Silylation of Azole *N*-Oxides

Mikael Begtrup [a] **and Per Vedsø** [b]
[a] *Department of Organic Chemistry, Royal School of Pharmacy, Universitetsparken 2, DK-2100 Copenhagen, Denmark*
[b] *Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark*

Pyrazole *N*-oxides and 1,2,3-triazole *N*-oxides can be *C*-silylated at ring and exocyclic α-positions in high yields in a one-pot procedure by treatment with trimethylsilyl triflate, trimethylsilyl iodide or *tert*-butyldimethylsilyl triflate in the presence of 1,2,2,6,6-pentamethylpiperidine, diisopropylethylamine or lithium tetramethylpiperidide. The reaction is initiated by *O*-silylation, followed by deprotonation of ring or exocyclic α-positions, and terminated by silylation of the generated anion. The activating *O*-silyl group is removed by hydrolysis.

Immonium ring carbon atoms are more reactive than enammonium ring carbon atoms. Silylation of exocyclic α-positions at enammonium ring carbon atoms require forcing conditions and give modest yields.

Ring protons adjacent to the positive heteroatoms of heteroaromatic *N*-oxides are activated towards deprotonation which leads to anions prone to attack by electrophiles with production of substituted *N*-oxides. 1-Substituted 1*H*-1,2,3-triazole 3-oxides‡ **13** react in this way,[1-3] while 2-substituted 2*H*-1,2,3-triazole 1-oxides‡ **6** do not.[4] 1-Benzyl-1*H*-pyrazole 2-oxide‡ **1** is deprotonated but the generated anion reacted only with dimethyl disulfide and chloroform.[3] Dimethyl disulfide reacts with poor selectivity and extensive deoxygenation. The reaction with chloroform is selective and followed by complete deoxygenation to give 1-benzyl-3-chloropyrazole. However the yield is only 9%.

Methylation, acylation or silylation of the *N*-oxygen atom increases the acidity of protons at the ring and at exocyclic α-positions.[5] The relative reactivity of different positions can be predicted on the basis of an extended donor–acceptor analysis.[6]

In the pyrazole 2-oxide series activation by silylation was found to be superior to alkylation and acylation. When trimethylsilyl iodide (TMSI) is used for this purpose, the liberated iodide attacks the *O*-silylated *N*-oxide.[5] Under these conditions methyl groups at immonium ring carbon atoms abstract a proton prior to the attack by the iodide ion which displaces the siloxy group in a 1,3- or 1,5-fashion.[5] In order to avoid nucleophilic substitution and allow reaction of the anion with an electrophile, a silylation agent with a non-nucleophilic leaving group was used.

Results and Discussion

Trimethylsilyl triflate is 10^9-times more powerful as a silylation agent than is trimethylsilyl chloride[7] and readily silylates the pyrazole- and triazole *N*-oxides **1**, **6** and **13**. The resulting siloxy compounds, *e.g.* **3**, **7** and **14**, could not be isolated, but were present in solution as was shown from ^{1}H and ^{13}C NMR spectra which exhibited chemical shifts and C–H coupling constants similar to the characteristic values of the corresponding *N*-methoxy compounds.[5] In the presence of a non-nucleophilic base, deprotonation of the siloxy compounds **3**, **7** and **14** took place, followed by silylation of the anion formed. In these reactions ring positions are most reactive while silylation at methyl groups situated at enammonium ring carbon atoms occurs rarely.

Silylation at Ring Positions.—Treatment of 1-benzyl-1*H*-pyrazole 2-oxide **1** with trimethylsilyl triflate (TMSTf) in the presence of lithium tetramethylpiperidide gave 1-benzyl-3,5-bis(trimethylsilyl)-1*H*-pyrazole 2-oxide **4** as the result of *O*-silylation followed by repeated deprotonation and *C*-silylation. Disilylation was predominant even when the base and silylating agent were used in deficient amounts. Presumably the first silyl group enhances the acidity of the remaining β-proton by speeding up its abstraction and hence the introduction of the second silyl group. The yield of compound **4** was only moderate, presumably due to its sensitivity to moisture causing extensive desilylation during work-up. The analogous *tert*-butyldimethylsilyl compound **4** (R = Bu^t) was stable and could be obtained in 74% yield when *tert*-butyldimethylsilyl triflate (TBDMSTf) was used as the silylating agent. In addition, a 13% yield of the 3-*tert*-butyldimethylsilyl compound **5** (R = Bu^t) was obtained but none of the isomeric 5-*tert*-butyldimethylsilyl compound **2** (R = Bu^t) could be detected.

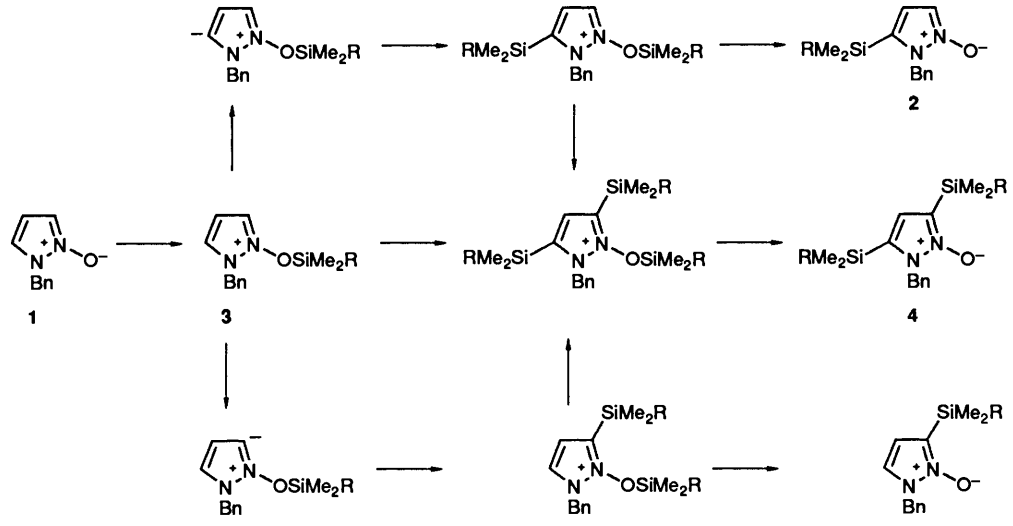
2-Methyl- and 2-phenyl-2*H*-triazole 1-oxide **6** (R^2 = Me and Ph) were silylated selectively at the 5-position to give stable 5-trimethylsilyl derivatives **8** (R^2 = Me and Ph) in high yields. Even weak bases, such as diisopropylethylamine, effected deprotonation. Since 5-H of the 1,2-dimethyltriazolium ion is 3.1×10^3-more acidic than both 3-H and 5-H of the 1,2-dimethylpyrazolium ion[2] it is reasonable that the same trend prevails in the corresponding siloxy ions **3** and **7**.

The 4-methyl-substituted triazole 1-oxide **6** (R^4 = Me) could be silylated stepwise at the 5-position to give compound **8** (R^4 = Me) and then at the methyl group to give compound **12**. Silylation at the methyl group, which is situated at an enammonium ring carbon atom, required forcing conditions and the use of lithium tetramethylpiperidide as the base.

