Rearrangement of 4*H*-Triazoles. Synthesis and Thermolysis of ^{15}N-Labelled 4-Ethyl-3,5-diphenyl-4*H*-1,2,4-triazole

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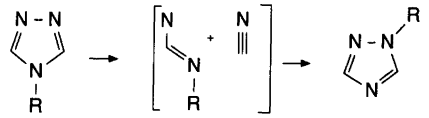
Thermolysis of [4-^{15}N]-4-ethyl-3,5-diphenyl-4*H*-1,2,4-triazole at 330 °C gave the rearranged product [4-^{15}N]-1-ethyl-3,5-diphenyl-1*H*-1,2,4-triazole together with small amounts of the elimination product [4-^{15}N]-3,5-diphenyl-1*H*-1,2,4-triazole. These results exclude ring cleavage mechanisms for the thermal reaction. They are in agreement with a mechanism where cleavage of the *N*-alkyl bond takes place in the course of the rearrangement.

From investigations of the thermal rearrangement of 4-alkyl-4*H*-1,2,4-triazoles to the corresponding 1-alkyl isomers[1] a working hypothesis for the mechanism has been formulated involving (*a*) a ring cleavage–recombination reaction, (*b*) a concerted group shift or (*c*) an inter- or intra-



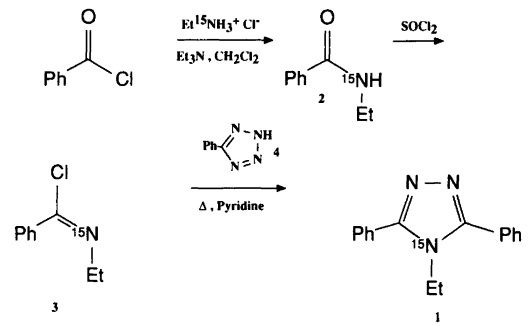
Scheme 1.

molecular ionic or radical mechanism. Our investigations so far, suggest an ion-pair mechanism or a bimolecular nucleophilic displacement reaction.[2] However, mechanism (*a*) or alternatively a ring rearrangement reaction may also represent a feasible reaction route. Characteristic for mechanism (*a*) is that during the reaction, no bond cleavage takes place between the alkyl group and the N-atom in the 4-position of the ring. This would therefore result in the migration of the N–R moiety as a group. We wish to exclude or confirm the ring cleavage–recombination as a viable route for the rearrangement mechanism. The reason for considering a ring cleavage mechanism is based on earlier observations, that under vacuum flash thermolytic conditions benzonitrile was formed in small amounts.[1] Formation of this product can only be explained by a ring cleavage mechanism. However, the reaction may take a different course in the condensed phase.

In order to clarify whether or not N–R bond cleavage takes place during the reaction, the N–R moiety must be identified as a clearly distinguishable entity prior to the rearrangement. This can be achieved by labelling of the 4-alkyltriazole, e.g. with ^{15}N in the 4-position. A dissociative mechanism according to Scheme 1 would result in a rearranged product with the alkylated ^{15}N in the 1-position, while the other suggested mechanisms would result in rearranged triazoles where ^{15}N remains in the 4-position. Triazoles labelled with ^{15}N in both the 1- and 2-positions would give the same mechanistic information. A method for the synthesis of [1,2-^{15}N$_2$]-1,2,4-triazole has been reported recently,[3] but can only be adapted to our purpose with difficulty. We therefore decided to prepare the isotopically labelled compound [4-^{15}N]-4-ethyl-3,5-diphenyl-4*H*-1,2,4-triazole, **1**, which has not previously been described in the literature. **1** was prepared here using known reactions.

Results and discussion

*[4-^{15}N]-4-Ethyl-3,5-diphenyl-4*H*-1,2,4-triazole,* **1**. This compound was prepared from [^{15}N]-*N*-ethylbenzamide, **2**, by reacting the corresponding imidoyl chloride **3** with phenyltetrazole, **4**, according to the reaction shown in Scheme 2. This is a modification of the synthetic method earlier developed by Huisgen.[4] Compound **2** was prepared by reaction between benzoyl chloride and [^{15}N]ethylammonium chloride in the presence of triethylamine in dichloromethane. Mass spectroscopic analysis of the ^{15}N source, revealed that



Scheme 2.

