^{13}C–H Coupling Constants as a Tool in Tautomerism Studies of 1,2,3-Triazole, 1,2,4-Triazole, and Tetrazole

By **Mikael Begtrup**, Department of Organic Chemistry, Technical University of Denmark, DK-2800 Lyngby, Denmark

Comparison of one or two bond ^{13}C–H coupling constants of azoles and their *N*-methylated derivatives indicates that 1,2,3-triazole, like pyrazole, in concentrated solutions exists as a cyclic associate, whereas 4-methyl-1,2,3-triazole, 1,2,4-triazole, and tetrazole are linearly associated, like imidazole. Similar results were obtained using ^{13}C–H couplings of azole–acetone adducts as reference. The results agree with other trends in physical properties.

THE tautomerism of 1,2,3-triazole,[1,2] 1,2,4-triazole,[2-8] and tetrazole [2,6-10] in solution has been studied by spectroscopic and physicochemical methods with conflicting or non-conclusive results.

Analysis of prototopy by applying one bond ^{13}C–H coupling constants $\{^1J(\text{C–H})\}$ was recently briefly introduced.[11] The coupling constants of the parent compounds were compared with analogous coupling constants of *N*-methylated derivatives with fixed structures representing each of the single possible tautomers. The method was based on scattered observations which indicate that replacement of hydrogen with methyl at amine or amide nitrogen hardly influences the one bond ^{13}C–H couplings to other carbon atoms in α-position. Thus, ^1J(C–H) in methyl- and trimethyl-amine is 133.2 ± 0.2 [12] and 131.7 ± 0.1 Hz,[13] respectively and $^1J[\text{H}_3\text{C(N)}]$ in methyl- and dimethyl-acetamide is 137.5 ± 1 and 138 ± 1 Hz,[14] respectively.

Accurate measurements of representative ^1J(C–H) values under conditions allowing a critical comparison confirm that *N*-methylation hardly influences one bond ^{13}C–H coupling constants to other α-carbon atoms, neither in amines, hydrazines, amides (Table 1), nor in pyrrole (Table 2). The same is true for one bond ^{13}C–H coupling constants to β-carbon atoms in diethylamine and pyrrole.

TABLE 1

^1J(C–H) Values of representative NH compounds and their *N*-methylated derivatives

Parent compound	J(C–H) (Hz)		Corresponding J(C–H) of *N*-methylated derivative (Hz)
Diethylamine	$^1J(\text{CH}_2)$	131.4	131.0
	$^1J(\text{CH}_3\text{–C})$	132.0	
N-Methylaniline [a]	$^1J(\text{CH}_3)$	135.0	134.9
Methylhydrazine [b]	$^1J(\text{CH}_3)$	133.1	133.3
N-Methylformamide [a]	$^1J[\text{CH}_3(E)]$	137.8	137.4
	$^1J[\text{CH}_3(Z)]$	137.8	137.8

[a] Neat. [b] 33% w/v in deuteriochloroform.

Therefore, one bond ^{13}C–H coupling constants of an *N*-methylazole are expected to reflect the corresponding coupling constants of the parent NH tautomer. As shown later, a similar relation exists between ^{13}C–H

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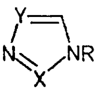
couplings through more than one bond, and *N*-methyl derivatives may be replaced by other derivatives or associates with certain solvents.

RESULTS AND DISCUSSION

In dissolved pyrazole, the *N*-proton undergoes rapid intermolecular exchange.[15] In connexion with observed self-association[16-18] and low concentration dependence of the dipole moment,[19] pyrazole seems best represented by a cyclic (dimer or trimer) associate (4a), at least in concentrated solutions.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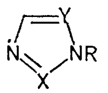
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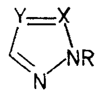
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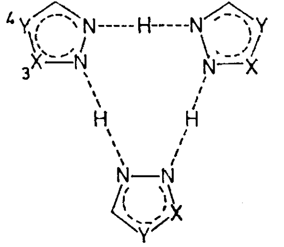

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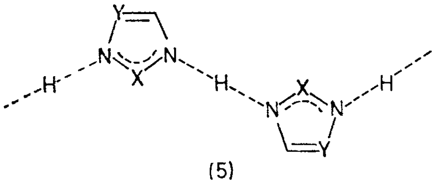
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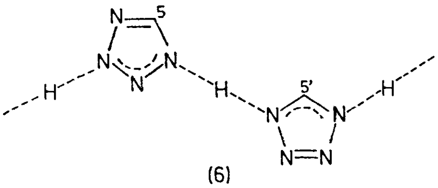

