Thermolysis of Triazoles as Melts − Is the 3,5-Diphenyl-1,2,4-triazole Group a Good Leaving Group?

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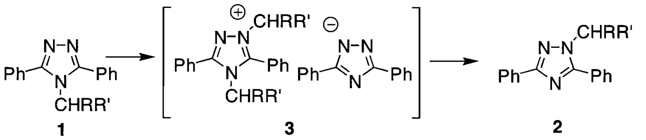
The mechanism of the rearrangement of 4-alkyltriazoles to the corresponding 1-alkyltriazoles on thermolysis at 330 °C is shown to involve initial formation of an intermediate 1,4-dialkyltriazolium triazolate salt. The triazolate ion subsequently attacks at the alkyl group bearing 1- and 4-positions of the dialkyltriazolium ion, yielding the observed products. No evidence for unimolecular reaction steps has been found. The triazole moiety in these compounds is only a weak leaving group, which requires activation by alkylation. Unimolecular reaction steps never take place, neither from neutral triazole species nor from activated dialkyl-substituted triazolium species.

Introduction

Studies of the thermal rearrangement of neat 4-alkyl-substituted 4*H*-1,2,4-triazoles, **1**, to the corresponding 1-alkyl-1*H*-1,2,4-triazoles, **2**, have been reported previously.[1] It was shown that the triazole moiety in such systems behaves as a leaving group, giving rise to products corresponding to both substitution and elimination reaction pathways.[2] The question now arises as to whether alkyl-substituted triazoles behave like alkyl halides or sulfonates or like, e.g., trialkylamines, which require activation by alkylation in order to function as leaving groups. We report herein on our efforts to further elucidate the mechanism of this rearrangement. This study is also of interest in view of the synthetic utility of *N*-substituted benzotriazoles.[3]

Results and Discussion

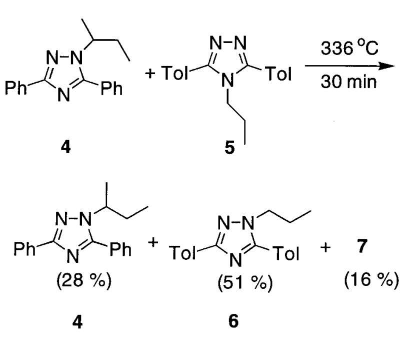
Previous work excluded a concerted, unimolecular mechanism, but gave evidence for a mechanism involving an initial bimolecular nucleophilic displacement reaction leading to formation of a triazolium triazolate "salt", **3**. As a consequence, the triazole ring was activated as a leaving group. Subsequent nucleophilic attack by the triazole anion at the alkyl group bearing positions of the triazolium ion of the ionic intermediate **3** led to formation of the products. This reaction scheme is bimolecular in nature (Scheme 1). In general, this reactivity resembles that of quaternary ammonium ions, which may undergo substitution as well as elimination reactions. Nucleophilic substitution and elimination are closely related.



Scheme 1

The rearrangement of optically active 4-(2-butyl)-substituted triazoles appeared to be in agreement with this mechanism, except that approximately 15% racemization occurred.[4] This was rationalized in terms of the nucleophilic attack taking place at both the 1- and 4-alkylated positions of the triazolium ion, but an alternative explanation may be that partial racemization takes place during the alkyl group transfer through a new 2-butyl carbocation−triazolate anion ion pair.

However, unimolecular pathways may also account for the racemization. There is a good deal of evidence to suggest that in most S_N1 reactions the carbenium ions are never removed far from their leaving groups. Instead, the nucleophile attacks an ion pair.[5] For triazoles bearing alkyl substituents that may form stable carbenium ions, cleavage of the alkyl−triazole bond may lead to ion-pair formation, which may facilitate racemization of the optically active group. This parallels the dual uni- and bimolecular reactivity of 2-bromobutane.[6] In previous work, we have also noted that all attempts to prepare 4-substituted triazoles where the substituent was capable of forming a stabilized carbenium ion, e.g. with *tert*-butyl and 1-adamantyl groups, met with failure and only the elimination products were isolated.[7]