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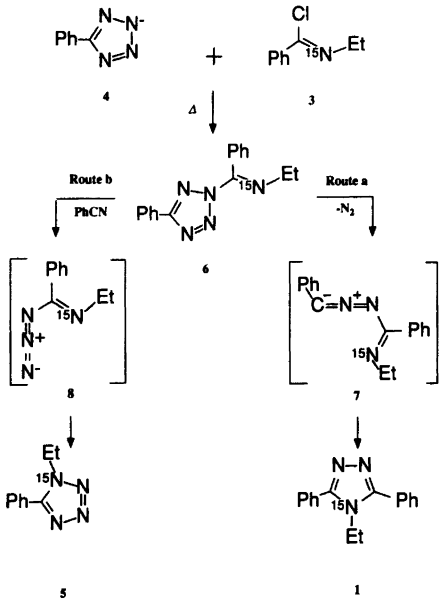
it was contaminated with approximately 20% of [^{15}N]-diethylamine. This was in agreement with a GLC analysis of the resulting product which indicated a mixture of 74% *N*-ethylbenzamine, **2**, together with 26% of *N,N*-diethylbenzamide. It was difficult to separate the latter from **2**, even by preparative thin layer chromatography. The presence of *N,N*-diethylbenzamide as an impurity, may also elude detection by GLC measurements. The formation of *N,N*-diethylbenzamide was not caused by the presence of diethylamine in the triethylamine, as MS analysis of the product indicated ^{15}N to be present in the molecular ion and fragments. Hoping that both of the benzamides upon treatment with thionyl chloride would yield the imidoyl chloride, **3**, the crude mixture of **2** was used without further purification. However, contrary to what has been reported by Braun and Pinkernelle,[5] treatment of *N,N*-diethylbenzamide with thionyl chloride, in our hands did not lead to the formation of **3**.

The isotopic purity of [^{15}N]-*N*-ethylbenzamide was determined by MS analysis to be 97.8% with respect to ^{15}N. All spectroscopic properties were in total agreement with those expected for this product. The imidoyl chloride **3** was not purified, but used as prepared in the subsequent reaction with phenyltetrazole, **4**, in refluxing pyridine. After purification of the crude product by preparative TLC and recrystallization, the yield of the ^{15}N-labelled triazole **1** was 14% based on [^{15}N]-*N*-ethylbenzamide. **1** was identified by comparison of its spectroscopic properties with those of an authentic, unlabelled sample and its straightforward spectral characteristics. With our instrumentation we were not able to detect any notable isotope shifts in the IR or NMR spectra.

The proton NMR spectrum exhibited the expected coupling between the ethyl group and the ^{15}N-nucleus. The methyl–^{15}N coupling constant, $^3J_{H\text{-}N15}$, was 3.2 Hz, while the methylene–^{15}N value, $^2J_{H\text{-}N15}$, was estimated to be approximately 0.5–1 Hz. The ^2J value was smaller than the ^3J-value. This is in agreement with observations for other ^{15}N-labelled compounds.[6] In the ^{13}C NMR spectrum a doublet was observed at 155.2 ppm with a coupling constant of 12.1 Hz, corresponding to the triazole carbon signal. The methylene carbon and ^{15}N coupled with J = 8.5 Hz. The spectroscopic data clearly showed that ^{15}N was present in the 4-position. The isotopic purity was determined to be 98.5% by MS measurements.

Unexpectedly we also isolated 1-ethyl-5-phenyltetrazole as a by-product in 5% yield, after purification by preparative TLC and recrystallization. This product was not reported by Huisgen.[4] Thus, the imidoyl chloride also appeared to function as an alkylating agent. However, the product was shown by MS and NMR analysis to be ^{15}N-labelled in the 1-position. The identity of the product, **5**, was further established by comparison of the spectroscopic properties with those of an authentic sample of unlabelled **5**, prepared by alkylation of phenyltetrazole with diethyl sulfate according to the method described by Lee and Wheeler.[7]

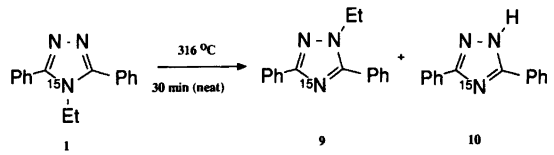
The straightforward NMR data clearly indicated the ^{15}N to be in the 1-position of the tetrazole and substituted by the ethyl group, as the ethyl proton signals exhibited the characteristic $^2J_{H\text{-}N15}$ and $^3J_{H\text{-}N15}$ values of 1.2 and 2.9 Hz, respectively. The large coupling constant, 12.2 Hz, observed for the ^{13}C doublet at 154 ppm and 9.8 Hz for the doublet at 43.3 ppm agrees well with the geminal ^{15}N–C relationships in structure **5**. The mechanisms for formation of the products can be rationalized as illustrated in Scheme 3. The triazole **1** may be formed according to the mechanism indicated by route (*a*), previously suggested for similar systems by Huisgen.[4] Addition of **3** to **4**, resulting in the



