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BENZOTRIAZOLE-ASSISTED SYNTHESIS OF ENAMINES

Alan R. Katritzky*, Qiu-He Long, Ping Lue, and Andrzej Jozwiak
Department of Chemistry, University of Florida, Gainesville, FL 32611, USA

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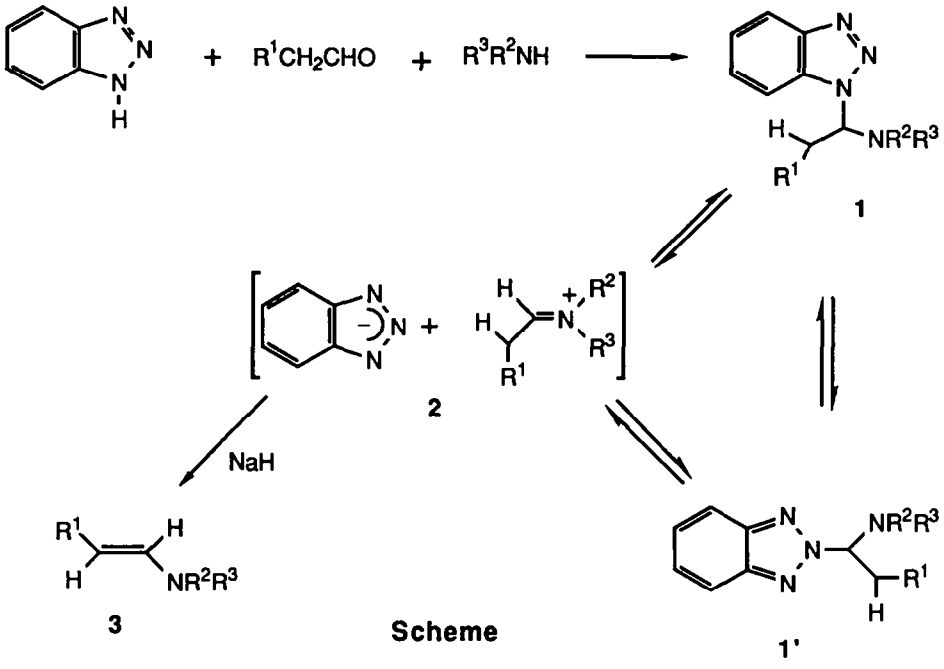
Abstract: *A new, facile preparation of enamines was achieved via a two-step sequence: (i) the ready formation of an N-(α-aminoalkyl)benzotriazole derivative from equimolar amounts of benzotriazole, an aldehyde, and a secondary amine, (ii) the elimination of benzotriazole from the derivative by sodium hydride in tetrahydrofuran (THF). The method provides enamines in good overall yields based on the quantity of amine used.*

Enamines have been important synthetic intermediates in organic synthesis since the discovery of the C-alkylation or acylation of enamines by Stork.[1] Several good methods have been developed for the preparation of enamines.[2,3] The most general route involves the condensation of aldehydes and ketones with secondary amines, either in the presence of a drying agent or by azeotropic distillation.[2,3] A crucial limitation of this method is that it requires, in most cases, a large excess of the amine (at least two equivalents). The good yields quoted are always based on the carbonyl component. Other procedures include the oxidation of tertiary amines by mercuric acetate,[4,5] the Horner-Wittig reaction,[6-10] and the reaction of aldehydes and ketones with metal-secondary amine complexes such as tin,[11-13] silicon,[14] germanium,[15] and titanium.[16-20] However, these methods have one or more limitations as regards the scope of the reaction, the use of toxic materials, tedious reaction procedures, large excesses of amines required, and/or relatively low yields of products.

