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A number of 4-allylic substituted 3,5-diphenyl-4*H*-1,2,4-triazoles were thermolyzed at 315-320° in evacuated glass ampoules. The main reaction in the melt was rearrangement to the corresponding 1-substituted triazoles, which appeared to proceed *via* competing $S_N2$ and $S_N2'$ mechanisms. The allylic systems were observed to undergo [2,3]-allyl walk reactions between the 1- and 2-ring positions. Allyl to vinyl isomerization also took place. Substitution of the allylic moiety increased the rate of reaction but decreased the rate of isomerization of allylic to the vinylic substituted triazoles. The 4-vinyl substituted triazoles were inert under the reaction conditions. Some triazoles were converted into substituted pyridines. This was proposed to proceed *via* nitrogen extrusion and formation of a 1,3-dipolar intermediate (nitrile ylide) which added intramolecularly to the allyl moiety and subsequently aromatized to the pyridine.

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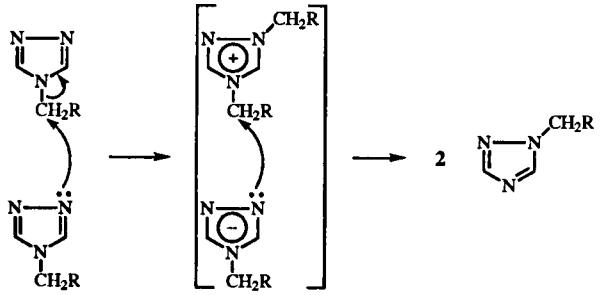
In recent publications the thermal rearrangements of 4-alkyl substituted 4*H*-1,2,4-triazoles to the corresponding 1-alkyl substituted triazoles were reported [1]. Thus, the neat 4-alkylated 3,5-diphenyl-4*H*-1,2,4-triazoles on thermolysis at 200-400° yielded the 1-alkylated 3,5-diphenyl-1*H*-1,2,4-triazoles as the predominant products. The rearrangement reaction appeared to be intermolecular of nature, involving a bimolecular nucleophilic type mechanism [2], where the *N*-1 atom of one molecule reacts in an $S_N2$ fashion at the α-carbon atom of the 4-alkyl group of another molecule, yielding an ion-pair intermediate which in a subsequent bimolecular group transfer reaction gave the rearranged triazole, (Scheme 1).

Scheme 1



As an extension of this work we undertook an investigation of the thermal behaviour of the 4-allyl substituted 4*H*-1,2,4-triazoles. For these compounds rearrangements may take place in $S_N2$ fashion described earlier, but $S_N2'$ type reactions at the allyl moiety now became feasible as well. We also wanted to establish possible allyl-walk reactions, such as aza-Cope type rearrangements and [2,3]-shift reactions.

Results and Discussion.

For the purpose of achieving this objective the 4-allyl substituted triazoles shown in Figure 1 were prepared.

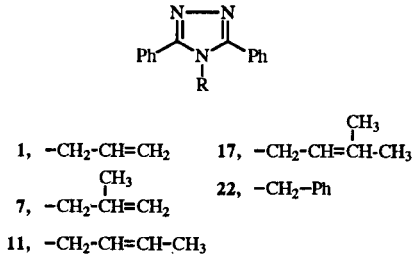
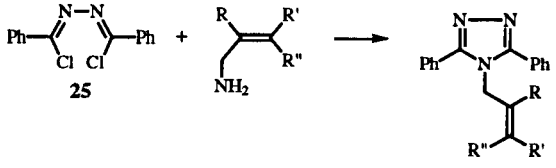


Figure 1

In this series was included the 4-benzyl substituted triazole, as this compound formally contain an α,β-unsaturation.

Synthesis of 4-substituted 4*H*-1,2,4-triazoles was accomplished applying a modification of the procedure described earlier by Gautun and Carlsen [3]. Thus, the desired products were obtained in satisfactory yields by reacting bis(α-chlorobenzylidene)hydrazine, **25**, with the appropriate allyl amine in refluxing toluene, (Scheme 2).

Scheme 2

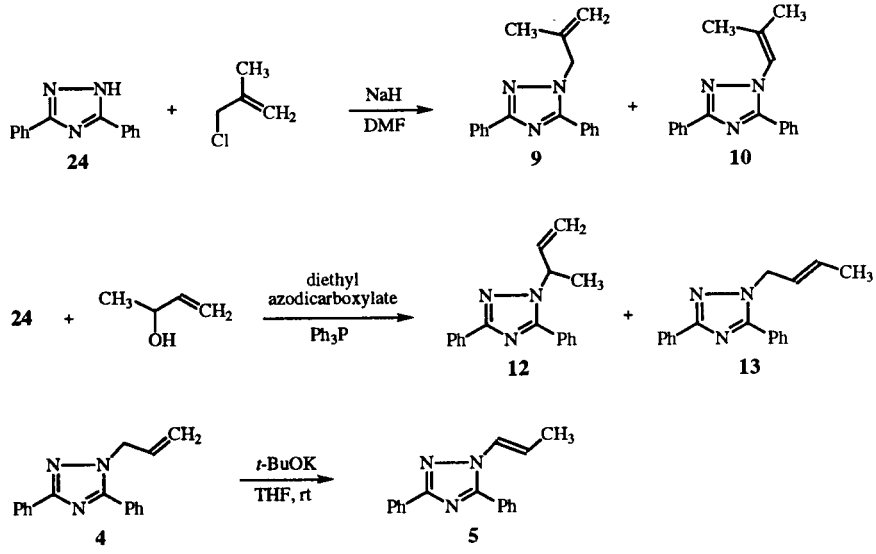


The corresponding 1-substituted triazoles were required as authentic samples in order to establish the identities of a number of products formed on thermolysis of the 4-substituted triazoles. These compounds were in general prepared by treating the sodium salt of 3,5-diphenyl-1,2,4-triazole, **24**, (**24**, sodium hydride in DMF) with the appropriate 2-alkenyl halides, (Scheme 3). In several of these cases, however, isomerization to the corresponding vinylic compounds was observed. Thus, reacting **24** with 1-chloro-2-methyl-2-propene under these conditions, resulted in a

product mixture consisting of 54% of **9** together with 36% of **10**. In order to alliviate this problem, the substitutions were carried out using a modification of the Mitsunobu reaction [4] as described earlier for similar systems [5]. Typically, alkylation of **24** under the Mitsunobu conditions with 2-methyl-2-propenol gave 44% of pure, recrystallized **9**. However, when reacting with 3-buten-2-ol the desired 1-(1-buten-3-yl)-3,5-diphenyl-1*H*-1,2,4-triazole, **12**, was produced as the main product (77%) together with 23% of the 1-crotyl product, **13**. Thus, alkylation by the Mitsunobu procedure eliminated the competing isomerization reactions, but instead what appeared as competing $S_N2$ and $S_N2'$ reactivity was encountered. The conversion of the allylic substituents into the corresponding vinylic substituted triazoles was easily accomplished by base catalyzed isomerization, (potassium *tert*-butoxide in THF).

molysis mixture by glc using authentic standard compounds, showed that products substituted in the 1-ring position gave a combined yield of 7%, consisting of a mixture of the allyl substituted triazole **4** together with the vinylic compounds **5** and **6**. A small amount of elimination product **24** was also detected, (3%). The 4-(1-propenyl) substituted triazole **2** was prepared by base catalyzed, (potassium *tert*-butoxide in THF), isomerization of **1** in 73% recrystallized yield. Surprisingly the *Z*-compound was the major product, even though the steric energies as determined by MMX calculations (using PCMODEL [6]), predicted the *E*-compound to be thermodynamically slightly more stable. However, the van der Waal repulsion was smaller for **2** than for **3**. Thermolysis of **2** under standard conditions resulted in formation of 28% of the corresponding *E*-isomer, **3**. Compound **2** was the sole product after isomerization of **1**

Scheme 3

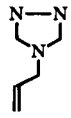
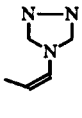
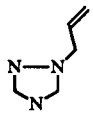
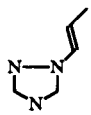
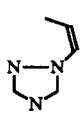
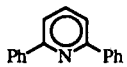
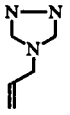
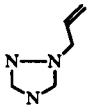



Thermolysis of triazoles was performed on approximately 50 mg samples in evacuated, sealed glass tubes at 315-320° for 20 minutes. The compositions of the reaction mixtures were determined by glc analysis. The identities of the products were all established by gc-ms, gc-ir, isolation by preperative tlc and comparison of the chromatographic and spectroscopic properties with those of authentic samples. The results are compiled in Tables 1-5. For clarity the 3,5-diphenyl-1,2,4-triazole ring systems are depicted as 5-membered rings omitting the phenyl groups and the multiple bonds.

