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ADDITIONS OF 5-PHENYLTETRAZOLE AND OTHER HETEROCYCLIC NH COMPOUNDS TO OLEFINS*

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The reactivity of a range of heterocyclic NH compounds toward cyclohexene under p-*toluenesulfonic acid catalysis was surveyed. 1,2,4-Triazole (38%), carbazole (67%) and 5-phenyltetrazole (83%) gave significant amounts of addition products. 5-Phenyltetrazole reacts with a wide range of unactivated olefins, to give addition products in 65% to 90% yield. This method represents a general, preparatively useful route to 2-alkyl-5-phenyltetrazoles.*

Michael additions of NH-functionality to electron-deficient olefins are well known in organic chemistry. By contrast, very few analogous additions to unactivated olefins have been documented, and most of these involve extreme temperature and pressure, as recently reviewed [1], or photochemical reactions of very specialized substrates [2]. Amines are reported to add π-allyl palladium complexes of 1,3-dienes and allenes to give allylic amines [3]. Previously, we reported the unprecedented addition of benzotriazole to phenylsubstituted, aliphatic, and alicyclic alkenes under *p*-toluenesulfonic acid catalysis [1]. We now report a survey of the reactivity of a range of heterocyclic NH compounds toward a simple unactivated olefin, i.e., cyclohexene, under similar conditions of acid catalysis. This survey indicated the superior reactivity of 5-phenyltetrazole, and its behavior toward a range of olefins was therefore examined.

RESULTS AND DISCUSSION

The heterocyclic compounds were reacted with a 50% excess of an olefin in the presence of either 0.1 or 1 equivalent of *p*-toluenesulfonic acid monohydrate (PTS · H_2O) without solvent in a sealed tube at 80-140°C. After aqueous workup the reaction mixture was examined by GC-MS and, where possible, the addition products were separated by column chromatography or preparative gas chromatography and identified by NMR and microanalysis.

Survey of Heterocyclic NH Addition to Cyclohexene. A group of seven NH-containing heterocyclic compounds (Scheme 1) were each reacted with cyclohexene and one equivalent of PTS · H_2O at 140°C for an extended period (30-45 h). The crude products were analyzed by GC-MS, and the yield of addition products was estimated by combining the integrations of all the GC peaks with the appropriate M^+ ion (Table 1). No addition products were found for benzimidazole, phthalimide, or saccharin, while 2-pyrrolidinone produced only traces (less than 1%) of addition products. Significant amounts of addition products were obtained with 1,2,4-triazole (38%), carbazole (67% of a mixture of four isomers), and 5-phenyltetrazole (83%, 2 isomers), and the results of these reactions are discussed in the following sections.

1,2,4-Triazole was reacted with cyclohexene for 35 h to give a 51% crude yield. GC-MS results showed a single compound with an M^+ 151, corresponding to the expected addition product, and column chromatography afforded 1-cyclohexyl-1,2,4-triazole in 23% isolated yield.

Carbazole was reacted with cyclohexene for 30 h to give a 78% crude yield. Analysis by GC-MS showed the presence of three isomeric compounds (57% GC) with an M^+ 249, corresponding to that of the expected addition product and one

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TABLE 1. Addition of Heterocyclic NH Compounds to Cyclohexane

Heterocycle	Crude yield, %	Isomers, GC%[a]
Benzotriazole[b]	54	6 (54)
Benzimidazole	0	—
Phthalimide	30	—
Saccharin	49	—
2-Pyrrolidinone	6	1 (0,4)
1,2,4-Triazole	51	1 (38)
Carbazole	78	4 (67)
5-Phenyltetrazole	95	2 (83)

