The Chemistry of *N*-Substituted Benzotriazoles. Part 1. 1-(Chloromethyl)-benzotriazole

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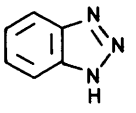
The *N*-chloromethyl group of 1-(chloromethyl)benzotriazole undergoes nucleophilic substitution by carbon, nitrogen, phosphorus, oxygen, and sulphur nucleophiles. α-Lithiation was achieved in high yield in 1-phenylthiomethyl-, 1-phenylsulphinylmethyl-, and 1-(phenylsulphonylmethyl)benzotriazoles and the lithio derivatives reacted with a variety of electrophiles. New benzotriazolium salts were prepared by quaternization of the N-3 nitrogen with methyl iodide.

N-Chloromethylheterocycles are important industrial intermediates. A substructure search for $ClCH_2$– attached to an N atom in a five- or six-membered ring [*cf.* (**1**)] revealed some 800 Chemical Abstracts entries over the period 1967—83 covering chloromethyl derivatives of 44 different heterocyclic systems. However, the vast majority of these references are to patents, and the few papers which mention compounds of this type either do so incidentally or are accounts of the preparation of large numbers of very similar derivatives for biological testing. Not even one of all these 44 systems has been systematically investigated. Nevertheless, the work reported contains hints of promise for such compounds as versatile synthetic intermediates. The chlorine atoms in compounds of type (**1**) are replaceable by nucleophiles as already demonstrated for many of the systems. Work in our laboratory[1] has shown that heterocycles can themselves be synthetically useful leaving groups. Furthermore, the ability of *N*-alkyl groups in azoles to undergo lithiation (for a summary see ref. 2) is powerfully increased by suitable activating groups as in the 9-(phenylthiomethyl)carbazoles.[3] Hence, compounds of type (**1**) represent synthons for $C^{+\,+\,-\,-}$ and allow, in principle, the transformation (**1**) ⟶ (**2**) in which the order of introduction of the substituents can be varied.

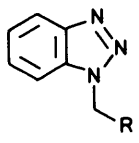
(**1**) (**2**)

The present series of papers will report work designed to exploit this synthetic potential, in particular the very different character of the two potential leaving groups, chlorine and heterocycle. The present paper deals with 1-(chloromethyl)-benzotriazole which is stable as the free base, unlike *N*-chloromethyl derivatives of more basic azoles which must be handled as hydrochloride salts.

1-(Chloromethyl)benzotriazole (**4**) was prepared from benzotriazole (**3**) *via* the hydroxymethyl derivative (**5**) in an overall yield of 91% following the literature procedure.[4] Previously reported reactions of (**4**) have all been concerned with the replacement of the chlorine atom by nucleophiles: with benzotriazole (**3**) to give the 1,1′-methylenebisbenzotriazole (**6**),[4] with morpholine to give (**7**),[4] with the appropriate dithiophosphate to give (**8**),[5] and with $LiAlH_4$ in a smooth reduction to give 1-methylbenzotriazole (**9**).[4]



(**3**)



(**4**), R = Cl
(**5**), R = OH
(**6**), R = Benzotriazolyl
(**7**), R = 1-Morpholinyl
(**8**), R = SP(O)(OEt)SPr
(**9**), R = H
(**10**), R = OEt
(**11**), R = OPh
(**12**), R = SPh
(**13**), R = SBz
(**14**), R = SO_2Ph
(**15**), R = Pyr^+Cl^-
(**16**), R = $DMAP^+Cl^-$
(**17**), R = 1-Pyrrolidyl
(**18**), R = N_3
(**19**), R = CN
(**20**), R = Ph
(**21**), R = Me
(**22**), R = $P(Ph_3)^+Cl^-$

Reactions of 1-(*Chloromethyl*)*benzotriazole with Nucleophiles.*—The chlorine atom is readily replaced by a wide range of nucleophiles (Table 1). Sodium ethoxide and sodium phenoxide gave the expected products (**10**) and (**11**) on refluxing in ethanol. Sulphur nucleophiles reacted particularly readily to form (**12**), (**13**), and (**14**) at 20 °C in methanol or dimethyl sulphoxide (DMSO) as solvent. Among nitrogen nucleophiles, tertiary amines [pyridine, 4-*N*,*N*-dimethylaminopyridine (DMAP)], a secondary amine (pyrrolidine), and sodium azide gave (**15**), (**16**), (**17**), and (**18**) as expected; these substitution reactions occurred readily at *ca.* 50 °C in various solvents.

Carbon nucleophiles also react to form the expected products, albeit in low yield. Thus sodium cyanide, phenylmagnesium bromide, and methylmagnesium iodide gave 1-(cyanomethyl)- (**19**), 1-benzyl- (**20**), and 1-ethylbenzotriazole (**21**), respectively. The last reaction was investigated in more detail: the major product was 1-methylbenzotriazole (**9**), which is likely produced by transmetallation of the Grignard reagent with 1-(chloromethyl)benzotriazole to give the 1-(magnesiomethyl)benzotriazole chloride which is then hydrolysed to (**9**) on hydrolytic work-up.

Nucleophilic substitution of the chlorine atom by phosphorus was accomplished by reaction of (**4**) with triphenylphosphine. Here, the low yield (23%) of phosphonium salt (**22**) resulted from incomplete reaction as both starting materials were observed in the reaction filtrate; no attempt was made to optimize its yield.

In some of these nucleophilic substitution reactions, low

Table 1. Reaction of 1-(chloromethyl)benzotriazole with nucleophiles.

Compound	Nu	Yield (%)	M.p. (°C)	Recryst. solvent	Crystal form	Found (%) C	H	N	Formula	Required (%) C	H	N
(10)	EtO^-	81	158(8)[c]	—	Oil		*e*		$C_9H_{11}N_3O$		*e*	
(11)	PhO^-	45	68—69	Hexane	Plates	69.55	4.95	18.95	$C_{13}H_{11}N_3O$	69.33	4.88	18.66
(12)	PhS^-	64	80	EtOH	Needles	64.70	4.65	17.15	$C_{13}H_{11}N_3S$	64.78	4.66	17.42
(13)	BnS^-	68	108—109	EtOH–H_2O	Needles	65.90	5.00	16.30	$C_{14}H_{13}N_3S$	65.85	5.14	16.46
(14)	$PhSO_2^-$	44	177—179	DMF–H_2O	Prisms	56.95	4.05	15.55	$C_{13}H_{11}N_3O_2S$	57.13	4.06	15.37
(15)	C_6H_5N	59	185	EtOH	Plates	46.20	3.65	18.10	$C_{12}H_{11}ClN_4O_4$	46.37	3.54	18.03
(16)	DMAP[a]	76	145	MeOH	Prisms	47.35	4.55	19.90	$C_{14}H_{16}ClN_5O_4$	47.52	4.52	19.80
(17)	C_4H_9N[b]	27	80	Light petroleum	Prisms	65.25	7.20	27.70	$C_{11}H_{14}N_4$	65.32	6.98	27.70
(18)	N_3^-	82	59	CCl_4–light petroleum	Neeldes	48.75	3.50	48.60	$C_7H_6N_6$	48.28	3.47	48.25
(19)	CN^-	49	85—86	Hexane–toluene	Grains	60.65	3.80	35.65	$C_8H_6N_4$	60.75	3.82	35.42
(20)	PhMgBr	15	114—115[d]	MeOH	Plates	—	—	—	$C_{13}H_{11}N_3$	—	—	—
(21)	CH_3MgI	11	150(10)[c,d]	—	Liquid	—	—	—	$C_8H_{11}N_3$	—	—	—
(22)	Ph_3P	23	274—275	—	Grains	60.65	4.30	16.35	$C_{25}H_{21}ClN_3P$	60.68	4.31	16.33

[a] DMAP = 4-Dimethylaminopyridine. [b] C_4H_9N = Pyrrolidine. [c] B.p. °C (mmHg). [d] See ref. 13. [e] Accurate *M*: *m/z* Found: 177.090 5; *m/z* Required: 177.090 2.

