STUDIES ON THE THERMAL DECARBOXYLATION OF 1-ALKOXYCARBONYLBENZOTRIAZOLES

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1-Alkoxycarbonylbenzotriazoles on thermolysis lose carbon dioxide; the decarboxylation is accompanied by the formation of a mixture of 1- and 2-alkylbenzotriazoles, with the N-1 isomer predominating over the N-2 isomer in all cases. A cross-over experiment, in which heating equimolar amounts of 1-benzyloxycarbonylbenzotriazole and 1-(4-methylbenzyloxycarbonyl)-5,6-dimethylbenzotriazole gave almost all the cross-over products, supports the proposed intermolecular mechanism for this decarboxylation and the formation of 1- and 2-alkylbenzotriazoles. No decarboxylation was observed for 1-phenoxycarbonylbenzotriazole.

INTRODUCTION

Many 1-substituted benzotriazoles undergo thermally induced reversible isomerization to N-2 isomers. The interconversions of N-[α -(N', N'-dialkylamino)alkyl]-, $N \left[\alpha - (alkoxy)alkyl \right]$ - and $N - \left[\alpha - (alkylthio)alkyl \right]$ -benzotriazoles have been extensively studied.¹⁻⁵ The thermolyses of N-benzyl-, N-diarylmethyl- and N-trityl-benzotriazoles in the absence of solvent have also been investigated.⁶ In all these isomerizations, a heterocyclic N-C bond breaks to form, as intermediates, the benzotriazole anion and the corresponding carbocations which are stabilized by an α -heteroatom (N, S or O) or by a conjugated π -system. The recombination of the intermediate ion pairs gives mixtures of the 1- and 2substituted isomers. We also reported a mechanistic study of the rearrangement of 1-benzovloxvbenzotriazole to 3-benzoylbenzotriazole 1-oxide in which the benzotriazole 1-oxide and RCO⁺ intermediates were formed. A cross-over experiment demonstrated an intermolecular process.⁷

We have now studied the thermolysis of 1-alkoxycarbonylbenzotriazoles. Our primary results show that 1-alkoxycarbonylbenzotriazoles on thermolysis lose carbon dioxide. This decarboxylation is accompanied by the formation of a mixture of 1- and 2-alkylbenzotriazoles. No isomerization to give 2-alkoxycarbonylbenzotriazoles was detected. The present study was undertaken because the chemistry of N-acylated benzotriazole derivatives in general and of N-alkoxycarbonylbenzotriazoles in particular is little known. Almost no synthetic applications as well as theoretical studies of *N*-alkoxycarbonylbenzotriazoles have been reported. The only known example is that 1-alkoxycarbonylbenzotriazoles react with secondary amines to give *N*,*N*-dialkyl carbamates.⁸ By contrast, the *O*-acyl derivatives of 1-hydroxybenzotriazole are of considerable importance in organic synthesis, especially in peptide chemistry,⁹ and many relevant mechanistic studies have been reported.^{7,10,11}

RESULTS AND DISCUSSION

Preparation of 1-alkoxycarbonylbenzotriazoles

1-Alkoxycarbonylbenzotriazoles have been prepared previously from benzotriazol-1-ylcarboxylic acid chloride and alcohols.^{8,12} 1-Alkoxycarbonylbenzotriazoles are also available in 11-22% yield from the reaction of benzotriazole and chloroformic acid esters.¹³ We now report a novel access to this type of compound by using 1,1'-carbonyldibenzotriazole.