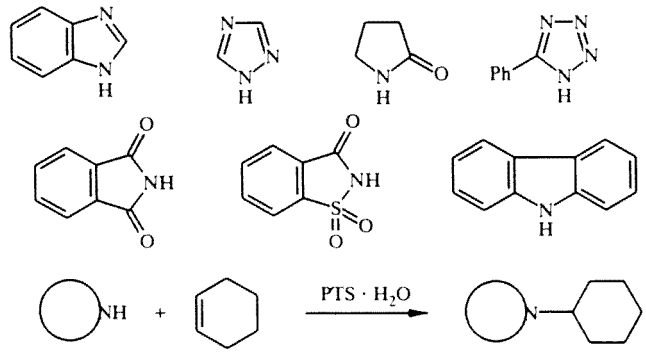
[a]Number of isomers by GC/MS (GC% = crude yield by GC integration).
[b]Data from [1].

TABLE 2. Addition of 5-Phenyltetrazole to Unactivated Olefins and Alkyne

Alkene	Products	Yield, %	Found, % / Calculated, %		
			C	H	N
Cyclohexene	Ia[a]	61	68,70 68,39	7,13 7,06	24,49 24,54
Styrene	II	68	72,42 71,98	5,80 5,64	22,09 22,38
2,4,4-Trimethyl-2-pentene	III	90	70,05 69,73	8,73 8,58	21,67 21,69
Octene	IV—VI[b]	85	70,02 69,73	8,85 8,58	21,86 21,69
	IV—VI[c]	10[d]	—	—	—
	IV—VI[e]	40[f]	—	—	—
2,3-Butadiene	VII and VIII	50	68,76 68,39	7,30 7,06	24,59 24,54
	IX	21	64,46 64,15	6,10 5,92	29,66 29,92
Phenylacetylene	X	—	—	—	—

[a]Compound Ib isolated in 4% yield.
[b]Reaction carried out at 140°C with 1 equivalent PTS · H_2O, IV:V:VI = 50:33:17.
[c]Reaction carried out at 100°C with 0.1 equivalent PTS · H_2O.
[d]Crude yield, IV:V:VI = 4.1:0.1:3.9.
[e]Reaction carried out at 140°C with 0.1 equivalent PTS · H_2O.
[f]Crude yield, IV:V:VI = 28.9:2.4:2.1.