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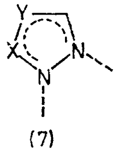
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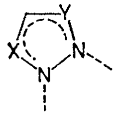
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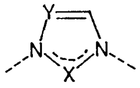
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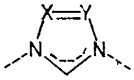
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	X	Y
a;	CH	CH
b;	N	CH
c;	CH	N
d;	N	N
e;	N	CMe

If ^{1}J(C–H) is not influenced by *N*-methyl substitution C-3 (≡C-5) in the associate (4a) is represented by an average between C-3 and C-5 in 1-methylpyrazole (3a; R = Me) with respect to one bond ^{13}C–H coupling constants. This was in fact observed in chloroform and acetone solutions (Table 2). The latter solvent may break self-association, characterized by N · · · H · · · N hydrogen bonds, taking over hydrogen transfer through a solute solvent associate held together by O · · · H · · · N hydrogen bonds. The two mechanisms of hydrogen transfer seem indistinguishable by ^{13}C n.m.r. However, self-association seems predominating in concentrated solutions of pyrazole[20] and imidazole[20,21] in acetone and this formulation is therefore used here for all compounds studied.

For dissolved imidazole, the linear (or macrocyclic) associate (5a) best accounts for the rapid intermolecular exchange of the NH protons,[22] the observed self-association,[17,23] and concentration dependent dipole moment.[19] Correspondingly, ^{1}J(H–C-4) ≡ ^{1}J(H–C-5) of imidazole equals the mean value of ^{1}J(H–C-4) and ^{1}J(H–C-5) of 1-methylimidazole (1a; R = Me) (Table 2).

The identity of C-4 and C-5 in 1,2,3 triazole[1,2] could indicate the presence of the 2*H*-tautomer (3b; R = H). However, observed self-association[1,24,25] is better accounted for by rapid exchange between 1*H*-forms, represented by the linear associate (5b), or by exchange between 1- and 2-*H*-forms through an associate combined in a more or less well defined way of the two possible units (7b) and (9b). ^{1}J(H–C-4) = ^{1}J(H–C-5) of 1,2,3 triazole (194.3 Hz in CDCl$_3$) is in the range between the value of ^{1}J(H–C-4) of 2-methyl-1,2,3-triazole (3b; R = Me) (192.5 Hz) representing the 2*H*-tautomer (1b; R = H) and the mean value between ^{1}J(H–C-4) and ^{1}J(H–C-5) (195.5 Hz) in 1-methyl-1,2,3-triazole (1b; R = Me) which reflects the averaged situation in the rapidly exchanging 1*H*-form (9b). The figures correspond to a 2 : 3 equilibrium mixture of the 2- and 1-*H*-forms. An associate combined solely of the unit (7b) also fits with the observed data and allows for the documented association. Thus, C-5 in (4b) is equivalent to the mean between C-5 in 1-methyl-1,2,3-triazole (1b; R = Me) and C-4 in 2-methyl-1,2,3-triazole (3b; R = Me), whereas C-4 in (3b) is equivalent to the mean between C-4 in (1b; R = Me) and C-4 in (3b; R = Me). Averaging C-4 and C-5 in (4b) renders its expected one bond ^{13}C–H coupling constant to $(196.5 + 192.5 + 194.3 + 192.5)/4 = 194.0$ Hz in good agreement with the value observed for 1,2,3-triazole. A

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cyclic (dimer or trimer) associate (4b) accounts better than a linear analogue for the low concentration dependence of the dipole moment of 1,2,3-triazole.[19] An alternative, random distribution of hydrogen between the three nitrogen atoms leads to an expected ^{1}J(C–H) value of $(196.5 + 192.5 + 194.3)/3 = 194.8$ Hz not fitting so well with the observed value.