Although 1,1'-carbonyldiimidazole is a valuable synthetic reagent with applications in the synthesis of esters, amides, amino acids, hydrazides and anhydrides, ^{14,15} most carbonyl transfer reactions using 1,1'-carbonyldibenzotriazole remain to be explored. 1,1'-Carbonyldibenzotriazole has previously been applied in the synthesis of adenosine 5'-diphosphate, ¹⁶ and of nucleoside and polyprenylpyrophosphate sugars. ^{17,18} The kinetics of the hydrolysis and methanolysis of N,N'-carbonyldibenzotriazole have also been studied. ¹⁹ We recently found that 1,1'-carbonyldibenzotriazole is a versatile dehydrating agent useful in the synthesis of nitriles. ²⁰

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We have now discovered that 1,1'-carbonyldibenzotriazole (3a), prepared from 1-(trimethylsilyl)benzotriazole (2a) and phosgene, ²¹ reacted with various alcohols at room temperature to give 1-alkoxycarbonylbenzotriazoles 4a-g (Scheme 1). Aliphatic, aromatic and allylic alcohols all reacted cleanly to give high yields of 4a-g (Table 1). However, the reaction of 1,1'-carbonyldibenzotriazole (3a) with 4-nitrophenol gave only benzotriazolium 4-nitrophenolate in 85% yield. Compounds 4a-g were characterized by their ¹H and ¹³C NMR spectra and elemental analyses (Tables 1-3). All the N-alkoxycarbonylbenzotriazoles prepared from 1,1'-carbonyldibenzotriazole (3a) were obtained solely in the N-1 isomeric form, and no 2-alkoxycarbonylbenzotriazoles were detected in the ¹H NMR spectra, indicating no isomerization of 1-alkoxycarbonylbenzotriazoles into their 2-isomers. In the ¹³C NMR spectra of 4a-g, the carbonyl carbon signals appear between 148.5 and 150.1 ppm.

Similarly, 1-alkoxycarbonyl-5,6-dimethylbenzotriazoles 4h-j were prepared in good yields from 1,1carbonyldi(5,6-dimethylbenzotriazole) (3b), available from the reaction of 1-(trimethylsilyl)-5,6-dimethylbenzotriazole (2b) and phosgene, and the appropriate alcohols (Scheme 1). Thus, 1-benzyloxycarbonyl- (4h), 1-(4-methylbenzyloxycarbonyl)- (4i) and 1-crotyloxycarbonyl-5,6-dimethyl-benzotriazole (4j) were each synthesized and characterized by their ¹H and ¹³C NMR spectra and analyses (Tables 1-3).

Decarboxylation

1-Alkoxycarbonylbenzotriazoles are readily decarboxylated to give the correspounding N-alkylbenzotriazoles in good yields. All the decarboxylations were carried out by heating the neat 1-alkoxycarbonylbenzotriazoles (without solvent) under an inert atmosphere at appropriate temperatures (Table 4). Even at elevated temperature, the decarboxylation is a slow process for many of the compounds studied, whereas all these compounds are stable at room temperature. All compounds, except 1-phenoxycarbonyl-benzotriazole (4d),



				M.p. (°C)	Formula	Calculated (%)			Found (%)		
No.	R	x	Yield (%)			С	Н	N	С	н	N
4 a	Ме	н	90	69–71ª	C ₈ H ₇ N ₃ O ₂	54.24	3.98	23.12	54.60	4.07	24.24
4b	Et	н	96	70–72 ^b	C ₉ H ₉ N ₃ O ₂	56.54	4.74	21.98	56.70	4.73	22.14
4c	n-Bu	н	95	Oil	C11H13N3O2	219 · 1008 °			219 · 1010°		
4d	Ph	н	79	108–110 ^d	$C_{13}H_9N_3O_2$	55.59	3.50	16.21	55-27	3-41	16.07
4e	PhCH ₂	н	95	98100 ^d	$C_{14}H_{11}N_3O_2$	66.40	4.38	16.59	66.72	4-41	16.91
4f	4-MeC ₆ H ₄ CH ₂	н	67	85-86	C15H13N3O2	67.41	4.90	15.72	67.30	4.88	15-45
42	$CH_2 = CHCH_2$	н	61	Oil	$C_{10}H_9N_3O_2$	203 · 0695 °			203 · 0520°		
4h	PhCH ₂	Me	94	109-110	C ₁₆ H ₁₅ N ₃ O ₂	68·31	5.37	14.44	68.04	5.35	14.16
4i	4-MeC ₆ H ₄ CH ₂	Me	72	138-139	C ₁₇ H ₁₇ N ₃ O ₂	69.14	5.80	14.23	68.77	5.83	13.93
4j	$CH_3CH = CHCH_2$	Me	93	74–76	$C_{13}H_{15}N_{3}O_{2}$	63.66	6.16	17.13	63·46	6.20	17.10

Table 1. Preparation of 1-Alkoxycarbonylbenzotriazoles (4)

^a This compound was reported previously without m.p.²⁴ ^b Lit.⁸ m.p. 71–73 °C. ^c High-resolution mass spectrum. ^d Lit.⁸ m.p. 108–110 °C.