Recent work in this group has amply demonstrated that N-(α-aminoalkyl)benzotriazole derivatives, which can easily be prepared by the condensation of benzotriazole, an aldehyde (or in some cases a ketone), and a primary or secondary amine, can be utilized advantageously in many synthetic transformations including the monoalkylation of aromatic and heteroaromatic amines,[21] the conversion of secondary aliphatic to tertiary aliphatic amines[22] and the preparation of symmetrical secondary and tertiary amines,[22] N,N-disubstituted hydroxylamines,[22] tertiary propargylamines[23] and tertiary cycloalkylamines,[24] the mono-*t*-butylation of aromatic and heteroaromatic amines,[25] the preparation of α-aminoesters,[26] β-aminoesters,[27] and β-aminoketones.[28] All these transformations depend on an intrinsic property of the intermediates: they exist in mobile equilibrium between the two isomers **1** and **1'** via the benzotriazolide-iminium ion pair **2**,[29-31] formation of which activates the C-N bond toward cleavage in compound **1** (Scheme). We now report another new, useful application of N-(α-

aminoalkyl)benzotriazole derivatives in the synthesis of enamines, based on this facile ionization process. An important feature of our method, in comparison with conventional methods[2,3] for the preparation of enamines, is that only one equivalent of amine is needed.



Scheme

Preparation of N-(α-aminoalkyl)benzotriazole derivatives 1: Each benzotriazole derivative **1** was readily prepared by mixing an equimolar amount of benzotriazole, an aldehyde and a secondary amine in dry diethyl ether with or without a drying agent (e.g. 3 Å molecular sieves). Under these conditions, the reaction took place smoothly at room temperature and led to the complete formation of the condensation product in about 4 hrs. The products (**1a - l**) were oils or low melting solids (see Table 1). Several difficulties were initially encountered in their isolation: they are unstable, do not withstand heating and decompose rapidly during distillation; thus making conventional methods of purification unusable. However, with our experience in the preparation of benzotriazole derivatives, we were able to overcome these problems successfully: after drying with magnesium sulfate and the removal of solvent, a solid was sometimes obtained by triturating the resulting oil with fresh diethyl ether in a solid CO_2-acetone bath. Compounds **1a - c** were obtained crystalline in this way, whereas **1d - l** remained as oils in which cases the ether was poured off and the oil dried in vacuo. All novel compounds were characterized by their NMR spectra (^1H and ^{13}C), and elemental analysis or mass spectra (low resolution and high resolution) (Table 1 and 2).

Table 1. Preparation of N-(α-aminoalkyl)benzotriazoles (1)

Compd	R^1	R^2R^3 of R^2R^3N	Yield(%)[a]	mp(°C)[b]	Formula	Found (calcd)		
						C	H	N
1a	CH_3	$N(CH_2CH_2)_2O$	95	98-101[c]	$C_{13}H_{18}N_4O$	63.39	7.36	22.75
						(63.46)	(7.57)	(23.20)
1b	CH_3CH_2	$N(CH_2CH_2)_2O$	87	64-65[c]	$C_{14}H_{20}N_4O$	64.59	7.74	21.52
						(64.56)	(8.00)	(21.75)
1c	H	$N(CH_2CH_2)_2O$	88	68-71[c]	$C_{12}H_{16}N_4O$	62.05	6.94	24.12
						(61.57)	(6.89)	(24.04)
1d	$CH_3(CH_2)_2$	$N(CH_2CH_2)_2O$	81	oil	$C_{15}H_{22}N_4O$	155.1310	(155.1310)[d]	
1e	$CH_3(CH_2)_3$	$N(CH_2CH_2)_2O$	93	oil	$C_{16}H_{24}N_4O$	169.1465	(169.1466)[d]	
1f	CH_3CH_2	$N(CH_2)_5$	97	oil	$C_{15}H_{22}N_4$	139.1362	(139.1361)[d]	
1g	CH_3	$N(CH_2)_5$	96	oil	$C_{14}H_{20}N_4$	126.1200	(126.1204)[d]	
1h	$CH_3(CH_2)_3$	$N(CH_2)_5$	98	oil	$C_{17}H_{26}N_4$	167.1674	(167.1672)[d]	
1i	CH_3CH_2	$N(CH_2)_4$	95	oil	$C_{14}H_{20}N_4$	125.1194	(125.1204)[d]	
1j	CH_3CH_2	$N(CH_2)_4NCH_3$	96	oil	$C_{15}H_{23}N_5$	154.1470	(154.1473)[d]	
1k	$CH_3(CH_2)_2$	$N(CH_2)_4NCH_3$	98	oil	$C_{16}H_{25}N_5$	182.1783	(182.1778)[d]	
1l	CH_3CH_2	$N(CH_3)C_6H_5$	91	oil	$C_{17}H_{20}N_4$	161.1211	(161.1204)[d]	

