PREPARATION AND PHOTOLYSIS OF 1-HETEROSUBSTITUTED 1-(1-ALKENYL)BENZOTRIAZOLES †

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Abstract -- A Peterson olefination reaction involving 1-trimethylsilanylmethyl-1*H*-benzotriazole and either adamantanone or acetone, in the presence of n-butyllithium, is used to prepare 1-adamantylidenemethyl-1*H*-benzotriazole and 1-(2-methylpropenyl)-1*H*-benzotriazole respectively. Further treatment of these compounds with n-butyllithium and an electrophile affords a variety of 1-heterosubstituted 1-(1-alkenyl)benzotriazoles. Photolysis of the latter compounds yields products from three competing pathways: cyclisation with C-C bond formation, cyclisation with C-S bond formation and halogen atom transfer.

Introduction

Over the past few years, Katritzky and his co-workers have amply demonstrated the synthetic versatility of benzotriazole and various substituted benzotriazoles.[1]

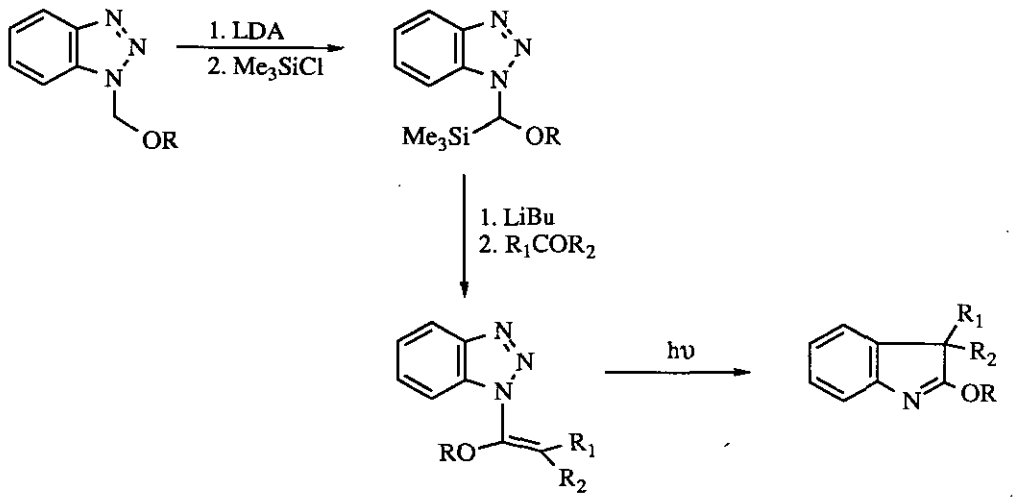
In addition, photolysis of 1-(1-alkenyl)benzotriazoles has proved to be an excellent route for the synthesis of indoles[2] and oxindoles[3a] and is one of the key steps in the synthesis of the complex oxindole alkaloid, gelsemine.[3b, 3c]

Several methods for the synthesis of specific 1-(1-alkenyl)benzotriazoles have been reported in the past. In the early work of Rees and Storr,[4] 1-chlorobenzotriazole was treated with a variety of olefins. A mixture of 1- and 2-(2-chloroalkyl)benzotriazoles was obtained (with the undesired 2- isomer always predominant). Subsequent dehydrochlorination of the adducts in the presence of 1,5-diazacyclo[4.3.0] non-5-ene (DBN) or potassium

† Dedicated to Professor Alan R. Katritzky on the occasion of his 65th birthday.

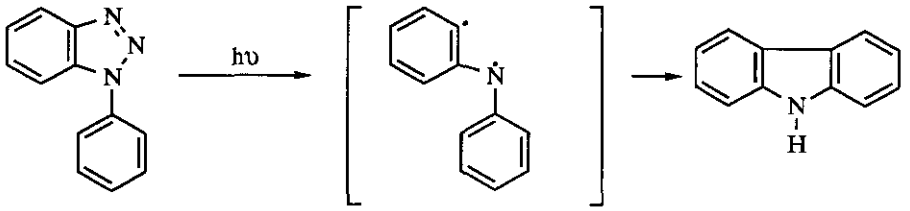
tert-butoxide in *tert*-butyl alcohol yielded the desired 1-(1-alkenyl)benzotriazoles. An alternative synthesis reported by Märky and co-workers[5] generated 1-(1-alkenyl)benzotriazoles in good yields by base-catalysed isomerisation of 1-allylbenzotriazoles. However, this method does not constitute a completely general route for 1-substituted 1-alkenyl-benzotriazoles. Katritzky and co-workers reported the preparation of a series of 1-(1-alkenyl)benzotriazoles *via* the Wittig reaction[6-8] which gave exclusively the *trans*-compounds in moderate yields (except in one example) and the Peterson olefination.[6,9]

In the course of a total synthesis of the alkaloid gelsemine, workers in this laboratory[3] devised a flexible and high yielding method for the preparation of 1-(1-alkoxy-1-alkenyl)benzotriazoles, which were then converted to the cyclic iminoethers by photolysis (shown in scheme 1).



Scheme 1

The thermal and photochemical decompositions of 1-(1-alkenyl)benzotriazoles have been investigated on several occasions in the past.[10-12] While the Graebe-Ullmann[10] thermal synthesis of carbazole from 1-phenylbenzotriazole is almost one hundred years old, paradoxically, the first photolytic preparation of carbazole from 1-phenylbenzotriazole was only published twenty-five years ago (Scheme 2).[11] Yonezawa *et al* .[12a] have provided strong evidence for the diradical nature of the presumed intermediate (i) (Scheme 2).



(i)

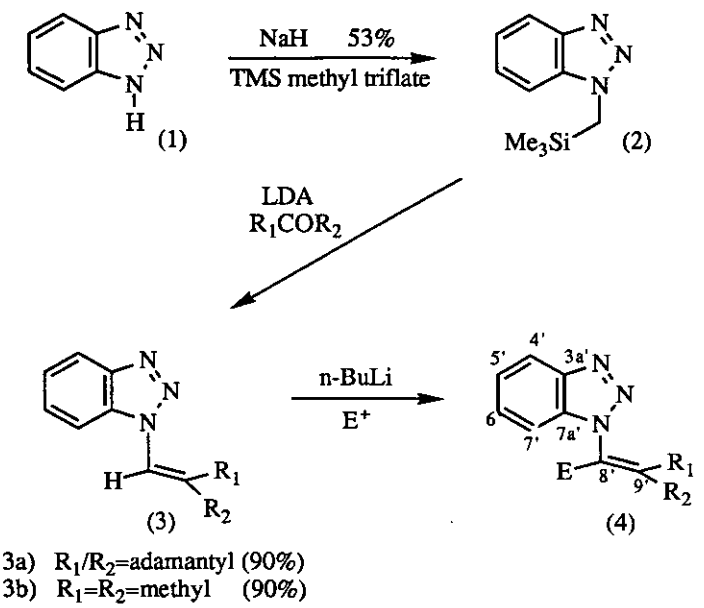
Scheme 2

Since then, there has been a considerable amount of work reported, concerning mechanistic differences between the thermal and photochemical processes.[12b,12c] Surprisingly, the application of this chemistry to an efficient synthesis of indoles has only been revealed quite recently.[2,5] Its extension to the synthesis of oxindoles was the basis of a key step in the recent total synthesis of gelsemine.[3c]

Results and Discussion

Preparation of 1-(1-alkenyl)benzotriazoles

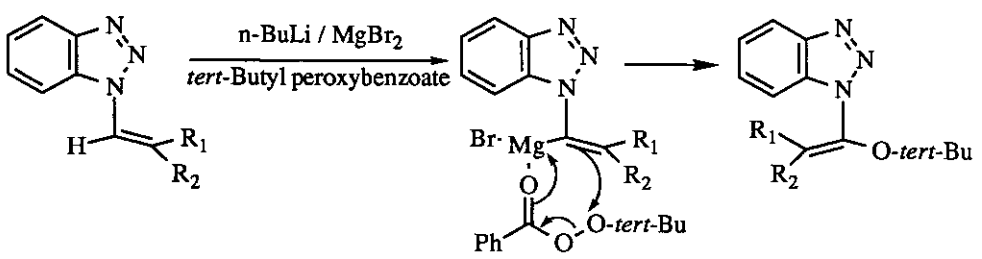
Preparation of 1-trimethylsilanylmethylbenzotriazole (2) was achieved by the action of the sodium salt of benzotriazole on trimethylsilanylmethyltrifluoromethane sulphonate (TMS methyl triflate). Treatment of 2 with lithium diisopropylamide at -78°C yielded the α–lithio intermediate (characteristic navy blue colour) which underwent a Peterson olefination reaction[13] with adamantanone (90%) and acetone (90%). The remaining vinylic proton could be removed easily by the action of n-butyllithium and the resulting vinyllithium intermediate reacted with a variety of electrophiles (trimethylsilanylchloride, *N*-chloro- and *N*-bromosuccinimides, disulphides) to afford α–substituted 1-(1-alkenyl)benzotriazoles (Scheme 3). The variations in reactants and yields of products are shown in Table 1.