Thermolysis of 4-allyl-3,5-diphenyl-4*H*-1,2,4-triazole, **1**, resulted in formation of a complex mixture of products, (Table 1). The main component, together with unreacted **1**, (35%) consisted of a mixture of the vinylic products **2** and **3** (53%) as indicated by nmr spectroscopic data. Separation of compounds **1** and **3** was unsuccessful by glc as well as preperative thin layer chromatography. Analysis of the thermolysis mixture by glc using authentic standard compounds, showed that products substituted in the 1-ring position gave a combined yield of 7%, consisting of a mixture of the allyl substituted triazole **4** together with the vinylic compounds **5** and **6**. A small amount of elimination product **24** was also detected, (3%). The 4-(1-propenyl) substituted triazole **2** was prepared by base catalyzed, (potassium *tert*-butoxide in THF), isomerization of **1** in 73% recrystallized yield. Surprisingly the *Z*-compound was the major product, even though the steric energies as determined by MMX calculations (using PCMODEL [6]), predicted the *E*-compound to be thermodynamically slightly more stable. However, the van der Waal repulsion was smaller for **2** than for **3**. Thermolysis of **2** under standard conditions resulted in formation of 28% of the corresponding *E*-isomer, **3**. Compound **2** was the sole product after isomerization of **1** with potassium *tert*-butoxide in THF at room temperature. No group migrations were observed for vinylic triazoles. Compound **4** was thermally relatively inert as formation of the vinylic compounds was not observed. A small amount of a new product (1%) was isolated, and identified as 2,6-diphenylpyridine, **28**, by comparison of its spectroscopic and chromatographic properties with those of an authentic sample. Formation of the 1-vinyl substituted products may take place at an early stage in the reaction.

In order to further elucidate the mechanisms involved in the thermal rearrangements of these compounds, the effect of substitution of the allyl moiety on the reactions was also investigated. Thermolysis of 4-(2-methyl-2-propenyl)-3,5-diphenyl-4*H*-1,2,4-triazole, **7**, appeared to proceed somewhat faster than for **1**. Thus, thermolysis under the standard condition (315-320° in 20 minutes), of **1**, gave approximately 40% unreacted starting material, while thermolysis

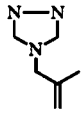
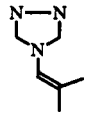
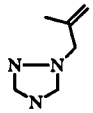
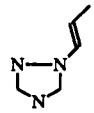
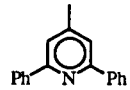
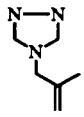
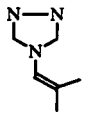
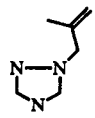
Table 1

| Products: / Starting material: |  **1** |  **2** |  **3** |  **4** |  **5** |  **6** |  **24** |  **28** |
|---|---|---|---|---|---|---|---|---|
|  **1** | 35 | 44 | 9 | 1 | 4 | 2 | 3 | – |
|  **2** | – | 71 | 28 | – | – | – | – | – |
|  **4** | – | – | – | 99 | – | – | – | <1 |

of **7** gave only 4% unreacted substrate, (Table 2). The main product was the corresponding 1-substituted triazole, **9**, together with small amounts of the vinylic products **8** and **10**. Some elimination was also observed, (**24**, 4%), as well as formation of small amounts (1%) of the substituted pyridine **29**. The latter product was also obtained after thermolysis of the primary rearrangement product, **9**.

minutes. A dramatic increase in pyridine formation was also observed for this triazole, as 9% of 2,6-diphenyl-3-methyl-pyridine, **30**, was formed. The same product was also formed on thermolysis of the pure 1-substituted allylic products **12** and **13**. Pyridine formation appeared to be associated with a high content of the 1-allyl substituted product in the thermolysis mixtures.

Table 2

| Products: / Starting material: |  **7** |  **8** |  **9** |  **10** |  **24** |  **29** |
|---|---|---|---|---|---|---|
|  **7** | 4 | 1 | 89 | 2 | 4 | 1 |
|  **8** | - | 100 | - | - | - | 1 |
|  **9** | - | - | 99 | - | - | 1 |

Thermolysis of the 4-crotyl substituted triazole, **11**, resulted in complete conversion under the standard reaction conditions, (Table 3). Reaction for shorter periods of time actually showed that **11** was fully converted after 5

Increased substitution of the allyl moiety resulted in a faster rearrangement reaction. Thermolysis of the 4-(3,3-dimethyl-2-propenyl)-substituted triazole, **17**, took place readily. However, only minor amounts of the 1-allyl

Table 3

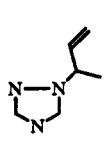
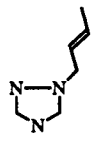
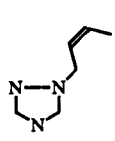
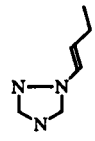
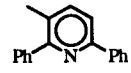
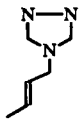
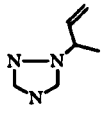
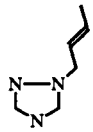
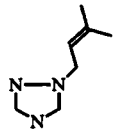
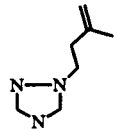
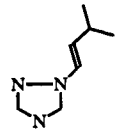
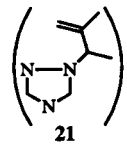
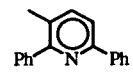
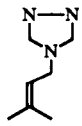
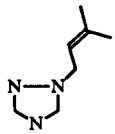
| Starting material: \ Products: |  **12** |  **13** |  **14** |  **15** |  **24** |  **30** |
|---|---|---|---|---|---|---|
|  **1** | 31 | 56 | 2 | - | 2 | 9 |
|  **12** | 81 | 6 | 1 | - | 2 | 9 |
|  **13** | 1 | 92 | 4 | 1 | – | 2 |

Table 4

| Starting material: \ Products: |  **18** |  **19** |  **20** |  **21** |  **24** |  **30** |
|---|---|---|---|---|---|---|
|  **17** | 5 | 3 | - | 3 | 89 | - |
|  **18** | 83 | 2 | 1 | - | 7 | 3 |

substituted triazoles were formed, (**18**, 5% together with **19**, 3% and **21**, 3%). The major product was the elimination product **24**, (89%). Thermolysis of **17** did not result in detectable amounts of pyridine, in contrast to that which was observed for thermolysis of the primary rearrangement product **18**, for which the pyridine **30**, (3%), was a major product, (Table 4). Thermolysis of the 4-benzyl substituted triazole, **22**, gave the 1-substituted compound, **23**, as the main product, together with 2% of isoquinoline **31**.

Mechanisms.

A product analysis of the above, indicates there is a number of reactions taking place, *i.e., a)* allyl group migration, *b)* elimination, *c)* allyl-vinyl isomerization and *d)* pyridine formation.