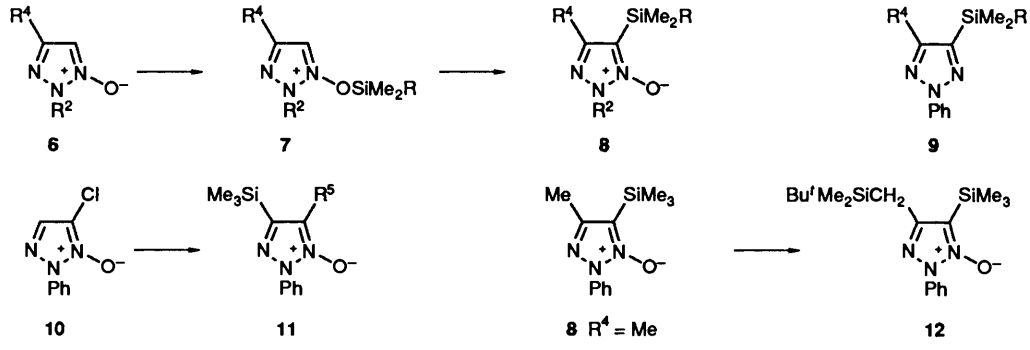
The *tert*-butyldimethylsilyl group could be introduced at ring positions in high yield, but this required that lithium tetramethylpiperidide be used as the base. Thus, 2-phenyl-2*H*-triazole 1-oxide **6** gave 5-*tert*-butyldimethylsilyl-2-phenyl-2*H*-triazole 1-oxide **8** (R = Bu^t) in 77% yield, together with 4-*tert*-butyldimethylsilyl-2-phenyl-2*H*-triazole **9** (R = Bu^t) (5%), presumably formed by deoxygenation of the initial product **8** (R = Bu^t).

If the 5-position of 2-substituted triazole 1-oxides is blocked

‡ The nomenclature used in the present paper for pyrazole *N*-oxides and triazole *N*-oxides is different from traditional use but follows the IUPAC rules strictly. The *N*-oxides are treated as *N'*-alkylated *N'*-H tautomers of *N*-hydroxyazoles in which the *N'*-atom adopts number one in the ring.



Scheme 1 R = Me unless stated otherwise



Scheme 2 R^2 = Ph, R^4 = R^5 = H, and R = Me unless stated otherwise

with a substituent the 4-position is silylated. Thus 5-chloro-2-phenyl-2*H*-triazole 1-oxide **10** produced 5-chloro-4-trimethylsilyl-2-phenyl-2*H*-triazole 1-oxide **11** (R^5 = Cl) in good yield. The reaction was only successful if a strong base, such as lithium tetramethylpiperidide, was employed. This agrees with the 1.2×10^5-lower acidity of 4-H than of 5-H in the corresponding 1,2-dimethyltriazolium ion.[2] The silylation of 5-chloro-2-phenyl-2*H*-triazole 1-oxide **10** gave a minute amount of 2-phenyl-4,5-bis(trimethylsilyl)-2*H*-triazole 1-oxide **11** (R^5 = $SiMe_3$) as a by-product. This is probably formed from the chief product **11** (R^5 = Cl) which in the pure state could be silylated to give the bis(trimethylsilyl) compound **11** (R^5 = $SiMe_3$), although in moderate yield. Most likely, this reaction involves a chlorometallation of compound **11** (R^5 = Cl) followed by silylation.

1-Benzyl- and 1-phenyl-1*H*-triazole 3-oxide **13** (R^3 = Bn and Ph) were selectively silylated at C-4 by treatment with trimethylsilyl triflate and diisopropylethylamine. The yields of products **15** (R^1 = Bn or Ph) were modest presumably due to desilylation during work-up.

The structure of 1-benzyl-4-trimethylsilyl-1*H*-triazole 3-oxide **15** (R^1 = Bn) was established through the coupling between C-5 and the CH_2 protons. The structure of the phenyl analogue **15** was confirmed by irradiation at the Me protons which gave a 6% NOE enhancement of the 5-H signal and no change of the intensity of the phenyl protons.

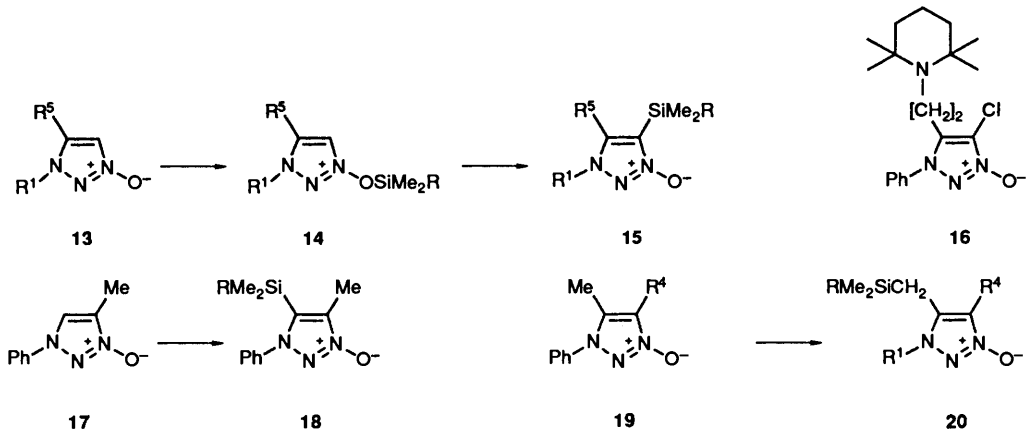
5-Methyl-1-phenyl-1*H*-triazole 1-oxide **13** (R^1 = Ph, R^5 = Me) was silylated quantitatively at C-4 by treatment with trimethylsilyl iodide and 1,2,2,6,6-pentamethylpiperidine at 80 °C to give compound **15** (R^5 = Me). Under similar conditions, 4-methyl-1-phenyl-1*H*-triazole 3-oxide **17** produced the isomeric but unstable silyl derivative **18**. The stable *tert*-butyldimethylsilyl analogue **18** (R = Bu^t) was obtained in high yield by treatment of compound **17** with *tert*-butyldimethylsilyl triflate and lithium tetramethylpiperidide.

The ready silylation of the 4- and 5-position of 1-substituted 1*H*-triazole 3-oxides **13** and **17** agrees with the relatively high acidity of the protons at these positions of 1,3-dimethyltriazolium salts.[8] The 1-substituted 1*H*-triazole 3-oxides are silylated more readily at C-4 than at C-5. The relative reactivity should be the reverse as predicted by an extended donor–acceptor analysis.[6] The high monoselectivity observed may be due to the bulk of the *C*-trialkylsilyl group which prevents a second silyl group from entering the adjacent position.

In some of the aforementioned *C*-silylation reactions minute amounts of deoxygenated starting material are observed.

Silylation at the α-Position of Side Chains.—Treatment of 5-methyl- or 3-methyl-1-benzyl-1*H*-pyrazole 2-oxide or of 2*H*-triazole 1-oxides possessing methyl groups at immonium ring carbon atoms, such as 5-methyl-2-phenyl-2*H*-1,2,3-triazole 1-oxide, with trimethylsilyl triflate in the presence of 1,2,2,6,6-pentamethylpiperidine gave complicated mixtures.