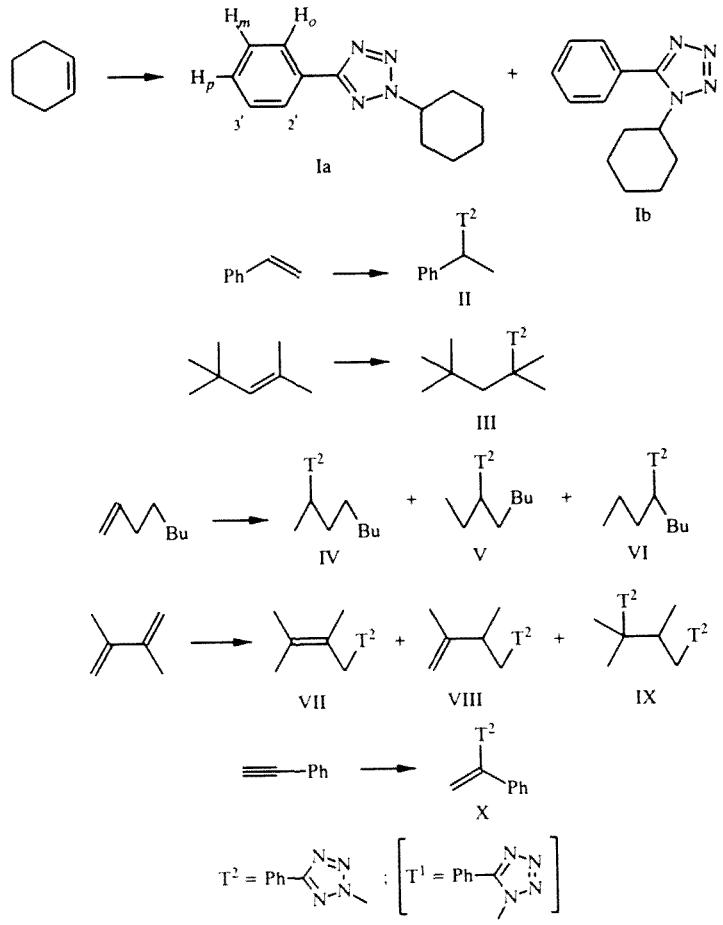
Scheme 1



compound (10% GC) with an M^+ 331, corresponding to two moles of alkene plus one of carbazole. This mixture could not be separated by column chromatography or preparative GC. It is well known that carbazole can react with electrophiles through one or more sites of its benzene rings which are activated by the nitrogen atom [4]. Therefore, it seems likely that benzene ring alkylation is responsible for the number of isomers produced in this reaction.

5-Phenyltetrazole was reacted with cyclohexene and 100% PTS · H_2O at 140°C for 24 h. The crude mixture of reaction products, obtained in 95% yield, was shown by GC-MS to be a mixture of two addition compounds. Column chromatography afforded compounds Ia and Ib (Scheme 2) in 61 and 4% isolated yields respectively (Table 2). 5-Phenyltetrazole, like benzotriazole, has the potential to be alkylated on either $N_{(1)}$ or $N_{(2)}$, and from ^1H and ^{13}C NMR it was apparent that both isomers had been produced. The ^1H and ^{13}C NMR of 1- and 2-methylphenyltetrazole were previously examined in detail [5, 6], and the chemical shifts of the methine hydrogen (4.16 and 4.25 ppm for $N_{(1)}$ and $N_{(2)}$ isomers respectively and the phenyl hydrogens (single multiplet 7.64 ppm for $N_{(1)}$ isomer; H_o 8.13, $H_{m,p}$ 7.41 ppm for $N_{(2)}$ isomer) were reported to be diagnostic of the site of alkylation [5]. Furthermore the chemical shifts of the ortho carbon on the phenyl group is 126.4 ppm for the $N_{(2)}$ isomer and 128.1 ppm for the $N_{(1)}$ isomer. This is because interannular conjugation is impeded in the latter case due to steric effects [6]. These reported diagnostic ^1H and ^{13}C chemical shifts of the 1- and 2-methyl-5- phenyltetrazoles correlated very well with those we now measured for the cyclohexyl-substituted isomers, and indicated that the major isomer produced in our reaction was alkylated on $N_{(2)}$ (Table 3). This assignment was confirmed by the preparation of authentic 2-cyclohexyl-5-phenyltetrazole from the reaction of the sodium salt of 5-phenyltetrazole with cyclohexyl bromide, a method which is known to lead to almost exclusive $N_{(2)}$ alkylation [7]. The compound produced in this fashion was identical in all respects to Ia.

Scheme 2



We found that in their mass spectra, 2-methyl- and 2-cyclohexyl-5-phenyltetrazoles had characteristic peaks at *m/z* (M — 28) and 104 corresponding to loss of N_2 and (RN_3 less H). By contrast, the $N_{(1)}$ isomers had intense peaks at *m/z* (M — 29) and 118 resulting from loss of HN_2 and (RN_2 less H). These spectra are similar to those of primary 1- and 2-alkyl-5-

phenyltetrazoles which have been discussed previously [5], and allows a reasonable degree of certainty in identifying by GC-MS the trace amounts of 1-alkyl-5-phenyltetrazoles which we were unable to isolate. Although in this, and all subsequent cases, the addition of olefins to phenyltetrazole occurred predominantly at $N_{(2)}$, small amounts of the $N_{(1)}$ substituted isomer were often detected by GC, and tentatively identified by analysis of the mass spectrum.

5-Phenyltetrazole Addition to Other Alkenes. Due to the outstanding reactivity of 5-phenyltetrazole toward cyclohexene, it was decided to investigate its reactivity toward a range of olefins (Scheme 2).