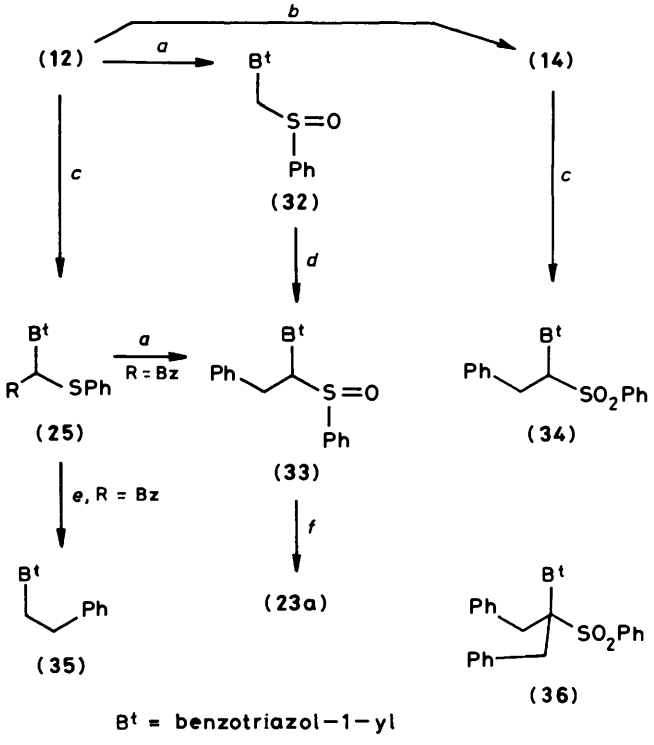
yields of the desired product seem to be caused by the preferential loss of the benzotriazolyl moiety over the chloride group. This is inferred by the isolation of compounds (**3**) and (**6**) from the reaction mixtures.

Preparation of Metallated 1-Methylbenzotriazole Derivatives for Reaction with Electrophiles.—We have employed two types of strategy to obtain metallated derivatives: (i) replacement of the chlorine atom of (**4**) by a metal such as magnesium, or by metal–halogen exchange with BuLi and (ii) proton loss from the CH_2 group in a derivative in which the chlorine atom had been replaced by PhS, PhSO, and $PhSO_2$, and PPh_3 as activating groups.

Grignard formation was found to be solvent dependent with formation of the metallated derivative occurring in tetrahydrofuran (THF), but not in ethereal solution. Even in THF fairly vigorous conditions (reflux for 6 h) were required for metallation to occur. Only a fair yield (21%) of 1-ethylbenzotriazole (**21**) was obtained when methyl iodide was the electrophile. Benzaldehyde gave a complex mixture of products, including 1-methylbenzotriazole (**9**), 1-styrylbenzotriazole (**23a**), and smaller amounts of unidentified materials, but none of the expected alcohol was isolated. Formation of these products may be envisaged as arising from hydrolysis of the Grignard reagent to give (**9**) and from dehydration of the initially formed alcohol during acidic work-up to give (**23a**).

Metallation was unsuccessful with either zinc metal (r.t., THF, 16 h) or BuLi (−30 °C, THF, 0.5 h). In the former case, only unchanged starting materials were recovered. In the latter case, a near quantitative recovery of benzaldehyde and formation of (**3**) and (**6**) was observed. Apparently, 1-(lithiomethyl)benzotriazole is so reactive under the conditions employed that it reacts immediately with (**4**) before benzaldehyde is added. Milder conditions (−78 °C, THF, 2 h) gave crude material after hydrolytic work-up. The ^1H n.m.r. spectrum suggested the formation of some of the desired addition product together with 1,2-dibenzotriazolylethane and *N*-pentylbenzotriazole.

Lithiation of 1-(Phenylthiomethyl)benzotriazole.—1-(Phenylthiomethyl)benzotriazole reacts with BuLi at −78 °C; the resulting carbanion can be trapped by various electrophiles (Scheme 1). Methyl iodide, benzyl chloride, and allyl bromide gave alkylated products (**24**), (**25**), and (**26**), respectively, in 37—68% yield (Table 2). With benzyl chloride as the electrophile, the dimeric product (**6**) was also isolated from the reaction mixture together with a small amount (5%) of 1-[dibenzyl(phenylthio)methyl]benzotriazole (**27**). Benzaldehyde and benzophenone gave alcohols (**28**) (44%) and (**29**) (76%), respectively. The former was isolated as a 1 : 1 mixture of diastereoisomers. Strong OH-stretching bands were observed at 3 280 for (**28**) and at 3 460 cm^{-1} for (**29**).



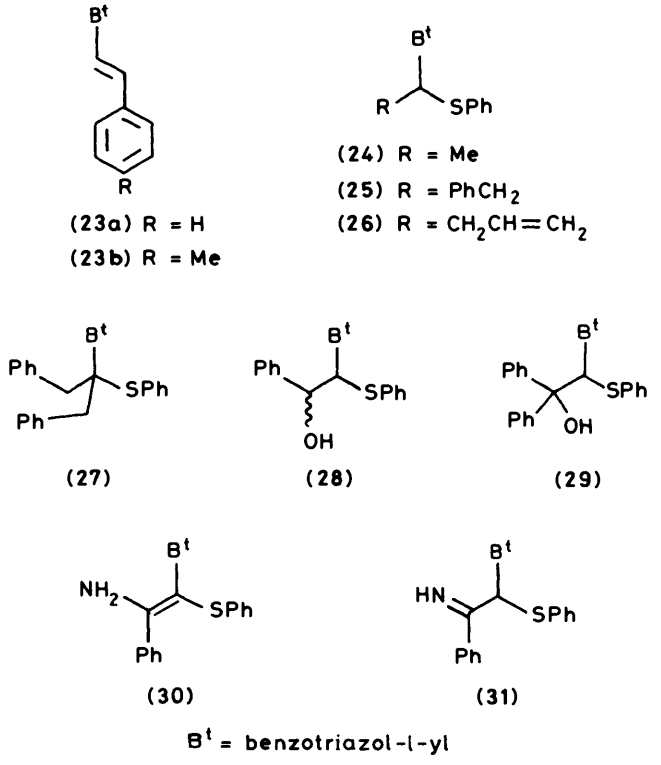
Scheme 1. *Reagents: a*, $NaIO_4$, H_2O/MeOH, 0 °C; *b*, MCPBA, CH_2Cl_2, 0 °C; *c*, BuLi, THF, −78 °C, Electrophile; *d*, LDA, THF, −78 °C, BzBr; *e*, Raney Ni, EtOH, heat; *f*, [$^2H_6$]-Me_2SO, 100 °C, 2 h.

Trapping of the anion with benzonitrile gave the enamino derivative (**30**). That the product was the enamine (**30**) rather than the imine (**31**) could be seen by the NH_2 stretching band at 3 380 and 3 280 cm^{-1} in its i.r. spectrum ($CHBr_3$). I.r. analysis of a highly diluted solution (CCl_4) of the product showed two strong bands for the enamine at 3 375 and 3 483 cm^{-1}; whereas, only one N–H stretching band would be expected in dilute

Table 2. Reaction of 1-(phenylthiomethyl)benzotriazole (**10**) with electrophiles.

Compound	Electrophile	Yield (%)	M.p. (°C)	Recryst.[a] solvent	Crystal form	Found (%) C	H	N	Formula	Required (%) C	H	N
(**24**)	MeI	49	Oil	—	Oil	65.60	5.20	16.40	$C_{14}H_{13}N_3S$	65.85	5.15	16.45
(**25**)	$PhCH_2Cl$	68	103—105	E–P	Needles	72.80	5.20	12.65	$C_{20}H_{17}N_3S$	72.50	5.15	12.70
(**26**)	CH_2=$CHCH_2Br$	46	46—48	P–H	Plates	68.10	5.40	14.95	$C_{16}H_{15}N_3S$	68.32	5.35	14.95
(**28**)	*p*-MeC_6H_4CHO	44	99—100	E–P	Plates	69.55	5.15	11.70	$C_{21}H_{19}N_3OS$	69.80	5.25	11.65
(**29**)	Ph_2CO	76	168—170	C–P	Prisms	73.70	5.00	9.85	$C_{26}H_{21}N_3OS$	73.75	4.95	9.90
(**30**)	PhCN	71	120—122	E	Plates	69.55	4.75	16.25	$C_{20}H_{16}N_4S$	69.75	4.65	16.25

[a] E = Diethyl ether; P = Light petroleum (35—48 °C); H = hexane; C = chloroform; B = benzene; T = carbon tetrachloride.



solution if the imine were the prevalent tautomer. Further support for (**30**) was obtained from ^1H and ^{13}C n.m.r. analysis (*vide infra*).