In the triazole series, silylation at the unreactive methyl groups at enammonium ring carbon atoms was observed only when methyl groups at the immonium ring carbon atoms were absent and when these carbon atoms were blocked by other substituents. The silylations required forcing conditions and yields were low to modest. Thus treatment of 4-methyl-2-phenyl-5-trimethylsilyl-2*H*-triazole 1-oxide **8** (R^4 = Me) with *tert*-butyldimethylsilyl triflate and lithium tetramethylpiperidide at best afforded 4-[(*tert*-butyldimethylsilyl)methyl]-2-phenyl-5-trimethylsilyl-2*H*-triazole 1-oxide **12** in only 14% yield. Similarly, 5-methyl-1-phenyl-4-trimethylsilyl-1*H*-triazole 3-



Scheme 3 R^1 = Ph, R^4 = R^5 = H, and R = Me unless stated otherwise

oxide **19** (R^4 = $SiMe_3$) gave 5-[(*tert*-butyldimethylsilyl)-methyl]-1-phenyl-4-trimethylsilyl-1*H*-triazole 3-oxide **20** (R = Bu^t, R^4 = $SiMe_3$) in 38% yield. In addition, 5([(*tert*-butyldimethylsilyl)methyl]-1-[2′-(*tert*-butyldimethylsilyl)phenyl]-4-trimethylsilyl-1*H*-1,2,3-triazole 3-oxide **20** (R^1 = 2-SiBu^{t}Me$_2$C$_6$H$_4$, R^4 = $SiMe_3$, R = Bu^t) (13%) and 4-(*tert*-butyldimethylsilyl)-5-[(*tert*-butyldimethylsilyl)methyl]-1-phenyl-1*H*-triazole 3-oxide **20** (R^4 = SiBu^{t}Me$_2$, R = Bu^t) (7%) were isolated. In general, *tert*-butyldimethylsilylation required definitely more forcing conditions than did trimethylsilylation. *tert*-Butyldimethylsilylation of 5-methyl-1-phenyl-1*H*-triazole 3-oxide **13** (R^1 = Ph, R^5 = Me) required such forcing conditions that selectivity was lost. The expected 4-(*tert*-butyldimethylsilyl)-5-methyl-1-phenyl-1*H*-triazole 3-oxide **15** (R^1 = Ph, R^5 = Me, R = Bu^t) was obtained in only 39% yield because it was further silylated to give 4-(*tert*-butyldimethylsilyl)-5-[(*tert*-butyldimethylsilyl)methyl]-1-phenyl-1*H*-triazole 3-oxide **20** (R^4 = SiBu^{t}Me$_2$, R = Bu^t) and the curious 4-{*tert*-butyl[(*tert*-butyldimethylsilyl)methyl]-methylsilyl}-5-[(*tert*-butyldimethylsilyl)methyl]-1-phenyl-1*H*-triazole 3-oxide **20** (R^4 = SiBu^{t}MeCH$_2$SiBu^{t}Me$_2$, R = Bu^t). The structure of the latter compound was supported by NOE experiments (see Experimental section).

Treatment of 4-chloro-5-methyl-1-phenyl-1*H*-triazole 3-oxide **19** (R^4 = Cl) with trimethylsilyl iodide and 1,2,2,6,6-pentamethylpiperidine gave 4-chloro-1-phenyl-5-trimethylsilylmethyl-1*H*-triazole 3-oxide **20** (R^4 = Cl) in 37% yield. In addition, 4-chloro-1-phenyl-5-[2-(2′,2′,6′,6′-tetramethylpiperidino)ethyl]-1*H*-triazole 3-oxide **16** was isolated. The formation of the latter compound remains unexplained.

Conclusions.—*O*-Silylation of pyrazole *N*-oxides **1** and triazole *N*-oxides **6**, **10**, **13** and **17** enhances the acidity of those ring protons which are situated adjacent to positive nitrogen atoms in the ring. The protons can be abstracted by non-nucleophilic bases and the anions thus generated can then be silylated to produce *C*-silylated *N*-oxides in good to excellent yields. The whole sequence can be run in one pot. The silylation conditions depend on the acidity of the ring protons. Positions of low acidity require trimethylsilyl triflate and lithium tetramethylpiperidide, while more acidic positions are silylated using trimethylsilyl iodide or trimethylsilyl triflate in the presence of 1,2,2,6,6-pentamethylpiperidine or diisopropylethylamine. *tert*-Butyldimethylsilylation is likewise feasible but requires the use of a stronger base such as lithium tetramethylpiperidide.

C-Silylation takes place selectively at ring carbon atoms provided that the more reactive exocyclic α-protons at immonium ring carbons atoms are absent.

In 1-benzyl-1*H*-pyrazole 2-oxide **1** C-3 and C-5 are more reactive than is C-4. Silylation at C-3 and C-5 is not monoselective and the relative reactivity of the 5- and 3-silyl derivatives **2** and **5** is unknown. Therefore the relative reactivity of C-3 and C-5 cannot be established. In contrast, the silylation of 2-methyl- and 2-phenyl-2*H*-triazole 1-oxide **6** (R^2 = Me and Ph), and of 1-benzyl- and 1-phenyl-1*H*-triazole 3-oxide **13** (R^3 = Bn and Ph) takes place exclusively at C-5 and C-4, respectively. Except for 1-substituted 1*H*-triazole 3-oxides the observed regioselectivity between different ring positions corresponds to that predicted on the basis of the extended donor–acceptor analysis.[6]

Methyl groups at immonium carbon atoms react readily but mixtures of products arise when the silylation is effected by trimethylsilyl triflate in contrast to the clean formation of iodomethyl derivatives brought about by trimethylsilyl iodide. Methyl groups at C-5 of 2-substituted 2*H*-triazole 1-oxides exhibited a higher reactivity than did methyl groups at C-4. Similarly, methyl groups at C-3 and C-5 of 1-substituted 1*H*-pyrazole 2-oxides exhibited a higher reactivity than methyl groups at C-4. Thus, methyl groups at enammonium ring carbon atoms were invariantly unreactive and could only be silylated in low yields under forcing conditions and only when other ring positions were blocked. The higher reactivity of methyl groups at immonium ring carbon atoms compared with that of methyl groups at enammonium ring carbon atoms agrees with the donor–acceptor analysis.

C-Silylated azole *N*-oxides of the type prepared in the present paper are expected to be useful intermediates for the regioselective preparation of substituted azoles since *C*-silyl groups are prone to undergo electrophilic halogenodesilylation or fluoride ion-catalysed carbodesilylation.[9-11]

Experimental

General.—Methylene dichloride was dried over sodium hydride. Tetrahydrofuran (THF) was distilled from lithium aluminium hydride. Diisopropylethylamine was distilled from sodium hydride. All reactions were performed with rigorous exclusion of moisture using syringe techniques and screw-cap-sealed reaction vessels[12] in an atmosphere of nitrogen dried over phosphorus pentaoxide. Magnesium sulfate for drying of solutions, was used unless otherwise stated. Solvents were removed under reduced pressure by rotary evaporation. Filtration through silica gel was performed using silica gel Merck 60 (70–230 mesh). The purity of all compounds was confirmed by m.p.s determined in open capillaries with a Büchi apparatus and are uncorrected. TLC, and ^{1}H and ^{13}C NMR

spectra recorded at 200 and 50.32 MHz, respectively, on a Bruker AC-200 instrument. NMR data are shown in Tables 1–4.