Scheme 2

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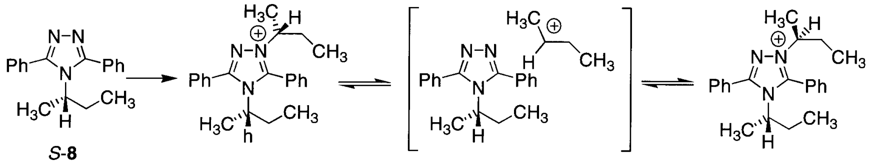


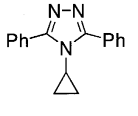
Scheme 3

Potentially borderline cases are the (2-butyl)triazoles, which may react along both uni- and bimolecular pathways. However, thermolysis of a melt containing 1-(2-butyl)-3,5-diphenyl-1*H*-1,2,4-triazole (**4**),[7] and 4-propyl-3,5-ditolyl-4*H*-1,2,4-triazole (**5**), led only to the products corresponding to the thermal rearrangement of **5**, without any signs of cross-over products (Scheme 2). These results indicated that ion-pair formation by heterolytic cleavage did not take place with the 2-butyl group in the 1-position, thus excluding unimolecular ion-pair formation by heterolytic cleavage of the non-activated triazole.

Alternatively, cleavage may take place from the dialkyltriazolium ion. Thus, the partial racemization observed[4] for (*S*)-**8** may occur via the activated triazole, i.e. the dialkyltriazolium ion, by cleavage of one of the triazole−alkyl bonds resulting in the formation of a free 2-butyl cation together with the neutral triazole, followed by recombination to give the triazolium ion. A driving force for this pathway would be the stability of the *sec*-butyl cation (Scheme 3).

In a quest for other substituents that may form more stable carbenium ions and which can also function as probes allowing assessment of full or partial unimolecular reaction steps, we investigated 4-cyclopropyl-substituted triazoles. Cyclopropyl halides are known to be resistant to nucleophilic attack and undergo unimolecular solvolysis reactions with concomitant ring-opening of the cyclopropane ring to give the corresponding allyl carbenium ion.[8] Cyclopropyl-substituted triazoles may therefore represent probes for unimolecular mechanisms. Thus, 4-cyclopropyl-3,5-diphenyl-4*H*-1,2,4-triazole (**9**), was prepared according to standard literature methods.[7] Neat **9** (Scheme 4) was then subjected to thermolysis at 330 °C for 30 min, but none of the anticipated products were produced. This was also the case when the experiment was repeated at 350 °C for 120 min. Some carbonation took place and 87% of the unchanged starting material was recovered after the thermolysis. Thus, in the neutral cyclopropyltriazole system, the triazole ring does not function as a leaving group. The resistance of **9** to reaction rules out a low-energy dissociative ion-pair mechanism.

The cyclopropylmethyl group, on the other hand, could be expected to promote formation of ion pairs as cyclopropylmethyl cations are known to be highly stabilized.[9] Ionic reactions, e.g. solvolyses of cyclopropylmethyl halides, give rise to product mixtures consisting of homoallyl-, cyclobutyl-, and cyclopropylmethyl products.[10] In many cases, such systems are known to undergo solvolysis much more rapidly than the corresponding alkyl compounds.[11] These reactions have been proposed to proceed through the formation of a non-classical cation, $C_4H_7^+$, the structure of which has been discussed by several groups.[12] The 4-cyclopropylmethyl-3,5-diphenyl-4*H*-1,2,4-triazole (**10**), was prepared according to established methods.[7] Thermolysis of **10** at 330 °C for 33 min yielded a product mixture consisting of 1-cyclopropylmethyl-3,5-diphenyl-1*H*-1,2,4-triazole (**11**), 1-cyclobutyl-3,5-diphenyl-1*H*-1,2,4-triazole (**12**), and 1-(3-butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole (**13**), in a 7.7:1.3:1.0 ratio, together with 33% of the unchanged starting material and traces of *cis*- and *trans*-crotyl-3,5-diphenyl-1*H*-1,2,4-triazole and 3,5-diphenyl-1*H*-triazole (**7**). These are the types of products generally obtained upon solvolysis of cyclopropylmethyl and cyclobutyl derivatives,[13] or by diazotization of cyclobutylamine or cyclopropylmethylamine.[14] With these results in mind, thermolysis of 4-cyclobutyl-3,5-diphenyl-4*H*-1,2,4-triazole (**14**), could therefore be expected to lead to similar products. Indeed, thermolysis of **14** at 330 °C for 30 min resulted in complete conversion with the generation of the same products **11**, **12**, and **13** in a 4.3:1.0:1.0 ratio, together with 30% of 3,5-diphenyltriazole, **7** (Scheme 5). It is noteworthy that **10** was not formed upon thermolysis of **14** or vice versa.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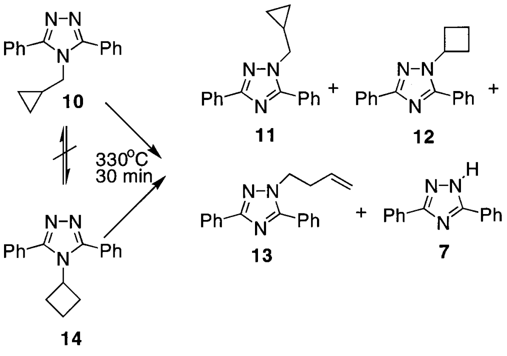
Scheme 4