[a]. Yield refers to the isolated product. [b]. Uncorrected. [c]. Triturated with Et_2O. [d]. MS(HR) for (M - benzotriazole)$^+$.

The derivatives **1** exist in solution as mixtures of the benzotriazol-1-yl and benzotriazol-2-yl isomers, as evidenced by their ^1H and ^{13}C-NMR spectra. Unlike formaldehyde derivatives where the benzotriazol-1-yl isomer normally predominates in the equilibrium,[29,30] the benzotriazol-1-yl isomer in compounds **1a - l** is only slightly in excess in the equilibrium (by about 5:4). This phenomenon is probably due to the steric influences which affect the relative stability of the 1- and 2-isomers.[31]

Preparation of enamines 3: Initial attempts for the preparation of the enamines **3** by the treatment of benzotriazoles **1** with lithium diisopropylamide (LDA) in THF at room temperature, or sodium hydride (NaH) in refluxing benzene failed. However, when benzotriazoles **1** were treated with NaH in refluxing THF, a precipitate of sodium benzotriazolate usually formed. The reaction proceeded smoothly and after the normal workup, furnished the enamines in high yields (Table 3). Such results reveal that the formation of iminium salts is favored in polar solvents and hence, the abstraction of the β-hydrogen of the iminium cation by a strong base is more facile.

The removal of sodium benzotriazolate was easily accomplished by aqueous extraction. Following this, hexane extraction gave in most cases a clean crude product which was further purified by distillation.

Table 2. ^{13}C-NMR Chemical Shifts (δ) for Products 1, BtCH(CH_2R^1)NR^2R^3 ($CDCl_3$)[a,b]

Compd	Bt						CH	NR^2R^3			CH_2R^1			
1a	145.6	133.8	127.2	123.8	119.9	110.0	81.1	66.8	48.9		24.3	10.4		
1'a	143.5	126.2	118.2				87.8	66.9	48.3		24.5	10.2		
1b	145.3	133.6	127.0	123.6	119.6	109.8	79.1	66.6	48.7		32.7	18.9	13.3	
1'b	143.3	125.9	118.0				85.9	66.7	48.1		33.0	18.7	13.3	
1c	145.9	133.1	127.3	123.8	119.9	110.5	75.4	66.8	48.7		17.4			
1'c	143.5	126.2	118.2				81.9	66.9	48.2		17.8			
1d	145.3	133.6	127.0	123.5	119.6	109.8	79.3	66.5	48.6		30.5	27.7	21.9	13.5
1'd	143.3	125.9	118.0				86.2	66.7	48.1		30.7	27.5	21.9	13.6
1e	145.4	133.7	127.1	123.6	119.7	109.9	79.5	66.6	48.7		31.0	25.3	22.1	13.7
1'e	143.3	126.0	118.0				86.2	66.8	48.2		30.6	25.1	22.1	13.7
1f	145.2	133.1	126.7	123.3	119.4	110.0	79.9	49.4	33.3	25.8	24.0	18.9	13.3	
1'f	143.2	125.6	117.9				86.9	49.0	33.3	25.8	24.0	18.8	14.9	
1g	145.2	133.9	126.6	123.2	119.4	110.0	80.2	49.4	30.1	25.8	22.0	13.6		
1'g	143.1	125.6	117.9				87.2	49.2	31.2	25.4	24.0	14.9		
1h	145.4	133.9	126.8	123.4	119.5	110.1	80.2	49.5	31.6	25.5	31.1	25.9	24.1	22.2
											13.7			
1'h	143.3	125.8	117.9				87.4	49.2	31.4	25.4	31.1	25.9	24.2	22.4
											13.6			
1j	145.4	133.6	126.8	123.4	119.5	110.0	78.9	54.8	48.0	45.5	32.9	18.9	13.3	
1'j	143.3	125.8	117.9				85.7	54.7	47.9	45.5	33.2	18.7	13.3	
1k	145.5	133.7	127.0	123.5	119.7	110.1	79.4	54.8	48.1	45.6	31.1	25.4	22.1	13.7
1'k	143.4	125.9	118.0				86.1	54.9	47.9	45.5	31.3	25.2	22.1	15.1