Preparation of N-*Oxides.*—Formic acid (20 cm^3), methylene dichloride (50 cm^3), and 1-benzyl-1*H*-pyrazole (15.0 g) were cooled to 0 °C. 60% Aq. hydrogen peroxide (30 cm^3) was added in *ca.* 1 min to the efficiently stirred mixture at 0 °C. The mixture was stirred at 0 °C for 3 h. The flask was kept in the bath while the ice was allowed to melt and the mixture was stirred at 20 °C for 24 h. Addition of water (25 cm^3), separation of the organic phase, extraction of the aqueous solution with further methylene dichloride (3 × 20 cm^3), washing of the organic solution with a solution of sodium sulfite (5 g) and potassium carbonate (5 g) in water (100 cm^3), extraction of the combined washings with methylene dichloride (4 × 20 cm^3), and drying and evaporation of the combined organic phase gave an oil (14.6 g), which was filtered through silica gel (20 g, 3 cm column) and elution with ethyl acetate–hexane (1:1) (250 cm^3). This gave unchanged starting material (12.3 g, 81% recovery). The column was then eluted with ethyl acetate–methanol (1:1) (250 cm^3) to give 1-benzyl-1*H*-pyrazole-2-oxide **1** (1.99 g, 11%) (R_f 0.68), identical with material described previously.[13]

Silylation at Ring Positions.—(*a*) 2-Methyl-2*H*-triazole 1-oxide **6** (R^2 = Me, R^4 = H)[14] (0.21 g), chloroform (0.5 cm^3), TMSI (0.99 cm^3) and dissopropylethylamine (0.89 cm^3) were stirred together at room temperature for 2 h. Evaporation to dryness (20 °C/12 mmHg), and filtration through silica gel (10 g, column diameter 2 cm) and elution with methylene dichloride–diethyl ether–hexane [2:2:1 (100 cm^3)] produced 0.32 g (91%) of 2-*methyl*-5-*trimethylsilyl*-2H-*triazole* 1-*oxide* **8** (R^2 = R = Me, R^4 = H), m.p. 83 °C (from EtOAc) (Found: C, 41.9; H, 7.5; N, 24.3. $C_6H_{13}N_3OSi$ requires C, 42.07; H, 7.65; N, 24.53%).

(*b*) 2-Phenyl-2*H*-triazole 1-oxide **6** (R^2 = Ph, R^4 = H)[15] (0.40 g), methylene dichloride (5 cm^3), TMSTf (1.5 cm^3) and diisopropylethylamine (0.86 cm^3) were stirred at room temperature for 5 h. Evaporation to dryness (20 °C/2 mmHg), and filtration through silica gel (10 g, column diameter 2 cm) with elution with methylene dichloride–diethyl ether–hexane [1:1:4 (250 cm^3)] produced 2-*phenyl*-5-*trimethylsilyl*-2H-*triazole* 1-*oxide* **8** (R^2 = Ph, R^4 = H, R = Me), (0.58 g, 99%) m.p. 97 °C (from hexane) (Found: C, 56.6; H, 6.55; N, 17.9. $C_{11}H_{15}N_3OSi$ requires C, 56.62; H, 6.48; N, 18.01%).

(*c*) A 1.6 mol dm^{-3} solution of butyllithium in hexane (0.47 cm^3) was added to 2,2,6,6-tetramethylpiperidine (0.13 cm^3) at −20 °C. After being stirred at −20 °C for 10 min the mixture was cooled to −78 °C. TBDMSTf (0.28 cm^3) and a solution of 2-phenyl-2*H*-1,2,3-triazole 1-oxide **6** (R^2 = Ph, R^4 = H)[15] (48 mg) in methylene dichloride (1.0 cm^3) were added. After being stirred at −78 °C for 30 min and at 20 °C for 1 h the mixture was filtered through silica gel (5.0 g, column diameter 1 cm) and eluted with diethyl ether–methylene dichloride–hexane (1:1:8) (60 cm^3). Removal of the solvents, drying over P_2O_5 at 0.2 mmHg, and recrystallization [hexane (0.7 cm^3)] gave 5-*tert*-*butyldimethylsilyl*-2-*phenyl*-2H-1,2,3-*triazole* 1-*oxide* **8** (R^2 = Ph, R^4 = H, R = Bu^t) (51 mg, 62%), m.p. 70–71 °C (from hexane) (Found: C, 61.2; H, 7.5; N, 15.1. $C_{14}H_{21}N_3OSi$ requires C, 61.05; H, 7.69; N, 15.26%). The solute from the mother liquor, obtained by preparative TLC (PLC) [diethyl ether–methylene dichloride–hexane (1:1:15)] gave a second crop of compound **8** (R^2 = Ph, R^4 = H, R = Bu^t) (12 mg, 15%) (R_f 0.38), bringing the total yield to 77%, and 4-*tert*-butyldimethylsilyl-2-phenyl-2*H*-1,2,3-triazole **9** (R^4 = H, R = Bu^t) (5 mg, 6%) (R_f = 0.94), *m/z* 259 (M^+, 10%) and 202 ($M^+ - C_4H_9$, 100).

4-Methyl-2-phenyl-2*H*-1,2,3-triazole 1-oxide **6** (R^2 = Ph, R^4 = Me)[15] (150 mg) was treated as in method (*b*) to give a reaction mixture which, after being stirred at 20 °C for 2 h, was evaporated to dryness. Addition of methylene dichloride (1.0 cm^3) and diisopropylethylamine (0.5 cm^3), stirring for 5 min, evaporation to dryness, filtration through silica gel (5 g, column diameter 1 cm) and elution with diethyl ether–methylene dichloride–hexane (1:1:4) (60 cm^3), and removal of the solvents gave an oil, which was recrystallized from hexane (1.5 cm^3) to give 4-*methyl*-2-*phenyl*-5-*trimethylsilyl*-2H-1,2,3-*triazole* 1-*oxide* **8** (R^2 = Ph, R^4 = Me) (159 mg, 75%), m.p. 78 °C (Found: C, 58.4; H, 6.9; N, 16.95. $C_{12}H_{17}N_3OSi$ requires C, 58.26; H, 6.93; N, 16.99%). PLC [diethyl ether–methylene dichloride–hexane (1:1:10)] of the mother liquor gave a further crop (28 mg, 13%) of compound **8** (R^2 = Ph, R^4 = Me) (R_f 0.26), bringing the total yield to 88%. The next fraction contained 5 mg (3%) of 4-methyl-2-phenyl-2*H*-1,2,3-triazole (R_f 0.65), described previously.[16] The third fraction contained 4-methyl-2-phenyl-5-trimethylsily-2*H*-1,2,3-triazole **9** (R^4 = R = Me)

Table 1 ^{1}H NMR spectroscopic data of 1*H*-pyrazole 2-oxides **4** and **5** in $CDCl_3$ with tetramethylsilane as internal standard

	δ_H				
Compound	5-H	4-H	Ph	CH_2	Me
4 (R = Me)		6.27	3: 7.20–7.34 2: 6.94–7.00	5.50	SiMe 0.38, 0.13
4 (R = Bu^t)		6.31	3: 7.18–7.33 2: 6.82–6.88	5.49	CMe 0.98, 0.85 SiMe 0.36, 0.16
5 (R = Me)	6.76[a]	6.09	7.28–7.38	5.33	SiMe 0.37
5 (R = Bu^t)	6.78[b]	6.11	7.25–7.39	5.33	CMe 0.98 SiMe 0.35

[a] $J_{4\text{-}H,5\text{-}H}$ 3.65 Hz. [b] $J_{4\text{-}H,5\text{-}H}$ 3.69 Hz.

