

182. Heterocyclic Rearrangement of 4,5,6,7-Tetrahydro-6,6-dimethyl-benzo[*c*][1,2,5]oxadiazol-4-one (*Z*)-Arylhydrazones into Corresponding 2-Aryl-4,5,6,7-tetrahydro-2*H*-benzo[*d*][1,2,3]triazol-4-one Oximes

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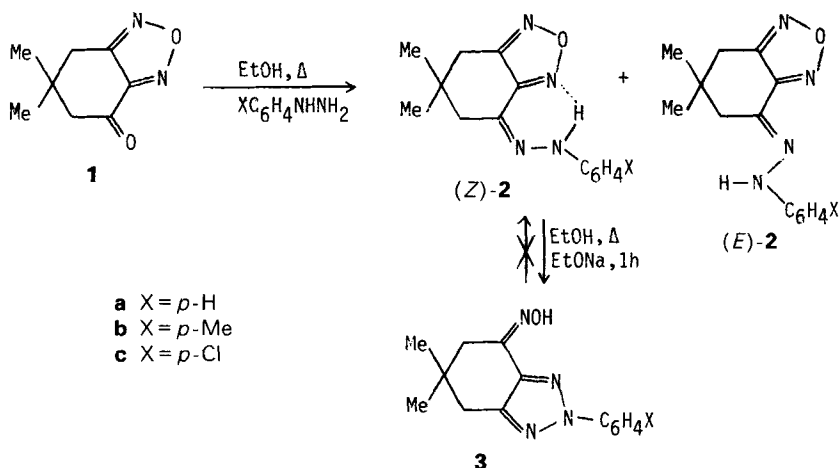
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The thermal base-catalysed and photochemical transformation (*Boulton-Katritzky* rearrangement) of the title tetrahydrobenzo[*c*][1,2,5]oxadiazoles to tetrahydro-2*H*-benzo[*d*][1,2,3]triazoles is studied. Attempts to induce analogous rearrangement in tetrahydro-2*H*-benzo[*d*][1,2,3]triazol-4-one arylhydrazones or oximes failed. Some CNDO/2 calculations are also carried out.

We have reported previously [1] [2] that attempts to induce thermal or photochemical mononuclear heterocyclic rearrangement in 2-aryl-4,5,6,7-tetrahydro-6,6-dimethyl-2*H*-benzo[*d*][1,2,3]triazol-4-one (*Z*)-arylhydrazones were unsuccessful. This prompted us to a more systematic study in order to examine whether this unsuccessful rearrangement [3] is either due to the thermodynamical stability of the triazole ring [4] [5] or to an unfavored geometry of the condensed ring system.

The present study is concerned with *Boulton-Katritzky*-type rearrangements [6] [7] of 4,5,6,7-tetrahydro-6,6-dimethylbenzo[*c*][1,2,5]oxadiazol-4-one (*Z*)-arylhydrazones (**2**) to the corresponding 2-aryl-4,5,6,7-tetrahydro-2*H*-benzo[*d*][1,2,3]triazol-4-one oximes (**3**). Comparatively few examples of ring transformations of 1,2,5-oxadiazoles to 1,2,3-

Scheme 1



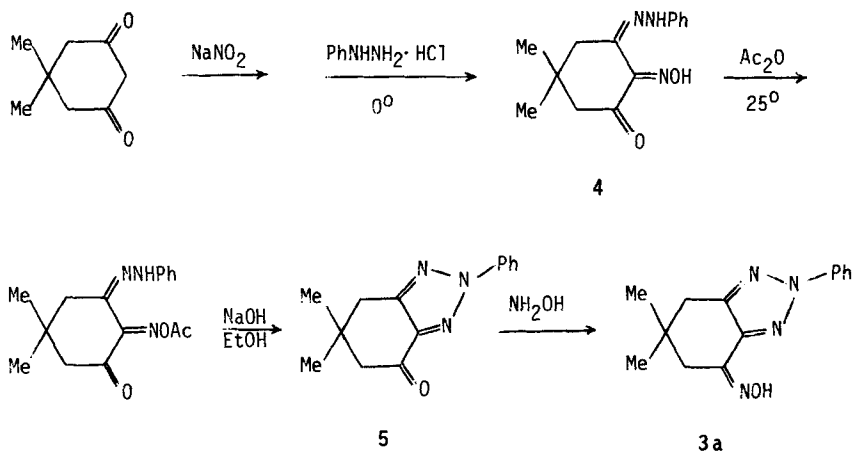
triazoles [5] [6] are known and it is postulated that 1,2,5-oxadiazoles are less reactive than 1,2,4-oxadiazoles and isoxazoles [7]. Furthermore, the condensed 1,2,5-oxadiazoles are less reactive than those of monocyclic ring systems [8].

