Organosilicon Chemistry. Part X.[1] The Reaction of Diazomethyltrimethylsilane with Trifluoroacetonitrile and Cyanogen Halides to give Triazoles

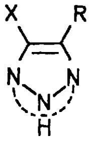
By **J. M. Crossman, R. N. Haszeldine,*** and **A. E. Tipping,** Chemistry Department, University of Manchester Institute of Science and Technology, Manchester M60 1QD

Reaction of diazomethyltrimethylsilane with trifluoroacetonitrile at room temperature gives 4-trifluoromethyl-2-trimethylsilyl-1,2,3-triazole in high yield, while reaction with cyanogen chloride or cyanogen bromide yields mixtures of the 4-halogeno-2-trimethylsilyl-1,2,3-triazole and an isomeric product, probably the 2-halogeno-2-(*N*-trimethylsilylimino)diazoethane. Hydrolysis of the 1 : 1 adducts gives, in each case, the corresponding 4-substituted-1,2,3-triazole in good yield.

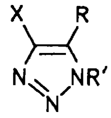
DIAZOALKANES are reported [2-5] to react with nitriles of the type XCN (where X is an electron-withdrawing group) to afford 1,2,3-triazoles (I). However, cyanogen reacts with diazomethane or diazoethane to give mixtures of (I) (where X = CN, R = H or Me) and the corresponding *N*-alkyl-1,2,3-triazole (II) (where X = CN, R = H or Me, R′ = Me or Et) formed *via* reaction of (I) with a second molecule of diazoalkane.[2] Cyanogen chloride and cyanogen bromide are reported [3] to react with diazomethane or diazoethane to give only *N*-alkylated products; a later investigation of the reaction of cyanogen bromide with diazomethane showed that all three *N*-alkyl-1,2,3-triazole isomers (IIa)—(IIc) (X = Br, R = H, R′ = Me) were formed.[4]

Diazomethyltrimethylsilane (III) has been synthesised only recently and its reactions have, as yet, been little studied.[6-8] In the present work the reactions of (III) with the nitriles CF_3·CN, ClCN, and BrCN have been investigated in order to compare the results obtained with those previously reported for reaction of nitriles with other diazoalkanes.

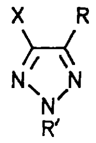
Diazoalkane (III), reacted with trifluoroacetonitrile (1·8 : 1·0 molar ratio), gave a 1 : 1 adduct (93%) (on the basis of elemental analysis and a molecular-weight determination) and recovered (III) (44%). The 1 : 1 adduct is considered to be an *N*-trimethylsilyl-4-trifluoromethyl-1,2,3-triazole, probably the 2-trimethylsilyl isomer (IVa), on the basis of the following evidence.



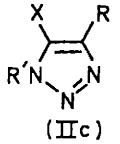
(I)



(IIa)



(IIb)



(IIc)

$Me_3Si·CHN_2$

(III)

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[1] Part IX, R. Fields, R. N. Haszeldine, and (Mrs.) A. F. Hubbard, *J.C.S. Perkin I*, 1972, 847.

[2] A. Peratoner and E. Alzarello, *Gazzetta*, 1908, **38**, 76.

[3] A. Tamburello and A. Milazzo, *Gazzetta*, 1908, **38**, 95.

[4] C. Pedersen, *Acta Chem. Scand.*, 1959, **13**, 888.

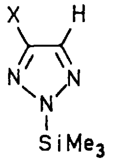
[5] J. M. Stewart, R. L. Clark, and P. E. Pike, *J. Chem. and Eng. Data*, 1971, **16**, 98.

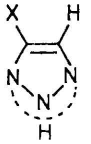
[6] M. F. Lappert and J. S. Poland, *Adv. Organometallic Chem.*, 1970, **9**, 397, and references contained therein.

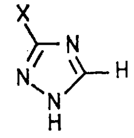
[7] D. Seyferth and T. C. Flood, *J. Organometallic Chem.*, 1971, **29**, C25.