Table 2 ^{13}C NMR spectroscopic data of 1*H*-pyrazole 2-oxides **4** and **5** in $CDCl_3$ with the solvent peak (δ_C 76.90) as internal standard

	δ_C					*J*/Hz	
Compound	C-5 (C-1′)	C-4 (C-2′)	C-3 (C-3′)	CH_2 (C-4′)	Me (C)	C-5	C-4
4 (R = Me)	132.0[a] (136.2)	115.3 (125.9)	129.0[a] (128.4)	47.7 (127.2)	SiMe −1.5, −2.7		178.3
4 (R = Bu^t)	129.6[a] (136.5)	117.9 (125.4)	127.6[a] (128.4)	48.5 (127.0)	26.6, 26.2 SiMe −6.65, −5.61 (17.5), (17.2)		177.8
5 (R = Me)	118.2 (134.4)	106.6 (128.4)	*b* (128.9)	48.6 (128.3)	SiMe −2.57		
5 (R = Bu^t)	118.4 (134.5)	107.8 (128.3)	128.9 (128.9)	48.8 (128.3)	26.6 SiMe −6.6 (17.5)	193.3 4-H 6.52 CH_2 2.7	180.6 5-H 5.41

[a] The assignments may have to be interchanged. [b] The signal could not be observed.

Table 3 ^{1}H NMR spectroscopic data of 1,2,3-triazole oxides in $CDCl_3$ with tetramethylsilane as internal standard

Compound	4-H	5-H	Ph	CH_2	Me[a]
8 (R^2 = Ph, R^4 = H, R = Me)	7.58		2: 7.92–7.98 3: 7.38–7.55		SiMe 0.40
8 (R^2 = R = Me, R^4 = H)	7.41				3.99 SiMe 0.36
8 (R^2 = Ph, R = R^4 = Me)			2: 7.90–7.96 3: 7.32–7.53		2.34 SiMe 0.42
8 (R^2 = Ph, R^4 = H, R = Bu^t)	7.61		2: 7.91–7.97 3: 7.38–7.56		1.02 SiMe 0.39
9 (R^4 = H, R = Bu^t)		8.07	2: 8.09–8.15 3: 7.36–7.58		1.00 SiMe 0.43
11 (R^5 = Cl)			2: 7.91–7.97 3: 7.42–7.59		SiMe 0.42
11 (R^5 = $SiMe_3$)			2: 7.94–8.00 3: 7.36–7.55		SiMe 0.45, 0.40
12			2: 7.93–7.99 3: 7.34–7.52	2.10	0.96 SiMe 0.43 (3), 0.05
15 (R^1 = Ph, R^5 = H, R = Me)		7.82	2: 7.64–7.70 3: 7.35–7.56		SiMe 0.39
15 (R^1 = Bn, R^5 = H, R = Me)		7.45	7.22–7.28	5.18	SiMe 0.23
15 (R^1 = Ph, R^5 = R = Me)			2: 7.39–7.46 3: 7.49–7.56		2.31 SiMe 0.45
15 (R^1 = Ph, R^5 = Me, R = Bu^t)			2: 7.35–7.41 3: 7.43–7.52		2.27, 0.98(3) SiMe 0.41
16			7.49–7.60	2.50–2.58 (4 H, m), 2.76–2.84 (4 H, m), 1.32–1.56 (2 H, m)	0.85(4)
18 (R = Bu^t)			2: 7.24–7.30 3: 7.33–7.50		2.31, 0.80(3) SiMe −0.12
20 [R^1 = Ph, R^4 = $SiBu^t(Me)CH_2SiBu^tMe_2$, R = Bu^t]			7.42–7.52	2.37 $SiCH_2$ −0.43, −0.58[b] (dd, *J* 13.9 Hz)	0.79, 0.77 SiMe 0.49, 0.43, −0.11, −0.19, −0.53
20 [R^1 = 2-(Bu^tMe_2Si)C_6H_4, R^4 = $SiMe_3$, R = Bu^t]			1: 7.66–7.71 2: 7.45–7.50 1: 7.27–7.32	2.10	0.90, 0.74 SiMe 0.45 (3), 0.04, −0.24
20 (R^1 = Ph, R^4 = Cl, R = Me)			2: 7.41–7.47 3: 7.52–7.58	2.28	SiMe −0.08
20 (R^1 = Ph, R^4 = $SiMe_2Bu^t$, R = Bu^t)			7.42–7.58	2.34	1.05, 0.74 SiMe 0.44, −0.38
20 (R^1 = Ph, R^4 = $SiMe_3$, R = Bu^t)			7.40–7.57	2.33	0.75 SiMe 0.46 (3), −0.34 (2)

[a] The number of methyl groups is given in parentheses in cases where it is needed for assignment. [b] The methylene protons are diastereotopic owing to the presence of a stereogenic silicon atom.

(4 mg, 2%) (R_f 0.86), *m/z* 231 (M^+, 29%), 216 (M^+ − Me, 13) and 91 (100).

(*d*) A. 1.6 mol dm^{-3} solution of butyllithium in hexane (1.3 cm^3) was added to 2,2,6,6-tetramethylpiperidine (0.34 cm^3) at −20 °C. After being stirred at −20 °C for 10 min the mixture was cooled to −78 °C. TMSTf (0.72 cm^3) and a solution of 5-chloro-2-phenyl-2*H*-1,2,3-triazole 1-oxide **10**[15] (165 mg) in methylene dichloride (2 cm^3) were added. After 30 min the temperature was increased during 45 min to 0 °C and was then kept here for 10 min. Evaporation to dryness, filtration through silica gel (5 g, column diameter 2 cm), elution with methylene dichloride (60 cm^3), removal of the eluting solvent, and PLC [diethyl ether–methylene dichloride–hexane (1:1:4)] afforded unchanged starting material (13 mg, 8% recovery) (R_f 0.59). The second fraction contained *5-chloro-2-phenyl-4-trimethylsilyl*-2H-1,2,3-*triazole 1-oxide* **11** (R^5 = Cl) (148 mg, 66%) (R_f 0.59), m.p. 50–52 °C (from hexane) (Found: C, 49.4; H, 5.3; N, 15.5. $C_{11}H_{14}ClN_3OSi$ requires C, 49.34; H, 5.27; N, 15.69%). The third fraction contained 2-phenyl-4,5-bis(trimethylsilyl)-2*H*-1,2,3-triazole 1-oxide **11** (R^5 = $SiMe_3$) (4 mg, 1.6%) (R_f 0.69) as an oil, *m/z* 305 (M^+, 2%) and 190 (100).

5-Chloro-2-phenyl-4-trimethylsilyl-2*H*-1,2,3-triazole 1-oxide **11** (R^5 = Cl) (51 mg) was treated as in method (*d*) to give a reaction mixture which, after being stirred at 20 °C for 21 h, was filtered through silica gel (5 g, column diameter 1 cm) and eluted with diethyl ether–methylene dichloride–hexane (1:1:1) (50 cm^3). Removal of the solvents and PLC [diethyl ether–methylene dichloride–hexane (1:1:4)] gave unchanged starting material (45 mg, 89% recovery) (R_f 0.59) and (4 mg, 7%) 2-phenyl-4,5-bis(trimethylsilyl)-2*H*-1,2,3-triazole 1-oxide **11** (R^5 = $SiMe_3$), identical with the material above.

(*e*) 5-Methyl-1-phenyl-1*H*-1,2,3-triazole 3-oxide **13** (R^1 = Ph, R^5 = Me)[1] (93 mg), chloroform (2.0 cm^3), TMSI (0.29 cm^3) and 1,2,2,6,6-pentamethylpiperidine (0.29 cm^3) were heated together to 80 °C for 3 h. Evaporation to dryness, filtration through silica gel (5 g, column diameter 1 cm) and elution with methylene dichloride–diethyl ether [1:1 (60 cm^3)] afforded *5-methyl-1-phenyl-4-trimethylsilyl*-1H-1,2,3-*triazole* 3-*oxide* **15** (R^1 = Ph, R^5 = Me), m.p. 139–142 °C. Low-temperature recrystallization from ethyl acetate gave m.p. 145 °C (Found: C, 58.2; H, 6.9; N, 16.9. $C_{12}H_{17}N_3OSi$ requires C, 58.26; H, 6.93; N, 16.99%).