The reaction of styrene and 5-phenyltetrazole in the presence of 10% PTS · H_2O at 140°C gave a crude product in 83% yield (Table 2). Purification of the mixture by column chromatography provided II in 68% isolated yield. GC-MS analysis of the crude mixture also showed small amounts (2.5%) of the $N_{(1)}$ isomer. When 100% PTS · H_2O was used, crude product (60%) was obtained, most of which (40%) consisted of dimers or trimers of styrene as analyzed by GC-MS.

Addition of 5-phenyltetrazole to 2,4,4-trimethyl-2-pentene at 140°C for 24 h gave a 95% yield of crude product. Purification by column chromatography provided a single compound isolated in 90% yield, which had ^1H and ^{13}C NMR and mass spectra consistent with structure III. Once again, only trace amounts of the corresponding $N_{(1)}$ isomer were detected by GC-MS.

5-Phenyltetrazole reacted with excess 1-octene (equimolar PTS · H_2O at 140°C for 40 h) and gave a 97% crude yield. Analysis by GC-MS showed this to be a mixture consisting mainly of three isomeric 2-octyl-5-phenyltetrazoles (IV, V, and VI), with trace amounts of the corresponding 1-octyl isomers [sic]. Column chromatography gave a mixture of the three main addition products IV, V, and VI in 85% yield; they were separated by preparative GC, the isomers were isolated and the ^1H NMR spectra were recorded for each. The isomer present in greatest proportion showed a 3H doublet at 1.66 ppm which in this system could only be produced by a methyl group alpha to a CH group, so this compound was assigned structure IV. The structures of the other two isomers were based on an analysis of their MS fragmentation patterns. Fragmentation of the octyl chain occurs readily on either side of the carbon bearing the tetrazole. For example, V shows enhanced loss of ethyl and pentyl, whereas VI loses propyl and butyl preferentially. This assessment is supported by ^1H and ^{13}C NMR chemical shift trends which were very similar to those observed for the benzotriazole series for which the isomers have been rigorously identified [1, 8].

The pattern of addition products was qualitatively similar to that of the 1- and 2-octylbenzotriazole series [1], with all possible isomers resulting from double bond migration of the starting olefin, as well as isomers from N1 and N2 substitution. For the 5-phenyltetrazole series, addition occurred through N2 almost exclusively, presumably because of crowding of N1 due to the phenyl group.

The reaction was repeated using a catalytic (10%) amount of PTS · H_2O at 100°C for 52 h, but only 10% crude yield of the same addition products was obtained; at 140°C for 52 h, the crude yield was improved to 40%.

When 2,3-dimethylbutadiene was reacted with 5-phenyltetrazole for 24 h, addition products were obtained in essentially quantitative crude yield. Column chromatography allowed the separation of two fractions. The first fraction consisted of a mixture of two isomers in a ratio of 70:30, which could not be further separated. These compounds were easily identified as being VII and VIII by ^1H and quantitative ^{13}C NMR, and a satisfactory microanalysis was obtained for the mixture. The second fraction consisted of a single compound IX, which was fully characterized by microanalysis, ^1H and ^{13}C NMR. Compound VII arises from 1,4-addition to the conjugated diene, while compound VIII is the product of double bond migration from VII under acid catalysis, and compound IX is the product of further reaction of VII or VIII with 5-phenyltetrazole, to give the double addition product.

When 5-phenyltetrazole was reacted with phenylacetylene and 10% PTS · H_2O at 80°C for 24 h, a crude mixture was obtained in 30% yield. Analysis of this mixture by GC-MS showed only 1% of a component corresponding to the expected addition product X (M^+ 248). Other components identified by GC-MS include 5% of phenylacetaldehyde, and unexpectedly, 3,5-diphenylpyrazole. The latter compound could arise from initial formation of the expected compound X, followed by loss of N2 from the tetrazole ring, then cyclization to form the pyrazole product. There are some literature procedures for the thermal fragmentation of 2,5-disubstituted tetrazoles resulting in the loss of nitrogen and generation of a reactive nitrilimine intermediate, which adds to multiple bonds giving 5-membered heterocyclic adducts [9]. Due to the complex nature of the mixture, no further purification was attempted. When the reaction was carried out using 5% PTS · H_2O, no addition products could be identified by GC-MS.