[8] M. F. Lappert and J. S. Poland, *J. Chem. Soc.* (*C*), 1971, 3910.

The adduct was readily hydrolysed by aqueous ethanol or even by atmospheric moisture to give 4-trifluoro*methyl*-1,2,3-triazole (Va). This product was identified


(IV)


(V)

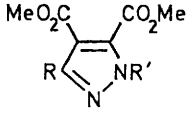

(VI)

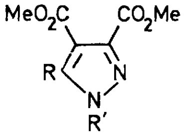
a; X = CF_3
b; X = Cl
c; X = Br

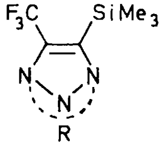
a; X = CF_3
b; X = Cl
c; X = Br

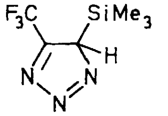
as having the 1,2,3-triazole structure and not the alternative 1,2,4-triazole structure (VI) (where X = CF_3), because of the similarity of its i.r. spectrum, mass spectral breakdown pattern, and ^1H n.m.r. spectrum with those of the positively identified 4-chloro- and 4-bromo-1,2,3-triazoles, (Vb) and (Vc), respectively, which were also prepared in the present work (see later).

The ^1H n.m.r. absorption of the trimethylsilyl group in the adduct (Table) is in the region reported for N–$SiMe_3$ (*ca.* τ 9·5) absorption rather than C–$SiMe_3$ (*ca.* τ 9·8) absorption in the trimethylsilyl-substituted pyrazoles of structure (VII) or less probably structure (VIII) (where R = R′ = Me_3Si;[7] R = Me_3Si, R′ = H;[8] R = H, R′ = Me_3Si[8]). An N–H n.m.r. absorption expected at *ca.* τ −6[9] if the adduct had structure (IX; R = H) was not observed.


(VII)


(VIII)


(IX)


(X)

This spectral evidence and the observation[7] that the N·$SiMe_3$ group in the pyrazole [(VII) or (VIII), R = R′ = Me_3Si] is hydrolysed preferentially to the C·$SiMe_3$ group and also under very mild conditions to give the pyrazole [(VII) or (VIII), R = Me_3Si, R′ = H] is strong evidence that the present adduct contains an N·$SiMe_3$ group and not a C·$SiMe_3$ group. Also the observation that the present adduct did not react further with an excess of diazoalkane (III) to give the product (IX; R = CH_2·$SiMe_3$) is consistent with the adduct containing an N·$SiMe_3$ group and not an NH group.

The exact attachment of the $SiMe_3$ group to the ring is not certain but, of the three possible structures for an *N*-trimethylsilyl-4-trifluoromethyl-1,2,3-triazole, structure (IVa) is the most likely. Thus trimethylsilyl azide and but-2-yne react to give 4,5-dimethyl-2-trimethylsilyl-1,2,3-triazole and not 4,5-dimethyl-1-trimethylsilyl-1,2,3-triazole as determined by i.r. and n.m.r. spectral evidence and also chemical evidence.[10] It is also reported[11] that with 3,5-bis(trifluoromethyl)-*N*-(trimethylsilyl)pyrazole n.m.r. coupling (0·76 Hz) is observed between the $SiMe_3$ group (in the 1-position) and the adjacent CF_3 group (in the 5-position); no such coupling was observed in the spectrum of adduct (IV).

Thus in the reaction of (III) with trifluoroacetonitrile the expected initial adduct (X) rearranged *via* trimethylsilyl migration to give adduct (IVa) rather than by hydrogen migration to give adduct (IX; R = H). This preferential migration of a trimethylsilyl group is as found by other workers in the preparation of trimethylsilyl-substituted pyrazoles.[6-8]

The reaction of the diazoalkane (III) with cyanogen chloride and cyanogen bromide gave relatively high-boiling products. These were readily hydrolysed by atmospheric moisture, and this, coupled with their low-volatility, made them difficult to purify. The cyanogen chloride product was isolated pure in low yield (19—45%) and identified as a 1 : 1 adduct by elemental analysis and a molecular-weight determination (mass spectrometry); the cyanogen bromide product (*ca.* 80%) was not purified, but its i.r. and n.m.r. spectra were very similar to those of the cyanogen chloride adduct.