For 4-methyl-1,2,3-triazole, one unit reflecting 1,3-exchange (9e) and two distinct units describing exchange between N-1 and N-2 exists [(7e) and (8e)]. The observed ^{1}J(H–C-5) of 4-methyl-1,2,3-triazole (191.8 Hz) exceeds the value calculated for any associate composed solely of the 1,2 units (7e) and (8e) using the data obtained for the *N*-methylated derivatives (1e)—(3e). In contrast, the observed coupling fits with the value [$(191.3 + 192.7)/2 = 192.0$ Hz] calculated for the associate (5e) composed of 1,3 units (9e). The figures allow for a certain contribution from 1,2 units corresponding to the presence of a mixture of linear (5e) or cyclic [*e.g.* (4e)] aggregates. Steric compression seems without significance in the cyclic associate (4e). Hence, the shift in favour of linear association induced by the *C*-methyl group is due rather to electronic release of the substituent which augments the basicity of N-1 in the 1,2,3-triazole system.

TABLE 2

^{13}C–H Coupling constants of azoles at 32°

Compound	^{1}J(C–H), ^{2}J(C–H), ^{3}J(C–H) (Hz) In deuteriochloroform [a,b]				In hexadeuterioacetone [b,c]			
	C-2	C-3	C-4	C-5	C-2	C-3	C-4	C-5
Pyrrole	184.4	170.2			182.9	169.0		
1-Methylpyrrole	184.0	170.0			183.0	169.1		
Pyrazole		185.5	176.7	185.5		185.1	176.0	185.1
		6.6	9.9	6.6		7.7	9.9	7.7
		6.6		6.6		6.6		6.6
1-Methylpyrazole		184.4	176.3	186.6		183.7	175.6	187.3
		8.1	9.6			8.4	8.8; 10.6	
		5.9				5.9		
Imidazole [d]	205.5		188.6	188.6	205.9		188.1	188.1
			13.2	13.2			13.2	13.2
	9.2		7.3	7.3	9.4		7.3	7.3
1-Methylimidazole			188.1	189.5	206.6		187.3	189.1
			10.5	16.9			10.6	6.71
			10.5	2.8			10.6	
1,2,3-Triazole			194.3	194.3			193.9	193.9
			13.2	13.2			13.6	13.6
1-Methyl-1,2,3-triazole			194.3	196.6				
			11.7	15.4				
2-Methyl-1,2,3-triazole			192.5	192.5				
			12.8	12.8				
4-Methyl-1,2,3-triazole				191.8				191.2
							0; 6.5	
								3.9
1,4-Dimethyl-1,2,3-triazole				192.7				
1,5-Dimethyl-1,2,3-triazole			191.3					
2,4-Dimethyl-1,2,3-triazole				189.5				
1,2,4-Triazole						208.6		208.6
						9.9		9.9
1-Methyl-1,2,4-triazole						205.3		210.1
						11.9		7.3
4-Methyl-1,2,4-triazole						209.7		209.7
						2.8		2.8
Tetrazole								217.0
1-Methyltetrazole								218.4
2-Methyltetrazole								213.7

[a] 33% w/v, except pyrazole and imidazole where spectra were taken in a saturated solution at 20°. [b] Coupling constants to methyl protons are not given. [c] 33% w/v, except 1,2,4-triazole, 1-methyl-1,2,4-triazole, and tetrazole whose spectra were taken in saturated solution (20°). [d] Concurrent data have been reported previously (M. C. Thorpe and W. C. Coburn, *J. Magnetic Resonance*, 1973, **12**, 225).

1,2,4-Triazole should be present mainly as the 1*H*-form (2c; R = H) according to pK_a[4] and dipole moment[19] measurements. The ^{1}H n.m.r. spectrum has been explained in terms of rapid exchange between 1*H*-forms.[5] ^{14}N[6,8] or ^{13}C[2] chemical shifts provide no conclusive information. Association in solutions of 1,2,4-triazole has been demonstrated by i.r. spectra.[3,17]

^{1}J(H–C-3) ≡ ^{1}J(H–C-5) of 1,2,4-triazole was in mid-range between ^{1}J(H–C-3) of 4-methyl-1,2,4-triazole (1c; R = Me) and the mean between ^{1}J(H–C-3) and ^{1}J(H–C-5) of 1-methyl-1,2,4-triazole (3c; R = Me) (Table 2), indicating rapid exchange between 1- and 2-*H*-tautomers, present in the ratio 1 : 1. An associate representing this exchange can be combinations of the units (7c) and (10b). However, only the associate (5c) combined solely of the units (10b) fits with the observed ^{1}J(C–H) values. Thus, averaging C-3 and C-5 of (5c) as above gives $(209.7 + 210.1 + 209.7 + 205.3)/4 = 208.7$ Hz as the expected value, agreeing well with 208.6 Hz found for 1,2,4-triazole. The associate (5c) is linear (or macrocyclic) as confirmed by the observed concentration dependence of the dipole moment.[19] This observation furthermore makes alternative random hydrogen exchange between the three nitrogen atoms, corresponding to a predicted value of (209.7 + 210.1 + 205.3)/3 = 208.4 Hz, unlikely.