The 1,2,5-oxadiazoles **2** were prepared from the furazan-4-one **1** [9] by refluxing in EtOH with the appropriate arylhydrazine [1] for 2 h (*Scheme 1*). The reaction afforded the (*Z*)- and (*E*)-isomers, which were separated in the case of **2a** by fractional crystallization from EtOH. In all other cases, only the (*Z*)-isomer could be isolated by fractional crystallization, whereas the (*E*)-isomer was obtained by prep. TLC. The (*E*)-oxadiazoles (*E*)-**2** isomerized to the corresponding (*Z*)-isomers either by heating at m.p. temperature or after a prolonged standing in solution. The characterization of the two isomers was based on data given by *Vivona et al.* [10] [11] and especially on the $^1\text{H-NMR}$ spectra where the NH proton of the (*Z*)-isomer resonates at *ca.* 10 ppm, whereas that of the (*E*)-isomer at *ca.* 7.70 ppm.

The thermal base-catalyzed rearrangement of the 1,2,5-oxadiazole ring system (*Z*)-**2** into 1,2,3-triazoles **3** was achieved in almost quantitative yield by refluxing a NaOEt/EtOH solution for 1 h. The (*E*)-isomers (*E*)-**2** also rearranged under the same conditions to the same triazoles **3** without any substantial difference in the reaction rates. However, a prior (*E*) $\rightarrow$ (*Z*) isomerization [11] should be involved. It is of interest to note that the rearrangement of **2a** to **3a** was reported [4] [5] to occur in very low yield (25%) after heating a DMSO solution at 120° for 24 h in the presence of K_2CO_3 .

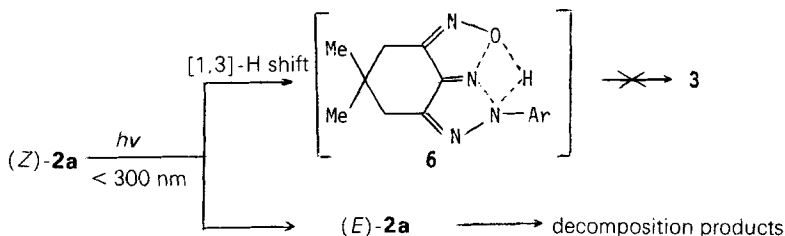
The structure of compounds **3** was based on their spectral data (IR, $^1\text{H-NMR}$, MS) and elemental analysis as well as on an independent synthesis (*Scheme 2*), from **4** via **5**, analogous to that described [12] for the synthesis of some dihydro-2-phenyl-2*H*-furotriazol-4-ones. It should be noticed that oximation of compound **5** gave a mixture **3** of (*E*)/(*Z*)-isomers which were separated by prep. TLC. In the $^1\text{H-NMR}$ (D_6)DMSO, the faster moving component showed a *s* for OH at 11.43 ppm, whereas the slower moving component, which was the only isomer obtained by *Boulton-Katritzky* rearrangement, showed a *s* at 11.32 ppm. Although the faster moving component could be assigned to the (*Z*)-isomer [13] [14], there is no conclusive evidence because of the small difference in the OH chemical shifts.

Scheme 2



Attempts to induce thermally the reverse rearrangement $3 \rightarrow 2$, either by heating the oxime **3a** at 220° for 30 min or by refluxing it in a NaOEt/EtOH solution, were unsuccessful, and in all cases **3a** remained unchanged.

