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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*-[α-(alkoxy)alkyl]- and *N*-[α-(alkylthio)alkyl]-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 2-substituted isomers. We also reported a mechanistic study of the rearrangement of 1-benzoyloxybenzotriazole 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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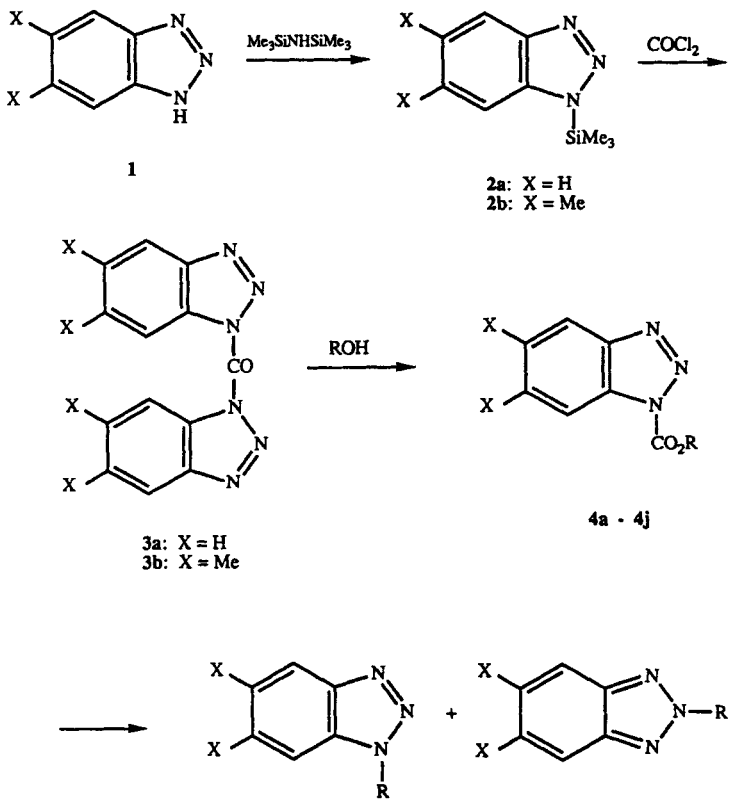
We have now discovered that 1,1′-carbonyldibenzotriazole (**3a**), prepared from 1-(trimethylsilyl)-benzotriazole (**2a**) and phosgene,[21] reacted with various alcohols at room temperature to give 1-alkoxycarbonyl-benzotriazoles **4a–g** (Scheme 1). Aliphatic, aromatic and allylic alcohols all reacted 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 ^{13}C 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-alkoxy-carbonylbenzotriazoles were detected in the ^1H NMR spectra, indicating no isomerization of 1-alkoxy-carbonylbenzotriazoles into their 2-isomers. In the ^{13}C 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 1,1-carbonyldi(5,6-dimethylbenzotriazole) (**3b**), available from the reaction of 1-(trimethylsilyl)-5,6-dimethyl-benzotriazole (**2b**) and phosgene, and the appropriate alcohols (Scheme 1). Thus, 1-benzyloxycarbonyl- (**4h**), 1-(4-methylbenzyloxycarbonyl)- (**4i**) and 1-crotyloxy-carbonyl-5,6-dimethyl-benzotriazole (**4j**) were each synthesized and characterized by their ^1H and ^{13}C 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**),



1

2a: X = H
2b: X = Me

3a: X = H
3b: X = Me

4a - 4j

5 **6**

Scheme 1

Table 1. Preparation of 1-Alkoxycarbonylbenzotriazoles (4)

No.	R	X	Yield (%)	M.p. (°C)	Formula	Calculated (%)			Found (%)		
						C	H	N	C	H	N
4a	Me	H	90	69–71[a]	$C_8H_7N_3O_2$	54·24	3·98	23·12	54·60	4·07	24·24
4b	Et	H	96	70–72[b]	$C_9H_9N_3O_2$	56·54	4·74	21·98	56·70	4·73	22·14
4c	*n*-Bu	H	95	Oil	$C_{11}H_{13}N_3O_2$	219·1008[c]			219·1010[c]		
4d	Ph	H	79	108–110[d]	$C_{13}H_9N_3O_2$	55·59	3·50	16·21	55·27	3·41	16·07
4e	$PhCH_2$	H	95	98–100[d]	$C_{14}H_{11}N_3O_2$	66·40	4·38	16·59	66·72	4·41	16·91
4f	4-$MeC_6H_4CH_2$	H	67	85–86	$C_{15}H_{13}N_3O_2$	67·41	4·90	15·72	67·30	4·88	15·45
4g	CH_2=$CHCH_2$	H	61	Oil	$C_{10}H_9N_3O_2$	203·0695[c]			203·0520[c]		
4h	$PhCH_2$	Me	94	109–110	$C_{16}H_{15}N_3O_2$	68·31	5·37	14·44	68·04	5·35	14·16
4i	4-$MeC_6H_4CH_2$	Me	72	138–139	$C_{17}H_{17}N_3O_2$	69·14	5·80	14·23	68·77	5·83	13·93
4j	CH_3CH=$CHCH_2$	Me	93	74–76	$C_{13}H_{15}N_3O_2$	63·66	6·16	17·13	63·46	6·20	17·10