In conclusion, 5-phenyltetrazole adds to a wide range of unactivated olefins in high yield under acid catalysis. This provides a preparative method for 2-alkyl-5-phenyltetrazoles superior to those previously available (a recent paper [10] should be mentioned, in particular, which reported a selective $N_{(2)}$ alkylation of tetrazole with limited success).

TABLE 3. ^1H and ^{13}C NMR Differences Between $N_{(1)}$ and $N_{(2)}$ Isomers of 5-Phenyltetrazole

Compound	δ_H, ppm[a]		δ_C, ppm[b]				
	δ_{Ho}	$\delta_{Hm,p}$	δ_{CH}	$\delta_{C2'}$	$\delta_{C3'}$	δ_{CH}	δ_C
2-Cyclohexyl-5-phenyltetrazole Ia[c]	8,13...8,18	7,45 7,52	4,70...4,79	126,7	128,8	63,1	164,5
1-Cyclohexyl-5-phenyltetrazole Ib[c]	7,58	7,58	4,29...4,37	128,7	129,2	58,1	153,5
2-Methyl-5-phenyltetrazole	8,13	7,41	4,25	126,4	128,5	39,4	—
1-Methyl-5-phenyltetrazole	7,64	7,64	4,16	128,1	128,8	35,0	—

[a]^1H NMR data of 1- and 2-methyl-5-phenyltetrazole from [5].
[b]^{13}C NMR data of 1- and 2-methyl-5-phenyltetrazole from [6].
[c]See structures in Scheme 2.

EXPERIMENTAL

Melting points were measured on a Thomas–Hoover melting point apparatus and are uncorrected. ^1H and ^{13}C NMR data were collected on a Varian VXR 300 NMR spectrometer (300 MHz and 75 MHz respectively), with TMS as internal reference in deutero-chloroform (except where indicated). All GC retention times and mass spectra were determined on a HP5890 Series II Capillary GC operating in split mode with helium carrier gas and fitted with a mass selective detector (MSD 5972). The column used was an HP5 capillary column 30 m × 0.25 mm, with 0.25 μ film thickness of 5% phenyl-methylsilicone gum. The temperature program used initial temperature 50°C for 1 min, then ramped at 16°C min^{-1} to 250°C. The GC yield was determined by integration of the total ion current of the MSD scaled to add up to the crude yield. The preparative GC separations were carried out on a GM 580 Isothermal GC fitted with a 1/4" stainless steel column packed with 10% OV-101 on Chromosorb W-HP with helium carrier gas using a thermal conductivity detector. Preparative GC (GOW-MAC GC 580) runs were carried out isothermally at 145-180°C, and separations were achieved on the basis of boiling point with compounds eluting from the packed column in the same order as on the capillary column specified above. All starting materials were supplied by Aldrich Chemical Co. or Fisher and used without further purification.

General Procedures. The heterocyclic NH compound (10 mmol) and an alkene (15 mmol) were heated under condition A (100% PTS · H_2O, 140°C) or condition B (10% PTS · H_2O, 80°C) or condition C (10% PTS · H_2O, 140°C) in a sealed tube for 24-45 h. The reaction mixture was dissolved in ethyl acetate (50 cm^3), washed with 10% NaOH (25 cm^3) three times, dried and evaporated to give a residue. Mixtures of compounds were separated by column chromatography or preparative gas chromatography where possible, and characterized by a combination of ^1H and ^{13}C NMR, and microanalysis as indicated.