Scheme 5

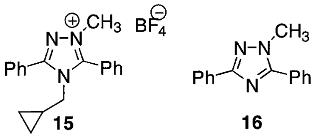
The products were isolated by preparative TLC and identified by comparison of their spectroscopic and chromatographic properties with those of authentic samples. The results are presented in Table 1.

The triazole−alkyl group C−N bond is activated towards cleavage in the triazolium salt. To elucidate this possible pathway, 4-cyclopropylmethyl-1-methyl-3,5-diphenyl-1,2,4-triazolium tetrafluoroborate (**15**), was subjected to thermolysis in solution. This salt was readily prepared by treating triazole **10** with trimethyloxonium tetrafluorobo-

Table 1. Product distributions on thermolysis of the neat triazoles **9**, **10**, and **14** at 330 °C for 30 min; ratios were determined by GC analysis

Triazole	Product **7** %	Conversion %	Product distribution Relative ratios of compounds: **11**	**12**	**13**
10	trace	77	7.7	1.3	1.0
14	30	100	4.3	1.0	1.0
9	0	0	−	−	−

rate in 1,2-dichloroethane at 60 °C for 3 h.[15] The NMR spectra of the crude thermolysate showed no sign of products in which the cyclopropylmethyl group had rearranged. When thermolysis was attempted in the more polar solvents acetonitrile and DMF (CD_3CN and [D_7]DMF) in sealed NMR tubes at 150 °C for 12 h, again no detectable amounts of rearrangement products were found. These results give the general impression that unimolecular reaction steps do not take place. When the triazolium salt was heated in acetonitrile at 200 °C for 3 h, however, 1-methyl-3,5-diphenyl-1*H*-1,2,4-triazole (**16**), was formed as the sole product (Scheme 6), presumably due to attack at the cyclopropylmethyl group by the solvent functioning as a weak nucleophile.



Scheme 6

The above results are consistent with mechanisms where no cleavage−recombination of the triazole−alkyl group C−N bonds takes place. This is further supported by the fact that **10** and **14** do not interconvert (Scheme 5). Elimination products were absent in the thermolysates derived from the cyclopropylmethyltriazole, whereas the cyclobutyltriazole formed appreciable amounts of elimination products. Substituted cyclobutanes are known to undergo elimination reactions, which rarely occur with cyclopropylmethyl compounds.[16] The results with cyclopropylmethyltriazole also excluded possible radical rearrangement mechanisms, as the cyclopropylcarbinyl radical undergoes rapid rearrangement to the homoallylcarbinyl radical. The use of the *radical clock* has been discussed.[17] Rate constants for this reaction have been determined to be of the order of $2 \cdot 10^7$ s^{-1} by Castellino and co-workers.[18]

Conclusion

This study confirms the previously proposed mechanism for the thermolysis of 4-alkyltriazoles to the corresponding 1-alkyltriazoles. This mechanism involves initial formation of an intermediate salt, a 1,4-dialkyltriazolium triazolate, from which the product is formed through attack of a nucleophile at the alkylated 4- and 1-positions. Thus, there is no evidence for unimolecular reaction steps. The present work furthermore confirms the previous hypothesis that the triazole moiety in these compounds functions as a weak leaving group, requiring activation by alkylation. Unimolecular reaction steps never take place, neither from the neutral triazole species nor from the activated dialkyl-substituted triazolium species. Among the systems we have studied, the course of the reaction has been found to be independent of the nature of the alkyl substituents. The 3,5-diphenyl-1,2,4-triazole ring can therefore be classified as a poor leaving group.