On hydrolysis the adducts formed the desilylated 1,2,3-triazoles (Vb) (84%) or (Vc) (61%), respectively. These were identified by spectral evidence (i.r., mass, and n.m.r.) and shown not to be the alternative 1,2,4-triazoles of type (VI) by a comparison of their melting points [(Vb), m.p. 71 °C; (Vc), m.p. 108 °C] with those reported for 4-chloro-1,2,4-triazole (m.p. 167 °C[12]) and 4-bromo-1,2,4-triazole (m.p. 188—189 °C[13]).

The reactions were expected to proceed similarly to that of (III) with trifluoroacetonitrile and thus afford 4-chloro- and 4-bromo-2-trimethylsilyl-1,2,3-triazole, (IVb) and (IVc), respectively. However, the ^1H n.m.r. spectra of the products showed the presence of two isomers and the spectra are compared in the Table with that of the trifluoroacetonitrile adduct (IVa).

N.m.r. spectra of nitrile–diazoalkane (III) 1 : 1 adducts

Nitrile	Chemical shift (τ)	Intensity	Assignment
ClCN	9·82	9	$SiMe_3$
	9·53	6	$NSiMe_3$
	6·03	1	CH
	2·40	0·67	CH
BrCN	*ca.* 9·7	9	$SiMe_3$
	ca. 9·5	6·7	$NSiMe_3$
	ca. 6·3	1	CH
	ca. 2·35	0·75	CH
CF_3·CN	9·40	9	$NSiMe_3$
	1·97	1	CH

The bands at τ 9·53 and 2·40 in the spectrum of the cyanogen chloride product are assigned to the $NSiMe_3$ and CH protons in the 4-chlorotriazole (IVb) and those

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[9] H. Gold, *Annalen*, 1965, **688**, 205.

[10] L. Birkhofer and P. Wegner, *Chem. Ber.*, 1966, **99**, 2512.

[11] D. H. O'Brien and C. P. Hrung, *J. Organometallic Chem.*, 1971, **27**, 185.

[12] J. Thiele and W. Manchot, *Annalen*, 1898, **303**, 33.

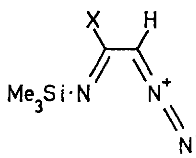
[13] W. Manchot and R. Noll, *Annalen*, 1905, **343**, 1.

at τ *ca.* 9·5 and *ca.* 2·35 in the spectrum of the cyanogen bromide adduct are assigned to the protons in the same groups in the 4-bromotriazole (IVc). The other bands present in the spectra of each of the products ($SiMe_3$: CH ratio 9 : 1) are assigned to a second major isomer; NH bands expected at *ca.* τ −6 were not observed, as in the spectrum of (IVa).

The ratio of the two cyanogen chloride isomers in a particular sample is invariant over the temperative range 0—100 °C (n.m.r.), but different ratios (from 2 : 1 to 1 : 2) are obtained depending on the reaction temperature used and whether the reaction is carried out in the absence or presence of a solvent. However, these different isomer ratios obtained may not be significant, because of the low yields of adducts isolated.

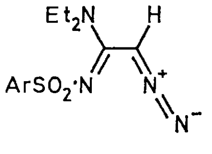
The i.r. spectra of the adduct mixtures each showed a weak band at 4·75 μm which is indicative of the presence of a diazo-grouping; the i.r. spectrum of the trifluoroacetonitrile adduct (IVa) did not contain this absorption.

These observations can be explained by the formation of the 2-halogeno-2-(*N*-trimethylsilylimino)diazoethanes (XIa) and (XIb) as the other 1 : 1 adducts in the cyanogen chloride and cyanogen bromide reactions.