Heterocyclic NH Addition to Cyclohexene

Benzimidazole. The reaction of benzimidazole was carried out under condition A for 45 h. After workup, only starting material was obtained.

Phthalimide. The addition reaction was carried out using condition A for 30 h, and crude products were obtained (30%). GC-MS analysis of this mixture showed no compound with an *m/z* corresponding to addition product.

Saccharin. Under condition A, saccharin was reacted with cyclohexene for 35 h to give a crude product (49%). Analysis of the GC-MS of this mixture showed that no addition product was formed.

1,2,4-Triazole. A crude product was obtained in the reaction of 1,2,4-triazole with cyclohexene under condition A (51%). Analysis by GC-MS showed the presence of one compound (38%) with an *m/z* corresponding to the expected addition compound. After column chromatography, 0.35 g of 1-cyclohexyl-1,2,4-triazole was obtained in 23% yield, as a white micro

crystalline powder; mp 59-61°C. ^{1}H NMR: δ 8.14 (1H, s), 7.95 (1H, s), 4.20 (1H, tt, J = 3.9 and 11.7 Hz), 2.18-2.24 (2H, m), 1.94 (2H, dt, J = 3.3 and 13.5 Hz), 1.72-1.98 (3H, m), 1.27-1.53 (3 H, m). ^{13}C NMR: δ 151.3, 140.7, 59.3, 33.0, 25.1, 25.0. MS, *m/z* (%): 151 (22) (M^+), 150 (22), 82 (30), 70 (100). Found, %: C 63.67; H 8.76; N 27.98. $C_8H_{13}N_3$. Calculated, %: C 63.55; H 8.67; N 27.79.

2-Pyrrolidinone. Using condition A, 2-pyrrolidinone was reacted with cyclohexene and provided a crude product (6%). Analysis by GC-MS showed the presence of one compound (0.4%) with an *m/z* (M^+ = 167) corresponding to the expected addition compound.

Carbazole. The addition reaction was carried out under condition A for 40 h, and a crude product was obtained (78%). Four additional compounds with appropriate *m/z* were detected in GC-MS (Table 1).

5-Phenyltetrazole Addition to Alkenes (Some Characteristics of Products are in Tables 2 and 3)

Cyclohexene. The addition reaction was carried out using condition A for 24 h, 2-cyclohexyl-5-phenyltetrazole Ia and 1-cyclohexyl-5 phenyltetrazole Ib were isolated by column chromatography.

2-Cyclohexyl-5-phenyltetrazole Ia (1.4 g, 61%), colorless oil. ^{1}H NMR: δ 8.13-8.18 (2H, m), 7.45-7.52 (3H, m), 4.70-4.79 (1H, m), 2.24-2.31 (2H, m), 1.93-2.10 (4H, m), 1.74-1.80 (1H, m), 1.34-1.56 (3H, m). ^{13}C NMR: δ 164.5, 130.0, 128.8, 127.7, 126.7, 63.1, 32.4, 25.0, 24.8. MS, *m/z* (%) : 228 (2) [M^+], 200 (92), 171 (16), 157 (54), 118 (15), 104 (100), 90 (60).

1-Cyclohexyl-5-phenyltetrazole Ib (90 mg, 4%), white prism; mp 135-137°C. ^{1}H NMR: δ 7.57-7.66 (5H, m), 4.35 (1H, tt, J = 4.4 and 11.0 Hz), 1.89-2.15 (6H, m), 1.75-1.77 (1H, m), 1.32-1.40 (3H, m). ^{13}C NMR: δ 153.6, 131.0, 129.2, 128.8, 124.4, 58.2, 33.2, 25.2, 24.7. MS, *m/z* (%): 228 (5) [M^+], 199 (12), 173 (8), 157 (88), 118 (100), 104 (33), 90 (25).

Styrene. Under condition C, 5-phenyltetrazole added to styrene in 98% crude yield.

