182. Heterocyclic Rearrangement of 4,5,6,7-Tetrahydro-6,6-dimethylbenzo[*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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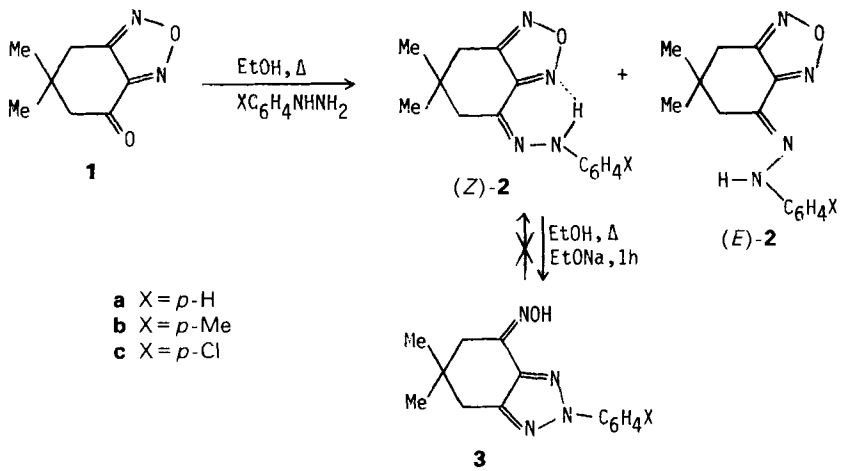
The thermal base-catalysed and photochemical transformation (*Boulton-Katritzky* rearrangement) of the title tetrahydrobenzo[*c*][1,2,5]oxadiazoles to tetrahydro-2*H*-benzo[*d*][1,2,3]triazoles is studied. Attempts to induce analogous rearrangement in tetrahydro-2*H*-benzo[*d*][1,2,3]triazol-4-one arylhydrazones 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



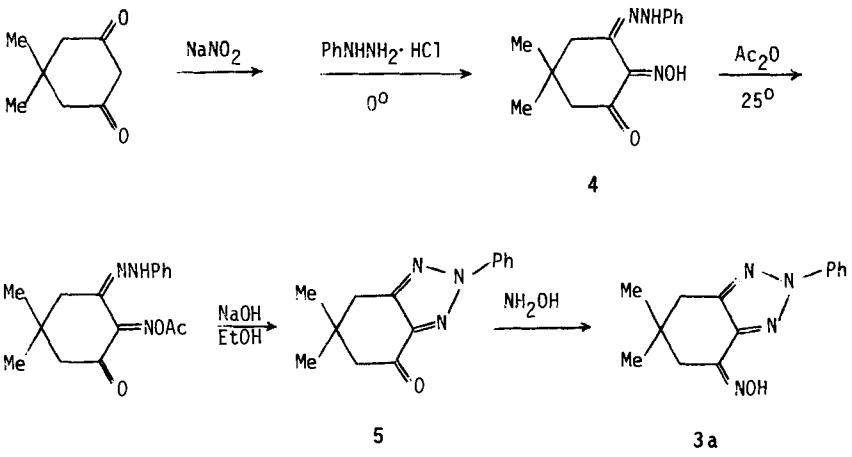
triazoles [5] [6] are known and it is postulated that 1,2,5-oxadiazoles are less reactive than 1,2,4-oxadiazoles and isoxazoles [7]. Furthermore, the condensed 1,2,5-oxadiazoles are less reactive than those of monocyclic ring systems [8].

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}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*)→(*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.