Dissolved tetrazole should be present predominantly as the 2*H*-tautomer (3d; R = H), according to ionisation constant [10] and ^{14}N n.m.r. measurements.[8] In contrast, dipole moment,[19] ^{1}H n.m.r.,[9] and ^{13}C n.m.r. chemical shift [2] data are in favour of the 1*H*-form (1d; R = H). I.r. spectra indicate intermolecular association.[17]

^1J(H–C-5) of tetrazole is close to the corresponding value of 1-methyltetrazole (1d; R = Me) and far from that of 2-methyltetrazole (2d; R = Me) (Table 1). In terms of an associate, predominance of the 1*H*-form in rapid equilibrium with the 2*H*-form using the 4 possible units (7d)–(10d), only the linear (or macrocyclic) combination (6d) agrees with the observed coupling constants. Averaging C-5 and C-5′ in (6d) as above gives an expected ^1J(C–H) value of (218.4 + 213.7 + 218.4 + 218.4)/4 = 217.2 Hz, matching much better with the observed coupling constant than that (216.0 Hz) expected assuming random hydrogen exchange. A linear (or macrocyclic) associate is confirmed by observed concentration dependency of the dipole moment.[19]

Like one bond ^{13}C–H coupling constants, two bond ^{13}C–H couplings of carbon atoms adjacent or remote to NH seem almost unaffected by *N*-methylation. Thus ^2J(H–C-4) of imidazole is almost equal to the mean value between ^2J(H–C-4) and ^2J(H–C-5) of 1-methylimidazole.

Therefore, two bond ^{13}C–H coupling constants are also applicable for analysis of tautomerism. The accuracy in assessment is comparable to that obtainable by ^1J(C–H) analysis since corresponding differences between two or one bond coupling constants are of the same order of magnitude (see data for 1-methylimidazole in Table 1).

For 1,2,3-triazole, results of ^2J(C–H) and ^1J(C–H) analysis agree perfectly. The averaged value for the two bond ^{13}C–H coupling constants of C-4 and C-5 in the associate (4b) is calculated to be (15.4 + 12.8 + 11.7 + 12.8)/4 = 13.2 Hz, the value actually observed for 1,2,3-triazole.

Neither in the imidazole nor in the 1,2,4-triazole series does comparison of three bond ^{13}C–H coupling constants of the methylated derivatives with those of the parent azole confirm the results based on one or two bond ^{13}C–H couplings. In both series the couplings transmitted through the methyl-substituted nitrogen atom are strikingly low (2.8 Hz), probably because they are actually four bond couplings, alternative transmission through a conjugated system being preferred.

The azoles, except pyrrole, form adducts with ketonic solvents at low temperature by which the n.m.r. signals of the adducts show up besides those of the self-associated azole.[7,25] The ^{13}C–H coupling constants of the pyrazole–acetone adduct [3a; R = C(OH)Me$_2$] are similar to those of 1-methylpyrazole and represent therefore, like these, the coupling constants of 1*H*-pyrazole (3a; R = H). Applying now the one bond ^{13}C–H coupling constants of the azole–solvent adduct (183.8 + 187.9)/2 = 185.9 Hz is expected for ^1J(H–C-3) of self-associated pyrazole (3a) in perfect agreement with the value observed under similar conditions (185.9 Hz, see Table 3).