4-Methyl-1-phenyl-1*H*-1,2,3-triazole 3-oxide **17**[1] (53 mg) was treated as in method (*c*) above to give a reaction mixture which, after being stirred at 20 °C for 3 h, was evaporated to dryness. The mixture was filtered through silica gel and eluted, first with diethyl ether–methylene dichloride–hexane (1:1:1) (30 cm^3) and then with ethyl acetate–methanol (4:1) (40 cm^3). The content of the latter eluate was purified by PLC [ethyl acetate–methanol (6:1)] to give 117 mg of 5-(*tert*-butyldimethylsilyl)-4-methyl-1-phenyl-1*H*-1,2,3-triazole 3-oxide **18** (R = Bu^t) (R_f 0.57)

Table 4 ^{13}C NMR spectroscopic data of 1,2,3-triazole oxides in $CDCl_3$ with the solvent peak (δ_C = 76.90) as internal standard

Compound	δ_C					J/Hz	
	C-4 (C-1')	C-5 (C-2')	(C-3')	CH_2 (C-4')	Me[a] (C)	C-4	C-5
8 (R^2 = Ph, R^4 = H, R = Me)	137.7 (134.9)	126.4 (122.7)	(128.7)	(128.6)	SiMe −3.1	196.0	4-H 15.9 $SiMe_3$ 2.3
8 (R^2 = R = Me, R^4 = H)	136.4	125.2			NMe 34.3 SiMe −3.3	195.6	4-H 15.9 $SiMe_3$ 2.3
8 (R^2 = Ph, R^4 = R = Me)	147.1 (134.9)	124.6 (122.6)	(128.6)	(128.2)	13.8 SiMe −2.2	Me 6.9	
8 (R^2 = Ph, R^4 = H, R = Bu^t)	138.8 (135.1)	125.1 (123.0)	(128.8)	(128.8)	26.5 SiMe −7.0 (17.4)	195.7	
11 (R^5 = Cl)	143.8 (134.9)	123.7 (122.2)	(128.7)	(128.9)	SiMe −2.6	$SiMe_3$ 2.2	
11 (R^5 = $SiMe_3$)	151.6 (135.2)	131.1 (122.9)	(128.8)	(128.5)	SiMe −0.6, −1.4		
12	150.1 (135.3)	124.6 (122.4)	(128.7)	12.9 (128.1)	26.5 SiMe −1.9, −6.1 (18.7)		

Compound	C-5 (C-1')	C-4 (C-2')	(C-3')	CH_2 (C-H')	Me[a] (C)	J/Hz C-5	J/Hz C-4
13 (R^1 = Bn, R^5 = H)	128.8 (132.7)	119.9 (128.1)	(128.7)	55.0 (128.7)		200.2 4-H, 12.6 CH_2 2.9	206.3 5-H 11.2
15 (R^1 = Ph, R^5 = H, R = Me)	130.4 (132.9)	131.0 (128.1)	(128.7)	54.5 (128.7)	SiMe −3.0	196.5 CH_2 3.0	5-H 13.6 $SiMe_3$ 2.2
15 (R^1 = Ph, R^5 = R = Me)	140.1 (134.7)	128.2 (125.5)	(129.4)	(129.5)	10.7 SiMe −1.8	Me 6.6	
15 (R^1 = Ph, R^5 = Me, R = Bu^t)	141.0 (134.5)	127.0 (125.4)	(129.3)	(129.4)	11.0, 27.3 SiMe −5.6 (18.1)	Me 6.7	
16	135.4 (134.6	119.4 (125.9)	(129.5)	42.1, 40.5, 17.1, NCH_2, 28.7 (130.4)	26.6 (54.4)	CH_2 6.4 NCH_2 2.1	CH_2 5.0
18 (R = Bu^t)	134.8 (137.6)	135.0 (127.8)	(128.7)	(130.3)	9.5, 26.4 SiMe −5.1 (18.1)		Me 6.8
20 [R^1 = Ph, R^4 = $SiBu^t(Me)CH_2SiBu^tMe_2$ R = Bu^t]	145.0 (136.0)	126.4 (1258.8)	(129.5)	12.4 $SiCH_2$ −8.3 (129.4)	27.2, 26.5, 26.1 SiMe −3.6, −3.7 −4.1, −4.7, −4.8 (18.5), (17.7), (17.0)	CH_2 7.1	
20 [R^1 = 2-(Bu^tMe_2Si)C_6H_4, R^4 = $SiMe_3$, R = Bu^t]	144.7 (139.6)	126.1 (137.2, 137.0, 129.6 128.7, 128.6)[b]		10.6	27.2, 25.9 SiMe −1.5, −5.1, −5.7 (17.8, (16.6)	CH_2 7.2	
20 (R^1 = Ph, R^4 = Cl, R = Me)	135.2[c] (136.1)[c]	116.6 (125.6)	(129.7)	14.2 (130.1)	SiMe −1.2		
20 (R^1 = Ph, R^4 = $SiMe_2Bu^t$, R = Bu^t)	144.9 (135.7)	126.3 (126.1)	(129.5)	10.0 (129.5)	27.3, 25.9 SiMe −4.6, −6.0 (18.2), (16.7)	CH_2 7.1	
20 (R^1 = Ph, R^4 = $SiMe_3$, R = Bu^t)	143.7 (135.4)	126.8 (125.8)	(129.4)	9.9 (129.3)	25.8 SiMe −1.6, −6.2 (16.5)		

[a] The number of methyl groups is given in brackets in cases where it is needed for assignment. [b] Signals for C-2' to C-6' have not been assigned. [c] The assignments may have to be interchanged.

contaminated with lithium triflate. Addition of 0.25 mol dm^{-3} tetraphenylboronate (1.0 cm^3), filtration, extraction of the residue with methylene dichloride (3 × 1 cm^3) and of the filtrate with methylene dichloride (4 × 2 cm^3), evaporation of the combined organic solutions to dryness, and PLC [ethyl acetate–methanol (5:1)] gave (76 mg, 86%) of 5-(tert-*butyldimethylsilyl*)-4-*methyl*-1-*phenyl*-1H-1,2,3-*triazole* 3-*oxide* **18** (R = Bu^t) (R_f 0.68), m.p. 155 °C (from ethyl acetate–hexane) (Found: C, 62.2; H, 8.1; N, 14.3. $C_{15}H_{23}N_3OSi$ requires C, 62.24; H, 8.01; N, 14.52%).

1-Benzyl-1*H*-1,2,3-triazole 3-oxide **13** (R^1 = Bn, R^5 = H) (91 mg) was treated as in method (*b*), with chloroform instead of methylene dichloride as solvent. The reaction mixture was then stirred at 50 °C for 6 h and evaporated to dryness. An NMR spectrum indicated complete and clean conversion of the starting material into the product **15** (R^1 = Bn, R^5 = H, R =

Me). Addition of diisopropylethylamine (0.2 cm^3) in order to assure basicity during work-up, evaporation to dryness, filtration through silica gel (5 g, column diameter 1 cm) with elution with methylene dichloride–diethyl ether (1:1) (75 cm^3), evaporation to dryness, and PLC [ethyl acetate–methanol (4:1)] afforded 1-*benzyl*-4-*trimethylsilyl*-1H-1,2,3-*triazole* 3-*oxide* **15** (R^1 = Bn, R^5 = H, R = Me), (74 mg, 57%) (R_f 0.55), m.p. 157 °C (from EtOAc) (Found: C, 58.0; H, 6.9; N, 16.2. $C_{12}H_{17}N_3OSi$ requires C, 58.27; H, 6.93; N, 16.99%).