3a) R_1/R_2=adamantyl (90%)
3b) $R_1=R_2$=methyl (90%)

Scheme 3

However, this method proved unsuccessful for the attempted preparation of 1-(adamantylidene-*tert*-butoxymethyl)-1*H*-benzotriazole ($4a_4$) and 1-(1-*tert*-butoxy-2-methylpropenyl)-1*H*-benzotriazole ($4b_2$) since no reaction took place between di-*tert*-butyl peroxide and the respective lithiated 1-(1-alkenyl)benzotriazole substrates. These compounds were eventually synthesised by the reaction of the Grignard reagent (prepared *in situ* from the organolithium derivative and $MgBr_2$) and *tert*-butyl peroxybenzoate.[14] In the case of $4b_2$, another addition product ($4b_3$) was also isolated (13%) (see experimental section). As shown in Table 1, in general the yields of these products are very good, the only exception being the preparation of the sterically hindered *tert*-butoxy compounds.



Scheme 4

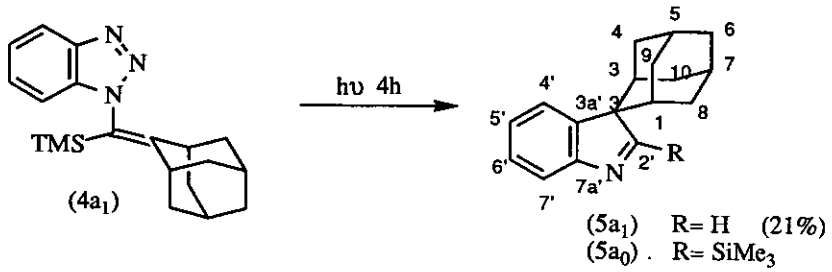
Note that $4a_8$ and $4a_9$ were formed by treatment of $4a_7$ with m-CPBA, $4a_8$ being formed initially, and then more slowly converting to $4a_9$ (see experimental).

Compound	Product	(E)	R_1	R_2	Yield (%)
3a	$4a_1$	$SiMe_3$	adamantyl	-	87
3a	$4a_2$	Cl	adamantyl	-	60
3a	$4a_3$	Br	adamantyl	-	93
3a	$4a_4$	*tert*-BuO	adamantyl	-	30(44)*
3a	$4a_5$	*tert*-BuS	adamantyl	-	66
3a	$4a_6$	PhS	adamantyl	-	86
3a	$4a_7$	MeS	adamantyl	-	85
$4a_7$	$4a_8$	MeSO	adamantyl	-	81
$4a_7$	$4a_9$	$MeSO_2$	adamantyl	-	41
3b	$4b_1$	Br	Me	Me	89
3b	$4b_2$	*tert*-BuO	Me	Me	27(30)*

Table 1: *Yields in parentheses are based on recovered starting material.

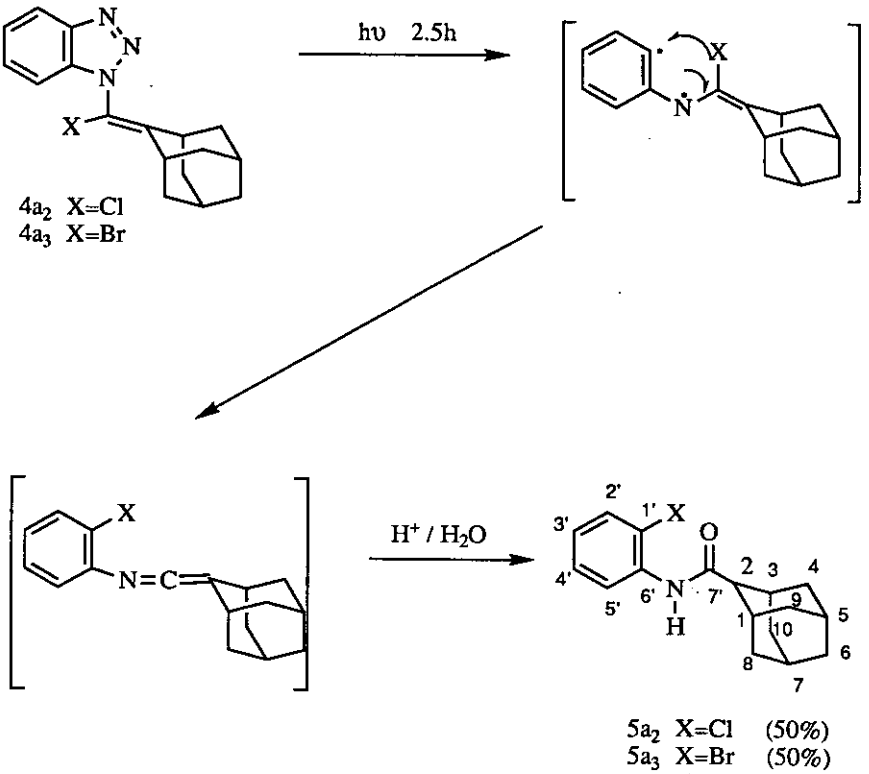
Photolyses of 1-(1-alkenyl)benzotriazoles

All the photolyses were conducted using pyrex glassware and dry acetonitile (see experimental section). Photolysis of $4a_1$ did not yield the expected indolenine ($5a_0$) but rather the desilylated product ($5a_1$) together with much recovered starting material. It is not known whether the desilylation occurs before or after the cyclisation step.



Scheme 5

As anticipated, photolyses of the 1-adamantylidene-halogenomethyl-1*H*-benzotriazoles ($4a_2$) and ($4a_3$) in each case led to the formation of amides, presumably *via* a keteneimine intermediate which results from the intramolecular transfer of Cl or Br to the intermediary aryl radical (Scheme 6).