Scheme 3.

intermediate **6**, upon elimination of N_2, would give the dipolar intermediate **7** which would subsequently cyclize to product **1**. The adduct **6** may also decompose by the alternative route (*b*), involving elimination of benzonitrile to form the imidoyl azide **8**, which would then cyclize to the ^{15}N-labelled tetrazole **5**. We note the low isolated yields in these reactions. This was not actually due to low chemical yields, but because high chemical purities were required for the isotope measurements, and purification by preparative TLC followed by recrystallization resulted in considerable losses of products.

Thermolysis of **1**. Triazole **1** was thermolyzed under standard conditions, i.e., in a sealed tube at 316–335 °C for 30 min.[2] The components of the resulting reaction mixture were separated by preparative TLC purification and subsequent recrystallization. Two products were isolated, the rearranged product, [4-^{15}N]-1-ethyl-3,5-diphenyl-1*H*-1,2,4-triazole, **9**, (84.6%) together with the elimination product [4-^{15}N]-3,5-diphenyl-1*H*-1,2,4-triazole, **10**, (4%), Scheme



1 9 10

Scheme 4.

4. NMR data for the triazole **9** clearly indicated the ^{15}N label to be in the 4-position, as no coupling of the ethyl signals due to ^{15}N was observed, either in the ^{1}H or in the ^{13}C NMR spectra. Two ^{13}C signals corresponding to the *ipso* phenyl carbons were observed at 128.5 and 131.1 ppm. The δ 131.1 signal appeared as a doublet with J = 7.3 Hz. The NMR data for **10** were in agreement with the symmetrical structure, as only one triazole ^{13}C signal was observed.

The results obtained above exclude a ring cleavage mechanism for the rearrangement of 4-alkyl-4*H*-1,2,4-triazoles to the corresponding 1-alkyltriazoles. They are in agreement with a mechanism in which cleavage of the *N*-alkyl bond takes place during the rearrangement.

Experimental

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL FX-100 NMR spectrometer, using $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. IR spectra were obtained on a Nicolet 20SXC FT-IR, and mass spectra on an AEI MS-902 spectrometer (Nier-Johnson geometry) at 70 eV (IP), 200 °C, unless otherwise stated. GLC measurements were performed on a Varian 3700 gas chromatograph equipped with a BP-5 capillary column (25 m). preparative TLC was performed on 20 × 20 cm glass plates covered by Merck silica gel HF254+366, using chloroform as the eluent. [^{15}N]Ethylamine hydrochloride (99 % ^{15}N) was purchased from ICN. MS of this compound showed it to contain approximately 20 % of ^{15}N-labelled diethylamine hydrochloride. MS [*m/z* (% rel. int.)] 74 (3), 73 (2), 59 (12), 47 (1), 46 (27), 45 (25), 44 (4), 43 (11), 42 (5), 38 (32), 37 (5), 36 (100), 35 (16), 31 (97), 30 (4).

[^{15}N]-N-*Ethylbenzamide,* **2**. A solution containing [^{15}N]ethylamine hydrochloride (0.40 g, 4.85 × 10^{-3} mol) and freshly distilled triethylamine (3.10 g) in dichloromethane (10 ml) was stirred under an atmosphere of nitrogen at room temperature for 1 h. The mixture was placed in an ice–water bath, and a solution of freshly distilled benzoyl chloride (0.85 g, 6.05 × 10^{-3} mol) in 3 ml of dichloromethane was added dropwise. The mixture was stirred at 0 °C for 1 h, and then allowed to reach room temperature and stirred at this temperature for another 24 h. Precipitated triethylamine hydrochloride was then filtered off, and washed with dichloromethane. The combined organic phases (ca. 30 ml) were washed with 1 M HCl (4 × 10 ml) and saturated sodium hydrogen carbonate and then dried over magnesium sulfate. Evaporation of the solvent gave 0.40 g of a colorless oil, which by GLC analysis was shown to consist of [^{15}N]-*N*-ethylbenzamide (74 %), and [^{15}N]-*N,N*-diethylbenzamide (26 %). The mass spectrum of the mixture, showed peaks for [^{15}N]-*N,N*-diethylbenzamide at *m/z* 177 (100.0 %) and 178 (M^+, 86.8 %). Unlabelled *N,N*-diethylbenzamide showed peaks at 176 (98.3 %), 177 (M^+, 100 %) and 178 (11.6 %). The ratio of unlabelled to labelled *N,N*-diethylbenzamide was calculated from the 177/178 ratio, after the method described by Creary and Sky.[8] It was assumed that the *m/z* 177 peak corresponded to unlabelled *N,N*-diethylbenzamide (M^+) and the (M^+-1) peak (98.3 %) of labelled *N,N*-diethylbenzamide. The *m/z* 178 peak was assumed to be due to labelled *N,N*-diethylbenzamide (M^+) and the (M^++1) peak (11.6 %) of the unlabelled diethylbenzamide. These values therefore correspond to 97.8 % ^{15}N incorporation in the product. The isotope contents in the other labelled compounds were calculated using the same procedure.