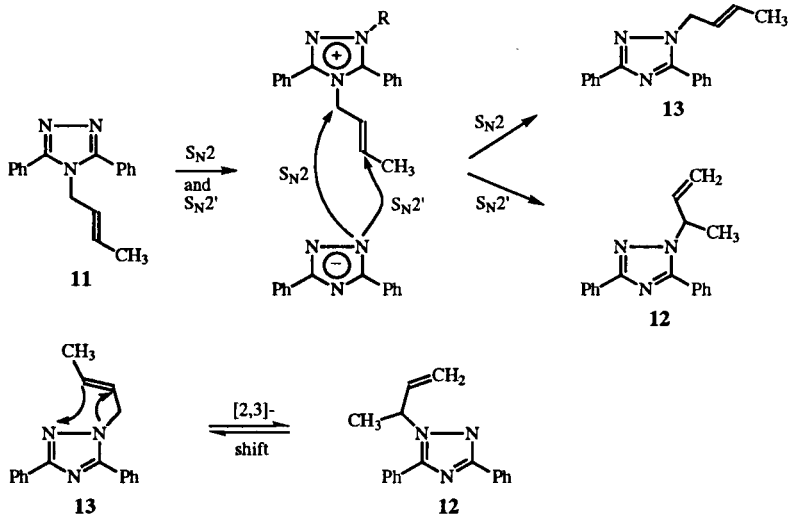
The mechanisms for the migration of the 4-allyl group to the 1-triazole positions can best be rationalized in terms of an ionic mechanism similar to the type described earlier [1] and as outlined in Scheme 1. The ion-pair intermediate initially formed (triazolium triazolate), may in a subsequent bimolecular $S_N2$-type nucleophilic group displacement result in formation of the rearranged products. For allylic substituents a corresponding $S_N2'$-type mechanism is possible, which will result in formation of an isomeric 1-allyl substitiuted triazole. That both mechanistic pathways take place here, was supported by the

results from thermolysis of **11**, which yield both the $S_N2'$-type product **12** and the $S_N2$-product **13**. These products may be interconverted in a [2,3]-allyl shift reactions between the *N*1 and *N*2 ring atoms. The results are shown in Table 3, however, it is indicated that **12** and **13** were only slowly interconverted under the reaction conditions, (Scheme 4). The results with triazoles **1** and **7** can not be used to distinguish between these reaction modes. That triazole **17** did not exhibit a similar reactivity can be understood in terms of the instability of the triazoles substituted with tertiary alkyl groups. All attempts to prepare such compounds have always failed. Compound **21**, was identified in a mixture of **18** and **19**, based on nmr spectroscopic data. The rearrangement of the 4-benzyl triazole, **22**, (Table 5) can be rationalized by the same mechanism.

Formation of the elimination product, **24**, from the various triazoles can also be explained to proceed *via* the ionic triazolium triazolate ion-pairs. The triazolate anion, acting as a base in an E2-like mechanism, form **24** together with the 4-allyl triazole. The amount of products formed by this elimination pathway, as expected, increased with increasing substitution of the allylic substituent. Thermolysis of **18** showed that only a minor amount (*ca.* 7%) of the elimination product **24** may be formed by unimolecular elimination. The activity of the triazolate anion as a base, may also account for the isomerization of the allyl species to the corresponding vinylic compounds.

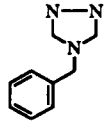
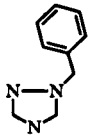
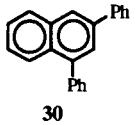
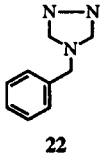
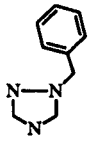
Thermolysis of **2** gave partial isomerization to **3**. However, thermolysis of **2** or **8** gave no sign of products due to thermal rearrangement. These observations were

Scheme 4




interesting as it allows for construction of the 4-substituted triazole ring systems that do not undergo thermal rearrangement.

Table 5

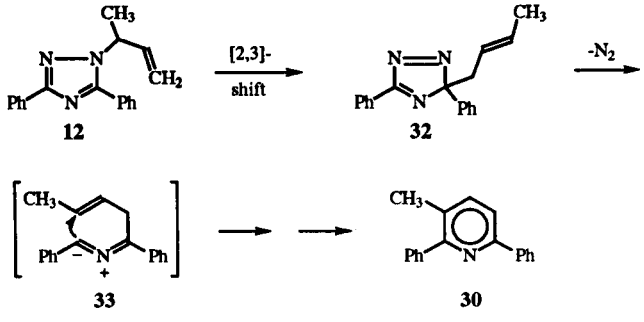
| Products: |  |  |  |  |
|---|---|---|---|---|
| Starting material: | **22** | **23** | **24** | **30** |
|  **22** | 7 | 91 | 1 | 2 |
|  **23** | 1 | 100 | - | - |

Pyridine Formation.

The results in Tables 1-5 indicated that formation of pyridines were related to the amounts of 1-allyl products in the reaction mixtures. Thus, conceivably the pyridines were formed in a reaction that involved the 1-allylated triazoles. It was also noted that pyridines vere not formed from the vinylic species. The mechanism for pyridine formation can be rationalized by assuming a thermal [2,3]-allyl shift reaction of the 1-allylated triazoles, forming a 5,5-disubstituted intermediate, **32**, which after elimination of nitrogen gave a 1,3-dipolar intermediate, (a nitrile ylide), **33**, which subsequently undergo a cyclization reaction and aromatization to the isolated pyridine product, Scheme 5. A similar type of reactivity has been reported by Gilchrist and Rees [7] for vacuum flash thermolysis at 750-800° of substituted triazoles

and by Padwa *et al.* on photolysis of allyl substituted 2*H*-azirines [8]. The reason for the shift reaction not taking place for the 4-allyl substituted triazoles, may be ascribed to a larger steric congestion around the C3-ring site, favoring alternative pathways, *e.g.*, allyl group migration to the *N*1-atom. Thermolysis of **18** produced the same product as the from compounds **11-13**. This must involve elimination of a $CH_3$-group instead of H in the aromatisation step.

Scheme 5




Thermolysis of the benzylated triazole **22** resulted in formation of small amounts of isoquiniline **31**. The mechanism for can be rationalized in terms of a similar mechanism as for formation of the pyridines.

## EXPERIMENTAL

### General.

The $^1H$ and $^{13}C$ nmr spectra are recorded on a JEOL JNM-EX 400 FT nmr system using tetramethylsilane (TMS) as the internal standard. Information from the DEPT technique are given in the $^{13}C$ nmr spectra when performed. All ir spectra were obtained as gc-ftir using a Nicolet 20-SXC FT-IR spectrometer in combination with a Carlo Erba HRGC 5160 Mega Series gas chromatograph equipped with a CP-Sil 5 CB capillary column (25 m). The glc analyses were performed on a Perkin-Elmer Autosystem gas chromatograph equipped with a CP-Sil 5 CB capillary column (25 m). For flash chromatography was used Silica gel 60, size 0.032-0.063 mm from Merck, and using the solvents described below. Thin layer chromatography was performed on 20 x 20 cm glass plates covered with 1-2 mm thick layer of Silica gel $HF_{254+366}$ (Type 60, Merck). All melting points are uncorrected.

### 4-Allylic Substituted 4*H*-1,2,4-Triazoles. General Procedure.

A mixture containing bis(α-chlorobenzylidene)hydrazine, **25**, 6-10 equivalents of triethylamine and 1.5-4 equivalents of the appropriate allylic amine in toluene was refluxed for 2-5 days. In some cases the neat amine was used as the solvent. The solvent was removed under reduced pressure, and the remaining oil dissolved in dichloromethane (50 ml/g). The solution was extracted trice with 0.1 *M* hydrochloric acid, twice with 0.1 *M* sodium hydroxide, water and brine. The solution was then dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure leaving behind the crude product, which after recrystalization (normally toluene) yielded the pure products.