Lithiation of 1-(Phenylsulphinylmethyl)benzotriazole.—The sulphoxide (**32**) (75%) was readily prepared by oxidation of the sulphide (**12**) with $NaIO_4$. ^1H and ^{13}C N.m.r. data (*vide infra*) for (**32**) were in good agreement with the assigned structure (Scheme 1).

The sulphoxide (**32**) was lithiated by BuLi, but in very low yield. Reaction of the anion with benzyl chloride gave 1-(2-phenyl-1-phenylsulphinylethyl)benzotriazole (**33**) (3%) after chromatography, together with recovered starting material (**32**),1-(2-phenethyl)benzotriazole (**35**), and 1-(2-phenylvinyl)-benzotriazole (**23a**). Compound (**23**) is likely produced during work-up of the reaction as (**33**) has been found to be unstable (*vide infra*). Variation of the reaction conditions gave similar results. Formation of the anion with lithium di-isopropylamide (LDA) provided the desired product (**33**) in good yield (63%).

This was found to be in good agreement with Durst's[6] report that lithiations of sulphoxides with alkyl-lithium reagents gave complex mixtures while LDA provided the expected product in good yield.

Lithiation of 1-(Phenylsulphonylmethyl)benzotriazole—Nucleophilic substitution of phenyl sulphinate on (**4**) gave sulphone (**14**) in moderate yield (see above), but the preferred route of oxidation of (**12**) with *m*-chloroperbenzoic acid (MCPBA) provided a quantitative yield of (**14**).

In a similar manner to (**12**) and (**32**), the sulphone (**14**) could be readily lithiated by BuLi and trapped with benzyl bromide yielding the benzyl derivative (**34**) in good yield (73%). Subsequent trapping of the anion when both an excess of benzyl bromide and BuLi were used, provided benzyl (**34**) and dibenzyl (**36**) derivatives in moderate yield.

Wittig Reaction of Benzotriazol-1-ylmethyl(triphenyl)-phosphonium Chloride.—Activation of the N-CH_2 carbon was also performed by formation of the ylide from phosphonium salt (**22**) and sodium methoxide in DMSO solution. Quenching the ylide with *p*-tolualdehyde gave the expected *trans*-alkene (**23b**) in moderate yield (43%). No other products were isolated from the reaction.

Transformation of Products—Although (**33**) was obtained in good yield by oxidation of the sulphide (**25**) with $NaIO_4$ (see above), some elimination of the phenylsulphinyl moiety also occurred during the oxidation yielding (**23a**). This elimination was found to occur quantitatively in a n.m.r. tube after heating a DMSO solution of (**33**) at 100 °C for 2 h.

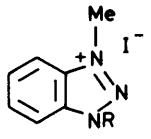
In our efforts to utilize the phenylthio and benzotriazolyl moieties for activation of the N–CH_2 group, we wished to investigate the selective removal of each of these groups from the methylene carbon under mild conditions. We found that indeed Raney nickel desulphurization of the benzyl derivative (**25**) yielded 1-(2-phenethyl)benzotriazole (**35**) (72%) (Scheme 1).

To activate the benzotriazole group for removal, quaternization by methyl iodide was carried out. Alkylation required the use of elevated temperatures (80 °C, sealed tube) and yielded products quaternized at N-3. The contrast with the 20 °C quaternization of a *N*-methylbenzotriazole[7] is apparently due to diminished nucleophilicity of the triazole system by electron withdrawal towards the phenylthio moieties.

Reaction with the more reactive alkylating agent, methyl tosylate, was attempted at room temperature; however, no quaternization was realized. The yields of methylation product obtained were 74% of (**37**) from the sulphide (**12**), 82% of (**38**) from the sulphoxide (**32**), and 35% of (**39**) from the sulphone (**14**).

1,3-Dimethylbenzotriazolium iodide (**40**) (26%) was also produced in the reaction of (**12**) with methyl iodide. This probably occurred *via* nucleophilic attack of the iodide ion on the methylene carbon of (**37**) to give *N*-methylbenzotriazole (**9**) and phenylthiomethyl iodide; treatment of (**9**) with methyl iodide yielding the product (**40**).[7]

The sulphide (**13**) gave, on reaction with methyl iodide, none of the N–CH_3 salt. Rather, 1,3-dimethylbenzotriazolium iodide (**40**) and trimethylsulphonium iodide were the only products



(37) R = CH_2SPh
(38) R = $CH_2S(O)Ph$
(39) R = CH_2SO_2Ph
(40) R = Me
(41) R = $CH \overset{t}{=} CHPh$

isolated from the reaction mixture. These products are a likely result of performing the reaction with an excess of methyl iodide, thus causing exhaustive methylation of all the products.

Reactions of the benzyl derivatives (**25**), (**33**), and (**34**) with methyl iodide under similar conditions gave in no case any of the simple methiodide. The sulphide (**25**) gave a mixture of 1,3-dimethylbenzotriazolium iodide (**40**) (6%) and starting material. With the sulphoxide (**33**), elimination of the phenylsulphinyl moiety occurred yielding (**23a**), which then quaternized giving 1-styryl-3-methylbenzotriazolium iodide (**41**) (66%). Evidence for this pathway was obtained by analysis of the crude product which showed the presence of (**23**) and the absence of starting material. Quaternization of the sulphone (**34**) provided the methiodide (**40**) (9%) along with starting material. Similarly, attempted quaternization of (**24**) was unsuccessful. Again, only the methiodide salt (**40**) was obtained. The lack of isolation of the simple methiodide salts is probably due to easy elimination of 1-methylbenzotriazole under the reaction conditions employed.

The chemistry of these novel benzotriazolium salts is being actively pursued and the results obtained will be reported on in due course.

^1H *and* ^{13}C *N.m.r.*—Spectral analysis of the compounds in this work allowed easy structure elucidation. In most instances, correct structure determinations were obtained by ^1H n.m.r. analysis. Any ambiguities in the assigned structure were clarified by the ^{13}C n.m.r. spectrum.

In the ^1H n.m.r. of (**10**)—(**19**) and (**32**), the NCH_2 protons resonate as a singlet in the range δ 5.7—8.0 (Table 3) while (**21**) and (**35**) displayed a quartet and a triplet, respectively. The deshielded methylene protons of (**22**) are unobservable due to severe signal overlap with a complex aromatic region. Typically, the benzotriazole protons[8–10] absorbed at δ 7.2—7.9 and δ 8.1—8.3 (4-H) as complex multiplets. Readily discernible in the ^{13}C spectra were the upfield NCH_2 carbons (35—76 p.p.m.). The benzotriazole[10,11] and substituent carbons were assigned by comparison with similar systems (Table 4).

1-(Disubstituted methyl)benzotriazoles (**24**)—(**26**), (**28**)—(**30**), and (**33**)—(**34**) displayed more interesting ^1H n.m.r. (Table 5). The NCH resonance for (**24**)—(**26**) and (**29**) was downfield (δ 6.3—6.5) with respect to the resonance of the NCH_2 in the starting sulphide (**12**). Upfield shifts due to the shielding effect exerted by the phenyl group(s) were observed for the methines of (**29**), (**33**), and (**34**). Compound (**28**), which showed a pair of doublets for the α-hydroxy protons and a pseudo triplet for the β-hydroxy protons, was found to be approximately a 1:1 mixture of diastereoisomers. Interestingly, the sulphone (**34**) exhibited characteristic triplet-doublet patterns for the CH and CH_2 protons, respectively. However, in the sulphoxide (**33**), the CH_2 protons were diastereotopic due to the asymmetric sulphinyl moiety thus providing a more complex pattern with the NCH as a doublet of doublets. The ^{13}C n.m.r. spectra helped to confirm the above structures; in the aliphatic region the NCH resonated in the range 62—81 p.p.m. (Table 6). The aromatic region was quite complex, rendering precise assignments uncertain.

That no methine proton was observed for the benzonitrile adduct suggested that the enamino (**30**) rather than the imino (**31**) form was the predominate tautomer. Indeed, its ^{13}C spectrum agreed well with this analysis. Clearly observable were the α- and β-amino carbons assigned to 156.5 and 92.7 p.p.m., respectively.