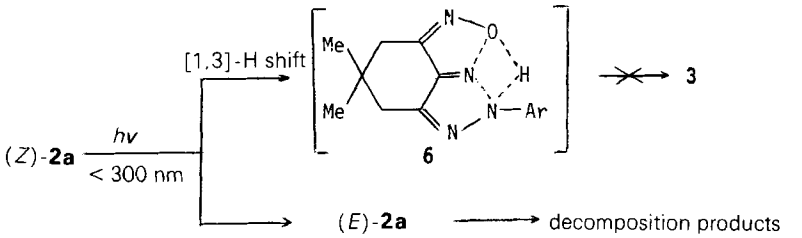
The structure of compounds **3** was based on their spectral data (IR, ^{1}H-NMR, MS) and elemental analysis as well as on an independent synthesis *(Scheme 2)*, from **4** *via* **5**, analogous to that described [12] for the synthesis of some dihydro-2-phenyl-2*H*-furotriazol-4-ones. It should be noticed that oximation of compound **5** gave a mixture **3** of (*E*)/(*Z*)-isomers which were separated by prep. TLC. In the ^{1}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**→**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.

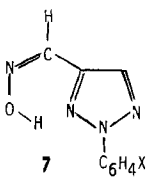
The possibility of a photochemically induced *Boulton-Katritzky* rearrangement **2a**→**3a** was also examined. This transformation should be a sigmatropic [1,3]-H shift (see **6**), photochemically allowed by the *supra-supra* process assuming that the uncatalyzed rearrangement is a pericyclic reaction [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**.



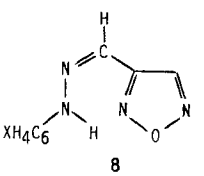
The conclusion from the above data is that the condensed 1,2,5-oxadiazoles very easily rearrange to 1,2,3-triazoles under appropriate experimental conditions, and the unsuccessful reverse rearrangement is probably due to the stability of the 1,2,3-triazole ring, in agreement with other analogous findings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



7



8

	X	$-E_{total}$ [au]		$\Delta E_{(7-8)}$ [kcal/mol]
		7	**8**	
a	*p*-H	135.0735	135.0386	21.9
b	*p*-Cl	150.5005	150.4675	20.7
c	*p*-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.

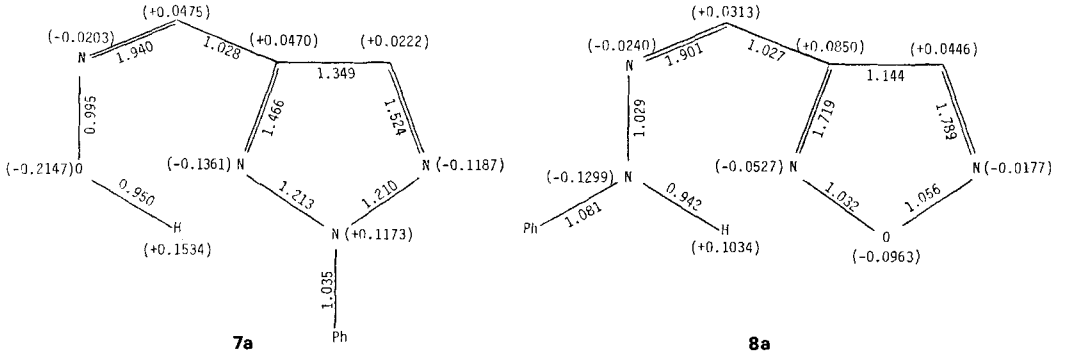


Fig. *Electrons in bond (B_{AB} values) and atom net charges (in parentheses) for* **7a** *and* **8a**. Very similar values are also obtained for the other triazole and oxadiazole derivatives.