[^{15}N]-N-*Ethylbenzimidoyl chloride,* **3**. This compound was prepared according to the procedure described by Huisgen[4] and Ugi.[9] The (74:26) mixture of [^{15}N]-*N*-ethylbenzamide and [^{15}N]-*N,N*-diethylbenzamide (0.40 g) was stirred with freshly distilled thionyl chloride (15 ml) for 45 h at room temperature under an atmosphere of nitrogen. Evaporation of the excess of thionyl chloride under reduced pressure gave a pale yellow oil (0.48 g), which upon being cooled in an ice bath crystallized to a white crystalline material. IR (neat): 3061, 3031, 2977, 2936, 1644, 1611, 1578, 1489, 1448, 1420, 1381, 1309, 1217, 1139, 1094, 1030, 995, 955, 888, 867, 768, 706, 690 cm^{-1}.

[4-^{15}N]-*4-Ethyl-3,5-diphenyl-4*H-*1,2,4-triazole,* **1**, was prepared according to the procedure described by Huisgen and coworkers.[4] A mixture of [^{15}N]-*N*-ethylbenzimidoyl chloride and [^{15}N]-*N,N*-diethylbenzamide, (74:26), (0.48 g) was dissolved in 2.5 ml of dry pyridine and cooled in an ice bath, under an atmosphere of nitrogen. A solution of 5-phenyltetrazole (0.75 g, 5.60 × 10^{-3} mol) in dry pyridine (4 ml) was then added dropwise. The reaction mixture was stirred at 0 °C for 0.5 h, and then gradually heated to reflux over a period of 1 h, and refluxed for 3 h. Some gas evolution was observed. The reaction mixture was then cooled, treated with water (20 ml) and extracted with dichloromethane (2 × 20 ml). The combined organic phase was washed with 2 M NaOH (4 × 20 ml), 1 M HCl (5 × 20 ml), and water (20 ml), and finally dried over anhydrous magnesium sulfate. Evaporation of the solvent under reduced pressure yielded 0.44 g of a dark oil that was purified by multiple preparative TLC (5 × $CHCl_3$). Two fractions were isolated.

Fraction 1 (R_f 0.07–0.35), contained 0.19 g of crude [4-^{15}N]-4-ethyl-3,5-diphenyl-4*H*-1,2,4-triazole, which was recrystallized from toluene (0.5 ml) to yield 0.0713 g (14 %) of white crystals of 99.9 % (GLC) purity, m.p. 159–160 °C. The mass spectrum of the product exhibited peaks at *m/z*

249 (70.7%) and 250 (M^+, 100.0%). Unlabelled 4-ethyl-3,5-diphenyl-4*H*-1,2,4-triazole showed peaks at *m/z* 248 (69.5%), 249 (M^+, 100%) and 250 (18.2%). The ratio of unlabelled to labelled triazole was calculated from the 249/250 ratio. These values correspond to 98.5% ^{15}N incorporation in the product.