The possibility of a photochemically induced *Boulton-Katritzky* rearrangement $2a \rightarrow 3a$ was also examined. This transformation should be a sigmatropic [1,3]-H shift (see **6**), photochemically allowed by the *supra-supra* process assuming that the uncatalyzed rearrangement is a pericyclic reaction [4]. The irradiation was carried out in an EtOH solution in a quartz tube for 6 h using a 125-W *Hanovia* medium-pressure mercury lamp. Instead of the ring transformation, an isomerization of the (*Z*)- to the (*E*)-isomer was observed. Further irradiation of the (*E*)-isomer led to decomposition products without any formation of **3**.



The conclusion from the above data is that the condensed 1,2,5-oxadiazoles very easily rearrange to 1,2,3-triazoles under appropriate experimental conditions, and the unsuccessful reverse rearrangement is probably due to the stability of the 1,2,3-triazole ring, in agreement with other analogous findings [3].

To examine the stability of the ring systems under question, we have carried out CNDO/2 calculations [15] on the model compounds **7** and **8** (Table). These compounds

Table. Calculated Energy Values (E_{total}) for 1,2,3-Triazoles **7** and 1,2,5-Oxadiazoles **8**

		$-E_{\text{total}}$ [au]		$\Delta E_{(7-8)}$ [kcal/mol]
X		7	8	
a	<i>p</i> -H	135.0735	135.0386	21.9
b	<i>p</i> -Cl	150.5005	150.4675	20.7
c	<i>p</i> -CH ₃	143.7714	143.7357	22.4

were chosen because of lack of any X-ray data on the condensed 1,2,5-oxadiazoles **2** and 1,2,3-triazoles **3**. The calculations were made for (*Z*)-isomers and for a coplanar conformation of the systems (Fig.) using for the geometries X-ray data of other simple 2*H*-1,2,3-triazole [16] and 1,2,5-oxadiazole [17] derivatives as well as data of other standard [18] bond angles and lengths.

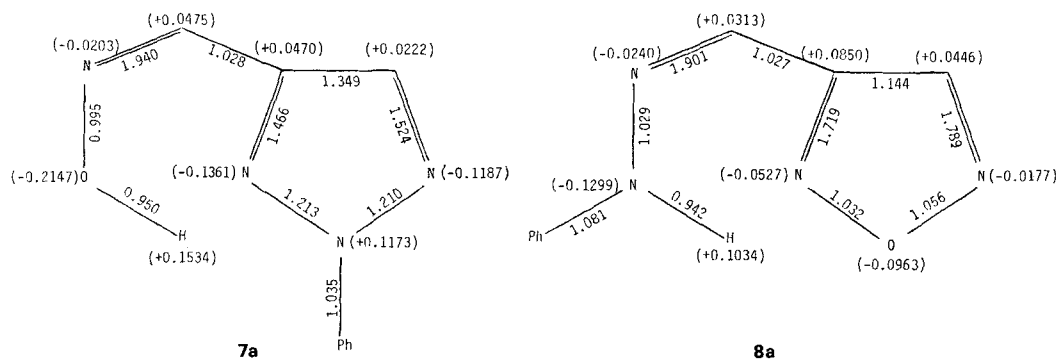


Fig. Electrons in bond (B_{AB} values) and atom net charges (in parentheses) for **7a** and **8a**. Very similar values are also obtained for the other triazole and oxadiazole derivatives.

From the energy values (E_{total}) given in the Table it is seen that the 1,2,3-triazole derivatives **7** are more stable than the isomeric 1,2,5-oxadiazoles **8** by ca. 20 kcal/mol. This energy difference also holds for other conformations of the phenyl group in **7** and **8**. Furthermore, the B_{AB} values (electrons in bond) [19] (Fig.) in N–N(Ar) bond in triazole systems are higher than the corresponding N–O bond values in 1,2,5-oxadiazoles. In addition, the net charge on the O-atom considered as H-receptor in oxadiazoles is negative, whereas the net charge on the N(2) atom in triazoles is positive. All these data could be considered as a good reasoning for the unsuccessful ring transformation of 2*H*-1,2,3-triazoles in several heterocyclic rearrangements.