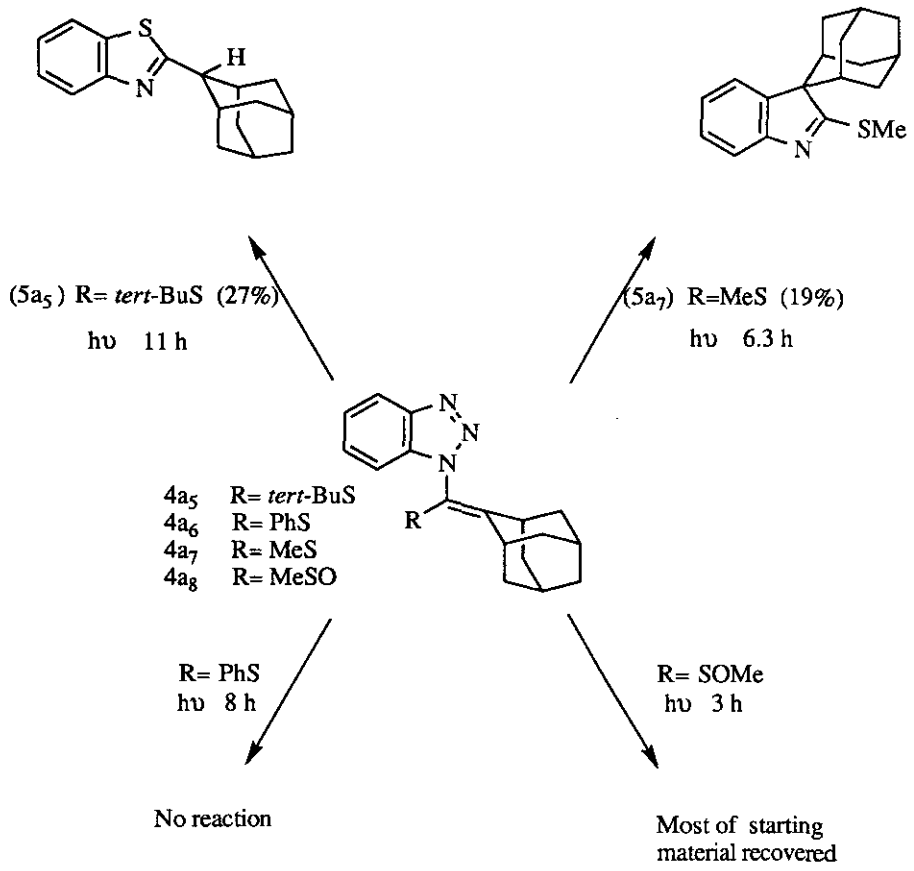


Scheme 6

This type of behaviour parallels the hydrogen transfer observed in thermal reactions studied by Barker and Storr[15] and Katritzky and co-workers.[16] In their flash pyrolysis studies of 1-pentylvinylbenzotriazoles, Barker

and Storr detected traces of *N*-phenylheptanamide, the product of the hydrolysis of the keteneimine intermediate. Katritzky and co-workers also detected keteneimines as intermediates in the flash vacuum pyrolysis (FVP) of *N*-vinylbenzotriazoles conducted at temperatures below 700°C.

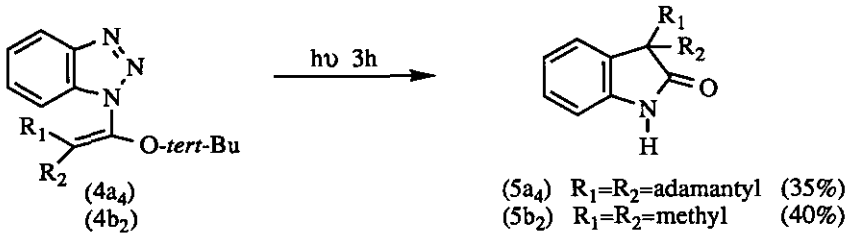
Photolyses of sulphur containing 1-(1-alkenyl)benzotriazoles (scheme 7) were disappointing, giving poor yields of isolated adducts.



Scheme 7

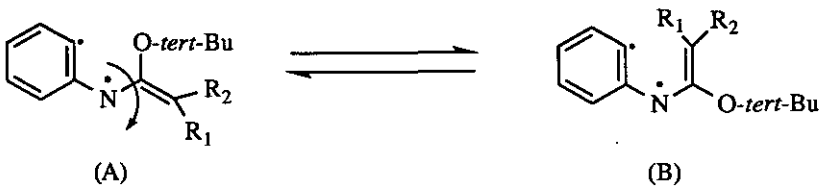
In the case of $4a_7$, only traces of $5a_5$ were detected after irradiation. The difference in behaviour of $4a_5$ and $4a_7$ can be understood by reference to Beckwith,[17] who argues that the rate of intramolecular homolytic substitution at sulphur, leading to $5a_5$, varies according to the alkyl group attached to sulphur in the order: benzyl> *tert*-butyl> methyl, which reflects the relative stabilisations of the expelled carbon radicals. Unfortunately, the photolyses of $4a_6$ and $4a_8$ did not prove very fruitful.

Surprisingly, photolyses of $4a_4$ and $4b_2$ afforded the respective oxindoles ($5a_4$) and ($5b_2$) directly, in moderate yields (Scheme 8), and the presumed intermediate, *tert*-butoxy-iminoether, could not be isolated.



Scheme 8

It is thought that the explanation for these moderate yields resides in the slow interconversion of two of the possible conformers of the diradical intermediate (Scheme 9), a process previously discussed by Barker and Storr.[15] Because of the very reactive nature of the aryl radical, cyclisation and/or fruitless side reactions perhaps occur much faster than the time required by the system to convert from (A) to (B), the conformation which would lead to the desired product.



Scheme 9

Conclusion

This publication reports a simple and efficient method for the preparation of α-heterosubstituted 1-(1-alkenyl)benzotriazoles. In the second part of this paper, the behaviour of 1-(1-alkenyl)benzotriazoles under photochemical conditions is investigated and reveals competing pathways of cyclisation and rearrangement.

EXPERIMENTAL SECTION

Proton (^1H) and carbon (^{13}C) nuclear magnetic resonance (nmr) spectra were recorded on GE QE-300 MHz and Bruker WP4W 400MHz spectrometers. Chemical shifts are reported in part per million (δ) relative to TMS (δ 0.0 ppm) in ^1H nmr and $CDCl_3$ (middle peak of triplet δ 77.0 ppm) in ^{13}C nmr. Infrared (ir) spectra were recorded on a Philips PU 9706 instrument as solutions in dichloromethane. Ultra-violet (uv) spectra were recorded on a PYE Unicam PU 8800. Mass spectra and accurate masses were obtained on a 70 eV VG Micromass 3D8 mass spectrometer. Microanalyses were determined by using a Carlo Erba Elemental Analyser MOD 1106. All the melting points were measured on a Kofler hot stage microscope and are uncorrected. Photolysis experiments were carried out in a Rayonet photochemical reactor, fitted with a high pressure mercury lamp, with the cooling fan on, unless otherwise indicated. Two varieties of silica gel were used in column chromatography purifications: Merck Kieselgel Silica gel 60G and Merck Flash Silica (230-400 mesh).

Trimethylsilanylchloride, diisopropylamine, acetonitrile were distilled from calcium hydride. *N, N*-Dimethylformamide and acetone were distilled and stored over 4Å molecular sieves. 1,2-Dibromoethane was distilled from calcium chloride and stored in the dark. n-Butyllithium was regularly titrated using diphenylacetic acid.[18]

1-Trimethylsilanylmethylbenzotriazole (2)

Benzotriazole (2.60 g, 21.6 mmol) was dissolved in dry DMF (10 ml) under a dry argon atmosphere. After benzotriazole had dissolved, NaH (0.888 g as a 60% dispersion in mineral oil, 22.22 mmol) was added slowly to the stirred solution. After NaH had reacted, the reaction mixture was cooled to 0°C and trimethylsilanylmethyltrifluoromethane sulphonate (4.23 g, 21.6 mmol) was introduced dropwise into the reaction flask. After all the trimethylsilanylmethyltrifluoromethane sulphonate had been added, the solution was stirred for 10 min at 0°C and was subsequently stirred at room temperature for 1.75 h. The reaction mixture was then transferred into a separating funnel using ether (2x30 ml) and was washed with water (3x20 ml), saturated $NaHCO_3$ solution (2x20 ml), brine (30 ml), dried with $MgSO_4$ and filtered. The crude mixture, obtained after removal of the solvent, was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. Two products were isolated: the title compound (2) as colourless crystals (2.35g, 53%) and 2-trimethylsilanylmethyl-2*H*-benzotriazole as a colourless oil (0.953 g, 22%).

