BECKMANN REARRANGEMENT OF (*Z*)- AND (*E*)-OXIMES OF 2-ARYL-4,5,6,7-TETRAHYDRO-6,6-DIMETHYL-2*H*-BENZO[*d*][1,2,3]-TRIAZOL-4-ONES AND 4,5,6,7-TETRAHYDRO-6,6-DIMETHYLBENZO-[*c*][1,2,5]OXADIAZOL-4-ONES

Sophia MITKIDOU, Julia STEPHANIDOU-STEPHANATOU, Constantinos A. TSOLERIDIS and Nicholas E. ALEXANDROU

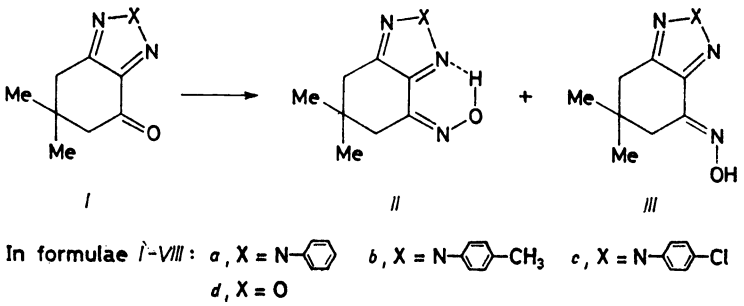
Laboratory of Organic Chemistry, University of Thessaloniki, Thessaloniki, Greece

Received February 2, 1989
Accepted May 3, 1989

Dedicated to Professor Otto Exner on the occasion of his 65th birthday.

The synthesis and geometry of (*Z*)- and (*E*)-oximes, *II* and *III*, derivatives of tetrahydro-2*H*-benzo[*d*][1,2,3]triazoles and tetrahydrobenzo[*c*][1,2,5]oxadiazoles, was investigated. The possibility of structural assignments of *II* and *III* by Beckmann rearrangement was examined. Some CNDO/2 calculations were also carried out on the oximes *II* and *III*.

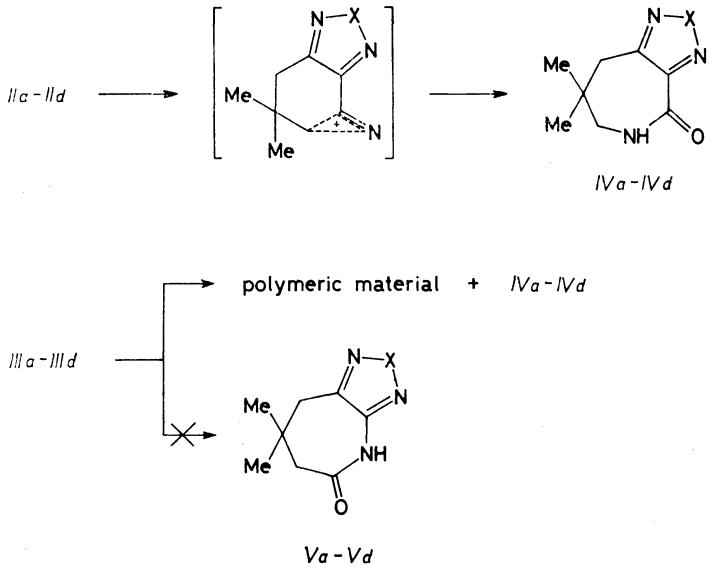
It has been recently described[1] that by Boulton–Katritzky rearrangement of 4-arylhydrazono-4,5,6,7-tetrahydro-6,6-dimethyl-benzo[*c*][1,2,5]oxadiazoles only one isomer 2-aryl-4,5,6,7-tetrahydro-4-hydroxyimino-6,6-dimethyl-2*H*-benzo[*d*][1,2,3]triazole is formed. On the other hand, oximation of 4,5,6,7-tetrahydro-6,6-dimethyl-4-oxo-2*H*-benzo[*d*]-[1,2,3]triazoles (*Ia*–*Ic*) and 6,7-dihydro-6,6-dimethyl-benzofurazan-4(5*H*)-one (*Id*) gives a mixture of (*Z*)- and (*E*)-oximes, *II* and *III* (Scheme 1). The two isomers were separated by fractional crystallization and show very similar R_F values on TLC. In all cases the slower moving isomer was identical with the oxime obtained by Boulton–Katritzky rearrangement of the correspoonding arylhydrazone.