Experimental Section

General: ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-EX400 FT NMR spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as an internal standard. − IR and GC-IR spectra were obtained on a Nicolet 20-SXC FT-IR (GC Carlo Erba 5160, 25 m, CP-Sil-5 CB). − Mass spectra were recorded on an AEI MS-902 spectrometer at 70 eV (IP) with an inlet temperature of 200 °C. − GC measurements were performed on a Varian 3700 gas chromatograph equipped with a BP-1 capillary column (24 m). All products were found to be stable under the GC conditions. − Melting points are uncorrected.

Thermolysis of 4-Alkyl-3,5-diphenyl-4*H*-1,2,4-triazoles. − General Procedure: The triazole (0.06−0.15 mmol) was placed in a thick-walled glass tube, which was evacuated and sealed. The sample tube was then placed in an oven at ca. 330 °C for 30 min. After cooling to room temperature, the tube was broken, the contents were dissolved in dichloromethane, and the composition of the crude product was determined by GC analysis. The components of the mixture were subsequently isolated by preparative TLC and their identities were confirmed by comparison of their spectroscopic and chromatographic properties with those of authentic samples. The identities of the products were similarly established by GC-FTIR analysis.

Synthesis of 4-Alkyl-3,5-diphenyl-4*H*-1,2,4-triazoles. − General Procedure: A solution of bis(α-chlorobenzylidene)hydrazone[19] (0.20 g, 0.72 mmol) and the appropriate amine (3.3 mmol) in dry benzene (10 mL) was placed in a glass ampoule, which was sealed and then heated in an oil bath at 140 °C for 40 h. After cooling, the ampoule was opened, the contents were taken up in dichloromethane (20 mL), and the resulting solution was washed sequentially with 1 M aq. HCl, 2 M aq. NaOH, and water. After drying with anhydrous magnesium sulfate, the solvent was evaporated and the crude product was recrystallized as detailed below.

4-Cyclopropyl-3,5-diphenyl-4*H*-1,2,4-triazole (9): After recrystallization from 75% ethanol, the yield of the pure product was 100 mg (53%) (> 99% pure by GC); m.p. 223.5−224.0 °C. − ^1H NMR (400 MHz, $CDCl_3$): δ = 0.39−0.44 (m, 2 H), 0.92 (q, J = 6.8 Hz, 2 H), 3.54 (sextet, J = 3.6 Hz, 1 H), 7.50−7.55 (m, 6 H), 7.87−7.90 (m, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 10.4, 27.6, 127.4, 128.4, 128.5, 129.6, 156.6. − IR (KBr): $\tilde{\nu}$ = 3068, 3061, 3049, 3041, 3017, 1472, 1467, 1442, 1415, 1287, 1076, 1062, 1030, 1023, 974, 929, 886, 848, 789, 773, 721 cm^{-1}. − MS: *m/z* (%) = 261 (100) [M^+], 260 (32), 144 (26), 131 (12), 130 (25), 104 (23), 103 (49), 89 (33), 77 (30), 63 (13). − Calcd. for $C_{17}H_{15}N_3$: M^+ 261.1266; found 261.1262. − $C_{17}H_{15}N_3$ (261.3): calcd. C 78.14, H 5.79, N 16.08; found C 78.01, H 6.03, N 15.87.

4-Cyclopropylmethyl-3,5-diphenyl-4*H*-1,2,4-triazole (10): After recrystallization from toluene, the yield of the pure product was