All the quaternized products were characterized by ^1H and ^{13}C n.m.r. spectroscopy. Generally, the NCH_3 was observed in a range from δ 4.67 to 4.86 while the NCH_2 was displayed from δ 6.7—δ 8.2. These protons appeared as a singlet in (**37**) and (**39**), but as an AB quartet in the sulphoxide (**38**). The aromatic protons appeared as complex multiplets. The olefinic signals in (**41**) were unobservable due to overlap with the aromatic signals.

^{13}C N.m.r. showed the NCH_3 at 38 p.p.m. for all of the quaternized products; the methylene carbon values ranged from 55 to 68 p.p.m. The sp^2 regions were rather complex, but

Table 3. ^1H N.m.r.[a] of 1-(Substituted methyl)benzotriazoles.

Compound	Aromatic-H	N-CH_2	Substituent-H
(**10**)[b]	8.32 (1 H, m), 8.1—7.4 (3 H, m)	6.18 (2 H, s)	3.67 (2 H, q, *J* 6), 1.18 (3 H, t, *J* 6)
(**11**)[b]	8.5—8.2 (1 H, m), 8.1—7.0 (8 H, m)	6.75 (2 H, s)	—
(**12**)[b]	8.3—8.1 (1 H, m), 7.8—7.4 (8 H, m)	6.10 (2 H, s)	—
(**13**)[b]	8.2 (1 H, m), 7.92—7.25 (8 H, m)	5.65 (2 H, s)	3.73 (2 H, s)
(**14**)[b]	8.2—7.5 (9 H, m)	6.71 (2 H, s)	—
(**15**)[c]	9.80 (2 H, d, *J* 7), 9.08 (1 H, m), 8.85 (4 H, m), 8.2—7.5 (2 H, m)[d]	8.03 (2 H, s)[d]	—
(**16**)[c,e]	8.83 (2 H, d, *J* 8), 8.42 (2 H, m), 7.84 (2 H, m), 7.27 (2 H, d, *J* 8)[d]	7.40[d]	—
(**17**)[b]	8.33 (1 H, m), 7.9—7.4 (3 H, m)	5.76 (2 H, s)	2.8 (4 H, m), 1.76 (4 H, m)
(**18**)[b]	8.35 (1 H, m), 7.9—7.5 (3 H, m)	6.10 (2 H, s)	—
(**19**)[b]	8.16 (1 H, s, 7.68 (3 H, m)	5.76 (2 H, s)	—
(**20**)[b]	8.35 (1 H, m, 7.56 (8 H, m)	6.03 (2 H, s)	—
(**21**)[b]	8.3—8.0 (1 H, m), 7.8—7.2 (3 H, m)	4.74 (2 H, q, *J* 7)	1.61 (3 H, t, *J* 7)
(**22**)[b]	8.3—7.15 (m)	8.3—7.15	—
(**32**)[b]	8.10 (1 H, m), 7.8—7.2 (8 H, m)	5.80 (2 H, s)	—
(**35**)[b]	8.17 (1 H, m), 7.37 (8 H, m)	4.92 (2 H, t, *J* 7)	3.36 (2 H, t, *J* 7)

[a] Chemical shift (δ) in p.p.m. and coupling constants (*J*) in Hz. [b] Solutions in $CDCl_3$. [c] Solutions in $[^2H_6]$-Me_2SO. [d] Signal overlap with other signals. [e] NMe_2: 3.30 (6 H, s).

Table 4. ^{13}C N.m.r. of 1-(substituted methyl)benzotriazoles

Compound	C-3a	C-4	C-5	C-6	C-7	C-7a	N-CH_2	C-*ipso*	C-*o*	C-*m*	C-*p*	Other	
(4)[c]	145.6	119.1	124.1	127.4	110.9	132.3	70.3	—	—	—	—	—	
(5)[c]	145.5	119.6	124.8	128.4	110.6	132.0	54.0	—	—	—	—	—	
(10)[a]	145.3	118.7	123.2	126.8	109.2	131.9	76.0	—	—	—	—	O-CH_2	64.0
												OCH_2CH_3	13.7
(11)[a]	146.0	119.8	124.2	127.9	109.7	132.6	74.7	156.0	116.1	129.5	122.9	—	
(12)[c]	145.3	119.1	124.0	127.2[b]	110.9	132.2[b]	50.8	131.9[b]	131.3	129.0	127.1[b]	—	
(13)[a]	146.1	119.7	123.9	127.1	110.0	131.7	47.5	150.5	128.3	129.0	136.3	s-CH_2Ph	34.7
(14)[c]	144.7	119.2	124.5	128.0	111.1	133.0	65.9	136.1	128.5	129.5	134.7	—	
(15)[c]	145.3	119.8	122.3	129.2	110.7	132.6	67.4	—	144.6	128.8	148.0	—	
(16)[c]	145.3	119.6	125.0	128.9	110.4	132.1	64.7	—	141.3	108.1	156.3	NMe_2	39.9
(17)[a]	145.6	119.6	123.6	127.2	109.8	133.8	65.0	—	—	—	—	NCH_2	50.1
												NCH_2CH_2	23.6
(18)[a]	146.3	120.3	124.7	128.4	109.2	132.4	61.7	—	—	—	—	—	
(19)[a]	146.2	120.6	125.0	128.9	108.7	132.3	35.7	—	—	—	—	CN	112.5
(20)[a]	146.4	120.0	123.9	128.4	109.8	134.8	52.2	132.8	129.0	127.5	127.4	—	
(22)[a,d]	144.7	118.8	124.3	128.2	112.0	135.2[e]	43.7	115.8	134.5	130.0	150.9[e]	—	
(32)[c]	144.7	118.9	124.2	127.4	111.2	133.7	67.4	140.5	124.6	129.1	131.6	—	
(35)[a]	145.8	119.9	123.7	127.0[b]	109.2	129.3	49.7	137.6	128.8	128.8	127.1[b]	NC*C*	36.4

[a] In $CDCl_3$ with 77.0 p.p.m. as reference. [b] Assignment could be reversed. [c] In [$^2H_6$]-Me_2SO with 39.5 p.p.m. as reference. [d] $^1J_{PC}$ 53.7 Hz, $^1J_{PC_i}$ 85.4 Hz, $^2J_{PC_o}$ 9.8 Hz, $^3J_{PC_m}$ 12.2 Hz, $^3J_{PC_{7a}}$ 2.4 Hz. [e] Tentative assignment.

Table 5. ^1H N.m.r. spectra[a] of 1-(disubstituted methyl)benzotriazoles.

	Aromatic-H			N-CH_2 (1 H)			Other-H
	4-posn	others					
Compound	(1 H, m)	δ	H	δ	M	*J*	
(24)	8.0	7.8—7.0	8	6.3	q	7	2.1 (3 H, d, *J* 7)
(25)	8.2	8.0—7.0	13	6.5	t	8	3.8 (2 H, d, *J* 8)
(26)	8.2	8.1—7.2	8	6.3	t	8	5.8 (1 H, m, =CH), 5.4—5.0 (2 H, m, $=CH_2$), 3.27 (2 H, t[b], CH_2)
(28)[c]		8.1—7.2	14	6.3	d	7	5.9—5.4 (m, C*H*OH), 4.3 (d, OH)
		8.1—7.0	14	6.4	d	6	4.2 (d, OH), 2.3 (s, CH_3)
(29)		8.3—6.8	19	5.4	s	—	—
(30)		8.1—7.0	14	—	—	—	5.2 (2 H, NH_2)
(33)	8.1	7.7—6.7	13	5.5	dd		4.1
(34)	8.1	7.9—7.2	13	6.1	t	8	4.1 (2 H, d, *J* 8, CH_2Ph)

[a] In $CDCl_3$; chemical shift (δ) in p.p.m. coupling constant (*J*) in Hz. [b] Apparent triplet. [c] Mixture of diastereoisomers in 1:1 ratio.

Table 6. ^{13}C N.m.r. spectra[a] of 1-(disubstituted methyl)benzotriazoles.