Table 2. ¹ H NMR spectral data for 1-alkoxycarbonylbenzotriazoles	(4	4	ļ	ĺ))
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No.	4-H (d)	5-H (t)	6-H (t)	7-H (d)	5-Me	6-Me	R
4a	8.13	7.65	7.49	8.10			4·24 (s. 3H)
4b	8.14	7.65	7.49	8.11			4.70 (q, J = 6.9, 2H), 1.58 (t, J = 6.9, 3H)
4c	8.13	7.66	7.49	8-11	_	_	4.64 (t, 1H), 1.93 (m, 2H), 1.55 (m, 2H), 1.02 (t, 3H)
4d	8.18	7.52	7.48	8.14			7.48 (t, 1H), 7.35 (m, 2H), 7.27 (d, 2H)
4e	8.11	а	а	8.08	_	_	7.65 - 7.53 (m, 2H), $7.48 - 7.37$ (m, 3H), 5.63 (s, 2H)
4f	8.10	7.61	7.46	8.07			7.45 (d, 2H), 7.22 (d, 2H), 5.58 (d, 2H), 2.36 (s, 3H)
4g	8.01	7.53	7.37	7 • 97	_	—	$6 \cdot 04$ (m, 1H), $5 \cdot 47$ (d, $J = 17 \cdot 21$ H), $5 \cdot 33$ (d, $J = 10 \cdot 41$ H), $5 \cdot 00$ (d, $J = 6 \cdot 1, 2$ H)
4h	7.85			7.83	2.42	2.40	7.54 (d, 2H), 7.42 (m, 3H), 5.61 (s, 2H)
4i	7.83		_	7.81	2.42	2.39	7.45 (d, 2H), 7.22 (d, 2H), 5.57 (s, 2H), 2.36 (s, 3H)
4j	7.84		_	7.81	2.44	2.41	6.05 (m, 1H), 5.85 (m, 1H), 5.02 (d, 2H), 1.80 (d, 3H)

^a Overlapping signals.

Table 3. ¹³C NMR spectral data for 1-alkoxycarbonylbenzotriazoles (4)

			Be	enzotriaz	ole moie	ety			
No.	C=0	C-4	C-5	C-6	C-7	C-3a	C-7a	5-Me, 6-Me	R
4a ²⁴	149.2	120.3	125.7	130-2	113.3	145.8	131.7	_	55.2
4b	149.0	120.3	125.6	130.1	113.4	145.8	132.2	_	65.1, 14.2
4c	148.7	120.0	125-5	129.9	113.2	145.6	131.5	_	68.7, 30.3, 18.7, 13.4
4d	150.0	120.6	126.0	129.8	113.5	146.0	130.5		127.0, 126.2, 121.1, 120.8
4e	148.8	120.3	125.7	130-1	113.4	145.8	131.7	_	133.8, 129.1, 128.8, 120.4, 70.3
4f	149-3	120-2	125.6	130-1	113.2	146.2	130.9	_	139.1, 129.5, 129.1, 129.0, 70.4,
									21.2
4g	148.5	120.2	125.6	130-0	113.2	145.7	131-5	_	130.2, 120.2, 69.1
4h	149.3	119.5	130.6	135-5	113.0	145.0	140.7	20.9, 20.3	134.1, 129.0, 128.8, 128.2, 70.1
4 i	149•4	119.5	131 · 1	135-4	113.0	145.7	140.7	20.9, 20.3	139.0, 129.4, 128.8, 128.7, 70.1, 21.2
4j	149-2	119-4	131.9	135-3	112.9	144.8	140.6	20.8, 19.1	134.3, 123.4, 79.2, 17.7

where no change could be detected, underwent clean decarboxylation to afford mixtures of 1-(5) and 2-alkybenzotriazoles (6) at ca 120 °C for 12-24 h.