Concerning the above discussed rearrangement, also the MS of compounds (*Z*)-**2** are informative: an interesting fragment [$M - 17$]⁺ in moderate relative intensity, attributable to a loss of an OH group, is observed. The composition of this ion is confirmed by HR-MS. This ion is explained assuming a *Boulton-Katritzky*-type rearrangement occurring under MS conditions. The same ion [$M - 17$]⁺ also appears in the MS of (*Z*)-**3**, but with higher relative intensity. On the other hand, the ion [$M - 17$]⁺ is absent in the spectra of tetrahydrobenzo[*c*][1,2,5]oxadiazol-4-ones and 2-aryl-tetrahydro-2*H*-benzo[*d*]-[1,2,3]triazol-4-one arylhydrazones.

We wish to thank Dr. N. Petasis, University of Pennsylvania, for high resolution mass measurements.

Experimental Part

General. M.p.: Kofler hot-stage apparatus; uncorrected. UV (λ_{max}): spectroscopic-grade EtOH; Shimadzu 210A spectrophotometer. IR: Perkin-Elmer-297 spectrometer [cm⁻¹]; Nujol. ¹H-NMR: CDCl₃ solns., if not otherwise stated; Varian-60A instrument; chemical shifts in δ with TMS as internal standard, coupling constants *J* in Hz. MS: Hitachi-Perkin-Elmer-RMU-6L single focusing spectrometer or VG-U-Mass-7070-H spectrometer (HR-MS) with ionization energy both at 70 eV, *m/z* (% of most important fragment). Elem. anal.: Perkin-Elmer-240B CHN analyzer.

4,5,6,7-Tetrahydro-6,6-dimethylbenzo[*c*][1,2,5]oxadiazol-4-one Phenylhydrazone (2a). For 2 h, 6,7-dihydro-6,6-dimethylbenzofuran-4(5*H*)-one (**1**; 415 mg, 2.5 mmol) [9] and phenylhydrazine (324 mg, 3 mmol) were refluxed in EtOH (20 ml). Upon cooling, (*E*)-**2a** (250 mg, 39%) was precipitated, which was recrystallized from EtOH. M.p. 220–222°. UV: 356. IR: 3280 (NH). ¹H-NMR: 1.13 (s, 2 Me); 2.41 (s, 2 H–C(5)); 2.78 (s, 2 H–C(7)); 7.20 (s, 5 arom. H); 7.75 (br. s, NH). MS: 256 (50, *M*⁺), 241 (8), 239 (10), 224 (8), 158 (8), 118 (26), 77 (100). Anal. calc. for C₁₄H₁₆N₄O (256.30): C 65.60, H 6.29, N 21.86; found: C 65.45, H 6.14, N 21.60.

The EtOH filtrate was concentrated (10 ml) and left at r.t. overnight whereupon (Z)-**2a** (225 mg, 35%) crystallized, m.p. 95°. UV: 367. IR: 3280 (NH). ¹H-NMR: 1.09 (s, 2 Me); 2.66 (s, 2 H–C(5)); 2.81 (s, 2 H–C(7)); 7.26 (s, 5 arom. H); 10.07 (br. s, NH). MS: 256 (10, *M*⁺), 241 (2), 239 (3), 224 (6), 158 (10), 118 (20), 77 (100). Anal. calc. for C₁₄H₁₆N₄O (256.30): C 65.60, H 6.29, N 21.86; found: C 65.71, H 6.19, N 22.08.

4,5,6,7-Tetrahydro-6,6-dimethylbenzo[c][1,2,5]oxadiazol-4-one (*p*-Tolyl)hydrazone (**2b**). As above by refluxing **1** (415 mg, 2.5 mmol) with (*p*-methylphenyl)hydrazine (366 mg, 3 mmol) in EtOH (20 ml) for 1 h. Upon cooling, (Z)-**2b** (170 mg) was precipitated, which was recrystallized from EtOH: M.p. 130–131°. IR: 3280 (NH). ¹H-NMR: 1.08 (s, 2 Me); 2.31 (s, *p*-Me); 2.64 (s, 2 H–C(5)); 2.78 (s, 2 H–C(7)); 7.13 (s, 4 arom. H); 10.05 (br. s, NH). MS: 270 (100, *M*⁺), 255 (11), 253 (10), 238 (7), 172 (13), 106 (66), 91 (83). Anal. calc. for C₁₅H₁₈N₄O (270.33): C 66.66, H 6.71, N 20.73; found: C 66.36, H 6.78, N 21.01.