### 4-Allyl-3,5-diphenyl-4*H*-1,2,4-triazole, **1**.

This compound was prepared from **25** (2.0 g, 7.2 mmoles) in allylamine (5 ml) after reflux for 2 days. Crystallization from 60% ethanol/water gave 1.78 g of pure **1** (94%), as white crystals (mp 142-143°). The product exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 4.63-4.66 (m, 2H), 4.96 (dt, J = 17.1, 2.0 Hz, 1H), 5.30 (dt, J = 10.7, 2.0 Hz, 1H), 5.88 (ddt, J = 10.7, 17.1, 4.4 Hz, 1H), 7.46-7.51 (m, 6H), 7.71-7.74 (m, 4H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform): δ 46.9, 118.1, 127.4, 128.8, 128.9, 130.1, 132.8, 155.7 ppm; ms: [m/z (% relative intensity)] 261 (100, $M^+$), 260 (27), 246 (6), 192 (6), 129 (8), 104 (8), 103 (8), 89 (63), 77 (10). Found: $M^+$ 261.1264 Calcd. for $C_{17}H_{15}N_3$: 261.1266.

*Anal.* Calcd. for $C_{17}H_{15}N_3$: C, 78.12; H, 5.79; N, 16.09. Found: C, 78.01; H, 5.77; N, 16.16.

### 4-(2-Methylallyl)-2,5-diphenyl-4*H*-1,2,4-triazole, **7**.

This compound was prepared by refluxing a solution containing **25** (0.88 g, 3.2 mmoles) and 2-methylallylamine (0.90 g, 12.7 mmoles) in benzene (10 ml) for 5 days. The yield of **7** was 0.52 g (59%) as white crystals (mp 158-159°); $^1H$ nmr (400 MHz, deuteriochloroform): d 1.69 (br s, 3H), 4.48 (br s, 2H), 4.62 (br s, 1H), 5.07 (br s, 1H), 7.47-7.50 (m, 6H), 7.73-7.76 (m, 4H); $^{13}C$ nmr (100 MHz, deuteriochloroform): d 20.1, 50.0, 112.9, 127.5, 128.7, 128.8, 130.1, 140.8, 155.8 ppm; gc-ftir: 3074, 2985, 2944, 1472, 1393, 1028,, 905, 783, 767, 695 $cm^{-1}$; ms: [m/z (% relative intensity)] 275 (100, $M^+$), 274 (36), 260 (11), 234 (5), 221 (3), 192 (4), 171 (3), 129 (8), 118 (3), 117 (4), 105 (3), 104 (13), 103 (6), 90 (5), 89 (53), 77 (11). Found: $M^+$ 275.1418. Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.50; H, 6.23; N, 15.27. Found: C, 78.26; H, 6.26; N, 15.24.

### Trans-4-crotyl-3,5-diphenyl-4*H*-1,2,4-triazole, **11**.

This compound was prepared from **25** (5.34 g, 19.3 mmoles), crotylamine, **26**, (1.90 g, 26.8 mmoles) and triethylamine (10.95 g, 108.2 mmoles) in toluene (100 ml) after refluxing for 4 days, yielding 2.13 g (40%) of the pure product as a crystalline material (mp 147-149°). The product contained 3% of the *cis*-isomer. The product exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.61-1.64 (m, 3H), 4.56-4.59 (m, 2H), 5.26-5.36 (m, 1H), 5.39-5.47 (m, 1H), 7.48-7.52 (m, 6H), 7.69-7.73 (m, 4H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform): δ 17.6, 46.5, 125.3, 127.7, 128.8, 129.0, 129.9, 130.0, 155.6 ppm; gc-ftir: 3073, 3038, 2954, 2933, 1472, 1396, 1351, 964, 766, 697 $cm^{-1}$; ms: [m/z (% relative intensity)] 275 (94, $M^+$), 274 (5), 261 (4), 260 (19), 222 (17), 221 (100), 193 (5), 192 (3), 157 (4), 131 (5), 130 (4), 129 (6), 128 (4), 119 (7), 118 (83), 104 (27), 103 (11), 91 (12), 90 (13), 89 (95), 86 (12), 84 (18), 77 (28). Found: $M^+$ 275.1427. Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.50; H, 6.23; N, 15.27. Found: C, 78.35; H, 6.22; N, 15.19.

### 4-(3-Methyl-2-butenyl)-3,5-diphenyl-4*H*-1,2,4-triazole, **17**.

This compound was prepared from **25** (2.22 g, 8.01 mmoles), 3,3-dimethylallylamine, **27**, (2.68 g, 31.5 mmoles) and triethylamine (8.08 g, 80 mmoles) in toluene (25 ml) after reflux for 5 days. The yield of pure **17** was 0.95 g (41%) as colourless crystals (mp 164-165°). The compound exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.32 (s, 3H), 1.63 (d, J = 1.0 Hz, 3H), 4.60 (d, J =

6.4 Hz, 2H), 5.06-5.10 (m, 1H), 7.48-7.51 (m, 6H), 7.67-7.71 (m, 4H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 17.8, 25.5, 43.5, 119.3, 127.8, 128.8, 129.1, 129.9, 137.0, 155.7 ppm; gc-ftir: 3073, 2979, 2926, 1471, 1446, 1396, 1361, 1316, 1258, 1026, 980, 912, 768, 697 cm$^{-1}$; ms: [m/z (% relative intensity)] 289 ($M^+$, 17), 222 (17), 221 (100), 193 (2), 118 (28), 89 (18). Found: $M^+$ 289.1576. Calcd. for $C_{19}H_{19}N_3$: 289.1579.

*Anal.* Calcd. for $C_{19}H_{19}N_3$: C, 78.85; H, 6.62; N, 14.53. Found: C, 78.65; H, 6.68; N, 14.44.

4-Benzyl-3,5-diphenyl-4*H*-1,2,4-triazole, **22**.

This compound was prepared from **25** (2.00 g, 7.22 mmoles), benzylamine (1.16 g, 10.83 mmoles) and triethylamine (7.32 g, 72.5 mmoles) in toluene (70 ml) and refluxed for 2 days, yielding 1.14 g (51%) of pure **22** as a white crystalline material (mp 215-217°). The product exhibited the following spectroscopic properties: $^1$H nmr (400 MHz, deuteriochloroform): δ 5.28 (s, 2H), 6.86-6.88 (m, 2H), 7.26-7.28 (m, 4H), 7.38-7.47 (m, 6H), 7.58-7.60 (m, 3H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 48.3, 125.9, 127.3, 128.1, 128.8, 128.9, 129.1, 130.1, 136.1, 156.0 ppm; gc-ftir: 3074, 3036, 1472, 1396, 1353, 1026, 981, 762, 725, 695 cm$^{-1}$; ms: [m/z (% relative intensity)] 311 (54, $M^+$), 310 (18), 91 (100), 89 (26). Found: $M^+$ 311.1428. Calcd. for $C_{21}H_{17}N_3$: 311.1423.

3,5-Diphenyl-1,2,4-triazole, **24**.

This compound was perpared as described by Kotone *et al* [9].

Bis(α-chlorobenzylidene)hydrazine, **25**.

This compound was prepared according to the procedure described by Lange and Tondys [10].

*Trans*-crotylamine, **26**.

This amine was prepared by a Delèpine reaction [11]. A solution containing hexamethyltetramine (42.5 g, 0.3 mole) and crotyl bromide (40.2 g, 0.3 mole) in 400 ml of chloroform was stirred at room temperature for 18 hours. Then heptane (1 l) was added, and the mixture stirred for 15 minutes. The solid crotyl bromide hexamethylamine adduct (79.1 g, 97%) was isolated as a white powder (dec 115°) by filtration and washed with small amounts of heptane.