Also the two bond ^{13}C–H coupling constant for C-3 of

TABLE 3

^{13}C Chemical shifts and ^{13}C–H coupling constants of azoles in [$^2H_6$]acetone at −40°.[a]

Compound		δ (p.p.m.)				^1J(C–H), ^2J(C–H), ^3J(C–H) (Hz)[b]			
	C-2	C-3	C-4	C-5	C–Me$_2$OH	C-2	C-3	C-4	C-5
Pyrrole						183.3	168.6		
1-Methylpyrrole						182.9	169.0		
Pyrazole		133.4	104.6	133.4			185.9	176.3	185.9
							7.0	9.5; 9.5	7.0
							7.0		7.0
N-1 solvent		138.4	104.6	126.1	86.4		183.8	176.3	187.9
adduct							8.4	8.8; 10.3	9.5
							6.1		4.6
1-Methylpyrazole							183.8	175.8	187.5
							8.3	9.0; 10.5	
							5.7		
1-Methylimidazole						210.1		187.4	189.2
								10.7	16.1
						3.3 3.6		10.7	
1,2,3-Triazole			129.8	129.8				194.5	194.5
								13.4	13.4
N-1 solvent			132.4	121.6	88.0			194.7	197.0
adduct								11.7	16.5
N-2 solvent			133.7	133.7	88.9			192.8	192.8
adduct								12.8	12.8
Tetrazole			143.2						217.9
N-1 solvent adduct			142.9		88.2				219.2
1-Methyltetrazole									218.1
2-Methyltetrazole									213.5

[a] 33% w/v, except pyrazole and tetrazole whose spectra were taken in saturated solution. [b] Coupling constants to methyl protons are not given.

(4a) calculated as the mean between ^{2}J(H–C-4) and ^{2}J(H–C-5) of the azole–solvent adduct agrees well with the observed coupling. Similarly, the average between the two two-bond ^{13}C–H couplings to C-4 of the azole–solvent adduct equals ^{2}J(H–C-4) in self-associated pyrazole. The mean value between ^{3}J(H–C-3) and ^{3}J(H–C-5) of [3a; R = $C(OH)Me_2$], is however different from ^{3}J(H–C-3) in self-associated pyrazole, again indicating that three bond ^{13}C–H coupling constants are not suitable for analysis of tautomerism. Values of ^{1}J(C–H) or ^{2}J(C–H) of the proposed 1,2,3-triazole associate (4b) calculated as above employing the one or two bond ^{13}C–H couplings of the 1,2,3-triazole solvent adducts [1b and 3b; R = $C(OH)Me_2$] also agree with the ^{13}C–H coupling constants of 1,2,3-triazole measured under similar conditions (Table 3).

Azole–solvent adducts do not possess signals which show long range couplings to *N*-methyl groups and therefore provide a better basis for analysis of tautomerism than *N*-methylated azoles. In addition, ^{13}C n.m.r. spectra of azoles are generally better resolved at the low temperature where azole–solvent adduct spectra are recorded.

If the structure of the azole–solvent adduct cannot be elucidated from the symmetry of its ring position as determined by ^{1}H or ^{13}C n.m.r., ^{13}C–H coupling constants may provide the necessary information.

Tetrazole forms only one of two possible solvent adducts of identical symmetry (1d or 3d; R = $C(OH)Me_2$]. ^{1}J(H–C-5) of the solvent adduct is however similar to that of 1-methyl- but far from that of 2-methyl-tetrazole indicating that association of tetrazole with acetone involves N-1.

Conclusions.—In the present investigation, one or two bond ^{13}C–H coupling constants of *N*-methylated azoles or the almost identical values of corresponding azole–solvent adducts have concurrently confirmed that pyrazole in concentrated solution is present as a cyclic (dimer or trimer) associate (4a) and shown that 1,2,3-triazole adopts an analogous structure (4b), whereas linear or macrocyclic association predominates in its *C*-methyl derivative. Imidazole was confirmed to exist as a linear or macrocyclic associate (5a) and analogous structures (5c) and (6d) were established for 1,2,4-triazole and tetrazole.

This division of azoles into linear or cyclic self-associates is in keeping with other physical characteristics. All the parent azoles, including pyrrole, possess similar dipole moments (1.7—2.7 D) in the diluted gas phase according to microwave spectroscopy.[26-30] In solution however, pyrazole and 1,2,3-triazole, like the unassociated pyrrole exhibit low dipole moments (1.6—1.8 D), whereas imidazole, 1,2,4-triazole, and tetrazole have higher values (3.2—5.1 D).[19] In addition, pyrazole and 1,2,3-triazole, like pyrrole, have lower m.p.s and b.p.s[19] and are more readily soluble in non-polar solvents than imidazole, 1,2,4-triazole, and tetrazole.