The EtOH filtrate was concentrated (10 ml) and left at r.t. overnight whereupon crystals of (Z)-**2b** and (E)-**2b** (380 mg) were obtained. The two isomers were separated on prep. TLC (silica gel, petroleum ether (60–80°)/AcOEt 10:1) yielding 40% of (Z)-**2b** (faster moving) and 30% of (E)-**2b**. (E)-**2b**: m.p. 120–122°. IR: 3290 (NH). ¹H-NMR: 1.12 (s, 2 Me); 2.30 (s, *p*-Me); 2.43 (s, 2 H–C(5)); 2.77 (s, 2 H–C(7)); 7.14 (s, 4 arom. H); 7.78 (br. s, NH). MS: 270 (83, *M*⁺), 255 (11), 253 (10), 238 (9), 172 (14), 106 (100), 91 (89). Anal. calc. for C₁₅H₁₈N₄O (270.33): C 66.66, H 6.71, N 20.73; found: C 66.45, H 6.85, N 20.51.

4,5,6,7-Tetrahydro-6,6-dimethylbenzo[c][1,2,5]oxadiazol-4-one (*p*-Chlorophenyl)hydrazone (**2c**). As above by refluxing **1** (415 mg, 2.5 mmol) with (*p*-chlorophenyl)hydrazine (427 mg, 3 mmol) in EtOH (20 ml) for 1 h. Upon cooling, (Z)/(E)-**2c** (550 mg) was obtained. By recrystallization from EtOH (Z)-**2c** (270 mg) was isolated as a pure compound, m.p. 138–139°. IR: 3280 (NH). ¹H-NMR: 1.09 (s, 2 Me); 2.66 (s, 2 H–C(5)); 2.82 (s, 2 H–C(7)); 7.22 (s, 4 arom. H); 10.09 (br. s, NH). MS: 290/292 (81, *M*⁺), 275/277 (6), 273/275 (4), 258/260 (3), 192/194 (4), 126/128 (50), 111/113 (100). Anal. calc. for C₁₄H₁₅ClN₄O (290.75): C 57.83, H 5.20, N 19.29; found: C 58.01, H 5.31, N 19.38.

The remainder was separated on prep. TLC (silica gel, petroleum ether (60–80°)/AcOEt 10:1) to give (Z)-**2c** (35 mg, 42%; faster moving) and (E)-**2c** (210 mg, 29%). (E)-**2c**: m.p. 138–140°. IR: 3310 (NH). ¹H-NMR: 1.12 (s, 2 Me); 2.43 (s, 2 H–C(5)); 2.79 (s, 2 H–C(7)); 7.19 (s, 4 arom. H); 7.74 (br. s, NH). MS: 290/292 (100, *M*⁺), 275/277 (10), 273/275 (12), 258/260 (11), 192/194 (17), 127/129 (98), 111/113 (55). Anal. calc. for C₁₄H₁₅ClN₄O (290.75): C 57.83, H 5.20, N 19.29; found: C 58.02, H 5.36, N 19.08.

Heating the isomers (E)-**2** at m.p. temperature, partial isomerization to the corresponding (Z)-**2** was observed. The same isomerization was observed after a prolonged standing of an EtOH soln. of the (E)-**2**.