The adduct (29.67 g, 108 mmoles) was decomposed in a solution containing ethanol (420 ml) and concentrated hydrochloric acid (56 ml), at 65-70°. After 15 minutes the solution was cooled in an ice bath, and the ammonium chloride formed was isolated by filtration. The filtrate was reduced to half volume under reduced pressure, resulting in precipitation of more ammonium chloride which was removed by filtration. Then the solution was evaporated to dryness by azeotropic destillation with toluene (3 x 100 ml). The dry solid (20.9 g, 195 mmoles), mainly crotylamine hydrochloride, was mixed with solid sodium hydroxyde (11.7 g, 293 mmoles) and distilled. The fraction with bp 75-78° contained 5.29 g (69%) of crotylamine (83% *trans*); $^1$H nmr (400 MHz, deuteriochloroform): δ 1.66-168 (m, 3H), 3.14-3.16 (m, 2H), 5.56-5.58 (m, 2H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 17.9, 44.3, 126.7, 132.6 ppm.

3,3-Dimethylallylamine, **27**.

This compound was prepared by the same procedure described above from hexamethyltetramine (8.54 g, 60.9 mmoles) and dimethylallyl bromide (8.21 g, 55.1 mmoles) after 2 hours yielding 14.00 g (88%) of 3,3-dimethylallyl bromide hexamethylamine adduct as a white powder (dec 162-163°). The adduct (16.98 g, 58.7 mmoles) was decomposed in a mixture of ethanol (170 ml) and concentrated hydrochloric acid (23 ml). Ammonium chloride was removed and the remaining solution was concentrated to dryness under reduced pressure, and then dissolved in water (100 ml). The *p*H was adjusted to 8 by 4*M* sodium hydroxide and the solution extracted with diethyl ether (2x100 ml). The *p*H was increased to above 11-12, and the solution was extracted with dichloromethane (3 x 100 ml). The dichloromethane phase was dried over sodium sulfate, filtered and distilled until the temperature reached 42°. The remnant consisted of approximately 2.68 g (54%) 3,3-dimethylallylamine in dichloromethane; $^1$H nmr (400 MHz, deuteriochloroform): δ 1.31 (s, 2NH), 1.63 (s, 3H), 1.71 (s, 3H), 3.2 (d, J = 6.83 Hz, 2H), 5.22-5.27 (m, 1H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 17.7, 25.7, 39.5, 126.0, 132.9 ppm.

1-Allylic Substituted 1*H*-1,2,4-Triazole. General Procedure.

3,5-Diphenyl-1,2,4-triazole, **24**, and 3 equivalents of sodium hydride were mixed in dry DMF (10 ml/g of triazole). After 1 hour, 1.5 equivalents of an appropriate allylic halide was added, and and the reaction mixture stirred over night at room temperature. The mixture was then poured in water (100 ml/g triazole), and the precipitated triazole isolated by filtration. The crude product was dissolved in dichloromethane (100 ml), and the solution extracted twice with 0.1 *M* hydrochloric acid, twice with 0.1 *M* sodium hydroxide, water and brine. The solution was dried over anhydrous magnesium sulfate, filtered and the solvent evaporated under reduced pressure. The crude product was finally recrystalized.

1-Allyl-3,5-diphenyl-1*H*-1,2,4-triazole, **4**.

This compound was prepared from **24** (0.300 g, 1.36 mmoles), sodium hydride (0.026 g, 1.08 mmoles) in dry DMF (4 ml) and allyl bromide (0.329 g, 2.71 mmoles). The reaction was stirred for two hours before work-up. The yield of **4** after recrystallization from toluene was 0.182 g (51%) as white crystals (mp 55-56°); $^1$H nmr (400 MHz, deuteriochloroform): δ 4.87 (dt, J = 4.8, 1.7 Hz, 2H), 5.18 (d, J = 17.1 Hz, 1H), 5.33 (d, J = 9.8 Hz, 1H), 6.11 (ddt, J = 10.4, 17.6, 4.8 Hz, 1H), 7.39-7.46 (m, 3H), 7.50-7.52 (m, 3H), 7.71-7.73 (m, 2H), 8.17-8.19 (m, 2H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 51.6, 118.2, 125.3, 126.4, 128.1, 128.2, 128.5, 128.8, 128.9, 129.0, 129.2, 130.2, 131.1, 132.4, 155.9, 161.6 ppm; gc-ftir: 3073, 1478, 1445, 1348, 1130, 1019, 926, 792, 732, 695 cm$^{-1}$; ms: [m/z (% relative intensity)] 261 (100, $M^+$), 260 (30), 246 (3), 234 (3), 221 (3), 158 (3), 157 (3), 129 (23), 115 (15), 104 (24), 103 (16), 91 (41), 89 (35), 77 (13). Found: $M^+$ 275.1424. Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{17}H_{15}N_3$: C, 78.12; H, 5.79; N, 16.09. Found: C, 78.28; H, 5.76; N, 16.00.

3,5-Diphenyl-1-(trans-1-propenyl)-1*H*-1,2,4-triazole, **5**, and 3,5-diphenyl-1-(*cis*-1-propenyl)-1*H*-1,2,4-triazole, **6**.

These compounds were prepared by reacting **24** (1.0 g, 4.5 mmoles), sodium hydride (0.36 g, 1.5 mmoles) and allyl bromide (0.91 g, 7.5 mmoles). The product was an oil, 0.91 g (77%), consisting of 55% of **5** and 42% of **6**. The two components were inseperable by the available chromatographic methods, but were identified by their characteristic nmr-spectra.

Compound **5** had $^1$H nmr (400 MHz, deuteriochloroform): δ 1.83 (dd, J = 1.6, 7.0 Hz, 3H), 6.52 (dq, J = 6.8, 14.0 Hz, 1H), 6.86 (dq, J = 14.0, 1.6 Hz, 1H), 7.36-7.50 (m, 6H), 7.68-7.71 (m, 2H), 8.18-8.23 (m, 2H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform)-[DEPT]: δ 13.0 ($CH_3$), 15.0 ($CH_3$), 118.8 (CH), 123.3 (CH), 123.7 (CH), 123.8 (CH), 126.5 (CH), 126.6 (CH), 127.8 (C), 128.0 (C), 128.5 (CH), 128.7 (CH), 128.8 (CH), 128.9 (CH), 129.3 (3 peaks,

CH), 130.1 (CH), 130.2 (CH), 130.8 (C), 130.9 (C), 154.0 (C), 155.4 (C), 161.4 (C) ppm; gc-ftir: 3073, 2935, 1676, 1521, 1480, 1446, 1397, 1347, 1175, 1130, 1019, 940, 731, 694 $cm^{-1}$.

Compound **6** had $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.92 (dd, J = 1.8, 7.1 Hz, 3H), 5.66 (dq, J = 7.2, 8.8 Hz, 1H), 6.75 (dq, J = 8.8, 1.8 Hz, 1H), 7.36-7.50 (m, 6H), 7.78- 7.81 (m, 2H), 8.18-8.23 (m, 2H) ppm; gc-ftir: 3072, 2932, 1666, 1521, 1482, 1445, 1381, 1346, 1177, 1128, 1027, 1017, 728, 693 $cm^{-1}$.

3,5-Diphenyl-1-(2-methyl-1-propenyl)-1*H*-1,2,4-triazole, **10**.

This compound was prepared from **24** (3.01 g, 13.6 mmoles), sodium hydride (0.84 g, 35 mmoles) and 1-chloro-2-methyl-2-propene (1.85 g, 20.4 mmoles). After work-up was obtained an oil that consisted of 54% of **9** and 36% of **10** (glc). The two products were inseperable by the available preperative chromatographic methods.

Compound **10**.

This compound $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.68 (d, J = 1.5, 3H), 1.88 (d, J = 1.0, 3H), 6.63 (m, 1H), 7.37-7.50 (m, 6H), 7.84-7.87 (m, 2H), 8.19-8.22 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform)[DEPT]: δ 18.2 ($CH_3$), 22.6 ($CH_3$), 119.8 (CH), 126.5 (CH), 128.2 (C), 128.5 (CH), 128.58 (CH), 128.63 (CH), 129.2 (CH), 130.0 (CH), 131.0 (C), 137.5 (C), 155.2 (C), 161.5 (C) ppm; gc-ftir: 3073, 2928, 1519, 1479, 1445, 1395, 1346, 1132, 1017, 812, 730, 694 $cm^{-1}$.

