

## Thermal Rearrangement of 4-Alkyl-3,5-diphenyl-1,2,4-4*H*-triazoles

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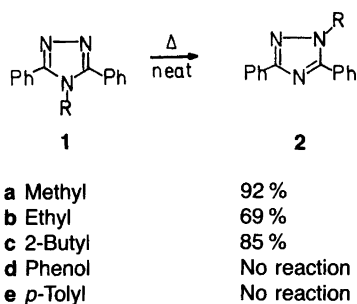
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A series of aryl substituted 1,2,4-triazoles has previously been studied by Gilchrist and co-workers.<sup>1</sup> These compounds undergo thermal transformations when subjected to vacuum flash thermolytic conditions at high temperatures, viz. 650–800 °C. Under these conditions several mechanistic pathways have been suggested, including pericyclic extrusion of nitrogen, scission of the 1,2-dinitrogen bond, and 1,2-aryl shift reactions.

In this communication we report a novel type of reaction for the fully substituted 1,2,4-4*H*-triazole system. Upon thermolysis of 4-alkyl-3,5-diphenyl-1,2,4-4*H*-triazoles, products are formed that can formally be derived from the starting material by a 1,3-alkyl shift reaction. Thus, heating the neat compounds, **1a–c**, to 350–400 °C yielded compounds **2a–c** as the exclusive products. Interestingly, thermolysis of the corresponding 4-aryl substituted triazoles, **2d–e**, under the same reaction conditions, gave no indication of any rearrangement products. The results are summarized in Scheme 1. The products **2a–c** were obtained in fair to good yields, and appear to be the exclusive products. Their identity was confirmed by comparison of their chromatographic and spectroscopic properties with those of authentic samples.

When **1a**, rather than being heated as the neat compound, was subjected to vacuum flash thermolysis conditions, a different reaction was observed. The required temperature in the experiments is approximately 700 °C at 10<sup>-3</sup> mmHg. In-



Scheme 1.

stead of yielding a single product, a complex mixture was obtained, together with 80 % recovered starting material. The reaction products are mostly intractable and extremely air sensitive. However, trace amounts of benzonitrile were identified, implying a possible dissociative mechanism.

It has thus been established that only 4-alkyl-substituted 1,2,4-4*H*-triazole systems appear to undergo the rearrangement reaction, and only in the condensed phase. To our knowledge, this type of alkyl shift reaction has not previously been reported.

### Experimental

*General.* NMR spectra were recorded on a Varian EM 390 NMR spectrometer. IR spectra were recorded on a Perkin-Elmer 257 grating

infrared spectrophotometer, and mass spectra on an AEI-MS 902 instrument. Vacuum flash thermolysis was performed by sublimation of the compounds at  $10^{-3}$  mmHg through a quartz tube (inner diam. 5 mm, length 20 cm) heated to 700°C. The reaction products were collected on a finger cooled with liquid nitrogen.

**4-Substituted 3,5-diphenyl-1,2,4-4H-triazoles (1a-5a)** were all prepared according to the procedure described by Huisgen and co-workers.<sup>2</sup> Compounds **1b** and **1c** are not described in the latter Ref.

**4-Ethyl-3,5-diphenyl-1,2,4-4H-triazole (1b)**, m.p. 130–132°C, exhibited the following spectroscopic properties. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ 1.07 (t, *J* = 7.3 Hz, 3H), 4.15 (q, *J* = 7.3 Hz, 2H), 7.5–7.75 (m, 10H). IR (KBr): 3060, 2980, 1488, 1480, 1450, 1418, 1390, 1355, 1253, 1080, 1030, 1004, 975, 805, 790, 784, 778, 736, 725, 718, 710, 695, 660 cm<sup>-1</sup>. MS [IP 70 eV; *m/e* (% rel. int.)]: 249 (100, M), 248 (72), 221 (8), 234 (3), 118 (15), 104 (53), 89 (21), 77 (16), 63 (9).