^1H NMR (100 MHz): δ 1.07 (dt, 3 H, $^3J_{N-H}$ = 3.2 Hz, J = 7.2 Hz, CH_3), 4.13 (q, 2 H, J = 7.5 Hz, CH_2), 7.30–7.80 (m, 10 H, Ph). ^{13}C NMR (25.0 MHz): 15.7 (CH_3), 39.8 (d, $^1J_{C-N}$ = 8.5 Hz, CH_2), 128.4, 128.9, 130.1, 155.2 (d, $^1J_{C-N}$ = 12.1 Hz, triazole) IR (KBr): 3029, 2968, 2937, 1480, 1472, 1445, 1403, 1079, 783, 778, 725, 720, 710, 704, 690, 583 cm^{-1}. MS (*m/z* (% rel. int.)]: 252 (2), 251 (17), 250 (100, M^+), 249 (71), 248 (5), 235 (2), 223 (2), 222 (8), 194 (2), 193 (2), 165 (2), 146 (2), 133 (8), 132 (3), 131 (2), 119 (3), 118 (27), 117 (3), 115 (2), 106 (4), 105 (48), 104 (40), 103 (8), 91 (6), 90 (6), 89 (43), 88 (2), 78 (4), 77 (33), 76 (7), 75 (2), 65 (2), 64 (3), 63 (17), 62 (4), 52 (3), 51 (13), 50 (5), 49 (2). Found M^+ 250.1238. Calc. for $C_{16}H_{15}\ ^{14}N_2{}^{15}N$: *M* 250.1236.

Fraction 2 (R_f 0.43–0.75), as an oil (ca. 0.20 g), was further purified by preparative TLC (5 × $CHCl_3$). Fraction, R_f 0.40–0.48, was identified as [1-^{15}N]-1-ethyl-5-phenyl-1*H*-1,2,3,4-tetrazole (0.0446 g, 82% GLC). Crystallization from 95% ethanol (0.2 ml), gave 0.0106 g of pure product as white crystals (93.3%, GLC) with m.p. 67–68 °C. The filtrate yielded a second crop which was recrystallized from 95% ethanol. The total yield of product was 0.0169 g (5% from [^{15}N]-ethylbenzamide). The mass spectrum of the product showed peaks at *m/z* 174 (6.3%) and 175 (M^+, 100%). Unlabelled 1-ethyl-5-phenyl-1*H*-1,2,3,4-tetrazole[7] showed peaks at 173 (4.9%), 174 (M^+, 100%) and 175 (11.4%). The ratio of unlabelled to labelled tetrazole was calculated from the 174/175 ratio. These values correspond to 98.5% ^{15}N incorporation of the product.

^1H NMR (100 MHz): δ 1.58 (dt, 3 H, $^3J_{N-H}$ = 2.9 Hz, J = 7.3 Hz, CH_3), 4.49 (dq, 2 H, $^2J_{N-H}$ = 1.2 Hz, J = 7.2 Hz, CH_2), 7.48–7.83 (m, 5 H, Ph). ^{13}C NMR (25.0 MHz): δ 15.2 (CH_3), 43.3 (d, $^1J_{C-N}$ = 9.8 Hz, CH_2), 126.2, 128.7, 129.3 and 131.2 (Ph), 154.0 (d, $^1J_{C-N}$ = 12.2 Hz, tetrazole). IR (KBr): 2997, 2966, 2952, 2930, 1530, 1467, 1457, 1384, 1369, 1352, 1287, 1078, 737, 695, 652 cm^{-1}. MS at 180 °C [*m/z* (% rel. int.)]: 177 (2), 176 (12), 175 (100, M^+), 174 (6), 149 (2), 133 (4), 132 (9), 131 (11), 120 (2), 119 (21), 118 (24), 117 (15), 115 (2), 106 (2), 105 (32), 104 (21), 103 (13), 92 (4), 91 (19), 90 (23), 89 (27), 78 (5), 77 (33), 76 (6), 75 (2), 65 (3), 64 (4), 63 (16), 62 (6), 61 (2), 58 (3), 57 (3), 55 (2), 52 (3), 51 (15), 50 (8), 44 (2), 43 (6), 42 (3), 41 (3). Found M^+ 175.0878. Calc. for $C_9H_{10}\ ^{14}N_3{}^{15}N$: *M* 175.0876.

Thermolysis of [4-^{15}N]-*4-ethyl-3,5-diphenyl-4*H-*1,2,4-triazole,* **1**. [4-^{15}N]-4-Ethyl-3,5-diphenyl-4*H*-1,2,4-triazole (0.0298 g, 1.19 × 10^{-4} mol) was placed in a sealed glass tube under reduced pressure (ca. 6 Pa), and heated in an oven at 332–336 °C for 30 min. After being cooled to room temperature, the reaction products were separated by preparative TLC.

