 6.77 (d, $J = 9.6$ Hz, 1H), 6.90 (t, $J = 7.6$ Hz, 1H), 7.47-7.60 (m, 3H), 8.07 (d of d, $J = 9.6$ Hz, $J = 2.6$ Hz, 1H), 8.22 (d, $J = 8.2$ Hz, 1H), 8.76 (s, 1H), 8.78 (d, $J = 2.6$ Hz, 1H), 11.69 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 14.7, 23.2, 112.5, 117.2, 121.2, 124.6, 126.2, 130.1, 131.2, 131.4, 132.9, 135.3, 139.0, 145.8, 146.3, 146.7 and 147.7; ir (KBr pellet) 1618 and 3294 cm^{-1} ; Hrms for $\text{C}_{17}\text{H}_{15}\text{N}_7\text{O}_4$ calcd 381.1186, found 381.1180.

(2E,4Z)-4-(2-Benzotriazolyl)-6-methyl-1-(2,4-dinitrophenyl)-1,2-diazahepta-2,4-diene (9c): This compound was prepared in 87% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6c) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 241 $^{\circ}\text{C}$; ^1H nmr (CDCl_3) δ 1.10 (d, J

= 6.6 Hz, 6H), 2.28-2.48 (m, 1H), 6.48 (d, J = 10.3 Hz, 1H), 6.91 (d, J = 9.1 Hz, 1H), 7.37-7.56 (m, 3H), 7.98-8.04 (m, 2H), 8.20 (d, J = 8.1 Hz, 1H), 9.03 (d, J = 3.7 Hz, 1H), 11.22 (s, 1H); ^{13}C nmr (CDCl_3) δ 24.3, 30.1, 112.0, 118.5, 122.3, 125.0, 126.2, 130.1, 131.7, 131.8, 132.0, 136.0, 140.7, 145.2, 146.3, 147.4 and 152.2; ir (KBr pellet) 1614 and 3295 cm^{-1} ; Hrms for $\text{C}_{18}\text{H}_{17}\text{N}_7\text{O}_4$ calcd 395.1342, found 395.1345.

(2E,4Z)-4-(2-Benzotriazolyl)-1-(2,4-dinitrophenyl)-1,2-diaza-2,4-diene (9d): This compound was prepared in 68% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6d) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 199-200 $^\circ\text{C}$; ^1H nmr (CDCl_3) δ 0.83 (t, J = 7.6 Hz, 3H), 1.28 (sextet, J = 7.6 Hz, 2H), 1.49 (pentet, J = 7.6 Hz, 2H), 2.14 (q, J = 7.6 Hz, 2H), 6.67 (t, J = 7.6 Hz, 1H), 6.96 (d, J = 9.5 Hz, 1H), 7.36-7.57 (m, 3H), 7.99-8.05 (m, 2H), 8.20 (d, J = 8.1 Hz, 1H), 9.04 (d, J = 1.4 Hz, 1H), 11.23 (s, 1H); ^{13}C nmr (CDCl_3) δ 15.7, 24.3, 30.1, 32.7, 112.1, 118.5, 122.3, 125.0, 126.2, 130.1, 131.7, 132.0, 133.8, 135.8, 140.7, 145.2, 145.8, 146.3 and 147.4; ir (KBr pellet) 1618 and 3294 cm^{-1} ; Hrms for $\text{C}_{19}\text{H}_{19}\text{N}_7\text{O}_4$ calcd 409.1499, found 409.1504.

(2E,4Z)-4-(2-Benzotriazolyl)-7-methyl-1-(2,4-dinitrophenyl)-1,2-diazaocta-2,4-diene (9e): This compound was prepared in 67% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6e) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 214 $^\circ\text{C}$; ^1H nmr (CDCl_3) δ 0.89 (d, J = 6.5 Hz, 6H), 1.83 (nonet, J = 6.5 Hz, 1H), 2.05 (t, J = 7.5 Hz, 2H), 6.69 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 9.5 Hz, 1H), 7.35-7.55 (m, 3H), 8.01 (d of d J = 9.5 Hz, J = 2.5 Hz, 1H), 8.07 (s, 1H), 8.20 (d, J = 8.6 Hz, 1H), 9.03 (d, J = 2.5 Hz, 1H), 11.22 (s, 1H); ^{13}C nmr (CDCl_3) δ 24.3, 30.3, 39.2, 112.1, 118.5, 122.3, 125.0, 126.2, 130.1, 131.7, 132.0, 134.4, 135.8, 140.7, 144.8, 145.2, 146.3 and 147.4; ir (KBr pellet) 1619 and 3295 cm^{-1} ; Hrms for $\text{C}_{19}\text{H}_{19}\text{N}_7\text{O}_4$ calcd 409.1499, found 409.1520.

(2E,4Z)-4-(2-Benzotriazolyl)-1-(2,4-dinitrophenyl)-1,2-diazadeca-2,4-diene (9f): This compound was prepared in 64% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6f) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 202 °C; ^1H nmr (DMSO- d_6) δ 0.77 (t, J = 6.5 Hz, 3H), 1.09-1.29 (m, 4H), 1.37-1.47 (m, 2H), 1.99 (q, J = 7.7 Hz, 2H), 6.75 (d, J = 9.6 Hz, 1H), 6.90 (t, J = 7.7 Hz, 1H), 7.47-7.61 (m, 3H), 8.07 (d of d J = 9.6 Hz, J = 2.6 Hz, 1H), 8.21 (d, J = 8.1 Hz, 1H), 8.76 (s, 1H), 8.78 (d, J = 2.6 Hz, 1H), 11.68 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 15.5, 23.4, 29.3, 29.4, 32.4, 112.6, 117.2, 121.3, 124.6, 126.1, 130.0, 131.4, 131.5, 133.7, 135.4, 139.1, 145.3, 145.9, 146.4 and 147.9; ir (KBr pellet) 1618 and 3294 cm^{-1} ; Hrms for $\text{C}_{20}\text{H}_{21}\text{N}_7\text{O}_4$ calcd 423.1655, found 423.1636.