Rearrangement of (Z)-**2a** and (E)-**2a**. A soln. of (Z)-**2a** (150 mg) in EtOH (45 ml) containing NaOEt (from 45 mg of Na) was refluxed for 1 h. After removal of EtOH, H₂O was added to the residue to give 4,5,6,7-tetrahydro-6,6-dimethyl-2-phenyl-2H-benzo[d][1,2,3]triazol-4-one oxime (**3a**; 139 mg, 93%) which was recrystallized from EtOH containing a few drops of H₂O. M.p. 164–166°. UV: 301. IR: 3240 (NOH). ¹H-NMR: 1.13 (s, 2 Me); 2.55 (s, 2 H–C(5)); 2.78 (s, 2 H–C(7)); 7.23–7.56 (*m*, 3 arom. H); 7.92–8.27 (*m*, 2 arom. H); 9.85 (br. s, NOH). ¹H-NMR ((D₆)DMSO): 1.03 (s, 2 Me); 2.75 (s, CH₂); 7.25–7.70 (*m*, 3 arom. H); 7.84–8.14 (*m*, 2 arom. H); 11.32 (s, NOH); the second CH₂ is obscured by the solvent. MS: 256 (100, *M*⁺), 241 (37), 239 (15), 224 (29), 91 (47), 77 (72). MS (HR): 256.1331 (*M*⁺, C₁₄H₁₆N₄O, calc. 256.1323); 239.1264 [(*M* – OH)⁺, C₁₄H₁₅N₄, calc. 239.1294], 224.1177 [(*M* – HNOH)⁺, C₁₄H₁₄N₃, calc. 224.1185]. Anal. calc. for C₁₄H₁₆N₄O (256.30): C 65.60, H 6.29, N 21.86; found: C 65.84, H 6.36, N 22.14.

Compound (E)-**2a**, under identical conditions, gave **3a** again in almost quantitative yield.

Rearrangement of (Z)-**2b** and (E)-**2b**. As above to give 4,5,6,7-tetrahydro-6,6-dimethyl-2-(*p*-tolyl)-2H-benzo[d][1,2,3]triazol-4-one oxime (**3b**) in 93% yield. M.p. 170–172°. IR: 3240 (NOH). ¹H-NMR: 1.13 (s, 2 Me); 2.38 (s, *p*-Me); 2.52 (s, 2 H–C(5)); 2.75 (s, 2 H–C(7)); 7.31, 7.99 (*AA'**BB'*, *J* = 8.5, 4 arom. H); 9.38 (br. s, NOH). MS: 270 (100, *M*⁺), 255 (22), 253 (12), 238 (14), 105 (31), 91 (41). Anal. calc. for C₁₅H₁₈N₄O (270.33): C 66.66, H 6.71, N 20.73; found: C 66.78, H 6.78, N 21.81.

Compound (E)-**2b**, under identical conditions, gave **3b** in almost quantitative yield.

Rearrangement of (Z)-**2c** and (E)-**2c**. As above to give 2-(*p*-chlorophenyl)-4,5,6,7-tetrahydro-6,6-dimethyl-2H-benzo[d][1,2,3]triazol-4-one oxime (**3c**) in 91% yield. M.p. 157–159°. IR: 3230 (NOH). ¹H-NMR: 1.11 (s, 2 Me); 2.53 (s, 2 H–C(5)); 2.76 (s, 2 H–C(7)); 7.45, 8.05 (*AA'**BB'*, *J* = 8.5, 4 arom. H); 9.31 (br. s, NOH). MS: 290/292 (100, *M*⁺), 275/277 (28), 273/275 (13), 258/260 (21), 125/127 (42), 111/113 (45). Anal. calc. for C₁₄H₁₅ClN₄O (290.75): C 57.83, H 5.20, N 19.29; found: C 57.64, H 5.19, N 19.11.

Compound (E)-**2c**, under identical conditions, gave **3c** in almost quantitative yield.

Attempted Rearrangement of **3a**. A soln. of **3a** (150 mg) in EtOH (45 ml) containing NaOEt (from 45 mg of Na) was refluxed for 7 h. The starting material remained unchanged. The rearrangement of **3a** was also attempted by heating without any solvent at 220° for 30 min. Again the starting material remained unchanged.

Irradiation of (Z)-2a. A soln. of (Z)-2a (80 mg) in EtOH (10 ml) was irradiated in a quartz tube for 6 h using a 125-W Hanovia medium-pressure mercury lamp. The irradiation was followed by TLC (silica gel, AcOEt/petroleum ether (60–80°) 1:1) which showed isomerization to (E)-2a. After evaporation of the solvent and addition of a small quantity of Et₂O/petroleum ether (60–80°), (E)-2a (60 mg) was crystallized. M.p. 220–222°. On further irradiation (ca. 10 h), various decomposition products were formed.