a. Bt represents the benzotriazol-1 or -2-yl group.

b. The spectral data of compounds **1i** and **1l** are not included because of the difficulty of assignment of the signals due to overlapping.

Enamines prepared by this method were derived from morpholine, piperidine, pyrrolidine, N-methylaniline and 1-methylpiperazine. While the first three are frequently used in the preparation of enamines, the other two are not. N-Methylaniline only gave very poor yields of enamines by the conventional method.[32] By our method, enamine **3l**, derived from N-methylaniline, was obtained in high yield (90%).

Table 3. Preparation of Enamines 3 from Benzotriazoles 1

Enamine	R^1	NR^2R^3	Yield(%)[a]	bp(°C/mm Hg)	Lit. bp(°C/mm Hg)
3a	CH_3	morpholino	75	49-51/11	45-56/12[35]
3b	CH_3CH_2	morpholino	81	60-63/7	74/13[33]
3c	H	morpholino	83	39-42/12[b]	-
3d	$CH_3(CH_2)_2$	morpholino	83	75-78/12	-
3e	$CH_3(CH_2)_3$	morpholino	92	92-94/10	-
3f	CH_3CH_2	piperidino	84	62-65/3	71/13[33]
3g	CH_3	piperidino	61	43-45/9	61-63/10[32]
3h	$CH_3(CH_2)_3$	piperidino	90	89-92/7	103/13[34]
3i	CH_3CH_2	pyrrolidino	92	45-48/5	58/13[33]
3j	CH_3CH_2	N-methylpiperazino	64	67-70/0.8[c]	-
3k	$CH_3(CH_2)_3$	N-methylpiperazino	80	76-79/1.1[d]	-
3l	CH_3CH_2	N-methylanilino	90	92-94/1.6	48-51/0.1[36]

[a] Isolated yield. [b] Contains a small amount of N-ethylmorpholine. [c] MS(HR) Calcd for $C_9H_{18}N_2$: 154.1470, found: 154.1473. [d] MS(HR) Calcd for $C_{11}H_{22}N_2$: 182.1783, found: 182.1774.

Table 4. ^{13}C-NMR Chemical Shifts (δ) for Enamines 3 ($CDCl_3$)

$R^1HC_\beta=C_\alpha HNR^2R^3$

Enamine	C_α	C_β	NR^2R^3					R^1			
3a	140.1	96.7	66.4	49.4				15.1			
3b	138.6	104.5	66.4	49.3				23.3	15.5		
3c	144.5	83.4	66.2	48.7				-			
3d	141.4	102.5	66.3	49.5				32.7	24.6	14.2	
3e	139.3	102.8	66.4	49.5				33.2	29.9	22.0	13.9
3f	139.4	103.1	50.0	25.4	24.3			23.6	15.7		
3g	140.9	95.1	50.0	25.4	24.3			15.3			
3h	140.1	101.4	50.0	25.3	24.3			33.5	30.1	22.0	13.9
3i	134.9	100.7	48.9	24.6				23.5	16.0		
3j	138.3	104.1	54.5	48.8	46.0			23.4	15.5		
3k	138.9	102.3	54.6	48.9	46.1			33.2	29.9	21.9	13.8
3l	132.3	106.1	147.8	129.0	119.5	116.1	34.8	23.7	15.8		