The mixtures of 1- and 2-alkylbenzotriazoles formed from the decarboxylation of 4a, b and c (R = Me, Et and *n*-Bu) were not separated, and their characterizations were achieved by comparisons of their ¹H and ¹³C NMR spectra (Tables 6 and 7) with those of authentic specimens²¹ and from spectra obtained by gas chromatography-mass spectrometry (GC-MS). All other mixtures of 1-alkyl- and 2-alkylbenzotriazoles, were separated by column chromatography and each was characterized by ¹H and ¹³C NMR spectra (Tables 6 and 7) and elemental analyses (Table 5).

We have recently reported that N-diarylmethyl- and N-tritylbenzotriazole undergo thermal isomerizations

with the N-1 isomers predominating over the N-2 isomers. However, no isomerization could be detected for N-benzylbenzotriazoles and N-alkylbenzotriazoles even after heating at 250 °C for 5 h.⁶ Our current results show that 1-alkoxycarbonylbenzotriazoles did not isomerize to their 2-isomers even at elevated temperatures as no 2-alkoxycarbonylbenzotriazoles were found when compounds 4 were heated for a short time. Further, when 4d (R = Ph), which did not decarboxylate at all, was heated at 120 °C for 24 h, only starting material was obtained and no isomerization to its 2-isomer was detected.

Cross-over experiment

To help determine the decarboxylation mechanism, a

				Produc	ts ratio ^b
Compound	R	x	Temperature (°C)	N-1 (5) (%)	N-2 (6) (%)
4a	Me	н	120	71	29
4b	Et	Н	120	73	27
4c	n-Bu	н	120	78	22
4d	Ph	н	120	0	0
4e	PhCH ₂	н	120	82	18
4f	4-MeC ₆ H ₄ CH ₂	н	118	74	26
4g	$CH_2 = CHCH_2$	Н	140	71	29
4h	PhCH ₂	Me	120	76	24
4i	4-MeC ₆ H ₄ CH ₂	Me	118	74	26
4j	$CH_3CH = CHCH_2$	Me	115	73	27

Table 4. Decarboxylations of 1-alkoxycarbonylbenzotriazoles (4)^a

^a 1-Alkoxycarbonylbenzotriazoles were heated for 12-24 h at the temperatures indicated.

^b Ratios were obtained from the relative intensities of the integration signals of ¹H NMR; N-1 = 1-alkylbenzotriazole and N-2 = 2-alkylbenzotriazole.

				T to make a	Calculated (%)			Found (%)		
No.	R	x	M.p. (°C)	or b.p. ($^{\circ}C$)	с	н	N	с	н	N
5e	PhCH ₂	н	113-115	114-11625				_		
6e	PhCH ₂	н	Oil	Oil ²⁵	209·0953*			209·0937ª		
5f	4-MeC ₆ H₄CH ₂	н	126-127	106–107 ²⁶	75.34	5.83	18.83	75.13	5.89	18 · 98
6f	4-MeC ₆ H ₄ CH ₂	н	Oil	Oil ²⁶				-		
5g	$CH_2 = CHCH_2$	н	Oil	161/15 mmHg ²⁷	159·0796 ^a			159·0781ª		
6g	$CH_2 = CH_2CH_2$	Н	Oil	$127/15 \text{ mmHg}^{27}$	159·0796ª			159·0780*		
5h	PhCH ₂	Me	165-166	· ·	75.92	6.37	17.71	75.84	6.65	17.78
6h	PhCH ₂	Me	Oil	—	75.92	6.37	17.71	75·94	6.66	17.79
5i	4-MeC ₆ H ₄ CH ₂	Me	142-144		76.46	6.82	16.72	76.29	6.87	16.74
6i	4-MeC ₆ H ₄ CH ₂	Me	102-103	_	76.46	6.82	16.72	76.47	6.84	16.77
5i	$CH_{3}CH = CHCH_{3}$	Me	61-62		71.61	7.51	20.88	71.71	7.58	21.13
6j	CH ₃ CH=CHCH ₂	Me	46-47		71.61	7.51	20.88	71.49	7.54	20.88

Table 5. Characterization of N-alkylbenzotriazoles (5 and 6)

^a High-resolution mass spectrum.