Compound	Aromatic-C	N-CH	Other-*C*
(24)	146.0—110.6	62.4	20.4 (CH_3)
(25)	146.2—110.6	68.5	40.5 (CH_2)
(26)	145.0—110.9	67.0	119.4 (=CH_2), 38.5 (CH_2)
(28)	145.6—111.3	73.2	75.3 (*C*HOH), 75.5 (*C*HOH)
		74.9	
(29)	144.7—110.3	76.4	81.9 (*C*-OH)
(30)	144.9—110.3	—	156.5 (=*C*-NH_2), 92.7 (-*C*=C-NH_2)
(33)	145.4—108.9	81.6	34.5 (CH_2Ph)
(34)[b]	144.5—110.8	76.3	31.7 (CH_2Ph)

[a] In $CDCl_3$ with 77.0 p.p.m. as reference. [b] In [$^2H_6$]-Me_2SO with 39.5 p.p.m. as reference.

distinctive [12] carbons (C-4 and C-7) could be easily seen upfield of the other signals. Assignment of these signals was aided by comparison of calculated values obtained from effects of quaternization on benzotriazole with those of the experimentally derived values (Table 7). Good agreement was seen in these comparisons.

1-(Trisubstituted methyl)benzotriazoles (**27**) and (**36**) showed the expected n.m.r. spectral data. The NCCH_2 protons in sulphide (**27**) are diastereotopic and are observed as an AB quartet; however, they appear as a singlet in the sulphone (**36**). Their ^{13}C spectra are complex due to the large number of aromatic signals (114 to 146 p.p.m.) but the NC and NCH_2, carbons are assignable: (**27**) (42.0 p.p.m. for the NCH_2 and 78.3 p.p.m. for the NC carbons), (**36**) (36.5 p.p.m. for the NCH_2 and 88.7 p.p.m. for the NC carbons).

The *N*-styrylbenzotriazoles (**23a**) and (**23b**) showed very complex ^1H n.m.r. spectra because of severe overlap of the olefinic signals with the aromatic signals. Similarly complex are the ^{13}C n.m.r. spectra due to the congested sp^2 region. As expected the benzotriazole carbons are easily observable as well as are the *p*-methyl of (**23b**). The styryl carbon assignments are uncertain because of the small chemical shift difference between the signals.

Experimental

M.p.s were determined with a hot-stage microscope and are uncorrected; b.p.s are uncorrected. I.r. spectra were recorded on a Perkin-Elmer Model 283B grating spectrophotometer. ^1H and ^{13}C N.m.r. chemical shifts are measured in δ from $SiMe_4$ or a specified internal standard. ^1H N.m.r. spectra were recorded

Table 7. ^{13}C N.m.r.[a] of benzotriazolium salts

Compound	3a	Carbon 4	5	6	7	7a	NCH	CH_3	C-*ipso*	C-*o*	C-*m*	C-*p*
(**37**)	135.1	114.4	130.8	131.0[b]	113.4	133.6	55.2	38.4	130.4[b]	132.5	129.4	128.9
(**38**)	135.4	113.9	131.8	130.7	114.0	134.4	68.6	38.6	139.1	124.5	129.3	132.2
(**39**)	135.1	113.4	131.1	131.9	114.7	135.0	67.0	38.9	135.6	129.1	129.8	134.7
(**41**)	135.3	114.2[b]	131.4[b]	131.1[b]	114.0[b]	132.3	120.7 130.0	38.4	133.2	128.9	128.0	128.1

[a] In [$^2H_6$]-Me_2SO with 39.5 p.p.m. as reference. [b] Assignment could be reversed.

on a Varian EM 360L (60 MHz) spectrometer, ^{13}C n.m.r. on a JEOL JNM-FX 100 (25.0 MHz) spectrometer, and mass spectra (m.s.) on a AEJ MS 30 mass spectrometer. Tetrahydrofuran (THF) was distilled from sodium–benzophenone prior to use.

The following compounds were prepared by the literature method quoted: 1-(chloromethyl)benzotriazole (**4**), m.p. 136—138 °C (lit.,[4] m.p. 136—138 °C) and 1-(hydroxymethyl)-benzotriazole (**5**), m.p. 148—151 °C (lit.,[4] m.p. 148—151 °C).

1-(*Ethoxymethyl*)*benzotriazole* (**10**).—To sodium ethoxide in EtOH [Na(0.23 g, 10 mmol) in EtOH (25 ml)] was added 1-(chloromethyl)benzotriazole (1.67 g, 10.0 mmol). The solution was refluxed for 6 h, cooled to room temperature, and the solvent removed under reduced pressure. The residue was dissolved in ether and was washed with water (3 × 100 ml). The ethereal solution was dried ($MgSO_4$) and concentrated by rotoevaporation. The resulting liquid was distilled to give (**10**) (1.43 g): $\nu_{max.}$($CHBr_3$) 3 070, 1 615, 1 590, 1 310, 1 271, 1 150, 1 090, and 750 cm^{-1} (Tables 1, 3, and 4)

1-(*Phenoxymethyl*)*benzotriazole* (**11**).—To sodium ethoxide in EtOH [Na (0.2 g, 8.7 mmol) in EtOH (10 ml)] was added phenol (0.73 g, 7.8 mmol) and the solution was heated at 50 °C for 10 min. 1-(Chloromethyl)benzotriazole (1 g, 6 mmol) was added, and the mixture refluxed with stirring for 4—5 h. On cooling to room temperature the precipitated solid was filtered off, washed with water (1 × 5 ml), dried, and recrystallized from hexane to give (**11**) (2.6 g) (Tables 1, 3, and 4).

1-(*Phenylthiomethyl*)*benzotriazole* (**12**).—To an ice-cold solution of thiophenol (11.0 g, 0.1 mol) in MeOH (100 ml) was added sodium metal (2.3 g, 0.1 mol). On complete dissolution of the metal, 1-(chloromethyl)benzotriazole (16.7 g, 0.1 mol) was added in small portions over 10 min. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under reduced pressure giving a solid which was stirred with water and then filtered. The solid was washed with water (2 × 100 ml) and then with EtOH–H_2O (30%). Drying in a vacuum oven gave a quantitative yield of (**12**): $\nu_{max.}$($CHBr_3$) 1 492, 1 450, 1 440, 1 284, 1 228, 1 145, 1 068, 780, 742, and 686 cm^{-1} (Tables 1, 3, and 4).

1-(*Benzylthiomethyl*)*benzotriazole* (**13**).—To a preformed mixture of sodium methoxide (2.70 g, 50 mmol), toluene-α-thiol (6.2 g, 50 mmol), and methanol (30 ml) that had been refluxed for 2 h was added 1-(chloromethyl)benzotriazole (8.35 g, 50 mmol). The mixture was stirred at r.t. overnight, filtered, and the solvent removed by rotoevaporation. The residue was stirred for several hours with MeOH (60 ml) and water (40 ml) containing KOH (1.12 g, 20 mmol). The precipitate was filtered off and washed with 5% NaOH and MeOH. Drying in a vacuum oven gave (**13**) as a white solid (8.63 g, 68%), $\nu_{max.}$($CHBr_3$) 2 980, 2 932, 1 491, 1 450, 745, 709, and 694 cm^{-1}; (Tables 1, 3, and 4).

1-(*Phenylsulphonylmethyl*)*benzotriazole* (**14**).—To DMSO (10 ml) was added 1-(chloromethyl)benzotriazole (1.67 g, 10 mmol) and sodium benzene sulphinate (1.64 g, 10 mmol). After being stirred overnight at room temperature, the mixture was taken up in $CHCl_3$ (200 ml) and washed with water (3 × 100 ml). The chloroform solution was dried ($MgSO_4$) and concentrated (60 °C/25 mmHg). The resulting solid was washed with ether and dried giving (**14**) (1.21 g): $\nu_{max.}$($CHBr_3$) 3 060, 1 610, 1 580, 1 330, 1 290, 1 230, 1 160, 1 155, 760, 740, and 683 cm^{-1} (Tables 1, 3, and 4).

1-(*Pyridiniomethyl*)*benzotriazole Perchlorates* (**15**) *and* (**16**).—To 1-(chloromethyl)benzotriazole (1 g, 6 mmol) in acetone–EtOH (2:1; 15 ml) for (**15**) and acetone (10 ml) for (**16**) was added the corresponding pyridine (7 mmol); the solution was refluxed with stirring for 1 h. On cooling, the precipitated solid was filtered off, dissolved in water (2 ml) and precipitated as the perchlorate salt with 50% $NaClO_4$ in water, (2 ml). The salt was filtered off, washed with water, and recrystallized (Tables 1, 3, and 4).