(XI)

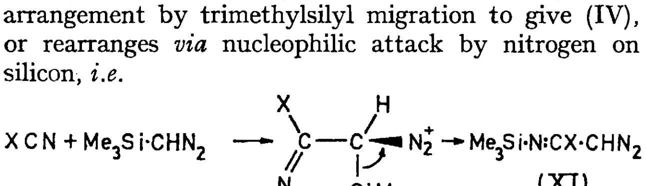
a; X = Cl
b; X = Br



(XII)

Similar open-chain isomers of type (XII) have been reported [14] as the products of reaction of *NN*-diethylethynylamines with substituted benzenesulphonyl azides; with such compounds the diazo-protons absorb at τ *ca.* 5·8 and weak i.r. diazo-group absorptions are observed at *ca.* 4·75 μm.

The observed slow rates of reaction of the diazoalkane (III) with the nitriles suggest that, rather than the reactions being 1,3-dipolar in type, they perhaps involve nucleophilic attack by the diazoalkane on the carbon atom of the nitrile to afford an intermediate of type (XIII), which either ring closes and then undergoes rearrangement by trimethylsilyl migration to give (IV), or rearranges *via* nucleophilic attack by nitrogen on silicon, *i.e.*



(XIII) (XI)

The absence of the diazo-imine in the products from the trifluoroacetonitrile reaction may be due to the strong −*I* effect of the CF_3 group which reduces the availability of the nitrogen lone-pair in the intermediate (XIII) (where X = CF_3) and thus renders nucleophilic attack by nitrogen on silicon unfavourable.

The ready hydrolysis of the initial 1 : 1 adducts to give, in each case, reasonable yields of the desilylated 1,2,3-triazoles (V) probably occurs *via* nucleophilic attack by water on silicon to give the stabilised triazole anion either directly or by ring closure of the desilylated diazoimine anion.

EXPERIMENTAL

Reactants and products were manipulated, where possible, in a conventional high-vacuum apparatus to avoid contact with air or moisture. Products were separated by repeated fractional distillation *in vacuo* and their identities were established by elemental analysis, i.r. spectroscopy (Perkin-Elmer spectrometer model 257 with sodium chloride optics), n.m.r. spectroscopy (Perkin-Elmer R10 or R20 spectrometers operating at 60·0 MHz for ^1H and 56·46 MHz for ^{19}F and using internal tetramethylsilane and external trifluoroacetic acid as the respective references and a Varian Associates HA 100 instrument operating at 100 MHz for ^1H), and mass spectrometry (A.E.I. M.S./902 instrument).

Cyanogen bromide was prepared according to the method of Hartman and Dreger [15] and was redistilled immediately before use. Trifluoroacetonitrile [16] and cyanogen chloride [17] were prepared as described and were purified by fractional distillation *in vacuo*. Diazomethyltrimethylsilane was prepared from chloromethyltrimethylsilane by the following series of reactions.

The preparation of the amine hydrochloride, $Me_3Si{\cdot}CH_2{\cdot}\overset{+}{N}H_3\overset{-}{Cl}$, was carried out as described by Sommer and Rockett.[18] This compound was converted into the diazoalkane by the method reported by Seyferth [19] with the following procedure used for the last stage. The *N*-nitroso-*N*-trimethylsilylurea (*ca.* 14 g) was suspended in n-pentane (30 ml) and treated with aqueous potassium hydroxide (12·5M; 10 ml) with the reaction mixture being stirred vigorously (0·5 h). The organic layer was separated, dried ($MgSO_4$; *ca.* 10 s), and then rapidly filtered. Repeated fractionation of the filtrate *in vacuo* yielded the diazoalkane, which was shown (n.m.r.) to be contaminated with hexamethyldisiloxane (*ca.* 5%).