No.	H-4	H-5	H-6	H-7	5-Me, 6-Me	R
	7.53 (d)	7.38 (t)	a	8·06 (d)		4·30 (s)
6a	7.85 (m)	7.38 (m)	7.38	7.85	_	4.52 (s)
5b	7.54 (d)	7.40 (t)	7 · 58 (t)	8·07 (d)	_	4.70 (q, CH ₂), 1.64 (t, CH ₃)
6b	7.86 (m)	7.35 (m)	7.35	7.86	_	4.79 (q, CH ₂), 1.72 (t, CH ₃)
5c	7.50 (d)	7.38 (t)	а	8·06 (d)	_	4.64 (t), 1.99 (m), 1.41 (m), 0.96 (t)
6c	7.86 (m)	7.38 (m)	7.38	7.86		4.73 (t), 2.10 (m), 1.41 (m), 0.96 (t)
5e	a	a	a	8·05 (d)	_	$7 \cdot 35 - 7 \cdot 16$ (m), $5 \cdot 76$ (s, 2H, CH ₂)
6e	7·81 (m)	a	a	7-81	_	$7 \cdot 10 \text{ (m)}, 5 \cdot 64 \text{ (s, CH}_4)$
5f	7.40 (d)	7·32 (t)	7·10 (t)	8·06 (d)	_	7.40 (d, 2H), 7.09 (d, 2H), 5.79 (s, CH ₂), 2.29 (s, CH ₃)
6f	7.86 (m)	7.35 (m)	7.36	7.86	_	$7 \cdot 22 (m, 4H), 5 \cdot 82 (s, 2H), 2 \cdot 30 (s, 3H)$
5g	7.51 (d)	7.36 (t)	7·44 (t)	8·04 (d)	_	$6.05 \text{ (m, 1H, CH=)}, 5.35 \text{ (m, 2H, =CH_2)}, 5.25 \text{ (d, CH_2)}$
6g	7.87 (m)	7.35 (m)	7.35	7.87		$6 \cdot 20 \text{ (m, 1H, CH}=), 5 \cdot 39 \text{ (d, 1H)}, 5 \cdot 33 \text{ (m, 3H)}$
5h	7·10 (s)		_	7·58 (s)	2.36, 2.33	$7 \cdot 32 - 7 \cdot 24$ (m, 5H), $5 \cdot 77$ (s, 2H, CH ₂)
6h	7 · 58 (s)			7 · 58 (s)	2·36 (s, 6H)	$7 \cdot 34 - 7 \cdot 29$ (m, 5H), $5 \cdot 81$ (s, 2H, CH ₂)
5i	7 · 10 (s)			7.77 (s)	2.35, 2.33	$7 \cdot 20 - 7 \cdot 10$ (m, 4H), $5 \cdot 72$ (s, 2H, CH ₂), $2 \cdot 30$ (s, 3H, CH ₃)
6i	7·49 (s)		_	7·49 (s)	2·29 (s, 6H)	7.19 (d, 2H), 7.05 (d, 2H), 5.69 (s, CH ₂), 2.22 (s, 3H)
5j	7·24 (s)			7·74 (s)	2.39, 2.36	$5 \cdot 76 - 5 \cdot 69$ (m, 2H, CH=CH), $5 \cdot 12$ (d, 2H), $1 \cdot 72$ (d, 3H, CH ₃)
6j	7 · 58 (s)		—	7 · 58 (s)	2·38 (s,6H)	5.85 (m, 2H, CH=CH), 5.20 (d, CH ₂), 1.75 (d, 3H, CH ₃)

Table 6. ¹H NMR spectral data for N-alkylbenzotriazoles (5 and 6)

^a Overlapping signals.