1-(*Pyrrolidylmethyl*)*benzotriazole* (**17**).—To pyrrolidine (10 ml) was added 1-(chloromethyl)benzotriazole (1.67 g, 10 mmol). After being stirred overnight at room temperature, the reaction mixture was evaporated under reduced pressure and the residue passed through a silica gel column with $CHCl_3$ as the eluant. Concentration (60 °C/25 mmHg) gave (**17**) (0.54 g) as a white solid: $\nu_{max.}$(Nujol) 3 060, 2 810, 1 610, 1 590, 1 294, 1 210, 1 145, and 750 cm^{-1} (Tables 1, 3, and 4).

1-(*Azidomethyl*)*benzotriazole* (**18**).—To DMSO (50 ml) was added 1-(chloromethyl)benzotriazole (1.67 g, 10 mmol) and sodium azide (1.30 g, 10 mmol). After being stirred overnight at room temperature, the solution was diluted with ether (150 ml) and water (150 ml). The layers were separated and the ethereal layer washed with water (3 × 100 ml). The organic layer was dried ($MgSO_4$) and concentrated (60 °C/25 mm Hg) giving (**18**) (1.97 g, 82%), as a white solid; $\nu_{max.}$(liquid) 3 010, 2 120, 2 080, 1 610, 1 590, 1 290, 1 230, 1 140, and 745 cm^{-1} (Tables 1, 3, and 4).

1-(*Cyanomethyl*)*benzotriazole* (**19**).—To DMSO (10 ml) was added 1-(chloromethyl)benzotriazole (1.67 g, 10 mmol) and NaCN (0.441 g, 9 mmol). The mixture was stirred under N_2 at 25 °C for 18 h and then poured into ice–water and extracted with $CHCl_3$ (3 × 20 ml). The combined organic layers were washed twice with water, dried ($MgSO_4$), and concentrated by rotoevaporation to give the crude product (1.176 g). Column chromatography on silica gel using $CHCl_3$ as eluant gave (**19**) as a white solid (0.693 g, 49%); $\nu_{max.}$($CHBr_3$) 2 980, 2 958, 1 612, 1 494, 1 453, 950, 917, 780, and 746 cm^{-1} (Tables 1, 3, and 4).

1-*Benzylbenzotriazole* (**20**).—To a solution of phenylmagnesium bromide, prepared from Mg turnings (0.24 g, 10 mmol) and bromobenzene (1.57 g, 10 mmol) in THF, (20 ml),

was added dropwise a solution of 1-(chloromethyl)benzotriazole (1.67 g, 10 mmol) in THF (15 ml) at 0 °C. The mixture was stirred at 0 °C for 3 h and then at r.t. for 1 h. The reaction was quenched by slow addition of a NH_4Cl solution. The mixture was extracted with ether (3 × 100 ml) and the combined ethereal layers were washed with water (2 × 100 ml) and dried ($MgSO_4$). The solvent was removed by rotoevaporation yielding (**20**) as a white solid (0.32 g, 15.1%) (Tables 1, 3, and 4).

1-*Methylbenzotriazole* (**9**).—To an ethereal solution (40 ml) of methylmagnesium iodide, prepared from methyl iodide (3.0 ml, 48 mmol) and Mg turnings (2.43 g, 100 mmol), was added 1-(chloromethyl)benzotriazole (4.2 g, 25 mmol) all at once. The mixture was stirred vigorously for 1 h at r.t. and then poured onto ice and neutralized with 5% HCl. The aqueous mixture was extracted with $CHCl_3$ (3 × 10 ml) and dried ($MgSO_4$). The mixture was filtered and the filtrate concentrated by rotoevaporation to give crude product (3.98 g) which contained 1-methylbenzotriazole (**9**) (83%), 1-ethylbenzotriazole (**21**) (11%), and some uncharacterized materials as determined by ^1H n.m.r. An analytical sample of (**9**) was obtained by treatment of the crude mixture with a $CHCl_3$ solution of picric acid. The resulting precipitate was filtered off, washed with ether, and then redissolved in a 10% solution of NaOH which was then extracted with $CHCl_3$ and dried ($MgSO_4$). The solution was concentrated by rotoevaporation to give pure (**9**) as white plates after recrystalization from ether–pentane (1:2); m.p. 60—62 °C (lit.,[4] m.p. 64—64.5 °C) (Found: C, 63.05; H, 5.4; N, 31.65; $C_7H_7N_3$ requires C. 63.14; H, 5.30; N, 31.56%); $\delta(CDCl_3)$ 4.36 (s, 3 H), 7.57 (m, 3 H), and 81.5 (m, 1 H).

1-*Ethylbenzotriazole* (**21**).—To Mg turnings (0.24 g, 10 mmol) and a catalytic amount of I_2 was added dropwise a solution of 1-(chloromethyl)benzotriazole (1.67 g, 10 mmol) in THF (20 ml). The reaction was started by warming in an oil-bath and after 3 h, the reaction was complete. The flask was cooled to room temperature and MeI (1.43 g, 10 mmol) was added and the mixture stirred at room temperature for 6 h. The solvent was removed under reduced pressure and the resulting solid was dissolved in a minimum amount of $CHCl_3$. The solution was chromatographed on silica gel using $CHCl_3$ as the eluant. The solvent was removed from the second band to give (**21**) (0.31 g, 21%) as a clear liquid), b.p. 150 °C (10 mmHg) [lit.,[13] b.p. 157—161 °C/(18 mmHg)] (Tables 1 and 3).

1-*Benzotriazol*-1-*ylmethyl*(*triphenyl*)*phosphonium Chloride* (**22**).—To dry THF (25 ml) was added 1-(chloromethyl benzotriazole (3.35 g, 20 mmol) and triphenylphosphine (6.55 g, 25 mmol). The mixture was heated under Ar at 50 °C for 96 h and the resulting precipitate was filtered off and washed with hexane. Drying in a vacuum oven (60 °C) gave (**22**) as a white solid (1.982 g, 23%): $\nu_{max.}(CHBr_3)$ 2 900, 1 588, 1 483, 1 311, 1 290, 858, 740, 704, and 685 cm^{-1} (Tables 1, 3, and 4).

General Procedure for the Lithiation of 1-(*Phenylthiomethyl*)-*benzotriazole* (**12**) *and Subsequent Trapping by Electrophiles.*—To 1-(phenylthiomethyl)benzotriazole (2 g, 83 mmol) in dry THF (20 ml) was added BuLi (1.5 M in hexane; 6 ml, 9 mmol) at −78 °C under Ar. The solution was stirred for 1.5 h at −78 °C and the electrophile (16.6 mmol) added. After 20 h at room temperature, the solvent was removed (40 °C/20 mmHg), extracted with CH_2Cl_2 (50 ml), washed with water (20 ml), and dried ($MgSO_4$). Evaporation of the solvent (30 °C/20 mmHg) gave an oily residue which solidified upon trituration with light petroleum. The solid after filtration was recrystallized from the appropriate solvent or purified by column chromatography (Tables 2, 5, and 6).

1-[*Dibenzyl*(*phenylthio*)*methyl*]*benzotriazole* (**27**).—This product was also obtained by the above procedure. It was isolated from the crude mixture by column chromatography on silica gel using benzene as the eluant (0.21 g, 5%), m.p. 140—142 °C (Found: C, 76.75; H, 5.6; N, 9.65. $C_{27}H_{23}N_3$ requires C, 76.93; H, 5.50; N, 9.97%); $\nu_{max.}(CHBr_3)$ 1 493, 1 450, 1 209, 1 070, 1 020, 742, and 693 cm^{-1}; $\delta_H(CDCl_3)$ 3.76 (d, *J* 15.6, 2 H, $PhCH_aH_b$), 4.23 (d, *J* 15.6, 2 H, $PhCH_aH_b$), 6.77—7.77 (m, 18 H, Ar*H*), and 8.34 (m, 1 H, Ar*H*); $\delta_C(CDCl_3)$ 42.0 (N-*C*), 78.3 (NC*C*Ph), 114.5 (C-7), 120.1 (C-4), 124.0 (C-5), 146.8 (C-3a), 127.0, 127.2, 128.0, 129.0, 130.2, 130.6, 133.1, 133.9, and 134.7; *m/z* (%) 312 (19), 302 (12), 284 (25), 211 (4), 193 (40), and 192 (16).