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. ^{1}H-NMR: $CDCl_3$ 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-dimethylbenzofurazan-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). ^{1}H-NMR: 1.13 (*s*, 2Me); 2.41 (*s*, 2H–C(5)); 2.78 (*s*, 2H–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 $C_{14}H_{16}N_4O$ (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). ^{1}H-NMR: 1.09 (*s*, 2Me); 2.66 (*s*, 2H–C(5)); 2.81 (*s*, 2H–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 $C_{14}H_{16}N_4O$ (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). ^{1}H-NMR: 1.08 (*s*, 2Me); 2.31 (*s*, *p*-Me); 2.64 (*s*, 2H–C(5)); 2,78 (*s*, 2H–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 $C_{15}H_{18}N_4O$ (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). ^{1}H-NMR: 1.12 (*s*, 2Me); 2.30 (*s*, *p*-Me); 2.43 (*s*, 2H–C(5)); 2.77 (*s*, 2H–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 $C_{15}H_{18}N_4O$ (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). ^{1}H-NMR: 1.09 (*s*, 2Me); 2.66 (*s*, 2H–C(5)); 2.82 (*s*, 2H–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 $C_{14}H_{15}ClN_4O$ (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). ^{1}H-NMR: 1.12 (*s*, 2Me); 2.43 (*s*, 2H–C(5)); 2.79 (*s*, 2H–C(7)); 7.19 (*s*, 4 arom. H); 7.74 (br. *s*, NH). MS: 290/292 (100, M^+), 275/277 (20), 273/275 (12), 258/260 (11), 192/194 (17), 127/129 (98), 111/113 (55). Anal. calc. for $C_{14}H_{15}ClN_4O$ (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, H_2O was added to the residue to give *4,5,6,7-tetrahydro-6,6-dimethyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazol-4-one oxime* (**3a**; 139 mg, 93%) which was recrystallized from EtOH containing a few drops of H_2O. M.p. 164–166°. UV: 301. IR: 3240 (NOH). ^{1}H-NMR: 1.13 (*s*, 2Me); 2.55 (*s*, 2H–C(5)); 2.78 (*s*, 2H–C(7)); 7.23–7.56 (*m*, 3 arom. H); 7.92–8.27 (*m*, 2 arom. H); 9.85 (br. *s*, NOH). ^{1}H-NMR ((D_6)DMSO): 1.03 (*s*, 2Me); 2.75 (*s*, CH_2); 7.25–7.70 (*m*, 3 arom. H); 7.84–8.14 (*m*, 2 arom. H); 11.32 (*s*, NOH); the second CH_2 is obscured by the solvent. MS: 256 (100, M^+), 241 (37), 239 (15), 224 (29), 91 (47), 77 (72). MS (HR): 256.1331 (M^+, $C_{14}H_{16}N_4O$, calc. 256.1323); 239.1264 [$(M - OH)^+$, $C_{14}H_{15}N_4$, calc. 239.1294], 224.1177 [$(M - HNOH)^+$, $C_{14}H_{14}N_3$, calc. 224.1185]. Anal. calc. for $C_{14}H_{16}N_4O$ (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.