120 mg (60%) (97.5% pure by GC). It was obtained as a white crystalline material, m.p. 194.0−195.5 °C. − ^{1}H NMR (100 MHz, $CDCl_3$): $\delta = (-0.39)-(-0.18)$ (m, 2 H), 0.16−0.35 (m, 2 H), 0.52−0.85 (m, 1 H), 3.97 (d, J = 6.8 Hz, 2 H), 7.49−7.78 (m, 10 H).[20] − ^{13}C NMR (25 MHz, $CDCl_3$): δ = 3.9, 11.4, 49.4, 127.8, 128.8, 129.1, 129.9, 155.5. − IR (KBr): $\tilde{\nu}$ = 3079, 3031, 3006, 2962, 2926, 1471, 1406, 1384, 1328, 1033, 830, 778, 744, 729, 707 cm^{-1}. − MS: *m*/*z* (%) = 275 (100) [M^+], 274 (19), 221 (45), 144 (17), 131 (72), 118 (29), 104 (29), 89 (42), 77 (20), 55 (77). − Calcd. for $C_{18}H_{17}N_3$: M^+ 275.1423; found 275.1418. − $C_{18}H_{17}N_3$ (275.4): calcd. C 78.52, H 6.22, N 15.26; found C 78.45, H 6.13, N 15.34.

4-Cyclobutyl-3,5-diphenyl-4*H*-1,2,4-triazole (14): After recrystallization from toluene, the yield of the pure product was 88 mg (44%) (> 99% pure by GC); m.p. 184.0−185.5 °C. − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.45−1.62 (m, 2 H), 1.81 (dq, J = 9.7 and 2.5 Hz, 2 H), 1.96−2.03 (m, 2 H), 4.90 (p, J = 8.2 Hz, 1 H), 7.48−7.51 (m, 6 H), 7.65−7.69 (m, 4 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 15.3, 31.2, 51.0, 128.4, 129.0, 129.8, 155.2. − IR (KBr): $\tilde{\nu}$ = 3060, 3043, 3009, 2997, 2977, 2947, 1471, 1444, 1413, 1342, 783, 774, 728, 716, 704 cm^{-1}. − MS: *m*/*z* (%) = 275 (100) [M^+], 274 (12), 248 (10), 247 (55), 246 (45), 245 (6), 222 (7), 221 (37), 144 (20), 143 (7), 132 (5), 131 (50), 130 (15), 118 (32), 117 (35), 116 (10), 115 (8), 104 (56), 103 (28), 91 (14), 90 (12), 89 (88), 77 (56), 63 (30). − Calcd. for $C_{18}H_{17}N_3$: M^+ 275.1423; found 275.1421. − $C_{18}H_{17}N_3$ (275.4): calcd. C 78.52, H 6.22, N 15.26; found C 78.64, H 6.39, N 15.04.

3,5-Bis(4-methylphenyl)-4-propyl-4*H*-1,2,4-triazole (5): From bis(α-chloro-4-methylbenzylidene)hydrazine (9.7 g, 0.032 mol) in propylamine (200 mL), 6.84 g (69%) of **5** was obtained after recrystallization from toluene (> 99% purity by GC); m.p. 202−203.5 °C. − ^{1}H NMR (100 MHz): δ = 0.60 (t, J = 7.3 Hz, 3 H), 1.39 (sextet, J = 7.3 Hz, 2 H), 2.43 (s, 6 H), 4.03 (t, J = 7.3 Hz, 2 H), 7.31 (d, J = 7.8 Hz, 4 H), 7.55 (d, J = 8.3 Hz, 4 H). − ^{13}C NMR (25 MHz): δ = 10.6, 21.4, 23.2, 46.3, 125.0, 128.7, 129.5, 140.0, 155.5. − IR (KBr): $\tilde{\nu}$ = 3068, 2976, 2958, 2944, 2921, 2876, 1479, 1474, 1465, 1449, 1417, 1383, 1347, 1339, 1021, 849, 822, 753 cm^{-1}. − MS: *m*/*z* (%) = 292 (23), 291 (100) [M^+], 290 (12), 276 (19), 249 (26), 132 (21), 118 (35), 103 (26), 91 (18), 77 (17). − Calcd. for $C_{19}H_{21}N_3$: M^+ 291.1735; found 291.1737. − $C_{19}H_{21}N_3$ (291.4): calcd. C 78.32, H 7.26, N 14.42; found C 78.23, H 7.38, N 14.38.