1-(2-*Phenyl*-1-*phenylsulphinylethyl*)*benzotriazole* (**33**).—To a dry THF solution (30 ml) containing 1-(phenylsulphinylmethyl)-benzotriazole (2.15 g, 8.3 mmol) at −78 °C under Ar was added BuLi (1.5 M in hexane; 6 ml, 9 mmol). After 15 min, benzyl chloride (1.27 ml; 11 mmol) was added all at once. The reaction mixture was allowed to slowly warm to r.t. and was kept there for 2 h. The reaction mixture was poured into ice–water and extracted with $CHCl_3$ (3 × 15 ml). The combined extracts were dried ($MgSO_4$) and concentrated by rotoevaporation. Recrystallization of the crude product gave starting material (**32**) (0.40 g, 19%). The filtrate was concentrated and chromatographed on silica gel. Elution with $CHCl_3$ and recrystallization from toluene–hexane (1:1) gave (**33**) (0.097 g, 3%) as white needles, m.p. 121—123 °C (Found: C, 69.25; H, 4.8; N, 12.00. $C_{20}H_{17}N_3OS$ requires C, 69.14; H, 4.93; N, 12.09%); $\nu_{max.}(CHBr_3)$ 1 492, 1 450, 1 442, 1 282, 1 220, 1 163, 1 145, 1 088, 1 040, 740, and 690 cm^{-1} (Tables 5–6).

This product was also produced by the following procedure: to a lithium di-isopropylamide (LDA) solution, prepared by the addition of BuLi (1.29 ml; 3.0 mmol) to di-isopropylamine (0.42 ml; 3.0 mmol) in THF (5 ml) at −78 °C followed by warming to r.t. and cooling back to −78 °C, was added dropwise at −78 °C a solution of the sulphoxide (**32**) (0.537 g, 2.1 mmol) in THF (25 ml). The mixture was stirred at −78 °C for 1 h and then warmed to −20 °C. To this was added benzyl bromide (0.48 ml, 4 mmol) and the mixture stirred at 0 °C for 14 h. Work-up of the reaction as described above gave pure (**33**) (0.455 g, 63%). ^1H N.m.r. spectra were identical with a sample as prepared above.

1-(2-*Phenethyl*)*benzotriazole* (**35**).—This product was also obtained by the above procedure with BuLi. Isolation from the crude mixture by column chromatography on silica gel using $CHCl_3$ as the eluant gave (**35**) (0.34 g, 18%) as a viscous liquid, $\nu_{max.}$(neat) 1 494, 1 452, 1 158, 1 093, 740, and 694 cm^{-1} (Tables 3–4) (Found: *M/z* 223.111 7. Calc. for $C_{14}H_{13}N_3$: 223.110 9).

This product was also obtained by Raney nickel reduction of sulphide (**25**). To a solution of 1-(2-phenyl-1-phenylthioethyl)-benzotriazole (**25**) (0.175 g, 0.53 mmol) in EtOH (20 ml) was added Raney nickel (1.00 g, 17 mmol). The mixture was refluxed with vigorous stirring for 2 h; the solution was filtered and the solvent evaporated. Column chromatography of the crude product on silica gel using benzene–$CHCl_3$ (1:1) as eluant gave (**35**) as a clear liquid (0.085 g, 72%). Spectral data were in agreement with those of an authentic sample.

1-*Styrylbenzotriazole* (**23a**).—This product was also obtained by the above procedure. Isolation from the crude mixture by column chromatography on silica gel using benzene–$CHCl_3$ (4:1) as the eluant gave (**23a**) as yellow needles (0.04 g, 2%), m.p. 115—116 °C (Found: C, 76.1; H, 4.85; N, 19.05. $C_{14}H_{11}N_3$ requires C, 75.99; H, 5.01; N, 18.99%); $\nu_{max.}$(neat) 1 453, 1 162, 1 140, 1 050, 936, 740, 688, and 648 cm^{-1}; $\delta_H(CDCl_3)$ 7.17—8.00 (m, 10 H) and 8.18 (m, 1 H).

1-(2-*Phenyl*-1-*phenylsulphonylethyl*)*benzotriazole* (**34**).—To a dry THF solution (30 ml) containing 1-(phenylsulphonylmethyl)benzotriazole (**14**) (0.396 g, 1.45 mmol) at −50 °C under argon was added BuLi (2.3 M in hexane; 0.63 ml, 1.45 mmol). After 15 min at −50 °C, benzyl bromide (0.174 ml; 1.45 mmol) was added and the mixture allowed to warm to r.t. over 1 h. The mixture was poured into ice–water and neutralized (phenolphthalein) with 5% HCl. After extraction with ether (3 × 15 ml), the combined ethereal layers were dried ($MgSO_4$) and concentrated by rotoevaporation. Recrystallization from hexane–toluene (1:1) gave (**34**) as white grains (0.387 g, 73%), m.p. 170—171 °C (Found C, 66.1; H, 4.55; N, 11.45. $C_{20}H_{17}N_3O_2S$ requires C, 66.10; H, 4.71; N, 11.56%); $\nu_{max.}$($CHBr_3$) 2 911, 1 458, 1 444, 1 318, 1 306, 1 080, and 968 cm^{-1}.

This product was also obtained with BuLi (0.38 mmol excess) and benzyl bromide (0.5 mmol excess) followed by chromatography of the crude mixture on silica gel using $CHCl_3$ as eluant and recrystallization of the product from the third fraction from EtOH. This gave (**34**) (29%) as white needles which showed spectra identical with an authentic sample prepared above.

1-[*Dibenzyl*(*phenyl*)*sulphonylmethyl*]*benzotriazole* (**36**).—This product was also obtained by the above procedure when an excess of BuLi and benzyl bromide were used. Isolation from the crude mixture by column chromatography on silica gel using $CHCl_3$ as the eluant gave (**36**) as a white solid after recrystallization from EtOH–toluene (1:1) (2.55 g, 28%), m.p. 154—156 °C (Found: C, 71.80; H, 5.30; N, 9.10. $C_{27}H_{23}N_3O_2S$ requires C, 71.50; H, 5.11; N, 9.27%); $\nu_{max.}$($CHBr_3$) 2 933, 1 602, 1 583, 1 492, 1 447, 1 306, 1 295, 1 140, 1 076, 1 024, 780, 759, 742, 723, 686, and 597 cm^{-1}; δ_H($CDCl_3$) 4.93 (s, PhCH_2, 4 H), 6.67—7.83 (m, ArH, 18 H), and 8.13 (m, 1 H); δ_C($CDCl_3$) 35.6 (Ph*C*H_2), 83.8 (NC), 114.3 (C-7), 120.3 (C-4), 124.6 (C-5), 127.0, 128.0, 128.4, 128.9, 129.3, 130.5, 133.2, 133.4, 133.8, 134.6, and 146.9 (C-3a).

1-[2-(p-*Tolyl*)*vinyl*]*benzotriazole* (**23b**).—To a solution of DMSO (10 ml), benzotriazol-1-ylmethylphosphonium chloride (0.86 g, 2 mmol) and *p*-tolualdehyde (0.235 ml; 2 mmol) under argon at r.t. was added slowly sodium methoxide solution (2 ml; Na 0.041 g, 1.8 mmol). The solution was stirred at r.t. for 3 h and then quenched by pouring into water. The aqueous solution was extracted with ether (3 × 20 ml) and the combined ethereal layers were dried ($MgSO_4$). Rotoevaporation of the solvent gave a solid which after recrystallization from MeOH gave (**23b**) (0.184 g, 43%), m.p. 149.5—150 °C (Found: C, 76.45; H, 5.6; N, 17.7. $C_{15}H_{13}N_3$ requires C, 76.55; H. 5.55; N, 17.85%); $\nu_{max.}$($CHBr_3$) 1 483, 1 446, 1 392, 1 281, 1 236, 1 206, 1 181, 1 165, 1 116, 1 050, 950, 932, 795, and 735 cm^{-1}; δ_H($CHBr_3$) 2.42 (s, 3 H), 7.13—8.00 (m, 9 H), and 8.20 (m, 1 H).