2-(1-Phenylethyl)-5 phenyltetrazole II was isolated by column chromatography (1.7 g, 68%), light yellow oil. ^{1}H NMR: δ 8.13-8.16 (2H, m), 7.31-7.48 (8H, m), 6.10 (1H, q, J = 7.1 Hz), 2.09 (3H, d, J = 7.1 Hz) .^{13}C NMR: δ 165.0, 138.9, 130.2, 128.9, 128.8, 128.6, 127.6, 126.8, 126.6, 63.6, 21.2. MS, *m/z* (%): 251 (58) [M^+ + 1], 250 (1) [M^+], 222 (2), 147 (62), 105 (100), 104 (12).

2,4,4-Trimethyl-2-pentene. Under condition C, 5-phenyltetrazole added to 2,4,4-trimethyl-2-pentene to give 2-(2-methyl-4,4-dimethyl-2-pentyl)-5-phenyltetrazole III (2.32 g, 90%), colorless oil. ^{1}H NMR: δ 8.17-8.20 (2H, m), 7.47-7.50 (3H, m), 2.15 (2H, s), 1.87 (6H, s) and 0.78 (9H, s) .^{13}C NMR: δ 164.2, 129.9, 128.7, 127.9, 126.8, 66.8, 54.1, 31.4, 30.3, 29.6. MS, *m/z* (%) : 258 (0.1) [M^+], 243 (4), 230 (8), 215 (16), 104 (8), 103 (9).

1-Octene. The reaction was carried out using condition A for 40 h, to give a mixture of three isomers (85%): 2-(2-octyl)-5-phenyltetrazole IV, 2-(3-octyl)-5-phenyltetrazole V, and 2-(4-octyl)-5-phenyltetrazole VI. Small amounts of each isomer were separated by preparative GC, and identified by NMR.

2-(2-Octyl)-5-phenyltetrazole IV, colorless oil. ^{1}H NMR: δ 8.14-8.17 (2H, m), 7.45-7.52 (3H, m), 4.94-5.01 (1H, m), 2.09-2.14 (1H, m), 1.87-1.94 (1H, m), 1.66 (3H, d, J = 6.8 Hz), 1.12-1.34 (8H, m), 0.85 (3H, t, J = 6.7 Hz). ^{13}C NMR (DMSO-D_6): δ 163.8, 129.6, 128.6, 127.4, 126.0, 60.05, 35.6, 30.9, 28.0, 25.1, 21.8, 19.9, 13.3. MS, *m/z* (%): 258 (0.2) [M^+], 230 (17), 215 (12), 201 (6), 173 (9), 159 (3), 145 (48), 104 (100).

2-(3-Octyl)-5-phenyltetrazole V, colorless oil. ^{1}H NMR: δ 8.16-8.20 (2H, m), 7.46-7.54 (3H, m), 4.73-4.80 (1H, m), 1.91-2.03 (2H, m), 2.07-2.15 (2H, m), 1.10-1.30 (6H, m), 0.82-0.91 (6H, m). ^{13}C NMR (DMSO-D_6): δ 164.0, 129.6, 128.6, 127.4, 126.0, 66.1, 33.8, 30.5, 27.5, 24.8, 21.7, 13.2, 9.6. MS, *m/z* (%): 258 (0.3) [M^+], 230 (9), 201 (52), 173 (3), 159 (26), 104 (100).

2-(4-Octyl)-5-phenyltetrazole VI, colorless oil. ^{1}H NMR: δ 8.16-8.19 (2H, m), 7.47-7.52 (3H, m), 4.80-4.90 (1H, m), 2.08-2.14 (2H, m), 1.89-1.94 (2H, m), 1.08-1.38 (6H, m), 0.79-0.93 (6H, m). ^{13}C NMR (DMSO-D_6): δ 164.0, 129.6, 128.6, 127.4, 126.0, 64.4, 36.3, 33.9, 27.3, 21.4, 18.4, 13.2, 12.8. MS, *m/z* (%): 230 (5) [$M^+ - N_2$], 215 (1), 201 (1), 187 (46), 173 (21), 159 (3), 104 (100).