Reactions of Diazomethyltrimethylsilane.—(a) *With trifluoroacetonitrile.* A mixture of the nitrile (0·95 g, 10·0 mmol) and the diazoalkane (2·08 g, 18·2 mmol) was sealed in a Pyrex tube (*ca.* 300 ml) *in vacuo* at −196 °C and the tube and contents were allowed to warm to room temperature and remain at that temperature for 12 weeks; the reaction gave (i) unchanged diazoalkane (0·97 g, 8·5 mmol, 44% recovered), (ii) *4-trifluoromethyl-2-trimethylsilyl-*1,2,3-*triazole* (1·95 g, 9·3 mmol, 93%) [Found: C, 34·5; H, 5·1%; *M* (mass spectrometry), 209. $C_6H_{10}F_3N_3Si$ requires C, 34·4; H, 4·8%; *M*, 209], $\lambda_{max.}$ 3·18w and 3·37m (C–H str.), 6·38m, 6·52s, 6·99w, 7·05w, 7·30s, 7·95s, 8·00s ($SiMe_3$), 8·20s, 8·40vs, 8·70vs, 8·75vs, 9·01m, 9·71m, 10·00s, 10·15w, 11·76vs ($SiMe_3$), 13·00s, 13·37s, 14·03w, and 15·67m μm; *m/e* 209 (39%, M^+), 194 [9%, $(M - Me)^+$], 118 (11%, $C_3H_2F_2N_3^+$),

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[14] M. Regitz and G. Himbert, *Tetrahedron Letters*, 1970, 2823.

[15] W. W. Hartmann and E. E. Dreger, *Org. Synth.*, 1948, Coll. Vol. II, p. 150.

[16] F. Swarts, *Bull. Sci. Acad. Roy. Belg.*, 1922, **8**, 343.

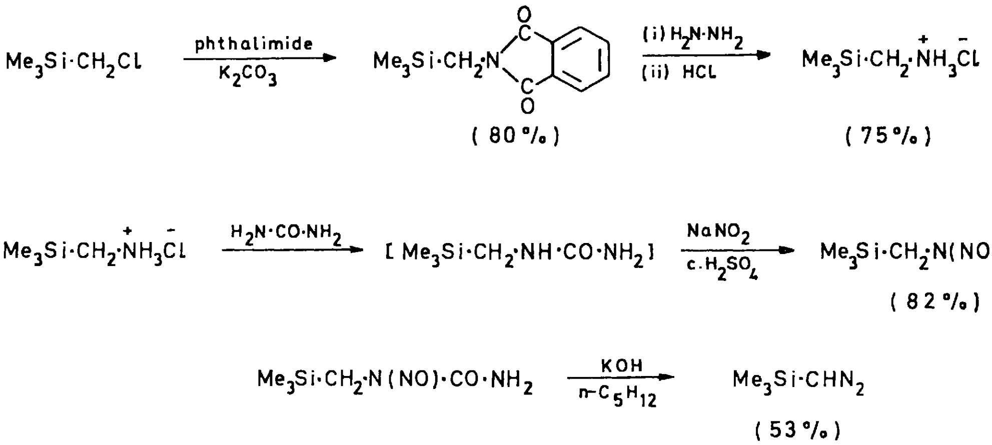
[17] R. P. Cook and P. L. Robinson, *J. Chem. Soc.*, 1935, 1001.

[18] L. H. Sommer and J. Rockett, *J. Amer. Chem. Soc.*, 1951, **73**, 5130.

[19] D. Seyferth, A. W. Dow, H. Menzel, and T. C. Flood, *J. Amer. Chem. Soc.*, 1968, **90**, 1080.

104 (13%, $C_2F_2N_3^+$), 91 (22%, $C_3H_8FSi^+$), 77 (100%, Me_2SiF^+), 73 (28%, Me_3Si^+), 45 (9%, CFN^+), and 43 (9%, $MeSi^+$), *and* (iii) non-volatile material (0·1 g).