1-Adamantylidenemethyl-1*H*-benzotriazole (3a)

Dry diisopropylamine (1.65 ml, 12 mmol) was dissolved in dry THF (45 ml), under a dry argon atmosphere and cooled to -78°C. n-BuLi (7.65 ml of a 1.47 M solution in hexanes, 11.24 mmol) was added dropwise with stirring. The mixture was stirred at -78°C for 15 min. 2 (2.16 g, 10.52 mmol) in dry THF (4 ml + 2x1 ml) was added dropwise with stirring to the LDA solution, at -78°C. The solution turned blue instantly and was stirred at -78°C for 1.5 h. 2-Adamantanone (1.61 g, 10.7 mmol), in dry THF (5 ml + 2x1 ml), was added and the reaction mixture was stirred at -78°C for 15 min before it was allowed to warm to room temperature over 2 h and subsequently was stirred at room temperature overnight (until the deep blue colour was discharged to brown). Ether (150 ml) and saturated NH_4Cl solution (40 ml) were added. The organic layer was washed successively with saturated NH_4Cl (2x30 ml), brine (30 ml) dried with $MgSO_4$ and filtered. Removal of the solvent under reduced pressure yielded a bright brown oil, which was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. 3a was isolated in 90% yield (2.51 g, mp 130 - 131°C); ^1H nmr (90 MHz, $CDCl_3$, δ): 8.05 (1H, d, J= 8 Hz, H-4), 7.60-7.30 (3H, m, H-5, H-6, H-7), 6.80 (1H, s, H-11), 2.75 (2H, br s, H-1, H-3), 2.20-1.80 (12H, m, adamantyl CH and CH_2); ^{13}C nmr (22.5 MHz, δ in ppm): 154.17 (C-2), 145.23 (C-3'a), 133.59 (C-7'a), 127.68 (C-6'), 123.81 (C-5'), 119.80 (C-4'), 109.78 (C-11), 109.45 (C-7'), 39.70, 39.22 (C-8, C-9, and C-4, C-10), 38.78, 36.72 (C-1, C-3), 37.21 (C-6), 28.05 (C-5, C-7); ms (%) 265 (M^+, 25), 238 (19), 237 (100, M-N_2), 236 (49), 194 (29), 180 (66), 134 (36, M-$C_6H_5N_3$), 119 (28, $C_6H_5N_3$), 104 (28, C_7H_6N), 79 (41), 77 (87), 41 (39); ir (cm^{-1})1450, 1150, 1080, 1050, 990, 950; Accurate Mass ($C_{17}H_{19}N_3$): calcd: 265.1571, found: 265.1578.

1-2-Methylpropenyl-1*H*-benzotriazole (3b)

The same procedure as the one described above was employed to prepare 3b in 90% yield.

1-Adamantyiledenetrimethylsilanylmethyl-1*H*-benzotriazole ($4a_1$)

3a (0.300 g, 1.13 mmol) was dissolved in dry THF (10 ml), under a dry argon atmosphere. The mixture was cooled to -78°C over 20 min. n-BuLi (0.84 ml of a 1.55 M solution in hexanes, 1.3 mmol) was added dropwise with stirring, at -78°C and the solution was stirred at -78°C for 90 min (the solution turned lime green). TMSCl (0.72 ml, 5.66 mmol), dissolved in dry THF (0.8 ml + 2x0.20 ml), was added dropwise. The reaction mixture was stirred at -78°C for 10 min, and then was allowed to warm to room temperature over 1 h. The reaction mixture turned pink and then colourless. Ether was added (30 ml). The organic layer was successively washed with saturated NH_4Cl (3x20 ml), brine (20 ml), dried with $MgSO_4$ and filtered. After

removal of the solvent, the crude mixture was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. $4a_1$ was isolated in 87% yield (331 mg, mp 155.3-155.7°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.05 (1H, d, J= 8 Hz, H-4), 7.32-7.45 (3H, m, H-7, H-5, H-6), 3.05 (1H, br s, adamantyl), 1.60-2.10 (13H, m, adamantyl), 0.10 (9H, s, TMS);^{13}C nmr (75 MHz, δ in ppm): 168.70 (C-2), 145.36 (C-3'a), 134.02 (C-7'a), 127.00 (C-8'), 125.03 (C-6'), 123.43 (C-5'), 119.77 (C-4'), 109.80 (C-7'), 39.64, 39.41, 39.23, 39.18, 36.54 (CH_2 adamantyl), 36.23, 33.67, 27.84, 27.76 (CH adamantyl), -0.60 (TMS); ms (%): 337 (M^+), 322 (8), 309 (32), 294 (11), 268 (8), 252 (15), 232 (19), 194 (9), 176 (5), 167 (12), 149 (11), 135 (7), 105 (10) ,91 (84), 80 (28), 73 (57), 65 (16), 51 (16); ir (cm^{-1}): 3070, 3000, 2940, 1430, 1270, 740; uv (in MeOH): λ_{max}= 208 nm, ε= 26945 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 260 nm, ε= 7567 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{20}H_{27}N_3Si$ (%): C 71.17, H 8.06, N 12.45. Found: C 70.85, H 7.75, N 12.55.

1-Adamantylidenechloromethyl-1*H*-benzotriazole ($4a_2$)

This compound was obtained by the above procedure using 2 (104 mg, 0.39 mmol), dry THF (10 ml), n-BuLi (0.29 ml of a 1.47 M solution in hexanes, 0.43 mmol) and sulphuryl chloride (0.16 ml, 1.96 mmol). The crude reaction mixture was purified by column chromatography, using silica gel, eluting with 10% ether / hexane. $4a_2$ was isolated in 60% yield (70 mg, mp 72.9-74.7°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.15 (1H, d, J= 8 Hz, H-4), 7.60-7.45 (3H, m, H-7, H-5, H-6), 3.40 (1H, br s, adamantyl), 2.15-1.75 (13H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 151.82 (C-2), 145.19 (C-3'a), 132.90 (C-7'a), 128.35 (C-6'), 124.35 (C-5'), 120.03 (C-4'), 109.83 (C-7'), 109.16 (C-8'), 38.86(2), 38.20(2), 36.16(1), (CH_2 adamantyl), 34.52(1), 34.21(1), 27.37(2) (CH adamantyl); ms (%): 301 (M^+, ^{37}Cl), 299 (M^+, ^{35}Cl), 273 (35), 271 (100), 236 (77) 214 (73), 194 (28), 180 (23), 143 (30), 117 (33), 91 (82), 77 (74), 65 (23), 41 (33); ir (cm^{-1}): 3050, 2920, 2850, 1450, 1260, 745; uv (in MeOH): λ_{max}= 206 nm, ε= 22311 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 250 nm, ε= 6877 $cm^{-1}mol^{-1}dm^3$; Accurate Mass ($C_{17}H_{18}N_3Cl$): calcd: 299.1202, found: 299.1189.

1-Adamantylidenebromomethyl-1*H*-benzotriazole ($4a_3$)

This compound was obtained by the above procedure using 3a (316 mg, 1.19 mmol), dry THF (15 ml), n-BuLi (0.89 ml of a 1.47 M solution in hexanes, 1.31 mmol) and *N*-bromosuccinimide (1.06 g, 5.96 mmol). The crude reaction mixture was purified by column chromatography, using silica gel, eluting with 10% ether / hexane. $4a_3$ was isolated in 93% yield (380 mg, mp 126.5-126.9°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.10 (1H, d, J= 8 Hz, H-4), 7.60-7.45 (3H, m, H-7, H-5, H-6), 3.35 (1H, br s, adamantyl), 2.20-1.60 (13H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 155.88 (C-2),

145.30 (C-3'a), 132.85 (C-7'a), 128.38 (C-6'), 124.47 (C-5'), 120.14 (C-4'), 110.14 (C-7'), 97.56 (C-8'), 38.98(2), 38.34(2), 36.24(1), (CH_2 adamantyl), 37.16(1), 35.11(1), 27.48(2) (CH adamantyl); ms (%): 345 (M^+, ^{81}Br), 343 (M^+, ^{79}Br), 317 (18), 315 (18), 260 (15), 258 (13), 36 (100), 204 (7), 194 (14), 180 (11), 167 (7), 149 (6), 134 (15), 117 (12), 105 (14), 91 (47), 77 (30), 41 (21); ir (cm^{-1}): 3050, 2920, 2850, 1450, 1265, 740; uv (in MeOH): λ_{max}= 206 nm, ε= 22934 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 249 nm, ε= 7204 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{17}H_{18}N_3Br$ (%): C 59.31, H 5.27, N 12.21. Found: C 58.85, H 5.15, N 12.15; Accurate Mass ($C_{17}H_{18}N_3{}^{79}Br$): calcd: 343.0684, found: 343.0674; ($C_{17}H_{18}N_3{}^{81}Br$): calcd: 345.0663, found: 345.0672.