[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)

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	[a]	[a]	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	—	—	6·04 (m, 1H), 5·47 (d, J = 17·2 1H), 5·33 (d, J = 10·4 1H), 5·00 (d, J = 6·1, 2H)
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. ^{13}C NMR spectral data for 1-alkoxycarbonylbenzotriazoles (4)

No.	C=O	Benzotriazole moiety						5-Me, 6-Me	R
		C-4	C-5	C-6	C-7	C-3a	C-7a		
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
4i	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 ^{1}H and ^{13}C NMR spectra (Tables 6 and 7) with those of authentic specimens[21] 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 ^{1}H and ^{13}C 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

Table 4. Decarboxylations of 1-alkoxycarbonylbenzotriazoles (**4**)[a]

Compound	R	X	Temperature (°C)	Products ratio[b] *N*-1 (**5**) (%)	*N*-2 (**6**) (%)
4a	Me	H	120	71	29
4b	Et	H	120	73	27
4c	*n*-Bu	H	120	78	22
4d	Ph	H	120	0	0
4e	$PhCH_2$	H	120	82	18
4f	4-$MeC_6H_4CH_2$	H	118	74	26
4g	CH_2=$CHCH_2$	H	140	71	29
4h	$PhCH_2$	Me	120	76	24
4i	4-$MeC_6H_4CH_2$	Me	118	74	26
4j	CH_3CH=$CHCH_2$	Me	115	73	27

[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 ^{1}H NMR; *N*-1 = 1-alkylbenzotriazole and *N*-2 = 2-alkylbenzotriazole.

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

No.	R	X	M.p. (°C)	Lit. m.p. or b.p. (°C)	Calculated (%) C	H	N	Found (%) C	H	N
5e	$PhCH_2$	H	113–115	114–116[25]	—	—	—	—	—	—
6e	$PhCH_2$	H	Oil	Oil[25]	209·0953[a]			209·0937[a]		
5f	4-$MeC_6H_4CH_2$	H	126–127	106–107[26]	75·34	5·83	18·83	75·13	5·89	18·98
6f	4-$MeC_6H_4CH_2$	H	Oil	Oil[26]	—			—		
5g	CH_2=$CHCH_2$	H	Oil	161/15 mmHg[27]	159·0796[a]			159·0781[a]		
6g	CH_2=CH_2CH_2	H	Oil	127/15 mmHg[27]	159·0796[a]			159·0780[a]		
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-$MeC_6H_4CH_2$	Me	142–144	—	76·46	6·82	16·72	76·29	6·87	16·74
6i	4-$MeC_6H_4CH_2$	Me	102–103	—	76·46	6·82	16·72	76·47	6·84	16·77
5j	CH_3CH=$CHCH_2$	Me	61–62	—	71·61	7·51	20·88	71·71	7·58	21·13
6j	CH_3CH=$CHCH_2$	Me	46–47	—	71·61	7·51	20·88	71·49	7·54	20·88

[a] High-resolution mass spectrum.

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

No.	H-4	H-5	H-6	H-7	5-Me, 6-Me	R
5a	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)	[a]	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)	—	7·35 – 7·16 (m), 5·76 (s, 2H, CH_2)
6e	7·81 (m)	[a]	[a]	7·81	—	7·10 (m), 5·64 (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	—	7·22 (m, 4H), 5·82 (s, 2H), 2·30 (s, 3H)
5g	7·51 (d)	7·36 (t)	7·44 (t)	8·04 (d)	—	6·05 (m, 1H, CH=), 5·35 (m, 2H, $=CH_2$), 5·25 (d, CH_2)
6g	7·87 (m)	7·35 (m)	7·35	7·87	—	6·20 (m, 1H, CH=), 5·39 (d, 1H), 5·33 (m, 3H)
5h	7·10 (s)	—	—	7·58 (s)	2·36, 2·33	7·32 – 7·24 (m, 5H), 5·77 (s, 2H, CH_2)
6h	7·58 (s)	—	—	7·58 (s)	2·36 (s, 6H)	7·34 – 7·29 (m, 5H), 5·81 (s, 2H, CH_2)
5i	7·10 (s)	—	—	7·77 (s)	2·35, 2·33	7·20 – 7·10 (m, 4H), 5·72 (s, 2H, CH_2), 2·30 (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	5·76 – 5·69 (m, 2H, CH=CH), 5·12 (d, 2H), 1·72 (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)

[a] Overlapping signals.