Table 7. ¹³C NMR spectra data for N-alkylbenzotriazoles (5 and 6)

No.			Benzotriaz	ole moiety	,			
	C-4	C-5	C-6	C-7	C-3a	C-7a	5-Me, 6-Me	R
5a	119.8	123.8	127.2	109.1	144.2	133.1		34.1
6a	117.7	126.2	_		144 • 2	_	_	42.3
5b	119-9	123.8	127.1	109.2	144 • 4	133.0	_	43.2. 14.9
6b	117.8	126 · 1	_		144 · 3		_	52.0, 15.0
5c	119.9	123.9	127.0	109.2	144 • 2	133.0		47.8, 31.6, 19.7, 13.4
6c	117.8	125.8	_	_	144.2			56.2, 31.9, 19.9, 13.4
5e	120.0	123.8	127.3	109.7	146.3	132.8	_	134.7, 128.9, 128.4, 127.5, 52.2
бе	118.0	125.8			145.5		_	135.0, 128.8, 128.5, 128.2, 60.1
5f	119.9	123.8	127.3	109.7	144 • 7	134.6	_	129.2, 128.8, 128.2, 124.6, 52.2, 21.3
6f	118.0	125.3			144.5		_	134.5, 129.3, 128.9, 126.2, 60.3, 21.2
5g	119-5	123.6	126.9	109.5	146.0	132.6	_	130.9, 118.9, 50.4
6g	117.8	126.2	_	_	144 · 3	_	_	130.9, 119.9, 51.2
5h	119.0	131.8	133.7	109.0	145.7	137.7	20.9, 20.3	135.0, 128.8, 128.2, 127.4, 51.9
6h	116.5	136.7			144.0	_	20.8	135.0, 128.7, 128.3, 128.1
5i	119.0	132.0	133.6	109.1	145.6	138.0	20.6, 20.3	137.6, 129.5, 127.5, 127.3, 51.8, 21.0
6i	116.5	136.6	_		144 • 3		20.8	138.2, 129.4, 128.8, 128.1, 59.8, 21.1
5j	118.6	131.6	133	108.9	145.2	137.2	20.7, 20.1	130.5, 124.2, 49.9, 17.4
6j	116.4	136.6	_		143.8		20.8	131.7, 124.3, 58.2, 17.7

cross-over experiment was performed by heating equimolar amounts of 1-benzyloxycarbonylbenzotriazole (4e) and 1-(4-methylbenzyloxycarbonyl)-5,6dimethylbenzotriazole (4i), at 120 °C for 2 h. GC-MS of the mixture of the products unambiguously revealed the formation of the cross-over products. Seven of the eight possible decarboxylation products were detected by GC-MS. The molecular ions of N-benzylbenzotriazole (M⁺ = 209), N-(4-methylbenzyl)benzotriazole $(M^+ = 223)$, N-benzyl-5,6-dimethylbenzotriazole $(M^+ = 237)$ and N-(4-methylbenzyl)-5,6-dimethylbenzotriazole $(M^+ = 251)$ were observed in the mass spectrum of the mixture. The NMR spectra were too complex to be assigned, and no attempt was made to separate the mixture. From this cross-over experiment, it is clear that the decarboxylation proceeds via an intermolecular process.

Mechanism

It has been clearly demonstrated by recent work 22 that benzotriazole can be alkylated effectively by alkyl halides in refluxing benzene in the absence of any added base. We therefore suggest the mechanism outlined in Scheme 2.