1-Adamantylidene-*tert*-butylsulphanylmethyl-1*H*-benzotriazole ($4a_5$)

This compound was obtained by the above procedure using 3a (500 mg, 1.89 mmol), dry THF (20 ml), n-BuLi (1.30 ml of a 1.6 M solution in hexanes, 2.08 mmol) and *tert*-butyl disulphide (1.82 ml, 9.43 mmol). The crude reaction mixture was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. $4a_5$ was isolated in 66% yield (435 mg, mp 110.1-111.1°C); ^1H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.05 (1H, d, J= 8 Hz, H-4), 7.70 (1H, d, J= 8 Hz, H-7), 7.50 (1H, t, J= 8 Hz, H-5 or H-6), 7.35 (1H, t, J= 8 Hz, H-5 or H-6), 3.75 (1H, br s, adamantyl), 1.75-2.20 (13H, m, adamantyl), 1.15 (9H, s, *tert*-butyl); ^{13}C nmr (75 MHz, δ in ppm): 164.45 (C-2), 146.25 (C-3'a), 134.94 (C-7'a), 127.20 (C-6'), 123.78 (C-5'), 119.67 (C-4'), 116.07 (C-8'), 111.52 (C-7'), 47.66 (C-9'), 39.42(2), 39.35(2), 36.59 (CH_2 adamantyl), 36.59, 34.76, 27.73(2) (CH adamantyl), 30.79 (*tert*-butyl); ms (%): 353 (M^+), 297 (12), 268 (29), 236 (9), 226 (5), 212 (10), 178 (100), 166 (25), 149 (5), 133 (6), 109 (5), 91 (22), 77 (12), 65 (6), 57 (36), 41(26); ir (cm^{-1}): 2940, 2870, 1470, 1370, 1175, 1080; uv (in EtOH): λ_{max}= 206 nm, ε= 24598 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 254 nm, ε= 10407 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{21}H_{27}N_3S$ (%): C 71.34, H 7.70, N 11.89, S 9.07. Found : C 71.25, H 7.95, N 12.00, S 9.15.

1-Adamantylidenephenylsulphanylmethyl-1*H*-benzotriazole ($4a_6$)

This compound was obtained by the above procedure using 3a (300 mg, 1.13 mmol), dry THF (10 ml), n-BuLi (0.84 ml of a 1.55 M solution in hexanes, 1.30 mmol) and phenyl disulphide (1.24 g, 5.66 mmol). The crude reaction mixture was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. $4a_6$ was isolated in 86% yield (240 mg, mp 128.3-130.1°C); ^1H nmr (300 MHz, $CDCl_3$, δ in ppm): 7.95 (1H, d, J= 8 Hz, H-4), 7.45 (1H, d, J= 8 Hz, H-7), 7.35 (1H, t, J= 8 Hz, H-5 or H-6), 7.25 (3H, m, H-5 or H-6 and 2xo-H), 7.10 (3H, 2xm-, p-H), 3.70 (1H, br s, adamantyl), 1.70-2.20 (12H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 162.63 (ipso C), 145.21 (C-3a'),

133.14, 133.00 (C-2, C-7a'), 129.80, 128.83 (o, m-C), 127.36 (p-C), 126.91 (C-6'), 123.73 (C-5'),.119.69 (C-4'), 114.76 (C-8'), 110.60 (C-7'), 39.38 (2), 39.33(2), 36.43 (CH_2 adamantyl), 36.01, 34.90, 27.67 (2) (CH adamantyl); ms (%): 373 (M^+), 345 (21), 312 (6), 288 (9), 268 (100), 243 (10), 236 (17), 212 (9), 194 (9), 184 (16), 166 (19), 152 (6), 133 (6), 117 (7), 109 (13), 91 (34), 77 (28), 65 (12), 51 (9), 41 (16); ir (cm^{-1}): 3060, 2990, 2920, 2300, 1440, 1260, 900, 730; uv (in MeOH): λ_{max}= 207 nm, ε= 30213 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 244 nm, ε= 16412 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd. for $C_{23}H_{23}N_3S$ (%): C 73.96, H 6.21, N 11 25, S 8.58. Found: C 73.65, H 6.25, N 11.50 , S 8.70.

1-Adamantylidenemethylsulphanylmethyl-1*H*-benzotriazole ($4a_7$)

This compound was obtained by the above procedure using 3a (142 mg, 0.54 mmol), dry THF (10ml), n-BuLi (0.40 ml of a 1.55 M solution) and methyl disulphide (0.25 ml, 2.68 mmol). The crude reaction mixture was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. $4a_7$ was isolated in 85% yield (143 mg, mp 79.8-81.0°C), ^1H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.05 (1H, d, J= 8 Hz, H-4), 7.60 (1H, d, J= 8 Hz, H-7), 7.45 (1H, t, J= 8 Hz, H-5 or H-6), 7.35 (1H, t, J= 8 Hz, H-5 or H-6), 3.60 (1H, br s, adamantyl), 1.60-2.10 (13H, m, adamantyl and methyl protons); ^{13}C nmr (75 MHz, δ in ppm): 158.29 (C-2), 145.21 (C-3'a), 132.95 (C-7'a), 127.50 (C-6'), 123.87 (C-5'), 119.63 (C-4'), 116.27 (C-8'), 110.21 (C-7'), 38.99(2), 38.92(2), 36.27 (CH_2 adamantyl), 35.33, 34.27, 27.54(2) (CH adamantyl), 15.88 (methyl); ms (%): 311 (M^+), 268 (100), 237 (36), 226 (6), 212 (8), 193 (9), 181 (31), 133 (6), 117 (8), 91 (31), 77 (27), 65 (9), 41 (20); ir (cm^{-1}): 2940, 2860, 1460, 1070; uv (in MeOH): λ_{max}= 206 nm, ε= 22634 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 254 nm, ε= 10664 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{18}H_{21}N_3S$ (%): C 69.42, H 6.80, N 13.49, S 10.29. Found: C 69.65, H 6.90, N 13.40, S 10.00.

1-1-Bromo-2-methylpropenyl-1*H*-benzotriazole ($4b_1$)

This compound was obtained by the above procedure using 3b (150 mg, 0.87 mmol), dry THF (10 ml), n-BuLi (0.60 ml of a 1.60 M solution in hexanes, 0.96 mmol) and *N*-bromosuccinimide (308 mg, 1.73 mmol). The crude reaction mixture was purified by column chromatography, using Kieselgel, eluting with 10% ether / hexane. $4b_1$ was isolated in 89% yield (194 mg, mp 61.4-62.4°C); ^1H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.15 (1H, d, J= 8 Hz, H-4), 7.60 (2H, m), 7.45 (1H, m, H-7, H-5, H-6), 2.20 (3H, s, methyl(b)), 1.70 (3H, s, methyl(a)); ^{13}C nmr (75 MHz, δ in ppm):145.21 (C-3'a(2)), 141.55 (C-9'(2)), 132.52 (C-7'a(2)), 128.41 (C-6'(2)), 124.57 (C-5'(2)), 120.17 (C-4'), 120.07 (C-4'), 110.30 (C-7'(2)), 104.74 (C-8'(2)), 33.47, 30.02, 23.86, 20.65 (methyl groups). ^{13}C revealed that $4b_1$ exists as an

equilibrium of two rotamers; ms (%): 253 (M^+, 37), 251 (M^+, 37), 224 (100), 222 (92), 210 (77), 208 (81), 184 (50), 182 (53), 172 (21), 157 (22), 155 (23), 144 (72), 103 (73), 91 (59), 76 (88) 50 (94), 41 (61); ir (cm^{-1}): 3040, 2980, 2900, 1600, 1440, 1370, 1270, 1160, 1030, 835, 740; uv (in MeOH): λ_{max}= 216 nm, ε= 11011 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 252 nm, ε= 7406 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{10}H_{10}N_3Br$ (%): C 47.55, H 3.99, N 16.63, Br 31.83. Found: C 47.35, H 4.10, N 16.50, Br 31.65; Accurate Mass ($C_{10}H_{10}N_3{}^{79}Br$): calcd: 251.0058, found: 251.0060; ($C_{10}H_{10}N_3{}^{81}Br$): calcd: 253.0037, found: 253.0040.