The product (0·43 g, 2·1 mmol) was treated with aqueous ethanol (90%, 1 ml) at room temperature (24 h) and the volatile material removed *in vacuo* to afford crystals of 4-*trifluoromethyl*-1,2,3-*triazole* (0·19 g, 1·4 mmol, 56%) [Found: C, 26·5; H, 1·6; N, 30·4%; *M* (mass spectrometry), 137. $C_3H_2F_3N_3$ requires C, 26·3; H, 1·5; N, 30·6%; *M*, 137], m.p. 78·5 °C; $\lambda_{max.}$ 3·04m, 3·15m, 3·44w, 6·34s, 6·84s, 7·12w, 7·35s, 7·58w, 8·07m, 8·62s, 8·70s, 9·05m, 9·43m, 10·01s, 10·22w, 12·20s, 13·42m, 13·83w, and 14·97m μm; *m/e* 137 (100%, M^+), 118 [13%, $(M - F)^+$], 110 (15%, $C_2HF_3N_2^+$), 108 (8%, $C_3HF_3N^+$), 42 (17%, $CH_2N_2^+$), and 31 (9%, CF^+); ^1H n.m.r. band [15% solution in $(CD_3)_2SO$] at τ 1·33 (s, CH) and ^{19}F n.m.r. band at −19·00 p.p.m. (s, CF_3) to low field of reference.



The reaction was repeated using a 1 : 1 molar ratio of reactants (*ca.* 10 mmol of each) both neat, in solvent ether (8 ml), and in solvent cyclohexane (8 ml). The yellow diazoalkane colour was discharged in 4, 4, and 5 h, respectively, to give the adduct triazole in 79, 84, and *ca.* 80% yield; in the last reaction hydrolysis of the adduct with aqueous ethanol afforded 4-trifluoromethyl-1,2,3-triazole (50%).

(b) *With cyanogen chloride.* In a typical experiment, a mixture of cyanogen chloride (0·54 g, 8·5 mmol) and the diazoalkane (0·97 g, 8·5 mmol), were allowed to react as in experiment (a) (5 days); the reaction gave (i) unchanged cyanogen chloride (trace), (ii) hexamethyldisiloxane (0·55 g, 3·4 mmol, 80%), formed by hydrolysis of the initial 1 : 1 adduct, (iii) a mixture of 4-chloro-2-trimethylsilyl-1,2,3-triazole and another 1 : 1 adduct (0·29 g, 1·6 mmol, 19%) [Found: C, 34·5; H, 5·8%; *M* (mass spectrometry), 175. Calc. for $C_5H_{10}ClN_3Si$: C, 34·2; H, 5·7%; *M*, 175], $\lambda_{max.}$ 3·12w, 3·18w, and 3·37m (C–H str.), 4·48w, 4·76w ($>CN_2$ group), 6·71m, 7·04w, 7·07w, 7·22w, 7·69s, 7·96s ($SiMe_3$), 8·13s, 8·40m, 9·09w, 9·52w, 10·00s, 11·76s ($SiMe_3$), 12·50m, 13·09m, 13·25m, and 14·10w μm; *m/e* 177 and 175 (66%, M^+), 134 and 132 (98%, $C_4H_7ClNSi^+$), 106 and 104 (100%, $C_2H_3ClNSi^+$), 73 (59%, Me_3Si^+), 66 (46%, $C_2N_3^+$), 45 (68%, CH_5Si^+), and 43 (67%, $MeSi^+$), and (iv) a mixture (0·65 g) of 4-chloro-1,2,3-triazole and an unidentified pink solid.