2-Hydroximino-5,5-dimethyl-3-(phenylhydrazono)cyclohexanone (4). NaNO₂ (3.45 g, 50 mmol) was added portionwise to a stirred suspension of 5,5-dimethyl-1,3-cyclohexadienone (7 g, 50 mmol) in H₂O (30 ml). The brown suspension was stirred for 2 h at r.t., filtered to remove the unreacted cyclohexanedione (2.5 g), and the filtrate was added dropwise to a vigorously stirred soln. of phenylhydrazine hydrochloride (5.57 g) in H₂O (65 ml) at 0°. After the end of the addition, the orange 4 was filtered off and recrystallised from EtOH: orange plates (4.5 g, 44%), m.p. 204–206°. IR: 3260 (NOH), 3190 (NH), 1690 (CO). ¹H-NMR: 1.17 (s, 2Me); 2.59 (s, 2CH₂); 6.83–7.45 (m, 5 arom. H). MS: 259 (13, M⁺), 242 (26), 241 (21), 226 (5), 200 (4), 77 (100). Anal. calc. for C₁₄H₁₇N₃O₂ (259.30): C 64.84, H 6.61, N 16.21; found: C 65.01, H 6.71, N 16.36.

4,5,6,7-Tetrahydro-6,6-dimethyl-2-phenyl-2H-benzof[d][1,2,3]triazol-4-one (5). A suspension of 4 (518 mg, 2 mmol) in Ac₂O (2.5 ml) was stirred at r.t. for 4 h and then at 40° for 1 more h. The red soln. was poured into ice/H₂O (25 ml) and the acetoxyated product which was separated was collected and suspended in warm 1N NaOH (2.5 ml). The suspension was stirred for 5 min, then warm EtOH (5 ml) was added and the stirring was continued for another 5 min. Upon cooling, 5 (275 mg, 57%) was precipitated. Recrystallization from EtOH. M.p. 116–118°. IR: 1690 (CO). ¹H-NMR: 1.17 (s, 2Me); 2.57, 2.91 (2s, 2CH₂); 7.07–7.73 (m, 3 arom. H); 7.90–8.45 (m, 2 arom. H). MS: 241 (100, M⁺), 226 (14), 185 (47), 105 (17). Anal. calc. for C₁₄H₁₅N₃O (241.28): C 69.69, H 6.27, N 17.42; found: C 69.39, H 6.30, N 17.62.

4,5,6,7-Tetrahydro-6,6-dimethyl-2-phenyl-2H-benzof[d][1,2,3]triazol-4-one Oxime (3a). To a suspension of 5 (241 mg, 1 mmol) in a soln. of NH₂OH · HCl (174 mg, 2.5 mmol) and NaOAc · 3H₂O (164 mg) in H₂O (15 ml), EtOH was added until a clear soln. was formed. The soln. was refluxed for 3 h and then left at r.t. for a night. The product 3a (203 mg) was filtered off, and the 2 isomers were separated on prep. TLC (silica gel, petroleum ether (60–80°)/AcOEt 8:1). The faster moving component was the major isomer (136 mg, 53%), m.p. 193–195°. UV: 305. IR: 3200 (NOH). ¹H-NMR: 1.15 (s, 2Me); 2.78 (s, 2CH₂); 7.28–7.55 (m, 3 arom. H); 8.05–8.20 (m, 2 arom. H). ¹H-NMR ((D₆)DMSO): 1.04 (s, 2Me); 2.72 (s, CH₂); 7.26–7.77 (m, 3 arom. H); 7.83–8.18 (m, 2 arom. H); 11.43 (s, NOH); the second CH₂ is obscured by the solvent. MS: 256 (39, M⁺), 241 (19), 239 (12), 224 (23), 91 (100). Anal. calc. for C₁₄H₁₆N₄O (256.13): C 65.60, H 6.29, N 21.86; found: C 65.48, H 6.34, N 21.71.

The slower moving component was the minor isomer and was also obtained by the Boulton-Katritzky rearrangement of 2a (72 mg, 28%), m.p. 164–166°.

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