*Trans*-1-crotyl-3,5-diphenyl-1*H*-1,2,4-triazole, **13**.

This compound was prepared from **24** (3.14 g, 14.2 mmoles), sodium hydride (1.0 g, 42 mmoles) and crotyl bromine (2.80 g, 20.7 mmoles) yielding after recrystallization from ethanol/water 2.14 g (57%) of **13** as white crystals (mp 80-82°). The product contained 3% of the *cis*-isomere **14**. The product exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.71 (ddt, J = 1.4, 6.0, 1.5 Hz, 3H), 4.77 (ddq, J = 1.0, 5.2, 1.0 Hz, 2H), 5.62 (dtq, J = 15.2, 1.2, 6.4 Hz, 1H), 5.72 (dtq, J = 14.8, 5.4, 1.6 Hz, 1H), 7.34-7.51 (m, 6H), 7.65-7.70 (m, 2H), 8.13-8.17 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform): δ 17.8, 51.1, 125.3, 126.5, 128.3, 128.5, 128.8, 128.9, 129.1, 129.9, 130.1, 131.1, 155.6, 161.4 ppm; gc-ftir: 3073, 2977, 1478, 1444, 1349, 1129, 964, 731, 695 $cm^{-1}$; ms: [m/z (% relative intensity)] 275 (75, $M^+$), 274 (7), 261 (7), 260 (33), 234 (3), 222 (17), 221 (100), 118 (47), 104 (24), 89 (38), 77 (11). Found: $M^+$ 275.1427: Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.50; H, 6.23; N, 15.27. Found: C, 78.42; H, 6.28; N, 15.12.

1-(3-Methyl-2-butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole, **18**.

This compound was prepared from **24** (2.99 g, 13.5 mmoles), sodium hydride (0.82 g, 34 mmoles) and 1-bromo-3-methyl-2-butene (3.08 g, 20.7 mmoles). The yield was 3.24 g (83%) of oil (100% pure by glc), which crystallized upon standing (mp 55°). The product exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.66 (s, 3H), 1.76 (s, 3H), 4.83 (d, J = 6.3 Hz, 2H), 5.47 (t, J = 6.3 Hz, 1H), 7.36-7.45 (m, 3H), 7.49-7.51 (m, 3H), 7.67-7.70 (m, 2H), 8.16-8.20 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform)[DEPT]: δ 18.1 ($CH_3$), 25.6 ($CH_3$), 47.7 ($CH_2$), 119.1 (CH), 126.4 (CH), 128.4 (CH), 128.4 (CH), 128.7 (CH), 128.9 (CH), 129.0 (CH), 130.0 (CH), 131.2 (C), 136.8 (C), 155.3 (C), 161.3 (C) ppm; gc-ftir: 3073, 2927, 1477, 1444, 1403, 1348, 1291, 1128, 1020, 775, 733, 694 $cm^{-1}$; ms: [m/z (% relative intensity)] 289 (14, $M^+$), 222 (17), 221 (100), 118 (38), 89 (17). Found: $M^+$ 289.1576 Calcd. for $C_{19}H_{19}N_3$: 289.1579.

*Anal.* Calcd. for $C_{19}H_{19}N_3$: C, 78.85; H, 6.62; N, 14.53. Found: C, 78.73; H, 6.59; N, 14.53.

1-Benzyl-3,5-dimethyl-1*H*-1,2,4-triazole, **23**.

This compound was prepared from **24** (0.49 g, 2.22 mmoles), sodium hydride (0.180 g, 7.50 mmoles) and benzyl bromide (0.60 g, 3.51 mmoles). The yield after recrystallization from toluene was 0.49 g (64%) of white crystals (mp 100-101°); $^1H$ nmr (400 MHz, deuteriochloroform): δ 5.45 (s, 2H), 7.19-7.21 (m, 2H), 7.26-7.35 (m, 3H), 7.37-7.47 (m, 6H), 7.60-7.63 (m, 2H), 8.18-8.21 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform): δ 52.8, 126.5, 126.8, 128.0, 128.1, 128.5, 128.82, 128.85, 128.9, 129.2, 130.2, 131.1, 136.1, 156.1, 161.6 ppm; gc-ftir: 3073, 3038, 1477, 1462, 1444, 1348, 1128, 1028, 731, 694 $cm^{-1}$; ms: [m/z (% relative intensity)] 311 (76, $M^+$), 310 (23), 91 (100), 89 (27), 77 (10). Found: $M^+$ 311.1428. Calcd. for $C_{21}H_{17}N_3$: 311.1423.

*Anal.* Calcd. for $C_{21}H_{17}N_3$: C, 80.99; H, 5.51; N, 13.50 Found: C, 80.90; H, 5.46; N, 13.53.

Synthesis of 1-Allyl Substituted 1*H*-1,2,4-Triazoles by the Mitsunobu Procedure. General Procedure.

3,5-Diphenyl-1,2,4-triazole, **24**, triphenylphosphine (1.2-2 equivalents) and the appropriate allylic alcohol (1.4-2 equivalents) was mixed in dry THF (15 ml) at room temperature. A mixture of diethyl azodicarboxylate (1.2-1.9 equivalents) in dry THF (5 ml) was added over a period of 2 hours. After stirring for an additional 2 hours, the solvent was evaporated under under reduced pressure. The product was purified by flash column chromatography on silica, using 20% ethyl acetate in hexane as the eluent.

1-(2-Methylallyl)-3,5-diphenyl-4*H*-1,2,4-triazole, **9**.

This compound was prepared from **24** (0.70 g, 3.17 mmoles), triphenylphosphine (1.00 g, 3.81 mmoles), 2-methyl-2-propenol (0.31 g, 4.30 mmoles) and diethyl azodicarboxylate (0.66 g, 3.79 mmoles) yielded after crystallization from toluene, 0.385 g (44%) of pure **9** as white crystals (mp 67-69°). The product exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.80 (s, 3H), 4.70 (s, 1H), 4.77 (s, 2H), 5.03 (s, 1H), 7.37-7.47 (m, 3H), 7.49-7.52 (m, 3H), 7.70-7.73 (m, 2H), 8.17-8.20 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform): δ 20.2, 54.7, 113.0, 126.5, 128.1, 128.5, 128.6, 128.7, 128.8, 129.2, 130.2, 131.1, 140.2, 156.1, 161.5 ppm; gc-ftir: 3073, 2985, 2943, 1476, 1445, 1348, 1129, 1025, 904, 799, 733, 694 $cm^{-1}$; ms: [m/z (% relative intensity)] 275 (100, $M^+$), 274 (49), 260 (10), 129 (11), 104 (27), 89 (25), 77 (11). Found: $M^+$ 275.1424. Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.50; H, 6.23; N, 15.27. Found: C, 78.39; H, 6.29; N, 15.15

1-(1-Buten-3-yl)-3,5-diphenyl-1*H*-1,2,4-triazole, **12**.