An alkyl group is transferred from one molecule of 4 to the nitrogen of another 4 with the loss of CO_2 and formation of the N-3-alkylated benzotriazole cation 7 and benzotriazole anion 8. The ambient anion 8 then reacts with 7 to give a mixture of the corresponding 1-alkylbenzotriazole 5 and 2-alkylbenzotriazole 6.

to 1-(trimethylsilyl)benzotriazole (2a) (19·1 g, 0·1 mol) at 0 °C in CH₂Cl₂ (30 ml). The mixture was stirred at room temperature for 1 h. The precipitate was filtered and washed with dried methylene chloride. Recrystallization from benzene gave 1,1'-carbonyldibenzotriazole as needles (3a) (50%); m,p. 183–185 °C (lit.²³ m.p. 182–183 °C). ¹H NMR: δ 8·25 (d, $J = 8\cdot3$ Hz, 1Hz, 8·21 (d, $J = 8\cdot3$ Hz, 1H), 7·78 (t, $J = 8\cdot1$ Hz, 1H), 7·62 (t, $J = 8\cdot1$ Hz, 1H). ¹³C NMR: δ 145·5, 132·3, 130·6, 126·5, 120·6, 113·2. Analysis Calculated for C₁₃H₈N₆O, C 59·09, H 3·05, N 31·80; found, C 58·87, H 2·99, N 32·25%.



EXPERIMENTAL

Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. The ¹H (300 MHz) and ¹³C (75 MHz) NMR spectra were taken on a VXR-300 spectrometer in CDCl₃ or DMSO- d_6 with tetramethylsilane as the internal standard. Mass spectra were obtained on an AEI MS 30 mass spectrometer. Elemental analyses were performed at the University of Florida. 1-(Trimethylsilyl)benzotriazole was prepared as reported previously.²¹

1.1'-Carbonyldibenzotriazole (3a). Phosgene (0.05 mol, 25 ml of 20% solution in toluene) was added

1,1'-Carbonyldi(5,6-dimethylbenzotriazole) (3b). This compound was prepared in 40% yield from 5,6dimethylbenzotriazole by the above procedure. ¹H NMR: δ 7.93 (s, 4H), 2.49 (s, 6H), 2.46 (s, 6H). ¹³C NMR: 144.8, 141.4, 136.5, 131.4, 120.0, 113.1, 21.0, 20.4. Analysis calculated for C₁₇H₁₆N₆O, C 63.74, H 5.03, N 26.23; found, C 63.53, H 5.02, N 26.39%.

General procedure for the preparation of 1-(alkoxycarbonyl)benzotriazoles (4a-j). 1,1'-Carbonyldibenzotriazole (20 mmol) was stirred with the appropriate alcohol (15 ml) at room temperature until the solid had completely dissolved. The excess alcohol was evaporated and the residue dissolved in methylene chloride, washed with KOH (3%, 15 ml) and dried over MgSO₄ (10 g). The solvent was evaporated and the residue recrystallized from the appropriate solvent and characterized (see Tables 1-3).

Benzotriazolium 4-nitrophenolate. This is the only product (85% yield) from the above procedure with 4nitrophenol; m.p. 77–78 °C (AcOEt-hexane). ¹H NMR (DMSO-d₆): $\delta 8.14$ (d, J = 9.2 Hz, 2H), 7.95 (m, 2H, BtH), 7.48 (m, 2H, BtH), 6.97 (d, J = 9.2 Hz, 2H). ¹³C NMR: $\delta 163.9$, 139.6, 126.3, 126.1, 125.4, 115.9, 106.6. Analysis calculated for C₁₂H₁₀N₄O₃, C 55.81, H 3.88, N 21.71; found, C 56.30, H 4.04, 21.79%.

Decarboxylation. All the decarboxylations of 1alkoxycarbonylbenzotriazoles were carried out with dry, pure samples under an argon atmosphere. Each sample (50–100 mg) of compounds 4a-j was heated alone at the specified temperature for 12–24 h. The products were cooled rapidly, dissolved in CDCl₃ and their spectra recorded. The mixtures of 1- and 2alkylbenzotriazoles 5a-6a (R = Me), 5b-6b (R = Et) and 5c-6c (R = Bu) were characterized without separation by their ¹H and ¹³C NMR spectra, which were consistent with those previously reported.²¹ Other mixtures were separated by column chromatography (silica gel, CDCl₃-hexane) and characterized (Tables 5–7).

Cross-over experiment. Finely powdered pure samples of compounds 4e and i (0.50 mmol each) were mixed well and heated at 120 °C for 2 h. The sample was then cooled and subjected to NMR spectrometry and GC-MS.

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