4-Cyclopropylmethyl-1-methyl-3,5-diphenyl-4*H*-1,2,4-triazolium Tetrafluoroborate (15): A solution of 4-cyclopropylmethyl-3,5-diphenyl-4*H*-1,2,4-triazole, **10**, (1.0 g, 3.7 mmol) and trimethyloxonium tetrafluoroborate (0.77 g, 4 mmol) in 1,2-dichloroethane (25 mL) was stirred at 60 °C for 3 h. The reaction mixture was then concentrated under reduced pressure and the residue was repeatedly washed with dry diethyl ether to yield 1.55 g of **15** (quantitative). − ^{1}H NMR (100 MHz, CD_3CN): $\delta = (-0.39)-(-0.44)$ (m, 2 H), 0.16−0.35 (m, 2 H), 0.52−0.90 (m, 1 H), 3.97 (d, J = 6.8 Hz, 2 H), 4.05 (s, 3 H), 7.49−7.78 (m, 10 H).

Thermolysis of 4-Cyclopropylmethyl-1-methyl-3,5-diphenyl-4*H*-1,2,4-triazolium Tetrafluoroborate (15): A solution of **15** (50 mg) in dry acetonitrile (2 mL) was placed in a glass tube, which was sealed and then heated at 205 °C for 3 h. After cooling, GC analysis of the contents of the tube showed that 1-methyl-3,5-diphenyl-1*H*-1,2,4-triazole, **16**, was the only product formed. The product was isolated by preparative TLC and its identity was confirmed by comparison of its spectroscopic properties with those of an authentic sample.[21]

Synthesis of 1-Alkyl-3,5-diphenyl-1*H*-1,2,4-triazoles. − General Procedure: To a solution of 3,5-diphenyl-1*H*-1,2,4-triazole[18] (5 mmol) in dry DMF (5 mL) under nitrogen was added NaH (0.2 g) and the mixture was stirred for 30 min. Then, the appropriate alkyl halide or sulfonate (5−7 mmol) was added. The resulting mixture was stirred overnight. Dichloromethane (20 mL) was then added and this solution was washed with 1 M aq. HCl, 1 M aq. NaOH, and water. After drying over anhydrous magnesium sulfate, evaporation of the solvent gave the product.

1-Cyclopropylmethyl-3,5-diphenyl-1*H*-1,2,4-triazole (11): From 3,5-diphenyl-1*H*-1,2,4-triazole and cyclopropylmethyl tosylate, **11** was obtained in 64% yield as white crystals (97% pure by GC). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.24 (q, J = 5.2 Hz, 2 H), 0.50 (q, J = 6.3 Hz, 2 H), 1.21−1.30 (m, 1 H), 4.05 (d, J = 6.8 Hz, 2 H), 7.30−7.40 (m, 3 H), 7.43−7.47 (m, 3 H), 7.59−7.63 (m, 2 H), 8.10 (d, J = 6.8 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 3.9, 11.5, 53.6, 126.3, 127.7, 128.5, 128.9, 129.5, 130.0, 131.1, 155.3, 161.1. − IR (KBr): $\tilde{\nu}$ = 3082, 3065, 3046, 3033, 3011, 2978, 2947, 1479, 1457, 1443, 1426, 1410, 1394, 1356, 1296, 1284, 1179, 1133, 1115, 1073, 1051, 1027, 1018, 983, 936, 926, 837, 791, 770, 763, 731, 704, 700 cm^{-1}. − MS: *m*/*z* (%) = 275 (100) [M^+], 274 (25), 248 (3), 221 (50), 144 (17), 131 (58), 118 (33), 104 (44), 103 (14), 91 (12), 89 (35), 77 (21), 63 (13). − Calcd. for $C_{18}H_{17}N_3$: M^+ 275.1423; found 275.1418.

1-(3-Butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole (13): From 3,5-diphenyl-1*H*-1,2,4-triazole and 1-bromo-3-butene, **13** was obtained in 74% yield as an oily product (> 99% pure by GC). − ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.70 (q, J = 7.2 Hz, 2 H), 4.29 (t, J = 7.6 Hz, 2 H), 5.04−5.09 (m, 2 H), 5.67−5.76 (m, 1 H), 7.38−7.47 (m, 3 H), 7.50−7.54 (m, 3 H), 7.64−7.68 (m, 2 H), 8.16 (d, J = 6.8 Hz, 2 H). − ^{13}C NMR (100 MHz, $CDCl_3$): δ = 34.2, 48.5, 117.9, 126.3, 128.5, 128.9, 129.0, 130.0, 131.1, 133.4, 155.7, 161.2. − IR (neat): $\tilde{\nu}$ = 3070, 3033, 3003, 2980, 2948, 1519, 1477, 1464, 1443, 1411, 1354, 1302, 1284, 1174, 1132, 1071, 1027, 1018, 996, 982, 922, 790, 773, 731 cm^{-1}. − MS: *m*/*z* (%) = 275 (62) [M^+], 274 (45), 221 (42), 131 (100), 118 (21), 104 (71), 103 (25), 91 (11), 89 (16), 77 (35). − Calcd. for $C_{18}H_{17}N_3$: M^+ 275.1423; found 275.1418.