This compound was prepared from **24** (0.57 g, 2.58 mmoles), triphenylphosphine (1.42 g, 5.41 mmoles), 3-buten-2-ol (0.45 g, 6.24 mmoles) and diethyl azodicarboxylate (0.85 g, 4.88 mmoles). The yield was 0.45 g (64%) of a colorless oil containing 77% of **12** and 23% of **13**. The components were separated by thin-layer chromatography on silica using chloroform as the eluent. Pure **12** formed a solid but failed to form well defined crystals. The spectroscopic properties of **13** were as described above. Compound **12** exhibited the following spectroscopic properties: $^1H$ nmr (400 MHz, deuteriochloroform): δ 1.67 (d, J = 6.8 Hz, 3H), 5.04-5.11

(m, 2H), 5.22 (d, J = 10.3 Hz, 1H), 6.14-6.23 (m, 1H), 7.36-7.45 (m, 3H), 7.50-7.52 (m, 3H), 7.64-7.67 (m, 2H), 8.17-8.20 (m, 2H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform)[DEPT]: δ 20.9 ($CH_3$), 5.68 (CH), 116.2 ($CH_2$), 126.5 (CH), 128.5 (CH), 128.8 (CH), 129.0 (CH), 130.1 (CH), 131.3 (C), 138.2 (CH), 155.2 (C), 161.4 (C) ppm; gc-ftir: 3074, 2988, 1520, 1479, 1445, 1397, 1362, 1297, 1177, 1132, 1014, 928, 769, 736, 695 cm$^{-1}$; ms: [m/z (% relative intensity)] 275 (100, M$^+$), 260 (5), 222 (15), 221 (91), 118 (40), 104 (12), 89 (15). Found: M$^+$ 275.1427. Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.50; H, 6.23; N, 15.27. Found: C, 78.35; H, 6.01; N, 15.39

Base Catalyzed Isomerization of Allylic Substituted Triazoles. General Procedure.

The isomerization was accomplished by exposing the appropriate triazole (0.15-0.25 g) to catalytic amounts of potassion *tert*-butoxide (0.02 g) in dry THF (4-5 ml) at room temperature for at least 5 days. The reaction mixture was then poured into water and the solid products isolated by filtration and recrystallized. For oily products, the product was dissolved in dichloromethane (50 ml) and the solution washed with water (25 ml) and brine (25 ml), dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure.

3,5-Diphenyl-4-(*cis*-1-propenyl)-4*H*-1,2,4-triazole, **2**.

This compound was prepared from **1** (0.16 g, 0.61 mmole). The product was recrystallized in toluene to yield 0.11 g (73%) of pure **2** as crystals (mp 165-166°); $^1$H nmr (400 MHz, deuteriochloroform): δ 1.19 (dd, J = 1.9, 6.8 Hz, 3H), 5.85 (dq, J = 7.6, 6.8 Hz, 1H), 6.66 (dq, J = 7.8, 1.9 Hz, 1H), 7.43-7.49 (m, 6H), 7.78-7.81 (m, 4H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 12.2, 122.5, 127.4, 128.5, 128.6, 129.2, 129.8, 130.5, 154.7 ppm; gc-ftir: 3073, 1509, 1471, 1398, 1029, 966, 762, 698 cm$^{-1}$; ms: [m/z (% relative intensity)] 261 (100, M$^+$), 260 (10), 246 (25), 144 (12), 131 (22), 130 (19), 104 (31), 103 (16), 77 (23). Found: M$^+$ 261.1272. Calcd. for $C_{17}H_{15}N_3$: 261.1266.

*Anal.* Calcd. for $C_{17}H_{15}N_3$: C, 78.12; H, 5.79; N, 16.09. Found: C, 78.05; H, 5.66; N, 16.08.

3,5-Diphenyl-4-(*trans*-1-propenyl)-4*H*-1,2,4-triazole, **3**.

This compound was formed on thermolysis of **2**. The compound was inseparable from **2**, but identified based on the characteristic $^1$H nmr data of the mixture; $^1$H nmr (400 MHz, deuteriochloroform): δ 1.72 (dd, J = 2.0, 6.8 Hz, 3H), 5.85 (dq, J = 7.3, 7.3 Hz, 1H), 6.66 (dq, J = 7.8, 2.0 Hz, 1H), 7.44-7.50 (m, 6H), 7.77-7.81 (m, 4H) ppm; ms: of the mixture was identical to that of **2**; gc-ftir: 3072, 1472, 1397, 1183, 1030, 937, 763, 696 cm$^{-1}$.

3,5-Diphenyl-4-(2-methyl-1-propenyl)-4*H*-1,2,4-triazole, **8**.

This compound was prepared from **7** (0.15 g, 0.55 mmoles). The product was recrystallized from toluene yielding 0.12 g (80%) of pure **8** as white crystals (mp 187°); $^1$H nmr (400 MHz, deuteriochloroform): δ 1.18 (s, 3H), 1.78 (s, 3H), 6.44 (s, 1H), 7.44-7.46 (m, 6H), 7.78-7.80 (m, 4H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform): δ 17.5, 21.9, 116.9, 127.7, 128.4, 128.5, 129.7, 140.3, 154.9 ppm; gc-ftir: 3072, 2926, 1680, 1469, 1339, 1028, 966, 823, 765, 712, 694 cm$^{-1}$; ms: [m/z (% relative intensity)] 275 (100, M$^+$), 260 (13), 171 (11), 158 (10), 145 (18), 144 (10), 130 (23), 104 (49), 103 (23), 89 (12), 77 (42), 76 (10). Found: M$^+$ 275.1424. Calcd. for $C_{18}H_{17}N_3$: 275.1423.

*Anal.* Calcd. for $C_{18}H_{17}N_3$: C, 78.50; H, 6.23; N, 15.27. Found: C, 78.42; H, 6.29; N, 15.09.

Isomerization of **13** gave an oil that was composed of **13** (54%), **14** (4%), **15** (36%) and **16** (6%). Compounds **13** and **14** were separated from **15** and **16** by thin-layer chromatography (silica and 75% chloroform in carbon tetrachloride). The *cis*- and *trans*-isomeres were identified by $^1$*H*-nmr.

*Cis*-1-crotyl-3,5-diphenyl-1*H*-1,2,4-triazole, **14**.

This compound had $^1$H nmr (400 MHz, deuteriochloroform): δ 1.64 (d, J = 4.5 Hz, 3H), 4.87 (d, J = 4.0 Hz, 2H) ppm; $^{13}$C nmr (100 MHz, deuteriochloroform)[DEPT]: δ 17.8 ($CH_3$), 46.7 ($CH_2$) ppm. The remaining nmr-data were not distinguishable from **13**.

The ms of the mixture of **13** and **14** was identical to that of pure **13**; gc-ftir: 3075, 3043, 2873, 1518, 1476, 1445, 1348, 1128, 1019, 799, 734, 695 cm$^{-1}$.

1-(*trans*-1-Butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole, **15**.

This compound had $^1$H nmr (400 MHz, deuteriochloroform): δ 1.13 (t, J = 7.3 Hz, 3H), 2.23 (ddt, J = 1.5, 7.4, 7.3 Hz, 2H), 6.58 (dt, J = 13.7, 6.8 Hz, 1H), 6.88 (dd, J = 1.6, 13.6 Hz, 1H), 7.38-7.54 (m, 6H), 7.71-7.73 (m, 2H), 8.20-8.22 (m, 2H) ppm; gc-ftir: 3074, 2976, 1522, 1481, 1446, 1394, 1349,1130, 1013, 733, 694 cm$^{-1}$.

1-(*cis*-1-Butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole, **16**.

This compound had $^1$H nmr (400 MHz, deuteriochloroform): δ 1.04 (t, J = 7.4 Hz, 3H), 2.44 (ddt, J = 1.6, 7.5, 7.5 Hz, 2H), 5.58 (dt, J = 8.9, 7.4 Hz, 1H), 6.72 (dd, J = 1.6, 8.9 Hz, 1H), 7.38-7.54 (m, 6H), 7.80-7.82 (m, 2H), 8.20-8.22 (m, 2H) ppm; gc-ftir: 3075, 3042, 2976, 2943, 1659, 1519, 1482, 1445, 1382, 1346, 1176, 1124, 1015, 775, 727, 695 cm$^{-1}$.

Compounds **15** and **16** (Mixture).