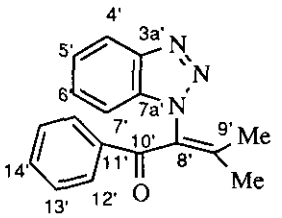
1-Adamantylidene-*tert*-butoxymethyl-1*H*-benzotriazole ($4a_4$)

3a (385 mg, 1.45 mmol) was dissolved in dry THF (10 ml), under a dry atmosphere of argon. It was cooled to -78°C over 20 min. n-BuLi (1.0 ml of a 1.60 M solution in hexanes, 1.60 mmol) was added dropwise with stirring, at -78°C. The mixture was stirred at -78°C for 90 min (the solution turned yellow instantly). In another flask (fitted with a condenser), magnesium turnings (42 mg, 1.75 mmol) were placed in dry THF (2.5 ml + 2 x 0.25 ml) under a dry atmosphere of argon, at room temperature. Dry 1,2-dibromoethane (1.74 mmol, 0.15 ml) was added to the magnesium turnings. After all the magnesium had reacted, the solution of the Grignard reagent was transferred by canulation into the flask containing the lithium salt. The reaction mixture was stirred at -78°C for 10 min before being allowed to warm -10°C and then stirred at -10°C for 1.5 h. *tert*-Butyl peroxybenzoate (7.26 mmol, 1.38 ml) in dry THF (1.4 ml) was added dropwise and the reaction mixture kept between -10° and -5°C. The mixture was then allowed to warm to 0 - +5°C and stirred at this temperature for 1.5 h. It was subsequently stirred at room temperature for 0.5 h. Removal of the solvent under reduced pressure yielded an oil which was purified by column chromatography, using silica gel, eluting with 10% ether / hexane. A second column was required (using Kieselgel, eluting with 98% toluene / ether) to isolate $4a_4$ in pure form and in 30% yield (141 mg, mp 157.2-159.8°C); ^1H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.05 (1H, d, J= 8 Hz, H-4), 7.70 (1H, d, J= 8 Hz, H-7), 7.50 (1H, t, J= 8 Hz, H-5 or H-6), 7.40 (1H, t, J= 8 Hz, H-5 or H-6), 3.25 (1H, br s, adamantyl), 1.75-2.20 (13H, m, adamantyl), 1.10 (9H, s, *tert*-butyl); ^{13}C nmr (75 MHz, δ in ppm): 145.33 (C-3'a), 135.59, 133.48 (C-2, C-8'), 129.45 (C-7'a), 127.62 (C-6'), 123.88 (C-5'), 119.63 (C-4'), 110.95 (C-7'), 77.20 (C-9'), 38.96(1), 38.87(1), 38.69(1), 36.77(2), (CH_2 adamantyl), 31.67, 3141, 27.93(2) (CH adamantyl), 28.20 (*tert*-butyl); ms (%): 337 (M^+), 317, 310, 281 (28), 264 (9), 253 (13), 225 (63), 162 (100), 146 (17), 133 (24), 118 (28), 105 (35), 91 (75), 79 (46), 57 (83), 41 (59); ir (cm^{-1}): 3050, 2980, 2920, 1265, 740; uv (in EtOH): λ_{max}= 208 nm, ε= 23456 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 252 nm, ε= 6605 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{21}H_{27}N_3O$ (%): C 74.74, H 8.06, N 12.45. Found: C 74.60, H 8.15, N 12.40.

1-(1-*tert*-Butoxy-2-methylpropenyl)-1*H*-benzotriazole ($4b_2$)

This compound was obtained by the above procedure using $4a_4$ (280 mg, 1.62 mmol), dry THF (10 ml), n-BuLi (1.11 ml of a 1.60 M solution in hexanes, 1.78 mmol), 1,2-dibromoethane (0.16 ml, 1.78 mmol), dry magnesium turnings (48 mg, 1.94 mmol) and *tert*-butyl peroxybenzoate (0.37 ml, 1.94 mmol). The crude reaction mixture was purified by column chromatography, using Kieselgel, eluting with 15% ether / hexane. $4b_2$ was isolated in 27% yield (107 mg, mp 46.1-47.2°C). Addition product ($4b_3$) was isolated as well (57 mg, 13%, mp 102.0-102.7°C); ($4b_2$) ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.05 (1H, d, J= 8 Hz, H-4), 7.65 (1H, d, J= 8 Hz, H-7), 7.55 (1H, t, J= 8 Hz, H-5 or H-6), 7.40 (1H, t, J= 8 Hz, H-5 or H-6), 2.00 (3H, s, methyl(b)), 1.60 (3H, s, methyl(a)), 1.10 (9H, s, *tert*-butyl); ^{13}C nmr (75 MHz, in ppm): 145.23 (C-3'a), 135.44 (C-9'), 133.15 (C-7'a), 127.70 (C-6'), 123.98 (C-5'), 120.57 (C-8'), 119.63 (C-4), 111.21 (C-7'), 80.96 (C-10'), 28.11 (C-11'), 18.72, 18.22 (methyl groups); ms (%): 245 (M^+, 3), 230, 189 (72), 176 (30), 160 (36), 146 (32), 132 (19), 120 (100), 91 (71), 77 (8), 70 (94), 64 (19), 57 (93), 50 (14), 41 (84); ir (cm^{-1}): 3050, 2960, 1440, 1360, 1140, 740; uv (in MeOH): λ_{max}= 214 nm, ε= 9967 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 254 nm, ε= 6146 $cm^{-1}mol^{-1}dm^3$; Anal. Calcd for $C_{14}H_{29}N_3O$ (%): C 68.54, H 7.81, N 17.13. Found: C 68.35, H 7.70, N 17.15; Accurate Mass ($C_{14}H_{29}N_3O$): calcd: 245.1528, found: 245.1521.

Addition product: 2-Benzotriazol-1-yl-3-methyl-1-phenylbut-2-en-1-one ($4b_3$)



^{1}H Nmr (300 MHz, $CDCl_3$, δ in ppm): 7.90 (1H, d, J= 8 Hz, H-4), 7.80 (2H, d, J= 8 Hz, H-7+H-5 or H-6), 7.40-7.20 (7H, m, H-5 or H-6 and phenyl protons), 2.10 (3H, s, methyl(b)), 1.80 (3H, s, methyl(a)); ^{13}C nmr (75 MHz, δ in ppm): 191.42 (C-10'), 147.14 (C-11'), 145.25 (C-3a'), 136.35 (C-7a'), 133.58 (C-9'), 133.39(C-6'), 129.08, 128.53 (C-12' and C-13'), 128.88 (C-8'), 128.20 (C-5'),.124.06 (C-14'), 119.98 (C-4'), 110.05 (C-7'), 21.70, 21.37 (methyl groups); ms (%): 277 (M^+), 263 (7), 248 (31), 234 (17), 220 (66), 208 (24), 180 (21), 160 (40), 120 (17), 105 (100), 91 (21), 77(84); ir (cm^{-1}): 2940, 1660, 1440, 1120, 1060. Accurate Mass ($C_{17}H_{15}N_3O$) : calcd: 277.1215, found: 277.1214.