(2E,4Z)-4-(2-Benzotriazolyl)-1-(2,4-dinitrophenyl)-5-phenyl-1,2-diazapenta-2,4-diene (9g): This compound was prepared in 57% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6g) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 231 °C; ^1H nmr (DMSO- d_6) δ 6.75-6.83 (m, 3H), 7.20-7.31 (m, 3H), 7.50-7.55 (m, 3H), 7.73 (s, 1H), 8.09 (d of d, J = 9.5 Hz, J = 2.6 Hz, 1H), 8.27 (d, J = 8.6 Hz, 1H), 8.79 (d, J = 2.6 Hz, 1H), 8.91 (s, 1H), 11.84 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 112.4, 117.3, 121.5, 124.6, 126.3, 130.3, 130.7, 131.0, 131.4, 131.6, 131.8, 131.9, 134.2, 134.9, 139.3, 145.6, 146.8 and 148.4; ir (KBr pellet) 1618 and 3284 cm^{-1} ; Hrms for $\text{C}_{21}\text{H}_{15}\text{N}_7\text{O}_4$ calcd 429.1186, found 429.1171.

(2E,4Z)-4-(2-Benzotriazolyl)-5-(4-fluorophenyl)-1-(2,4-dinitrophenyl)-1,2-diazapenta-2,4-diene (9i): This compound was prepared in 73% yield in a manner identical to the preparation of compound (9g) with the exception that aldehyde (6i) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp 275 °C decomp.; ^1H nmr (DMSO- d_6) δ 6.76 (d, J = 9.6 Hz, 1H), 6.83-6.90 (m, 2H), 7.07-7.15 (m, 2H), 7.50-7.60 (m, 3H), 7.72 (s, 1H), 8.07 (d of d, J = 9.6 Hz, J = 2.6 Hz, 1H), 8.27 (d, J = 8.9 Hz, 1H), 8.78 (d, J = 2.6 Hz, 1H), 8.88 (s, 1H), 11.84 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 112.4, 117.3, 117.8 (d, J = 19.9 Hz), 121.5, 124.6,

126.4, 130.4, 130.8 (d, $J = 2.9$ Hz), 131.3, 131.8, 133.3 (d, $J = 13.5$ Hz), 134.9, 137.9, 139.2, 145.6, 146.8, 148.2 and 164.4 (d, $J = 248.7$ Hz); ir (KBr pellet) 1617 and 3294 cm^{-1} ; Hrms for $\text{C}_{21}\text{H}_{14}\text{FN}_7\text{O}_4$ calcd 447.1091 found 447.1091.

(2E,4Z)-4-(2-Benzotriazolyl)-5-(4-(1,1-dimethylethyl)phenyl)-1-(2,4-dinitrophenyl)-1,2-diazapenta-2,4-diene (9j): This compound was prepared in 89% yield in a manner identical to the preparation of compound (9h) with the exception that aldehyde (6j) was used as one of the starting materials. The purified product of this reaction exhibited the following properties: mp >300 °C decomp.; ^1H nmr (DMSO- d_6) δ 1.19 (s, 9H), 6.71 (d, $J = 8.7$ Hz, 3H), 7.26 (d, $J = 8.5$ Hz, 2H), 7.52 (m, 3H), 7.68 (s, 1H), 8.07 (d of d, $J = 9.6$ Hz, $J = 2.6$ Hz, 1H), 8.25-8.30 (m, 1H), 8.78 (d, $J = 2.6$ Hz, 1H), 8.88 (s, 1H), 11.82 (s, 1H); ^{13}C nmr (DMSO- d_6) δ 32.5, 36.4, 108.4, 112.4, 117.3, 121.5, 124.6, 126.3, 127.6, 130.4, 130.8, 131.0, 131.4, 131.7, 135.0, 139.2, 139.4, 145.6, 146.8, 148.6 and 155.1; ir (KBr pellet) 1613 and 3292 cm^{-1} ; Hrms for $\text{C}_{25}\text{H}_{23}\text{N}_7\text{O}_4$ calcd 485.1811 found 485.1822.

Z-2-(4-Methoxyphenyl)but-2-enal (8a): This compound was prepared in 83% yield in a manner identical to the preparation of compound (6a) with the exception that methyl magnesium bromide and 2-(4-methoxyphenyl)-1,1,5,5-tetramethyl-1,5-diazapentadienium hexafluorophosphate^{4b} were used as the starting materials. The residue was purified by bulb-to-bulb distillation. The purified product had the following properties: bp 88 °C at 0.4 torr; ^1H nmr (CDCl_3) δ 2.02 (d, $J = 7.1$ Hz, 3H), 3.83 (s, 3H), 6.80 (q, $J = 7.1$ Hz, 1H), 6.94 (d, $J = 8.8$ Hz, 2H), 7.12 (d, $J = 8.8$ Hz, 2H), 9.60 (s, 1H); ^{13}C nmr (CDCl_3) δ 18.1, 57.3, 115.7, 126.3, 132.7, 146.5, 153.1, 161.2, and 196.0; ir (neat) 1687 cm^{-1} ; Hrms for $\text{C}_{11}\text{H}_{12}\text{O}_2$ calcd 176.0837 found 176.0830.

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