1-Phenyl-1*H*-1,2,3-triazole 3-oxide **13** (R^1 = Ph, R^5 = H) (73 mg) was treated as in method (*b*), but with chloroform instead of methylene dichloride. The reaction mixture was then stirred for 1.5 h and evaporated to dryness. An NMR spectrum indicated complete and clean conversion of the starting material into the product **15**. Addition of diisopropylethylamine (0.2 cm^3), evaporation to dryness, filtration through silica gel (5 g, column diameter 1 cm), elution with methylene dichloride–diethyl ether–hexane (1:1:1) (110 cm^3) and removal of the solvents gave (64 mg, 60%) 1-*phenyl*-4-*trimethylsilyl*-1H-1,2,3-*triazole* 3-*oxide* **15** (R^1 = Ph, R^5 = H, R = Me), m.p. 185–186 °C (from EtOAc) (Found: C, 56.5; H, 6.3; N, 18.25. $C_{11}H_{15}N_3OSi$ requires C, 56.62; H, 6.48; N, 18.01%).

(*f*) To a solution of lithium tetramethylpiperidide at −78 °C, prepared as in method (*d*) above from 2,2,6,6-tetramethylpiperidine (0.49 cm^3), were added TBDMSTf (1.1 cm^3) and a solution of 1-benzyl-1*H*-pyrazole 2-oxide **1**[13] (166 mg) in methylene dichloride (2.0 cm^3). After being stirred at −78 °C for 10 min and at 20 °C for 20 h the reaction mixture was filtered through silica gel (10 g, column diameter 2 cm) and eluted, first with diethyl ether–methylene dichloride–hexane (1:1:15) (50 cm^3), then with these solvents in the proportions 1:1:1 (50 cm^3), and finally with diethyl ether–methylene dichloride (1:1) (50 cm^3). The content of the second eluate was filtered through a second column of silica gel (10 g, column diameter 2 cm) and eluted with diethyl ether–methylene dichloride–hexane (1:1:8) (100 cm^3) and then with these solvents in the proportions 1:1:1 (75 cm^3). The latter eluate contained 1-*benzyl*-3,5-*bis*(tert-*butyldimethylsilyl*)-1H-*pyrazole* 2-*oxide* **4** (R = Bu^t) (283 mg, 74%), m.p. 84 °C (from hexane) (Found: C, 65.7; H, 9.5; N, 7.0. $C_{22}H_{38}N_2OSi_2$ requires C, 65.61; H, 9.51; N, 6.96%).

The content of the third eluate from the first column was purified by PLC [Et_2O–CH_2Cl_2 (1:1)] to give 1-*benzyl*-3-tert-*butyldimethylsilyl*)-1H-*pyrazole* 2-*oxide* **5** (R = Bu^t) (35 mg, 13%) (R_f 0.68), m.p. 47 °C (from hexane) (Found: C, 66.7; H, 8.3; N, 9.7. $C_{16}H_{24}N_2OSi$ requires C, 66.62; H, 8.39; N, 9.71%).

1-Benzyl-1*H*-pyrazole 2-oxide **1** (166 mg) was treated as in method (*f*) except that TMSTf (0.86 cm^3) was used in place of TBDMSTf, to give a reaction mixture, which was filtered through silica gel (10 g, column diameter 2 cm) and eluted, first with diethyl ether–methylene dichloride–hexane (1:1:15) (60 cm^3), then with these solvents in the proportions 1:1:1 (90 cm^3), and finally with diethyl ether–methylene dichloride (1:1) (60 cm^3). The second fraction contained 1-*benzyl*-3,5-*bis*(*trimethylsilyl*)-1H-*pyrazole* 2-*oxide* **4** (R = Me) (94 mg, 31%) as an oil, which was reprecipitated from hexane (Found: C, 60.7; H, 8.4; N, 8.4. $C_{16}H_{26}N_2OSi_2$ requires C, 60.32; H, 8.23; N, 8.79%). The third fraction after PLC gave 1-*benzyl*-3-*trimethylsilyl*-1H-*pyrazole* 2-*oxide* **5** (R = Me) (7 mg, 3%) (R_f 0.53), m.p. 47–52 °C (from hexane) (Found: C, 63.4; H, 7.5; N, 11.4. $C_{13}H_{18}N_2OSi$ requires C, 63.37; H, 7.36; N, 11.37%).

Silylation at α-Side Chain Positions.—(*g*) To a solution of lithium tetramethylpiperidide prepared as in method (*d*) from 2,2,6,6-tetramethylpiperidine (57 mm^3), TBDMSTf (0.16 cm^3) and a solution of 4-methyl-2-phenyl-5-trimethylsilyl-2*H*-1,2,3-triazole 1-oxide **8** (R^2 = Ph, R^4 = Me) (42 mg) in THF (1.2 cm^3) were added. After 30 min the temperature was increased during 1 h to 20 °C and kept at 50 °C for 45 min. Subsequent filtration through silica gel (5 g, column diameter 1 cm), elution with diethyl ether–methylene dichloride–hexane (1:1:4) (50 cm^3), removal of the solvent and PLC [diethyl ether–methylene dichloride–hexane (1:1:8)] gave starting material **8** (16 mg, 39% recovery) (R_f 0.40) and (8 mg, 14%) of 4-[(tert-*butyldimethylsilyl*)*methyl*]-2-*phenyl*-5-*trimethylsilyl*-2H-1,2,3-*trizole* 1-*oxide* **12** (R_f 0.53), m.p. 101–102 °C (from hexane) (Found: C, 59.8; H, 8.7; N, 11.7. $C_{18}H_{31}N_3OSi_2$ requires C, 59.78; H, 8.64; N, 11.62%).

5-Methyl-1-phenyl-1*H*-1,2,3-triazole 3-oxide **13** (R^1 = Ph, R^5 = Me)[1] (83 mg) was treated as in method (*f*) but using THF instead of methylene dichloride. After 15 min the temperature was increased during 40 min to 20 °C and kept there for 30 min. Filtration through silica gel (10 g, column diameter 2 cm) and elution with diethyl ether–methylene dichloride–hexane (1:1:8) and then with diethyl ether–methylene dichloride (1:1) (100 cm^3) gave an eluate which, by PLC [diethyl ether–methylene dichloride–hexane (1:1:1)] afforded 4-(tert-*butyldimethylsilyl*)-5-*methyl*-1-*phenyl*-1H-1,2,3-*triazole* 3-*oxide* **15** (R^1 = Ph, R^5 = Me, R = Bu^t) (53 mg, 39%) (R_f 0.37), m.p. 195–197 °C (from EtOAc–THF) (Found: C, 62.3; H, 7.9; N, 14.4. $C_{15}H_{23}N_3OSi$ requires C, 62.24; H, 8.01; N, 14.52%). The second fraction contained 4-(tert-*butyldimethylsilyl*)-5-[(tert-*butyldimethylsilyl*)*methyl*]-1-*phenyl*-1H-1,2,3-*triazole* 3-*oxide* **20** (R^1 = Ph, R^4 = $SiBu^tMe_2$, R = Bu^t) (28 mg, 15%) (R_f 0.51), m.p. 109–110 °C (from hexane) (Found: C, 62.3; H, 9.2; N, 10.3. $C_{21}H_{37}N_3OSi_2$ requires C, 62.48; H, 9.24; N, 10.41%). The third fraction contained 4-{tert-*butyl*[(tert-*butyldimethylsilyl*)-*methyl*]*methylsilyl*}-5-[(tert-*butyldimethylsilyl*)*methyl*]-1-*phenyl*-1H-1,2,3-*triazole* 3-*oxide* **20** (R^1 = Ph, R^4 = $SiBu^tMe$-$CH_2SiBu^tMe_2$, R = Bu^t) (27 mg, 11%) (R_f 0.74), m.p. 129–130 °C (from hexane) (Found: C, 62.7; H, 10.0; N, 8.15. $C_{27}H_{51}N_3OSi_3$ requires C, 62.60; H, 9.92; N, 8.11%). The structure of the compound was confirmed by an NOE experiment with irradiation at the phenyl protons. This caused a 1.3% enhancement of the CCH_2Si signal, all other signals remaining unchanged.