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

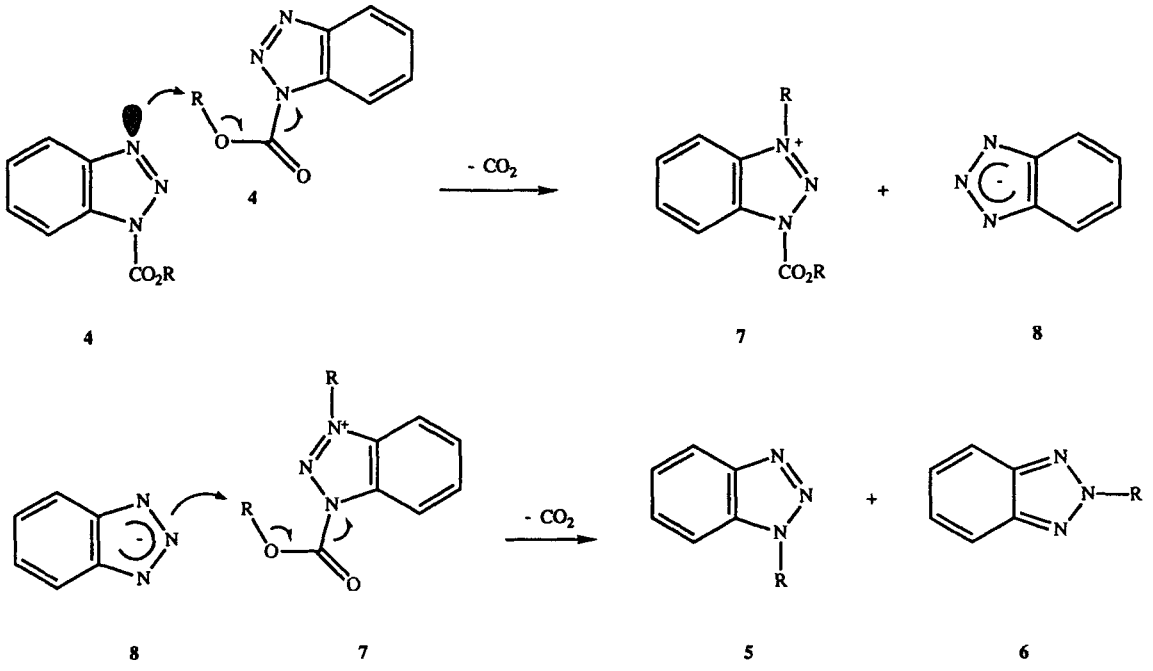
	Benzotriazole moiety							
No.	C-4	C-5	C-6	C-7	C-3a	C-7a	5-Me, 6-Me	R
5a	119·8	123·8	127·2	109·1	144·2	133·1	—	34·1
6a	117·7	126·2	—	—	144·2	—	—	42·3
5b	119·9	123·8	127·1	109·2	144·4	133·0	—	43·2, 14·9
6b	117·8	126·1	—	—	144·3	—	—	52·0, 15·0
5c	119·9	123·9	127·0	109·2	144·2	133·0	—	47·8, 31·6, 19·7, 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
6e	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)-5,6-dimethylbenzotriazole (**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 correspounding 1-alkylbenzotriazole **5** and 2-alkylbenzotriazole **6**.



Scheme 2

EXPERIMENTAL

Melting points were determined with a Thomas–Hoover melting point apparatus and are uncorrected. The ^1H (300 MHz) and ^{13}C (75 MHz) NMR spectra were taken on a VXR-300 spectrometer in $CDCl_3$ 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 to 1-(trimethylsilyl)benzotriazole (**2a**) (19·1 g, 0·1 mol) at 0 °C in CH_2Cl_2 (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 = 8·3 Hz, 1Hz, 8·21 (d, J = 8·3 Hz, 1H), 7·78 (t, J = 8·1 Hz, 1H), 7·62 (t, J = 8·1 Hz, 1H). ^{13}C NMR: δ 145·5, 132·3, 130·6, 126·5, 120·6, 113·2. Analysis Calculated for $C_{13}H_8N_6O$, C 59·09, H 3·05, N 31·80; found, C 58·87, H 2·99, N 32·25%.

1,1'-Carbonyldi(5,6-dimethylbenzotriazole) (**3b**). This compound was prepared in 40% yield from 5,6-dimethylbenzotriazole by the above procedure. ^1H NMR: δ 7·93 (s, 4H), 2·49 (s, 6H), 2·46 (s, 6H). ^{13}C NMR: 144·8, 141·4, 136·5, 131·4, 120·0, 113·1, 21·0, 20·4. Analysis calculated for $C_{17}H_{16}N_6O$, 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 $MgSO_4$ (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 4-nitrophenol; m.p. 77–78 °C (AcOEt–hexane). ^{1}H NMR (DMSO-d_6): δ 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). ^{13}C NMR: δ 163·9, 139·6, 126·3, 126·1, 125·4, 115·9, 106·6. Analysis calculated for $C_{12}H_{10}N_4O_3$, C 55·81, H 3·88, N 21·71; found, C 56·30, H 4·04, 21·79%.

Decarboxylation. All the decarboxylations of 1-alkoxycarbonylbenzotriazoles 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 $CDCl_3$ and their spectra recorded. The mixtures of 1- and 2-alkylbenzotriazoles **5a–6a** (R = Me), **5b–6b** (R = Et) and **5c–6c** (R = Bu) were characterized without separation by their ^{1}H and ^{13}C NMR spectra, which were consistent with those previously reported.[21] Other mixtures were separated by column chromatography (silica gel, $CDCl_3$–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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