*Rearrangment of (*Z*)-***2b*** and (*E*)-***2b***.* As above to give *4,5,6,7-tetrahydro-6,6-dimethyl-2-(*p*-tolyl)-2*H*-benzo[d][1,2,3]triazol-4-one oxime* (**3b**) in 93% yield. M.p. 170–172°. IR: 3240 (NOH). ^{1}H-NMR: 1.13 (*s*, 2Me); 2.38 (*s*, *p*-Me); 2.52 (*s*, 2H–C(5)); 2.75 (*s*, 2H–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 $C_{15}H_{18}N_4O$ (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-2*H*-benzo[*d*][1,2,3]triazol-4-one oxime* (**3c**) in 91% yield. M.p. 157–159°. IR: 3230 (NOH). ^{1}H-NMR: 1.11 (*s*, 2Me); 2.53 (*s*, 2H–C(5)); 2.76 (*s*, 2H–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 $C_{14}H_{15}ClN_4O$ (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 Et_2O/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**). $NaNO_2$ (3.45 g, 50 mmol) was added portionwise to a stirred suspension of 5,5-dimethyl-1,3-cyclohexadienone (7 g, 50 mmol) in H_2O (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 H_2O (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). ^{1}H-NMR: 1.17 (*s*, 2Me); 2.59 (*s*, $2CH_2$); 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 $C_{14}H_{17}N_3O_2$ (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-2*H*-benzo[*d*][1,2,3]triazol-4-one* (**5**). A suspension of **4** (518 mg, 2 mmol) in Ac_2O (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/H_2O (25 ml) and the acetoxylated 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). ^{1}H-NMR: 1.17 (*s*, 2Me); 2.57, 2.91 (2*s*, $2CH_2$); 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 $C_{14}H_{15}N_3O$ (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-2*H*-benzo[*d*][1,2,3]triazol-4-one Oxime* (**3a**). To a suspension of **5** (241 mg, 1 mmol) in a soln. of $NH_2OH \cdot HCl$ (174 mg, 2.5 mmol) and $NaOAc \cdot 3H_2O$ (164 mg) in H_2O (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). ^{1}H-NMR: 1.15 (*s*, 2Me); 2.78 (*s*, $2CH_2$); 7.28–7.55 (*m*, 3 arom. H); 8.05–8.20 (*m*, 2 arom. H). ^{1}H-NMR ((D_6)DMSO): 1.04 (*s*, 2Me); 2.72 (*s*, CH_2); 7.26–7.77 (*m*, 3 arom. H); 7.83–8.18 (*m*, 2 arom. H); 11.43 (*s*, NOH); the second CH_2 is obscured by the solvent. MS: 256 (39, M^+), 241 (19), 239 (12), 224 (23), 91 (100). Anal. calc. for $C_{14}H_{16}N_4O$ (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°.

REFERENCES

[1] Taken in part from the Ph.D. Thesis of S. Lefkopoulou, University of Thessaloniki, 1984.
[2] S. Lefkopoulou, J. Stephanidou-Stephanatou, N.E. Alexandrou, *J. Chem. Res.*, (5), **1985**, 82.
[3] H. Balli, S. Gunzenhauser, *Helv. Chim. Acta* **1978**, *61*, 2628.
[4] M. Ruccia, N. Vivona, D. Spinelli, *Adv. Heterocycl. Chem.* **1981**, *29*, 141.
[5] A.J. Boulton, 'Lectures in Heterocyclic Chemistry', Hetero-Corporation, Provo, Utah, 1973.
[6] A.J. Boulton, A.R. Katritzky, A.M. Hamid, *J. Chem. Soc. (C)* **1967**, 2005.
[7] For a recent review on the subject, see G. L'abbé, *J. Heterocycl. Chem.* **1984**, *21*, 627.
[8] A.J. Boulton, F.J. Frank, M.R. Huckstep, *Gazz. Chim. Ital.* **1982**, *112*, 181.
[9] J. Ackrell, A.J. Boulton, *J. Chem. Soc., Perkin Trans. 1* **1973**, 351.
[10] N. Vivona, M. Ruccia, V. Frenna, *J. Heterocycl. Chem.* **1980**, *17*, 401.
[11] N. Vivona, G. Macaluso, V. Frenna, M. Ruccia, *J. Heterocycl. Chem.* **1983**, *20*, 931.
[12] P. Pollet, S. Gelin, *Synthesis* **1979**, 977.
[13] N. Vivona, G. Macaluso, V. Frenna, *J. Chem. Soc., Perkin Trans. 1* **1983**, 483.
[14] N. Vivona, V. Frenna, S. Buscemi, M. Ruccia, *J. Heterocycl. Chem.* **1985**, *22*, 97.
[15] CNINDO program (QCPE 141).
[16] A. Kalman, L. Parkanyi, J. Schawartz, *Acta Crystallogr., Sect. B* **1977**, *33*, 3097.
[17] D. Viterbo, A. Serafino, *Acta Crystallogr. Sect. B* **1978**, *34*, 3444.
[18] 'Interatomic Distances (Supplement)', Chemical Society, London, 1965.
[19] D.R. Armstrong, P.G. Perkins, J.P. Stewart, *J. Chem. Soc., Dalton Trans.* **1973**, 838.