1-(*Phenylsulphinylmethyl*)*benzotriazole* (**32**).—To a solution of 1-(phenylthiomethyl)benzotriazole (**12**) (7.96 g, 33 mmol) in MeOH (400 ml) was added a solution of $NaIO_4$ (10.65 g, 50 mmol) in water (100 ml). The solution was stirred for 24 h at room temperature. After concentration of the solvent, the residue was treated with $CHCl_3$ (200 ml). NaI was filtered off and the filtrate was dried ($MgSO_4$). The $CHCl_3$ solution was concentrated to a small volume (10 ml) and added slowly to stirred hexane (100 ml). The precipitate was filtered off and washed with hexane. Drying in a vacuum oven gave (**32**) (4.24 g, 75%) (Found: C, 60.65; H, 4.30; N, 16.35. $C_{13}H_{11}NOS$ requires C, 60.68; H, 4.31; N, 16.33%) which was recrystallized from toluene to give white needles (Tables 1, 3, and 4).

Preparation of 1-(2-*Phenyl*-1-*phenylsulphinylethyl*)*benzotriazole* (**33**) *by Oxidation of* 1-(2-*Phenyl*-1-*phenylthioethyl*)*benzotriazole* (**25**).—To an ice-cold stirred solution of $NaIO_4$ (2.56 g, 12 mmol) in MeOH (40 ml) was added in one portion a solution of 1-(2-phenyl-1-phenylthioethyl)benzotriazole (**25**) (0.99 g, 3 mmol) in dioxane–MeOH (1:1) (10 ml). The mixture was stirred at 0 °C for 1 h after which the temperature was allowed slowly to rise to room temperature and was kept there for 40 h. To this was added $CHCl_3$ (30 ml) and the mixture was stirred for 1 h. The resulting solid was filtered off and the filtrate concentrated (60 °C/25 mmHg). The residue was crystallized from toluene–hexane (1:1) yielding (**33**) (0.64 g, 61%) which had ^1H n.m.r. characteristics identical with an authentic sample prepared as described above.

Preparation of 1-(*Phenylsulphonylmethyl*)*benzotriazole* (**14**) *by Oxidation of* 1-(*Phenylthiomethyl*)*benzotriazole* (**12**).—To an ice-cold solution of 1-(phenylthiomethyl)benzotriazole (7.96 g, 33 mmol) in CH_2Cl_2 (50 ml) was added slowly over 1 h a warm solution of *m*-CPBA (3.80 g, 80 mmol) in CH_2Cl_2 (60 ml). The mixture was stirred at 0 °C for 3 h. T.l.c. analysis showed the presence of (**12**). Thus, an additional quantity of *m*-CPBA (1.63 g, 10 mmol) was added and the mixture was stirred at room temperature for 1 h. The solvent was concentrated (60 °C/25 mmHg) and the resulting solid taken up in water (150 ml) and neutralized with 2M aqueous NaOH (phenolphthalein). Saturated brine (50 ml) was added and the mixture was chilled and filtered. The solid so obtained was washed with water and dried in a vacuum oven yielding (**14**) as small white needles (9.05 g, 100%) after recrystallization from EtOH. This had ^1H n.m.r. spectral characteristic identical with those of an authentic sample prepared as described above.

Thermolysis of 1-(2-*Phenyl*-1-*phenylsulphinylethyl*)*benzotriazole* (**33**).—To a 5 mm n.m.r. tube was added a solution of 1-(2-phenyl-1-phenylsulphinylethyl)benzotriazole (**33**) in [$^2H_6$]-DMSO. The sample was heated at 100 °C for 2 h. ^1H N.m.r. analysis showed complete decomposition of (**33**) with the formation of 1-(2-phenylvinyl)benzotriazole (**23a**) as the sole product.

3-*Methyl*-1-(*phenylthiomethyl*)*benzotriazolium Iodide* (**37**).—To a glass vial was added 1-(phenylthiomethyl)benzotriazole (0.965 g, 4 mmol), toluene (10 ml), and MeI (10 ml, 161 mmol). The vial was sealed and heated in an oil-bath at 80 °C for 16 h. The mixture was cooled and THF (6 ml) and MeOH (3 ml) were added. After rewarming and cooling, the resulting solid was filtered off yielding (**37**) as yellow crystals (0.991 g, 65%), m.p. 165—166 °C (Found: C, 43.65; H, 3.6; N, 10.90. $C_{14}H_{14}IN_3S$ requires C, 43.88; H, 3.68; N, 10.97%); δ_H($CDCl_3$/[$^2H_6$]-DMSO) 4.67 (s, NCH_3, 3 H), 6.70 (s, NCH_2, 2 H), 7.47 (s, Ar*H*, 5 H), and 7.92—8.60 (m, Ar*H*, 4 H); ^{13}C N.m.r. (Table 7).

1,3-*Dimethylbenzotriazolium Iodide* (**40**).—This compound was obtained in the above reaction by evaporation of the solvent from the filtrate after separation from (**37**). Recrystallization of the residue from dioxane–EtOH (1:1) gave (**40**) as yellow needles (0.29 g, 26%), m.p. 188—189 °C (lit.,[7] m.p. 185 °C); δ_H($CDCl_3$/[$^2H_6$]-DMSO) 4.83 (s, CH_3, 6 H), 8.13 (m, ArH, 2 H), and 8.45 (m, Ar*H*, 2 H).

3-*Methyl*-1-(*phenylsulphinylmethyl*)*benzotriazolium Iodide* (**38**).—This compound prepared similarly to (**37**) (except that a 24 h reflux time was used), was found to give yellow needles [from THF–MeOH (2:1)] (82%), m.p. 172—174 °C (Found: C, 42.05; H, 3.45; N, 10.45. $C_{14}H_{14}IN_3OS$ requires C, 42.12; H, 3.53; N, 10.53%); $\nu_{max.}$($CHBr_3$) 2 920, 1 601, 1 444, 1 405, 1 346,

1 265, 1 150, 1 080, 1 045, 1 017, 995, and 739 cm^{-1}; $\delta_H(CDCl_3/[^2H_6]$-DMSO) 4.68 (s, CH_3, 3 H), 6.46 (d, J_{ab} 14 Hz, N–CH_aH_b, 1 H), 6.78 (d, J_{ab} 14 Hz, N–CH_aH_b, 1 H), 7.65 (s, Ar*H*, 5 H), 8.04 (m, Ar*H*, 3 H), and 8.50 (m, Ar*H*, 1 H); ^{13}C N.m.r. (Table 7).

3-*Methyl*-1-*(phenylsulphonylmethyl)benzotriazolium Iodide* (**39**).—Compound (**39**) prepared similarly to (**37**) (except that a 72 h reflux time was used), was found to give prisms (from MeOH) (35%) m.p. 188—190 °C (Found: C, 40.6; H, 3.35; N, 9.80. $C_{14}H_{14}IN_3O_2S$ requires C, 40.49; H, 3.40; N, 10.12%); $\nu_{max.}(CHBr_3)$ 3 097, 2 998, 2 888, 2 817, 1 446, 1 343, 1 332, 1 285, 1 272, 1 178, 1 150, 1 140, 1 081, 1 022, 803, 761, 739, and 683 cm^{-1}; $\delta[^2H_6]$-DMSO 4.78 (s, CH_3, 3 H), 7.18 (s, CH_2, 2 H), 8.00 (m, ArH, 7 H), and 8.47 (m, Ar*H*, 2 H); ^{13}C N.m.r. (Table 7).

3-*Methyl*-1-*styrylbenzotriazolium Iodide* (**41**).—Compound (**41**) prepared similarly to (**37**) from (**25**) (except that $CHCl_3$ was used as the solvent and that a 15 h reaction time was used), was found to give needles (from $CHCl_3$) (66%), m.p. 188—190 °C (Found: C, 49.60; H, 3.80; N, 11.7. $C_{15}H_{14}IN_3$ requires C, 49.60; H, 3.89; N, 11.57%); $\nu_{max.}(CHBr_3)$ 3 100, 2 950, 1 608, 1 445, 1 362, 1 340, 1 230, 1 138, 950, 760, 740, and 690 cm^{-1}; $\delta([^2H_6]$-DMSO) 4.86 (s, NCH_3, 3 H), 7.47 (m, 3 H), 8.00 (m, 5 H), 8.41 (m, 1 H), and 8.78 (m, 2 H); ^{13}C N.m.r. (Table 7).

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