1-Adamantylidenemethanesulphinylmethyl-1*H*-benzotriazole ($4a_8$)

1-Adamantylidenemethylsulphanylmethyl-1*H*-benzotriazole ($4a_7$) (169 mg, 0.54 mmol) was dissolved in DCM (10 ml) and 10% solution of potassium carbonate (7 ml). The reaction mixture was vigourously stirred at room temperature for 5 min and m-CPBA (188 mg, 1.09 mmol) was added to it. The subsequent reaction mixture was stirred for 5 h at room temperature. The reaction was quenched by addition of sodium sulphite (10 ml) and DCM (40 ml). The organic layer was separated and the aqueous layer was extracted with DCM (20 ml). The combined organic portions were washed with water (3x20 ml), brine (25 ml), dried with $MgSO_4$ and filtered. The crude mixture was then purified by column chromatography, using silica gel, eluting with 30% ethylacetate / hexane. $4a_7$ was isolated in 81% yield (142 mg, mp 124.6C-125.7°C) and 13 mg of $4a_9$ were also obtained. ^{1}H Nmr (300 MHz, $CDCl_3$, δ in ppm): 8.00 (1H, d, J= 8 Hz, H-4), 7.60 (1H, d, J= 8 Hz, H-7), 7.45 (1H, t, J= 8 Hz, H-5 or H-6), 7.25 (1H, t, J= 8 Hz, H-5 or H-6), 3.60 (1H, br s, adamantyl), 1.60-2.10 (13H, m, adamantyl), 2.55 (3H, s, methyl protons); ^{13}C nmr (75 MHz, δ in ppm):165.97 (C-2), 144.70 (C-3'a), 135.90 (C-7'a), 128.36 (C-6'), 126.18 (C-8'),.124.08 (C-5'), 119.19 (C-4'), 110.69 (C-7'), 39.13, 38.98, 38.92, 38.85, 35.68 (CH_2 adamantyl), 34.17, 34.06, 27.10(2) (CH adamantyl), 37.97(C-9'); ms (in %): 328 (M^+, 1), 311 (13), 264 (100), 237 (29), 194 (30), 180 (36), 168 (21), 156 (18), 142 (16), 130 (18), 116 (11), 105 (19), 91 (55), 77 (46), 55 (18), 41 (36); ir (cm^{-1}): 3050, 2920, 2850, 1610, 1450, 1265, 1060, 745; uv (in MeOH): λ_{max}= 208 nm, ε= 25197 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 250 nm, ε= 8070 $cm^{-1}mol^{-1}dm^3$; Accurate Mass ($C_{18}H_{21}N_3OS$) : calcd: 327.1405, found: 327.1399.

1-Adamantylidenemethanesulphonylmethyl-1*H*-benzotriazole ($4a_9$)

This compound was obtained by a similar procedure using $4a_7$ (133 mg, 0.43 mmol), 10% solution of potassium carbonate (7 ml), m-CPBA (185 mg, 1.07 mmol). The reaction mixture was stirred at room temperature for 26 h. The crude mixture was purified by column chromatography, using silica gel, eluting with 30 % ethylacetate / hexane. $4a_9$ was isolated in 41% yield (60 mg, mp 186.4-187.0°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.10 (1H, d, J= 8 Hz, H-4), 7.60 (1H, m, H-7), 7.45 (2H, m, H-5, H-6), 4.35 (1H, br s, adamantyl), 1.60-2.20 (13H, m, adamantyl), 3.10 (3H, s, methyl protons); ^{13}C nmr (75 MHz, δ in ppm):172.10 (C-2), 145.31 (C-3'a), 134.88 (C-7'a), 128.90 (C-6'), 124.58 (C-5'), 123.98 (C-8'), 119.99 (C-4'), 110.24 (C-7'), 42.82 (C-9'), 39.99, 39.44, 39.54, 39.34, 35.85 (CH_2 adamantyl), 35.56, 33.19, 27.02, 26.93 (CH adamantyl); ms (%): 343 (M^+, 9), 264 (100), 252 (18), 236 (20), 213 (9), 151 (46), 117 (12), 104 (14), 91 (34), 77 (31), 41 (26); ir (cm^{-1}): 3050, 2980, 2920, 2850, 1650, 1450, 1320, 1265, 1145, 740; uv (in MeOH): λ_{max}= 206 nm, ε= 21162 $cm^{-1}mol^{-1}dm^3$, λ_{max}= 248 nm, ε= 7193 $cm^{-1}mol^{-1}dm^3$.

Accurate Mass ($C_{18}H_{21}N_3O_2S$): calcd: 343.1354, found: 343.1345.

Photolysis of 1-adamantylidenetrimethysilanylmethyl-1*H*-benzotriazole ($4a_1$)

$4a_1$ (0.100 g, 0.30 mmol) was dissolved in dry acetonitrile (10 ml) under an atmosphere of dry argon. The solution was subsequently subjected to ultrasound for 20 min under a positive pressure of dry argon and photolysed in a pyrex vessel for 4 h (fan off). Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. The cyclised product ($5a_1$) was isolated in 21% yield (15 mg, mp 84.4-84.9°C) and much starting material was recovered (56 mg). ^{1}H Nmr (300 MHz, $CDCl_3$, δ in ppm): 8.75 (1H, s, H-2'), 7.90 (1H, d, J= 8 Hz, H-4), 7.70 (1H, d, J= 8 Hz, H-7), 7.40 (1H, t, J= 8 Hz, H-5 or H-6), 7.30 (1H, t, J= 8 Hz, H-5 or H-6), 1.60-2.55 (14H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm):176.86 (C-2'), 155.11 (C-3'a), 143.10 (C-7'a), 127.54 (C-6'), 126.00 (C-5'), 124.95 (C-4'), 121.38 (C-7'), 63.29 (C-3'), 38.79, 36.55(2), 33.26(2) (CH_2 adamantyl), 33.26(2), 27.67, 26.85 (CH adamantyl); ms (%): 237 (M^+), 222 (5), 194 (13), 180 (24), 168 (11), 156 (6), 143 (6), 130 (6), 115 (6); ir (cm^{-1}): 3070, 3000, 2310, 1430, 1265, 900, 740; Anal. Calcd for $C_{17}H_{19}N$ (%): C 86.00, H 8.10, N 5.90. Found: C 85.00, H 8.10, N 5.90; Accurate Mass ($C_{17}H_{19}N$): calcd 237.15183, found: 237.15175.

Photolysis of 1-adamantylidenechloromethyl-1*H*-benzotriazole ($4a_2$)

$4a_2$ (0.056 g, 0.19 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 2.5 h (fan on) according to the procedure described above. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using Kieselgel, eluting with 5% ether / hexane. $5a_2$ was isolated in 50% yield (27 mg, mp 129.5-131.5°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.45 (1H, d, J= 8 Hz, H-5'), 7.95 (1H, br s, N-H), 7.35 (1H, d, J= 8 Hz, H-2'), 7.30 (1H, dd, J= 8 Hz, J= 8 Hz, H-3' or H-4'), 7.05 (1H, dd, J= 8 Hz, J= 8 Hz, H-3' or H-4'), 2.75 (1H, br s), 2.40 (2H, br s), 2.10-1.60 (11H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 172.44 (C-7'), 134.74 (C-6'), 128.87, 127.72, 124.20, 121.46 (C-2', C-3', C-4', C-5'), 122.66 (C-1'), 51.30 (C-2), 38.27(2), 37.23(1), 33.29(2) (CH_2 adamantyl), 30.17(2), 27.39, 27.35 (CH adamantyl); ms (%): 291 (M^+, 3), 289 (M^+, 10), 254 (14), 211 (43), 162 (45), 135 (100), 127 (36), 107 (06), 93 (21), 79 (22), 67 (21), 41 (15); ir (cm^{-1}): 3050, 2900, 1680, 1500, 1420, 1250, 735; Accurate Mass ($C_{17}H_{20}NOCl$): calcd: 289.1233, found: 289.1240.