2,3-Dimethyl Butadiene. Addition of 5-phenyltetrazole to 2,3-dimethyl butadiene under condition C gave a mixture of two isomers of 2,3-dimethyl-1-(5-phenyltetrazol-2-yl)-2-butene VII and 2,3-dimethyl-3-(5-phenyltetrazol-2-yl)-1-butene VIII (1.14 g, 50%), colorless oil; and a double addition product 2,3-dimethyl-1,3-bis(5 phenyltetrazol-2-yl)-pentane IX (0.8 g, 21%). The structures of compounds VII and VIII were identified by ^{1}H and quantitative ^{13}C NMR of the mixture.

2,3-Dimethyl-1-(5-phenyltetrazol-2-yl)-2-butene VII, ^{1}H NMR: δ 8.12-8.16 (2H, m), 7.43-7.51 (3H, m), 5.23 (2H, s), 1.94 (3H, s), 1.75 (3H, s), 1.70 (3H, s). ^{13}C NMR: δ 164.6, 133.0, 129.8, 128.5, 127.4, 126.5, 120.4, 55.4, 20.7, 20.2, 16.5. MS, *m/z* (%): (mixture of VII and VIII) 229 (58) [M^+ + 1], 228 [M^+, 6], 200 (1), 147 (100), 104 (11).

2,3-Dimethyl-4-(5-phenyltetrazol-2-yl)-1-butene VIII, ^{1}H NMR: δ 8.12-8.16 (2H, m), 7.43-7.51 (3H, m), 4.75-4.77 (1H, m), 4.71-4.72 (1H, m), 4.68 (1H, dd, J = 7.5 and 13.3 Hz), 4.53 (1H, dd, J = 7.7 and 13.3 Hz), 2.99-3.06 (1H, m), 1.78 (3H, s), 1.10 (3H, d, J = 7.0 Hz). ^{13}C NMR: δ 164.6, 144.6, 129.8, 128.5, 127.3, 126.5, 112.1, 56.6, 41.1, 19.0, 16.4.

2,3-Dimethyl-1,3-bis(5-phenyltetrazol-2-yl)pentane IX, white needles; mp 90-92°C. ^{1}H NMR: δ 8.16-8.20 (2H, m), 8.10-8.13 (2H, m), 7.44-7.51 (6H, m), 4.67 (1H, dd, J = 4.3 and 13.5 Hz), 4.55 (1H, dd, J = 10.0 and 13.5 Hz), 3.13-3.20 (1H, ddt, J = 4.3, 6.9 and 10.0 Hz), 1.94 (3H, s), 1.90 (3H, s), 0.88 (3H, d, J = 6.9 Hz). ^{13}C NMR: δ 165.2, 164.8, 130.3, 130.2, 128.8, 127.4, 127.2, 126.9, 126.8, 67.8, 54.7, 43.4, 25.7, 24.2, 12.8.

Phenylacetylene. The reaction was carried out under condition B for 24 h, and a crude product was obtained (30%). Analysis of GC-MS showed the presence of one compound (1%) corresponding to the expected addition product X.

Reaction of 5-phenyltetrazole Sodium Salt with Cyclohexyl Bromide. Sodium hydride (50 mmol) was added to 5-phenyltetrazole (50 mmol) in acetonitrile (75 cm^3) and stirred for 20 min. Then cyclohexyl bromide (50 mmol) was added, and the reaction mixture was heated to reflux for 5 days.

2-Cyclohexyl-5-phenyltetrazole Ia (1.1 g, 10%, colorless oil) and 1-cyclohexyl-5-phenyltetrazole Ib (90 mg, 0.8%, white prism) were obtained.

Their NMR spectra are exactly the same as compounds synthesized from 5-phenyltetrazole with cyclohexene.

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