With regard to the stereochemistry, the reaction gives exclusively E-isomers. Thus the ^1H NMR spectra of all enamines prepared show coupling constants of the α-olefin protons in the range 13-14 Hz (see experimental section). The ^{13}C-NMR chemical shifts listed in Table 4 are also in good agreement with literature data for E-isomers.[37]

While the unhindered intermediates (1) derived from straight chain aldehydes were readily converted to their enamines by this methods, a major limitation of this method is that more hindered examples were not. For example, derivatives of isobutyraldehyde were found to decompose under these reaction condtions, and derivatives (1) are not readily available for most ketones.

In conclusion, the present method provides an attractive route for the preparation of enamines derived from unhindered aldehydes. Of particular importance is that only one equivalent of amine is used which is more economical than most of the methods previously reported. The easily accessible starting materials, the general scope of the reaction, the high yields and the straightforward laboratory procedure, further demonstrate the utility and the generality of the method.

Experimental section

General. Melting points were measured with a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on a Varian VXR 300 MHz spectrometer in $CDCl_3$ (unless otherwise stated) using TMS as an internal reference for ^1H spectra and $CDCl_3$ for ^{13}C NMR spectra (abbreviations used: s singlet; d doublet; t triplet; m multiplet; dd doublet of doublets). Elemental analyses were performed on a Carlo Erba-1106 instrument under the supervision of Dr. D. Powell. Tetrahydrofuran (THF) and diethyl ether (Et_2O) were predried and distilled from sodium/benzophenone before use.

Preparation of N-(α-aminoalkyl)benzotriazole adducts 1. General procedure: Benzotriazole (5.96 g, 0.05 mol) and the secondary amine (0.052 mol) were mixed in 75 mL of Et_2O. The mixture was stirred for 5 min and the aldehyde (0.052 mol) added. The homogeneous solution was stirred at room temperature for several hours (with or without 3 Å molecular sieves) and dried with magnesium sulfate. The solvent was evaporated and the resulting oil was triturated with Et_2O (10 mL) at -70 °C (CO_2/acetone bath). Derivatives **1a-c** were obtained as solids by this procedure, whereas **1d-l** remained as oils which were used in the next step without further purification.

Preparation of enamines 3. General procedure: The benzotriazole derivative (0.02 mol) and sodium hydride (1 g, 0.04 mol) were mixed in 60 mL of THF under nitrogen. The mixture was heated under reflux for 2-3 hours. A heavy precipitate usually formed within 15-30 min. The solution was then cooled to room temperature and poured into ice-H_2O (200 mL). To the aqueous solution hexane (100 mL) was

added and the organic layer separated. The organic layer was dried with magnesium sulfate and evaporated to give the crude product. Distillation under reduced pressure gave pure product.

1-Morpholino-1-propene 3a: ^{1}H NMR δ 1.64 (dd, *J* = 6.5, 1.4 Hz, 3 H), 2.75 (t, *J* = 4.9 Hz, 4 H), 3.70 (t, *J* = 4.9 Hz, 4 H), 4.46 (m, 1 H), 5.79 (d, *J* = 13.9 Hz, 1 H).

1-Morpholino-1-butene 3b: ^{1}H NMR (C_6D_6) δ 1.52 (t, *J* = 7.5 Hz, 3 H), 2.53 (m, 2 H), 2.98 (t, *J* = 4.8 Hz, 4 H), 3.98 (t, *J* = 4.8 Hz, 4 H), 4.87 (m, 1 H), 6.19 (d, *J* = 13.8 Hz, 1 H).