**4-(2-Butyl)-3,5-diphenyl-1,2,4-4H-triazole (1c)**, m.p. 175–176°C, exhibited the following spectroscopic properties. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ 0.65 (t, *J* = 7 Hz, 3H), 1.34 (d, *J* = 7 Hz, 3H), 4.10 (hex, *J* = 7 Hz, 1H), 7.4 (m, 10H). IR (KBr): 3060, 1990, 2970, 1530, 1465, 1450, 1415, 1390, 1330, 1240, 1180, 1160, 1120, 1100, 1080, 1030, 1000, 935, 770, 750, 735, 705 cm<sup>-1</sup>. MS [IP 70 eV; *m/e* (% rel. int.)]: 277 (71, M), 221 (100), 118 (54), 104 (20), 89 (27), 77 (14).

**Thermolysis of 1,2,4-4H-triazoles. General procedure.** Approximately 50 mg of the triazole is placed under nitrogen in a closed glass tube, which is then heated in an oven at 350°C for 10 min. After cooling, the contents are purified by chromatography and the products identified by comparison of their spectroscopic properties with those of authentic samples, prepared either by alkylation of the 2,4-diphenyl-1,2,4-triazole anion with the appropriate alkyl halide<sup>3</sup> or by the reaction between dibenzoylamine and alkylhydrazines.<sup>4</sup>

**3,5-Diphenyl-4-methyl-1,2,4-4H-triazole (1a)** yielded upon thermolysis 92% of 3,5-diphenyl-1-

methyl-1,2,4-1H-triazole (**1b**), m.p. 81–82°C. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ 3.92 (s, 3H), 7.39 (m, 6H), 7.63 (m, 2H), 8.02 (m, 2H). IR (KBr): 3060, 2920, 1605, 1520, 1475, 1440, 1395, 1350, 1270, 1225, 1132, 1070, 1029, 1018, 923, 790, 780, 758, 732, 700 cm<sup>-1</sup>. MS [IP 70 eV; *m/e* (% rel. int.)]: 235 (100, M), 221 (31), 193 (2), 118 (60), 91 (16), 89 (14), 77 (16).

**3,5-Diphenyl-4-ethyl-1,2,4-4H-triazole (2a)** gave 69% of 3,5-diphenyl-1-ethyl-1,2,4-1H-triazole (**2b**) m.p. 74–75°C. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ 1.50 (t, *J* = 7.5 Hz, 3H), 4.30 (q, *J* = 7.5 Hz, 2H), 7.4–7.8 (m, 8H), 8.1–8.2 (m, 2H). IR (KBr): 3075, 2980, 1480, 1445, 1415, 1382, 1300, 1285, 1200, 1135, 1075, 1030, 1020, 912, 795, 780, 735, 700 cm<sup>-1</sup>. MS [IP 70 eV; *m/e* (% rel. int.)]: 249 (100, M), 234 (10), 221 (14), 146 (10), 131 (68), 118 (6), 89 (27), 77 (23).

**4-(2-Butyl)-3,5-diphenyl-1,2,4-4H-triazole (3a)** yielded 85% of 1-(2-butyl)-3,5-diphenyl-1,2,4-1H-triazole (**3b**), m.p. 102–104°C. <sup>1</sup>H NMR (90 MHz, CDCl<sub>3</sub>): δ 0.74 (t, *J* = 7.3 Hz, 3H), 1.57 (d, *J* = 6.8 Hz, 3H), 1.95 (m, 1H), 2.24 (m, 1H), 4.29 (m, 1H), 7.3–7.5 (m, 8H), 8.1–8.3 (m, 2H). IR (KBr): 3060, 2960, 2930, 1472, 1440, 1400, 1380, 1370, 1350, 1340, 1300, 1280, 1190, 1175, 1155, 1130, 1112, 1073, 1030, 1010, 996, 980, 964, 932, 925, 852, 808, 790, 780, 740, 730, 708, 695 cm<sup>-1</sup>. MS [IP 70 eV; *m/e* (% rel. int.)]: 277 (74, M), 248 (34), 221 (32), 131 (13), 118 (63), 104 (66), 89 (100), 77 (66), 63 (32).

**3,4,5-Triphenyl-1,2,4-4H-triazole (4a)** on thermolysis yielding only starting material.

**3,5-Diphenyl-4(4-tolyl)-1,2,4-4H-triazole (5a)** on thermolysis yielded only starting material.

## References

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