1-Cyclobutyl-3,5-diphenyl-1*H*-1,2,4-triazole (12): As expected, reaction of 3,5-diphenyl-1*H*-1,2,4-triazole with cyclobutyl bromide gave a mixture of products, from which 1-cyclopropylmethyl-3,5-diphenyl-1*H*-1,2,4-triazole (**11**) (67%), 1-(3-butenyl)-3,5-diphenyl-1*H*-1,2,4-triazole (**13**) (8%), and the desired product 1-cyclobutyl-3,5-diphenyl-1*H*-1,2,4-triazole (**12**) (25%) were isolated by preparative TLC. The overall yield was merely 15%. Spectroscopic details for **12**: ^{1}H NMR (400 MHz): δ = 1.75−1.87 (m, 1 H), 1.94−2.02 (m, 1 H), 2.39−2.46 (m, 2 H), 2.89 (dp, J = 9.6, J = 2.4 Hz, 2 H), 4.90 (p, J = 8.3 Hz, 1 H), 7.37−7.47 (m, 3 H), 7.50−7.55 (m, 3 H), 7.60−7.69 (m, 2 H), 8.15−8.21 (m, 2 H).

3,5-Bis(4-methylphenyl)-1-propyl-1*H*-1,2,4-triazole (6): After recrystallization from toluene, 90 mg (79%) of **6** was obtained; m.p. 101−102.5 °C (> 99% purity by GC). − ^{1}H NMR (100 MHz): δ = 0.91 (t, J = 7.3 Hz, 3 H), 1.93 (sextet, J = 7.3 Hz, 2 H), 2.38 (s, 3 H), 2.43 (s, 3 H), 4.16 (t, J = 7.3 Hz, 3 H), 7.28 (m, 4 H), 7.55 (d, J = 7.8 Hz, 2 H), 8.04 (d, J = 8.3 Hz, 2 H). − ^{13}C NMR (25 MHz): δ = 11.0, 21.4, 23.5, 50.7, 125.5, 126.2, 128.4, 128.7, 129.2, 129.5, 138.8, 140.0, 155.5, 161.1. − IR (KBr): $\tilde{\nu}$ = 2962, 2947, 2934, 2917, 2877, 1472, 1468, 1425, 1352, 1182, 1129, 1018, 840, 826, 759 cm^{-1}. − MS: *m*/*z* (%) = 292 (24), 291 (100) [M^+], 263 (12), 262 (58), 249 (48), 145 (48), 132 (13), 119 (21), 118 (76), 117 (28), 116 (17), 103 (28), 91 (21), 77 (21). − Calcd. for $C_{19}H_{21}N_3$: M^+ 291.1736; found 291.1731. − $C_{19}H_{21}N_3$ (291.4): C 78.32, H 7.26, N 14.42; found C 78.47, H 7.41, N 14.67.

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[1] O. R. Gautun, P. H. J. Carlsen, *Acta Chem. Scand.* **1992**, *46*, 469; P. H. J. Carlsen, K. B. Jørgensen, O. R. Gautun, S. Jagner, M. Håkansson, *Acta Chem. Scand.* **1995**, *49*, 676.

[2] O. R. Gautun, P. H. J. Carlsen, *Acta Chem. Scand.* **1994**, *48*, 411.

[3] A. R. Katritzky, X. Lan, J. Z. Yang, O. V. Denisko, *Chem. Rev.* **1998**, *98*, 409−548.

[4] P. H. J. Carlsen, O. R. Gautun, *Acta Chem. Scand.* **1990**, *44*, 485.

[5] D. J. Raber, J. M. Harris, P. v. R. Schleyer, *Ions and Ion Pairs in Organic Reactions*, vol. 2 (Ed.: M. Szwarc), Wiley, New York, **1974**.