4-Chloro-5-methyl-1-phenyl-1*H*-1,2,3-triazole 3-oxide **19** (R^4 = Cl)[1] (68 mg) was treated as in method (*e*) to give a reaction mixture which, after being stirred at 70 °C for 26 h, was evaporated to dryness. Filtration through silica gel (column diameter 2 cm, 10 g), the column was eluted with methylene dichloride–diethyl ether–hexane (1:1:1) (40 cm^3) and then with methylene dichloride–diethyl ether (1:1) (40 cm^3). The latter fraction contained 4-*chloro*-1-*phenyl*-5-*trimethylsilylmethyl*-1H-1,2,3-*triazole* 3-*oxide* **20** (R^1 = Ph, R^4 = Cl, R = Me) (34 mg, 37%), m.p. 116 °C (from EtOAc) (Found: C, 51.3; H, 5.7; N, 15.0. $C_{12}H_{16}ClN_3OSi$ requires C, 51.14; H, 5.72; N, 14.91%). Elution with ethyl acetate–methanol [4:1 (45 cm^3)], removal of solvents, addition of 2 mol dm^{-3} aq. sodium hydroxide (3 cm^3), extraction with methylene dichloride (3 × 5 cm^3), drying of the extract, removal of the solvent and PLC [ethyl acetate–methanol (8:1)] gave starting material (18 mg, 26% recovery) (R_f 0.64) and 4-*chloro*-1-*phenyl*-5-[2-(2,2,6,6-*tetramethylpiperidino*)*ethyl*]-1H-1,2,3-*triazole* 3-*oxide* **16** (16 mg, 14%) (R_f 0.81), m.p. 191 °C (from EtOAc) (Found: C, 62.9; H, 7.5; N, 15.3. $C_{19}H_{27}ClN_4O$ requires C, 62.88; H, 7.50; N, 15.44%).

In a similar manner to that in method (*g*), 5-methyl-1-phenyl-4-trimethylsilyl-1*H*-1,2,3-triazole 3-oxide **19** (R^4 = $SiMe_3$) (52 mg) gave a reaction mixture which, after being stirred at 20 °C for 3 h was filtered through silica gel (5 g, column diameter 1 cm), and the column was washed with diethyl ether–methylene dichloride–hexane (1:1:10) (40 cm^3) and then eluted with diethyl ether–methylene dichloride (1:1) (60 cm^3). The eluate, upon work-up by PLC [diethyl ether–methylene dichloride–hexane (7:7:5)], gave unchanged starting material (16 mg, 31% recovery). The second fraction contained 5-[(tert-*butyldimethyl*-

*silyl)methyl-1-phenyl-4-trimethylsily-*1H-1,2,3-*triazole* 3-*oxide* **20** (R^1 = Ph, R^4 = $SiMe_3$, R = Bu^t) (R_f 0.32) (29 mg, 38%), m.p. 123 °C (from ethyl acetate–hexane) (Found: C, 59.7, H, 8.6; N, 11.5. $C_{13}H_{31}N_3OSi_2$ requires C, 59.78; H, 8.64; N, 11.62%). The third fraction contained 6 mg (7%) 4-*tert*-butyldimethylsilyl)-5-[(*tert*-butyldimethylsilyl)methyl]-1-phenyl-1*H*-1,2,3-triazole 3-oxide **20** (R^1 = Ph, R^4 = $SiBu^tMe_2$, R = Bu^t) (6 mg, 7%), identical with the material described above. The last fraction contained 5-[(*tert*-butyldimethylsilyl)methyl]-1-[2'-(*tert*-butyldimethylsilyl)phenyl]-4-trimethylsilyl-1*H*-1,2,3-triazole 3-oxide **20** (R^1 = 2-(Bu^tMe_2Si)C_6H_4, R^4 = $SiMe_3$, R = Bu^t] (13 mg, 13%) (R_f 0.56) as an oil, *m/z* 460 (M^+ − Me, 2%), 418 (M^+ − C_4H_9, 11) 346 (M^+ − 2 × C_4H_9Me, 90) and 73 (100).

Acknowledgements

This work was supported by the Danish Technical Research Council. P. V. thanks the Technical University of Denmark for a grant. The NMR spectrometer is a gift from the Velux Foundation of 1981, The Danish Technical Research Council, The Ib Henriksen Foundation, and the Torkil Steenbeck Foundation.

References

1 M. Begtrup and G. Jonsson, *Acta Chem. Scand., Ser. B*, 1987, **41**, 724.
2 M. Begtrup, *Bull. Soc. Chim. Belg.*, 1988, **97**, 573.
3 I. Almena, M. Begtrup and A. de la Hoz, *Acta Chem. Scand.*, 1992, **46**, 1096.
4 M. Begtrup, unpublished results.
5 M. Begtrup and P. Vedsø, *J. Chem. Soc., Perkin Trans. 1*, 1992, 2555.
6 M. Begtrup, *Heterocycles*, 1992, **33**, 1129.
7 H. Emde, D. Domsch, H. Feger, U. Frick, A. Götz, H. H. Hergott, K. Hoffmann, W. Kober, K. Krageloh, T. Oesterle, W. Steppan, W. West and G. Simchen, *Synthesis*, 1982, 1.
8 M. Begtrup and K. V. Poulsen, *Acta Chem. Scand.*, 1971, **25**, 2087.
9 F. Effenberger and W. Spiegler, *Chem. Ber.*, 1985, **118**, 1643.
10 F. Effenberger and A. Krebs, *J. Org. Chem.*, 1984, **49**, 4687.
11 F. Effenberger, M. Roos, R. Ahmad and A. Krebs, *Chem. Ber.*, 1991, **124**, 1639.
12 M. Begtrup, *J. Chem. Educ.*, 1987, **64**, 974.
13 M. Begtrup, P. Larsen and P. Vedsø, *Acta Chem. Scand.*, 1992, **46**, 972.
14 M. Begtrup and H. P. Nytoft, *Acta Chem. Scand., Ser. B*, 1986, **40**, 262.
15 M. Begtrup and J. Holm, *J. Chem. Soc., Perkin Trans. 1*, 1981, 503.
16 J. L. Riebsomer and D. A. Stauffer, *J. Org. Chem.*, 1951, **16**, 1643.

Paper 2/04400E
Received 13*th August* 1992
Accepted 15*th October* 1992