Fraction 1 (R_f 0.42–0.62), as a colorless oil, contained 0.0252 g (84.6%) of [4-^{15}N]-1-ethyl-3,5-diphenyl-1*H*-1,2,4-triazole (98.3%, GLC). The mass spectrum of the product showed peaks at *m/z* 249 (8.0%) and 250 (M^+, 100%). Unlabelled 1-ethyl-3,5-diphenyl-1*H*-1,2,4-triazole showed peaks at 248 (3.7%), 249 (M^+, 100%) and 250 (18.7%). The ratio of unlabelled triazole to labelled triazole was calculated from the 249/250 ratio. These values correspond to 95% ^{15}N incorporated of the product.

^1H NMR (100 MHz): δ 1.54 (t, 3 H, J = 7.3 Hz, CH_3), 4.28 (q, 2 H, J = 7.3 Hz, CH_2), 7.37–7.86 (m, 8 H, Ph), 8.10–8.27 (m, 2 H, Ph). ^{13}C NMR (25.0 MHz): δ 15.5 (CH_3), 44.3 (CH_2), 126.3, 128.5, 128.8, 129.0, 130.0, 131.1 (d, $^2J_{C-N}$ = 7.3 Hz, Ph), 155.1 and 161.2 (triazole). IR (neat): 3067, 2979, 2938, 1475, 1463, 1442, 1352, 1126, 1071, 1027, 1019, 787, 772, 740, 728, 695, 575 cm^{-1}. MS [*m/z* (% rel. int.)]: 252 (2), 251 (18), 250 (100, M^+), 249 (8), 235 (3), 223 (2), 222 (13), 146 (10), 132 (6), 131 (62), 125 (2), 118 (6), 105 (8), 104 (45), 103 (6), 91 (3), 90 (6), 89 (22), 78 (2), 77 (18), 76 (4), 63 (9), 62 (3), 51 (6), 50 (3), 44 (3), 43 (2), 42 (6), 41 (2). Found M^+ 250.1238. Calc. for $C_{16}H_{15}\ ^{14}N_2{}^{15}N$: *M* 250.1236.

Fraction 2 (R_f 0.11–0.18) contained 0.0033 g of crude [4-^{15}N]-3,5-diphenyl-1*H*-1,2,4-triazole. It was dissolved in dichloromethane and extracted with 2 M NaOH (3 × ml), the combined aqous phases were acidified with conc. HCl and then extracted with dichloromethane (6 × 5 mol). After drying over anhydrous magnesium sulfate the solvent was evaporated under reduced pressure, to give 0.0011 g (4%) of the product as a white solid. The mass spectrum of the product exhibited peaks at *m/z* 221 (21.7%) and 222 (M^+, 100%). Unlabelled 3,5-diphenyl-1*H*-1,2,4-triazole showed peaks at 220 (0.5%), 221 (M^+, 100%) and 222 (16.4%). The ratio of unlabelled to labelled triazole was calculated from the 221/222 ratio. These values correspond to 79.8% ^{15}N incorporation of the product.

^1H NMR (100 MHz): δ 7.30–7.64 (m, 6 H, Ph), 7.94–8.22 (m, 4H, Ph). ^{13}C NMR (25.0 MHz): δ 126.5, 128.8 and 130.0 (Ph), 159.5 (triazole). IR (KBr): 3133, 3057, 3000, 2923, 2853, 1560, 1492, 1469, 1442, 1390, 1380, 1261, 1174, 1135, 1096, 1070, 1026, 1001, 989, 803, 788, 719, 710, 691, 686, 671, 529 cm^{-1}. MS [*m/z* (% rel. int.)]: 223 (16), 222 (100, M^+), 221 (22), 194 (2), 119 (8), 118 (89), 111 (6), 105 (5), 104 (5), 103 (9), 96 (2), 92 (3), 91 (21), 90 (6), 89 (19), 85 (3), 84 (2), 83 (3), 81 (2), 78 (3), 77 (22), 76 (5), 75 (2), 72 (4), 71 (3), 70 (2), 69 (4), 67 (2), 64 (5), 63 (12), 62 (3), 59 (8), 57 (8), 56 (2), 55 (5), 52 (2), 51 (9), 50 (4), 49 (3), 44 (7), 43 (6), 42 (2), 41 (6). Found M^+ 222.0926. Calc. for $C_{14}H_{11}\ ^{14}N_2{}^{15}N$: *M* 222.0923.

Fraction 3 (R_f 0.01–0.7) contained 0.0061 g unchanged [4-^{15}N]-4-ethyl-3,5-diphenyl-4*H*-1,2,4-triazole. The mass spectrum was identical with that of the starting material, corresponding to a 98.5% ^{15}N content.

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