The 1 : 1 adduct (0·27 g, 1·5 mmol) reacted with aqueous ethanol (90%, 1 ml, 1 min), gave 4-*chloro*-1,2,3-*triazole* (0·13 g, 1·25 mmol, 84%) [Found: C, 23·3; H, 1·9; Cl, 34·1; N, 40·7%; *M* (mass spectrometry), 103. $C_2H_2ClN_3$ requires C, 23·2; H, 1·9; Cl, 34·3; N, 40·6%; *M*, 103], m.p. 71 °C; $\lambda_{max.}$ 3·15s, 3·22w, 3·27m, 3·37m, 3·44m, 6·55s, 7·58s, 7·94m, 7·97m, 8·20s, 8·73s, 8·86s, 9·26s, 9·95s, 10·14m, 11·66m, 12·25s, 13·74w, 14·28w, and 15·36m μm; *m/e* 105 and 103 (100%, M^+), 78 and 76 [28%, $(M - HCN)^+$], 76 and 74 [21%, $(M - HN_2)^+$, 50 and 48 (26%, $CHCl^+$), 49 and 47 (19%, CCl^+), and 42 (6%, $CH_2N_2^+$); ^1H n.m.r. band [15% solution in $(CD_3)_2SO$] at τ 1·90 (s, CH).

In a second experiment reaction of cyanogen chloride (0·50 g, 7·8 mmol) with the diazoalkane (1·01 g, 8·9 mmol) at 70 °C (8 h) and then at room temperature (48 h), gave trimethylsilyl-4-chloro-1,2,3-triazole (0·61 g, 3·5 mmol, 45%).

Reaction was also carried out (*ca.* 10 mmol of each reactant) in solvent ether (8 ml) and cyclohexane (8 ml) at room temperature and gave the 1 : 1 adduct (*ca.* 25%) after 8 and 5 days, respectively.

(c) *With cyanogen bromide.* A mixture of the diazoalkane (1·71 g, 16·0 mmol) and cyanogen bromide (1·70 g, 16·0 mmol) in solvent diethyl ether (8 ml), sealed in a Pyrex tube (*ca.* 300 ml) *in vacuo* and kept at room temperature (8 days), gave a moisture-sensitive brown oil identified as a mixture of 4-bromo-2-trimethylsilyl-1,2,3-triazole and another 1 : 1 adduct (*ca.* 3 g, *ca.* 14 mmol, *ca.* 85%), $\lambda_{max.}$ 3·10w, 3·18w, 3·37m, and 3·43m (C–H str.), 4·48w, 4·76vw (CN_2 group), 6·93m, 7·10m, 7·33m, 7·68m, 7·78s, 7·98s ($SiMe_3$), 8·16s, 8·33m, 8·48m, 9·10m, 9·47m, 9·60m, 10·12s, 10·39m, 11·90vs ($SiMe_3$), 12·50m, 13·05m, 13·90m, and 14·15m μm, which was not purified, but which was treated with water (1 ml) and the resultant material extracted with chloroform (3 × 5 ml). The chloroform extract was dried ($MgSO_4$) and the solvent removed *in vacuo* to afford 4-*bromo*-1,2,3-*triazole* (1·45 g, 9·8 mmol, 61% based on CNBr) [Found: C, 16·4; H, 1·45; N, 28·6%; *M* (mass spectrometry), 148. $C_2H_2BrN_3$ requires C, 16·2; H, 1·35; N, 28·4%; *M*, 148], m.p. 108 °C; $\lambda_{max.}$ 3·15s, 3·22w, 3·34m, 3·40m, 3·57w, 6·60s, 6·83m, 7·58s, 8·02m, 8·06w, 8·28s, 8·73s, 8·81m, 9·22m, 9·32s, 10·12s, 10·20m, 11·63m, 12·18s, 13·79w, 14·33w, and 15·38m μm; *m/e* 149 and 147 (100%, M^+), 122 and 120 [97%, $(M - HCN)^+$], 94 and 92 (32%, $CHBr^+$), 93 and 91 (35%, CBr^+), 68 [49%, $(M - Br)]^+$, 42 (24%, $CH_2N_2^+$), 41 (49%, CHN_2^+), 40 (47%, CN_2^+ and $C_2H_2N^+$), 39 (47%, C_2HN^+), and 38 (45%, C_2N^+); ^1H n.m.r. band [15% solution in $(CD_3)_2SO$] at τ 1·90 (s, CH).

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