1-Morpholinoethene 3c: ^{1}H NMR (C_6D_6) δ 2.62 (t, *J* = 4.9 Hz, 4 H), 3.70 (t, *J* = 4.9 Hz, 4 H), 3.95 (d, *J* = 15.4 Hz, 1 H), 4.03 (d, *J* = 8.8 Hz, 1 H), 5.94 (dd, *J* = 6.6, 8.8 Hz, 1 H).

1-Morpholino-1-pentene 3d: ^{1}H NMR (C_6D_6) δ 0.94 (t, *J* = 7.2 Hz, 3 H), 1.39 (m, 2 H), 1.98 (q, 2 H), 2.49 (t, *J* = 4.7 Hz, 4 H), 3.48 (t, *J* = 4.7 Hz, 4 H), 4.35 (m, 1 H), 5.68 (d, *J* = 13.7 Hz, 1 H).

1-Morpholino-1-hexene 3e: ^{1}H NMR δ 0.89 (m, 3 H), 1.31 (m, 4 H), 1.97 (m, 2 H), 2.76 (t, *J* = 4.7 Hz, 4 H), 3.71 (t, *J* = 4.7 Hz, 4 H), 4.47 (m, 1 H), 5.77 (d, *J* = 13.9 Hz, 1 H).

1-Piperidino-1-butene 3f: ^{1}H NMR δ 0.99 (t, *J* = 7.4 Hz, 3 H), 1.48-1.60 (m, 6 H), 1.97 (m, 2 H), 2.73 (m, 4 H), 4.39 (m, 1 H), 5.78 (d, *J* = 13.9 Hz, 1 H).

1-Piperidino-1-propene 3g: ^{1}H NMR δ 1.45-1.60 (m, 6 H), 1.61 (d, *J* = 6.6 Hz, 3 H), 4.38 (m, 1 H), 5.79 (d, *J* = 15.1 Hz, 1 H).

1-Piperidino-1-hexene 3h: ^{1}H NMR δ 0.88 (t, *J* = 7.4 Hz, 3 H), 1.30 (m, 4 H), 1.45-1.61 (m, 6 H), 1.94 (m, 2 H), 2.72 (m, 4 H), 4.43 (m, 1 H), 5.78 (d, *J* = 13.7 Hz, 1 H).

1-Pyrrolidino-1-butene 3i: ^{1}H NMR δ 0.97 (t, *J* = 7.4 Hz, 3 H), 1.83 (m, 4 H), 2.02 (m, 2 H), 2.95 (m, 4 H), 4.16 (m, 1 H), 6.15 (d, *J* = 13.7 Hz, 1 H).

1-(N-Methylpiperazino)-1-butene 3j: ^{1}H NMR δ 0.97 (t, *J* = 7.4 Hz, 3 H), 1.98 (m, 2 H), 2.28 (s, 3 H), 2.42 (t, *J* = 5 Hz, 4 H), 2.79 (t, *J* = 5 Hz, 4 H), 4.43 (m, 1 H), 5.80 (d, *J* = 13.7 Hz, 1 H).

1-(N-Methylpiperazino)-1-pentene 3k: ^{1}H NMR δ 0.89 (t, *J* = 7.4 Hz, 3 H), 1.32 (m, 4 H), 1.97 (m, 2 H), 2.29 (s, 3 H), 2.42 (t, *J* = 5 Hz, 4 H), 2.80 (t, *J* = 5 Hz, 4 H), 4.42 (m, 1 H), 5.79 (d, *J* = 13.7 Hz, 1 H).

1-(N-Methylanilino)-1-butene 3l: ^{1}H NMR δ 1.03 (t, *J* = 7.4 Hz, 3 H), 2.09 (m, 2 H), 3.05 (s, 3 H), 4.68 (m, 1 H), 6.67 (d, *J* = 13.4 Hz, 1 H), 6.81-7.22 (m, 5 H).

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