EXPERIMENTAL

^{13}C N.m.r. spectra were recorded on a Bruker WH-90 instrument using fast Fourier transform pulse technique. 1 000—3 500 Scans were accumulated at 6.0 s intervals with a pulse tilt angle of 60° applying the gated decoupling technique.[31] 8 K Computer memory was used at 1 500 Hz sweep and at least two measurements were averaged. This corresponds to an accuracy of ± 0.2 Hz in the coupling constants obtained by first-order analysis. A slightly increased uncertainty obtains for most couplings to carbon atoms adjacent to *N*-methyl groups due to signal broadening or splitting caused by long range coupling to the methyl protons.

Pyrazole, imidazole, 1-methylimidazole, and 1,2,4-triazole were commercial products (Fluka; purum). The following compounds were prepared by literature methods: 1-methylpyrazole,[32] 1,2,3-triazole,[33] 1-methyl- and 2-methyl-1,2,3-triazole,[33] 1 methyl-1,2,4-triazole,[34] 4-methyl-1,2,4-triazole,[34-35] tetrazole,[36] 1-methyl- and 2-methyl-tetrazole.[20]

4-*Methyl*-1,2,3-*triazole* (1e; R = H).[37]—Dry triphenylacetylmethylenephosphorane [38] (17.4 g) and *m*-nitrophenyl azide [39] (10.5 g) were dissolved in dry methylene chloride (130 ml). After standing overnight the solvent was removed and the residue recrystallized from methylene chloride–hexane (1 : 10) with cooling to −30°. The precipitate was treated with boiling ether (150 ml). Cooling to −30°, decanting, and washing with cold ether (2 × 25 ml) gave a yellow residue (22.1 g) which was refluxed for 6 h in methanol (350 ml). Methanol was removed at 50° and 100 mmHg, the residue was dried (P_2O_5; atmospheric pressure), and treated with hydrogen chloride in ether (500 ml). After precipitation, decanting, and washing with ether (2 × 50 ml) the residue was extracted with boiling water (2 × 50, 30, and 15 ml). The solution was cooled to 0°, filtered, neutralized with sodium hydrogen carbonate, saturated with potassium chloride, and extracted with ether (4 × 75 ml). The ether phase was dried ($MgSO_4$), filtered through activated carbon, and the solvent removed by distillation. Distillation of the residue afforded 4-methyl-1,2,3-triazole (3.6 g, 79%), b.p. 88° at 5 mmHg, m.p. 23° (lit.,[40] b.p. 203° at 752 mmHg, m.p. 23.5°).

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1,4- (1e; R = Me), 1,5- (2e; R = Me), *and* 2,4-*Dimethyl*-1,2,3-*triazole* (3e; R = Me).—These were obtained by methylation of 4-methyl-1,2,3-triazole (5.57 g) with distilled etheral diazomethane. Distillation gave 2,4-dimethyl-1,2,3-triazole (2.70 g, 41%) as a colourless oil, b.p. 123—124°, δ ($CDCl_3$) 7.59br (s, H-5), 4.27 (s, NMe), and 2.36br (s, CMe), ^{13}C n.m.r. δ ($CDCl_3$) 142.9 (C-4), 132.3 (C-5), 40.2 (NMe), and 9.4 (CMe), and a mixture of 1,4- and 1,5-dimethyl-1,2,3-triazole (2.05 g), b.p. 96—97° at 5.0 mmHg in the ratio 1.54 : 1 (^1H n.m.r.) corresponding to 19 and 12% yields. Attempts to separate the latter two compounds by distillation or chromatography proved unsuccessful. 2,4-Dimethyl-1,2,3-triazole was identified through its low b.p., characteristic of 2-substituted 1,2,3-triazoles.[33,41] 1,5-Dimethyl-1,2,3-triazole was identified through comparison with an authentic sample,[42] δ ($CDCl_3$), 7.69 (q, 4-H, J 1.0 Hz), 4.08 (s, NMe), and 2.38 (s, CMe), ^{13}C n.m.r. δ ($CDCl_3$) 131.9 (C-5), 131.4 (C-4), 32.8 (NMe), and 6.8 (CMe). 1.4-Dimethyl-1,2,3-triazole was identified through its spectra, δ ($CDCl_3$) 7.54 (q, H-5, J 0.9 Hz), 4.19 (s, NMe), and 2.40 (d, CMe), ^{13}C n.m.r. δ ($CDCl_3$) 141.9 (C-4), 121.4 (C-5), 35.0 (NMe), and 9.4 (CMe).

[5/1671 *Received, 29th August*, 1975]

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