These two compound had the following data: $^{13}$C nmr (100 MHz, deuteriochloroform)[DEPT]: δ 13.4 ($CH_3$, **16**), 13.6 ($CH_3$, **15**), 20.7 ($CH_2$, **16**), 23.1 ($CH_2$, **15**), 122.2 (CH), 122.3 (CH), 125.3 (CH), 126.5 (CH), 126.6 (CH), 128.0 (CH), 128.5 (CH), 128.7 (CH), 128.9 (CH), 129.0 (CH), 129.3 (CH), 129.4 (CH), 130.2 (CH), 130.3 (CH), 130.8 (C), 154.2 (C), 161.5 (C) ppm; ms: [m/z (% relative intensity)] 275 (100, M$^+$), 274 (36), 260 (11), 234 (25), 208 (10), 180 (9), 172 (8), 157 (8), 105 (37), 104 (83), 103 (16), 77 (16).

Isomerization of **18** after boiling for 16 hours gave an oil that contained **18** (72%), **19** (7%), **20** (8%) and **24** (11%). **20** was isolated by thin-layer chromatography (Silica/ $CHCl_3$). **19** was inseperable from **18**.

1-(*cis*-3-Methyl-3-butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole, **19**.

This compound had $^1$H nmr (400 MHz, deuteriochloroform): δ 1.63 (br s, 3H), 2.62 (t, J = 7.32 Hz, 2H), 4.33 (t, J = 7.32, 2H), 4.63 (br s, 1H), 4.75 (br s, 1H) ppm. Further data were not distinguishable from **18**; $^{13}$C nmr (100 MHz, deuteriochloroform)-[DEPT]: δ 22.3 ($CH_3$), 38.0 ($CH_2$), 112.9 ($CH_2$), 141.2 (C), 155.8 (C) ppm. Further data were not distinguishable from **18**; gc-ftir: 3075, 2978, 2953, 1650, 1519, 1477, 1445, 1350, 1128, 1018, 900, 731, 694 cm$^{-1}$; gc-ms: [m/z (% relative intensity)] 289 (41, M$^+$), 288 (36), 274 (24), 222 (17), 221 (96), 132 (10), 131 (100), 118 (50), 105 (10), 104 (97), 103 (20), 91 (12), 89 (26), 77 (57).

1-(*trans*-3-Methyl-1-butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole, **20**.

This compound had $^1$H nmr (400 MHz, deuteriochloroform): δ 1.12 (d, J = 6.85 Hz, 6H), 2.44-2.56 (m, 1H), 6.53 (dd, J = 7.32, 13.67 Hz, 1H), 6.86 (dd, J = 1.46, 13.67 Hz, 1H), 7.38-

7.56 (m, 6H), 7.70-7.73 (m, 2H), 8.19-8.23 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform): δ 22.4, 29.2, 121.1, 126.7, 128.0, 128.5, 128.9, 129.4, 130.3, 130.4, 130.8, 154.4, 161.5 ppm; gc-ftir: 3074, 2971, 2882, 1666, 1522, 1480, 1446, 1395, 1349, 1299, 1177, 1129, 1018, 946, 732, 695 $cm^{-1}$; ms: [m/z (% relative intensity)] 289 (77, $M^+$), 288 (25), 274 (15), 234 (15), 221 (20), 208 (16), 171 (9), 145 (11), 118 (13), 105 (69), 104 (100), 103 (21), 89 (10), 83 (25), 77 (23).

Compound **21**.

The compound was detected in the reaction mixture from thermolysis of **17**; gc-ftir: 3074, 2935, 1519, 1477, 1445, 1404, 1348, 1288, 1174, 1129, 1026, 769, 733), 693 $cm^{-1}$; gc-ms: [m/z (% relative intensity)] 289 (3, $M^+$, 274 (5), 222 (8), 221 (30), 118 (78), 104 (57), 103 (16), 91 (28), 90 (15), 89 (100), 77 (54), 76 (16).

Thermolysis of 1,2,4-Triazoles. General Procedure.

Samples (50 mg) of the appropriate triazoles were placed in closed, evacuated glass ampoules (40 x 3 mm id) and heated to 315-320° for 20 minutes. The ampoules were then crushed and the resulting reaction products extracted with dichloromethane. The compositions of the product mixtures were determined by glc and gc-ftir analyses. The single components of the product mixtures were next separated by thin-layer chromatography, and their identity determined by comparison of their characteristic spectroscopic properties with those of authentic samples. The results are reported in Tables 1-5. The products were identified by comparison with those described above. Thermolysis of several of the triazoles also yielded a variety of pyridine products.

2,6-Diphenylpyridine, **28**.

This compound was isolated in small quanities upon thermolysis of **4**. The product exhibited spectroscopic properties similar to those described in the literature [12]; cg-ftir: 3070, 2043, 1589, 1569, 1443, 1181, 1025, 749, 691 $cm^{-1}$; ms: [m/z (% relative intensity)] 231 (100, $M^+$), 230 (43), 149 (25), 109 (12), 91 (11), 85 (15), 83 (24), 82 (15), 81 (14), 77 (12). Found: $M^+$ 231.1050. Calcd. for $C_{17}H_{13}N$: 231.1048.

2,6-Diphenyl-4-methyl-pyridine, **29**.

This compound was isolated from the thermolysis mixture of **7**. The product exhibited spectroscopic properties similar to those described in the literature [13]; $^1H$ nmr (400 MHz, deuteriochloroform): δ 2.48 (s, 3H), 7.41-7.53 (m, 8H), 8.13-8.15 (m, 4H) ppm; gc-ftir: 3070, 3041, 2931, 1600, 1559, 1497, 1414, 735, 691 $cm^{-1}$; gc-ms: [m/z (% relative intensity)] 245 (100, $M^+$), 244 (59), 243 (8), 242 (5), 230 (17), 228 (5), 202 (7), 115 (9), 114 (5), 102 (8). Found: $M^+$ 245.1202. Calcd. for $C_{18}H_{15}N$: 245.1204.

2,6-Dipenyl-3-methylpyridine, **30**.

This compound was isolated from the thermolysis mixture of **11**. The product exhibited spectroscopic properties similar to those described in the literature [14]; $^1H$ nmr (400 MHz, deuteriochloroform): δ 2.40 (s, 3H), 7.35-7.49 (m, 6H), 7.61-7.65 (m, 4H), 8.05-8.07 (m, 2H) ppm; $^{13}C$ nmr (100 MHz, deuteriochloroform)[DEPT]: 19.9 ($CH_3$), 118.7 (CH), 126.8 (CH), 127.9 (CH), 128.1 (CH), 128.6 (CH), 128.6 (CH), 129.3 (CH), 139.4 (CH), 140.9 (C), 154.6 (C), 158.2 (C) ppm; gc-ftir: 3069, 3040, 2942, 1454, 1226, 752, 697 $cm^{-1}$; ms: [m/z (% relative intensity)] 245 (57, $M^+$), 244 (100), 243 (11). Found: $M^+$ 245,1198. Calcd. for $C_{18}H_{15}N$: 245.1204.

1,3-Diphenylisoquinoline, **31**.

This compound was isolated after thermolysis of **22**. The product exhibited spectroscopic properties similar to those described in the literature [14-15]; $^1H$ nmr (400 MHz, deuteriochloroform): δ 7.38-7.42 (m, 1H), 7.48-7.58 (m, 6H), 7.67-7.71 (m, 1H), 7.80-7.82 (m, 2H), 7.94 (d, J = 7.8 Hz, 1H), 8.01 (s, 1H), 8.13 (d, J = 8.8 Hz, 1H), 8.21-8.22 (m, 2H) ppm; gc-ftir: 3069, 1619, 1562, 1495, 1440, 1384, 1336, 1029, 976, 861, 766, 693 $cm^{-1}$; ms: [m/z (% relative intensity)] 281 (77, $M^+$), 280 (100), 202 (10), 149 (10). Found: $M^+$ 281.1198. Calcd. for $C_{21}H_{15}N$: 281.1204.

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