Photolysis of 1-adamantylidenebromomethyl-1*H*-benzotriazole ($4a_3$)

$4a_3$ (0.071 g, 0.21 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 2.5 h, according to the

procedure described above. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using Kieselgel, eluting with 10% ether / hexane. $5a_3$ was isolated in 50% yield (35 mg, mp 128.2-130.2°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.45 (1H, d, J= 8 Hz, H-5'), 7.95 (1H, br s, N-H), 7.55 (1H, d, J= 8 Hz, H-2'), 7.30 (1H, dd, J= 8 Hz, J= 8 Hz, H-3' or H-4'), 6.95 (1H, dd, J= 8 Hz, J= 8 Hz, H-3' or H-4'), 2.75 (1H, br s), 2.45 (2H, br s), 2.10-1.60 (11H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 172.41 (C-7'), 135.85 (C-6'), 132.09, 128.35, 124.74, 121.76 (C-2', C-3', C-4', C-5'), 113.41 (C-1'), 51.33 (C-2), 38.28(2), 37.25(1), 33.33(2) (CH_2 adamantyl), 30.14(2), 27.40, 27.37 (CH adamantyl); ms (%): 335 (M^+, 6), 333 (M^+, 6), 254 (32), 211 (18), 173 (23), 171 (24), 162 (42), 135 (100), 93 (23), 91 (23), 79 (23), 67 (21), 41 (14); ir (cm^{-1}): 3050, 2900, 1680, 1500, 1420, 1250, 735; Anal. Calcd for $C_{17}H_{20}NOBr$ (%): C 61.09, H 6.03, N 4.19, Br 23.91. Found: C 61.20, H 6.15, N 4.10, Br 23.95; Accurate Mass ($C_{17}H_{20}NO^{79}Br$): calcd: 333.0728, found: 333.0739; ($C_{17}H_{20}NO^{81}Br$): calcd: 335.0707, found: 335.0713.

Photolysis of 1-adamantylidene-*tert*-butylsulphanylmethyl-1*H*-benzotriazole ($4a_5$)

$4a_5$ (0.100 g, 0.28 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 11 h (fan on) according to the procedure described above. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using silica gel, eluting with 5% ether / hexane. $5a_5$ was isolated in 27% yield (20 mg, mp 110.4-112.2°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.05 (1H, d, J= 8 Hz, H-4), 7.90 (1H, d, J= 8 Hz, H-7), 7.45 (1H, t, J= 8 Hz, H-5 or H-6), 7.35 (1H, t, J= 8 Hz, H-5 or H-6), 3.40 (1H, br s, adamantyl), 2.60 (2H, s, adamantyl), 1.60-2.10 (13H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 176.33 (C-2'), 153.29 (C-3'a), 134.90 (C-7'a), 125.59 (C-6'), 124.44 (C-5'), 122.62 (C-4'), 121.41 (C-7'), 49.60 (C-3'), 38.53(2), 37.58(2), 32.60 (CH_2 adamantyl), 32.54 (2), 27.86, 27.60 (CH adamantyl); ms (%): 269 (M^+), 226 (16), 212 (14), 201 (11), 186 (15), 175 (18), 162 (26), 149 (78), 136 (19), 109 (15), 91 (34), 71 (4), 77 (27), 65 (18), 53 (12); ir (cm^{-1}): 3080, 3000, 2320, 1430, 1270, 900, 740; Anal. Calcd for $C_{17}H_{19}NS$ (%): C 75.79, H 7.11, N 5.20, S 11.90. Found: C 75.35, H 7.20, N 4.90, S 11.70.

Photolysis of 1-adamantylidenephenylsulphanylmethyl-1*H*-benzotriazole ($4a_6$)

$4a_6$ (0.100 g, 0.28 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 8 h (fan on) according to the procedure described above. The reaction was very messy and no product was detected.

Photolysis of 1-adamantylidenemethylsulphanylmethyl-1*H*-benzotriazole ($4a_7$)

$4a_7$ (0.120 g, 0.38 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 6.3 h (fan on) according to

the procedure described above. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using silica gel, eluting with 5% ether / hexane. $5a_7$ was isolated in 19% yield (20 mg, mp 103.6-104.6°C) as well as $5a_5$ (8 mg). ^{1}H Nmr (300 MHz, $CDCl_3$, δ in ppm): 7.80 (1H, d, J= 8 Hz, H-4), 7.45 (1H, d, J= 8 Hz, H-7), 7.30 (1H, t, J= 8 Hz, H-6), 7.10 (1H, t, J= 8 Hz, H-5), 3.10 (2H, d, J= 14 Hz, adamantyl), 2.75 (2H, d, J= 14 Hz, adamantyl), 2.65 (3H, s, methyl), 1.60-2.15 (10H, m, adamantyl); ^{13}C nmr (75 MHz, δ in ppm): 186.43 (C-2'), 154.08 (C-3'a), 143.98 (C-7'a), 127.59 (C-6' and C-5'), 122.55 (C-4'), 118.89 (C-7'), 68.21 (C-3'), 40.01, 33.83(2), 33.51(2) (CH_2 adamantyl), 32.97 (2), 27.96, 26.45 (CH adamantyl), 16.57 (methyl); ms (%): 283 (M^+,46), 268 (100), 250 (13), 236 (13), 194 (6), 148 (15), 128 (7), 115 (8), 91 (7), 79 (10), 41 (12); ir (cm^{-1}): 3070, 3000, 2930, 2320, 1510, 1470. 1430, 1270, 905, 740; Anal. Calcd for $C_{18}H_{21}NS$ (%): C 76.28, H 7.47, N 4.94, S 11.30. Found: C 76.20, H 7.35, N 4.65, S 11.55.

Photolysis of 1-adamantylidenemethanesulphinylmethyl-1*H*-benzotriazole ($4a_8$)

$4a_8$ (0.100 g, 0.28 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 8 h (fan on) according to the procedure described above. Only starting material was recovered (40 mg).

Photolysis of 1-adamantylidene*tert*-butoxymethyl-1*H*-benzotriazole ($4a_4$)

$4a_4$ (0.065 g, 0.19 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 3 h (fan on) according to the procedure described above. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using silica gel, eluting with 20% ether / hexane. $5a_4$ was isolated in 35% yield (17 mg).

Photolysis of 1-(1-*tert*-butoxy-2-methylpropenyl)-1*H*-benzotriazole ($4b_2$)

$4b_2$ (0.063 g, 0.26 mmol), dissolved in dry acetonitrile (10 ml), was photolysed for 2.75 h (fan on) according to the procedure described above. Removal of the solvent under reduced pressure gave an oil, which was purified by column chromatography, using Kieselgel, eluting with 10% ether / hexane (first column) and 30% ether / ethylacetate (second column). $5b_2$ was isolated in 40% yield (22 mg, mp 118-122°C); ^{1}H nmr (300 MHz, $CDCl_3$, δ in ppm): 8.65 (1H, br s, N-H), 7.25-7.15 (2H, m)), 7.05 (1H, m), 6.95 (1H, m, aromatic protons), 1.40 (6H, s , methyl groups); ^{13}C nmr (75 MHz, δ in ppm): 184.15 (C-2'), 139.79 (C-3a'), 136.24 (C-7a'), 127.61 (C-6'), 122.56 (C-5'), 122.41 (C-4'), 109.87 (C-7'), 44.66 (C-3'), 24.29 (methyl groups); ms (%): 161 (M^+, 83), 146 (100), 132 (22), 128 (34), 118 (21), 103 (5), 91 (16), 77 (13), 65 (10), 51 (8), 39 (11); ir (cm^{-1}): 3050, 2980, 1705, 1260, 730; Accurate Mass ($C_{10}H_{11}NO$): calcd: 161.0840, found: 161.0840.

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Received, 24th Novemver, 1993