[6] C. K. Ingold, *Structure and Mechanism in Organic Chemistry*, Cornell University Press, Ithaca, N.Y., **1953**, p. 318.

[7] O. R. Gautun, P. H. J. Carlsen, *Acta Chem. Scand.* **1991**, *45*, 609.

[8] P. v. R. Schleyer, T. Su, M. Saunders, J. C. Rosenfeld, *J. Am. Chem. Soc.* **1969**, *91*, 5174; L. Radom, P. C. Hariharan, J. A. People, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1973**, *95*, 6531.

[9] S. Sarel, J. Yovell, M. Sarel-Imber, *Angew. Chem.* **1968**, *80*, 592; H. G. Richey, in: *Carbonium Ions* (Eds.: G. A. Olah, P. v. R. Schleyer), Wiley, New York, **1972**, p. 1243.

[10] K. B. Wiberg, B. A. Hess, A. J. Ashe, H. G. Richey, in: *Carbonium Ions*, vol. 3 (Eds.: G. A. Olah, P. v. R. Schleyer), Wiley, New York, **1972**, p. 1295.

[11] J. D. Robert, *J. Org. Chem.* **1964**, *29*, 294; J. D. Robert, *J. Org. Chem.* **1965**, *30*, 23; M. C. Caserio, W. H. Graham, J. D. Roberts, *Tetrahedron* **1960**, *11*, 171.

[12] P. C. Myhre, G. G. Webb, C. S. Yannoni, *J. Am. Chem. Soc.* **1990**, *112*, 8992; M. Saunders, K. E. Laidig, K. B. Wiberg, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1988**, *110*, 7652; W. Koch, B. Lui, D. J. DeFrees, *J. Am. Chem. Soc.* **1988**, *110*, 7325; R. F. W. Bader, K. E. Laidig, *J. Mol. Struct. (Theo.)* **1992**, *261*, 1; G. A. Olah, V. P. Reddy, G. K. S. Prakash, *Chem. Rev.* **1992**, *92*, 69.

[13] J. S. Staral, J. D. Roberts, *J. Am. Chem. Soc.* **1978**, *100*, 8018.

[14] J. D. Roberts, R. H. Mazur, *J. Am. Chem. Soc.* **1951**, *73*, 2509; R. H. Mazur, W. N. White, D. A. Semenov, C. C. Lee, M. S. Silver, J. D. Roberts, *J. Am. Chem. Soc.* **1959**, *81*, 4390.

[15] L. A. Lee, R. Evans, J. W. Wheeler, *J. Org. Chem.* **1972**, *37*, 343; H. Meerwein, *Org. Synth.* **1966**, *46*, 113.

[16] S. Halazy, A. Krief, *Tetrahedron Lett.* **1980**, *21*, 1997.

[17] V. W. Bowry, J. Lusztyk, K. U. Ingold, *J. Chem. Soc. Chem Commun.* **1990**, 923; V. W. Bowry, J. Lusztyk, K. U. Ingold, *J. Am. Chem. Soc.* **1991**, *113*, 5687; V. W. Bowry, K. U. Ingold, *J. Am. Chem. Soc.* **1991**, *113*, 5699; P. S. Engel, J. T. He, K. U. Banks, K. U. Ingold, J. Lusztyk, *J. Org. Chem.* **1997**, *62*, 7211.

[18] A. J. Castellino, T. C. Bruice, *J. Am. Chem. Soc.* **1988**, *110*, 1313; A. J. Castellino, T. C. Bruice, *J. Am. Chem. Soc.* **1988**, *110*, 7511.

[19] J. Lange, H. Tondys, *Dissert. Pharm. Pharmacol. XXII*, **1980**, 217.

[20] The extreme high-field NMR shifts observed for the cyclopropyl protons are due to two of the protons being forced into the shielding region of the phenyl rings. Molecular modeling studies indicated that the phenyl rings lie approximately 56° out of the plane of the triazole ring and that the cyclopropylmethyl substituent is essentially perpendicular to this plane. The molecular modeling studies were performed using PCModel, Version 7, from Serena Software, Box 3076, Bloomington, IN 47402−3076, USA; E-mail: gilbert@serenasoft.com.

[21] P. H. J. Carlsen, *Acta Chem. Scand.* **1987**, *B41*, 302.

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