SCHEME 1

Structural *Z* and *E* assignments based on the –OH chemical shift differences[2,3] in the ^{1}H NMR of the two isolated isomers could not be unambiguously established due to the small chemical shift difference of these protons (see Experimental). Furthermore, the results based on other physical properties like R_F values on TLC, of these isomers could also be inconclusive. Thus, in some oximes the faster moving component was assigned *Z* configuration[2], but in other[3] *E*.

Structural *Z*, *E* assignment of the oximes *II* and *III* could be established[3–5] by means of Beckman rearrangement and characterization of the amides formed (Scheme 2). The rearrangement was carried out with phosphorus pentachloride in dry ether

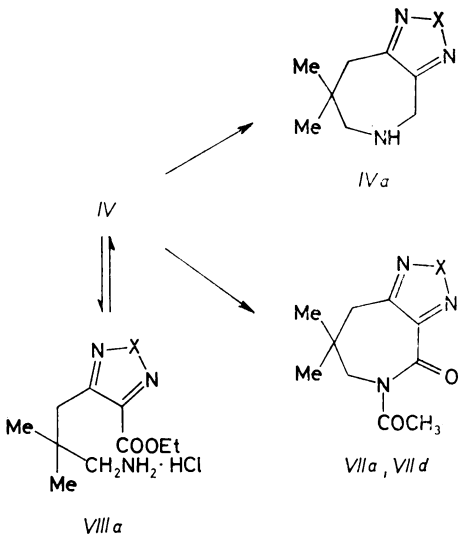


SCHEME 2

at room temperature to minimize possible isomerization[6,7]. In all cases from the slower moving oxime only the azepinone *IV* was isolated in moderate yield (25 – 60%) without isolation of any other product, whereas from the faster moving oxime mainly polymeric material and a small amount (c. 5%) of the azepinone *IV* was obtained. The azepinone *V* expected from Beckmann rearrangement of (*E*)-isomer was not isolated. From the above results the conclusion can be drawn, that the slower moving component, corresponds to (*Z*)-isomer also obtained by Boulton–Katritzky rearrangement[1] and this isomer by Beckmann rearrangement gives the expected azepinone *IV* (Table I). The fact that the azepinone *V* was not obtained by Beckmann rearrangement, from the faster moving isomer, considered as (*E*)-oxime *III*, could

be explained assuming that the bond under rearrangement is much stronger than the bond involved in (*Z*)-isomer as evidenced also by CNDO/2 calculations. The azepinone *IV* obtained in very low yield is attributed to a partial *E* to *Z* isomerization in starting oximes during the reaction process and no substantial difference was observed when the Beckmann rearrangement was carried out at 0°C.

The structure of azepinone *IV* was elucidated by spectral and chemical means (Table II). The protons of the methylene group adjacent to the NH were represented as a doublet centered at c. δ 3·12 (J = 6 Hz) collapsable into a singlet upon addition of deuterium oxide and this feature argues in favor of structure *IV* and against the isomeric azepinone *V*. Additional proof for the formation of *IV* was obtained by lithium aluminium hydride reduction of *IVa* in refluxing tetrahydrofuran, from which the azepinotriazole *VIa* was isolated in 90% yield. The structure of *VIa* is supported by the ^{1}H NMR spectrum, where three separate singlets at δ 3·95, 2·72, and 2·84 were observed for the C-4, C-6, and C-8 methylene protons, respectively. Acylation of the NH group of azepinones *IVa* and *IVd* was achieved with sodium hydride and acetyl chloride to produce the N-acetylated products *VIIa* and *VIId*, respectively. Finally, hydrolysis of the azepinone *IVa* by refluxing in ethanolic hydrochloric acid gave compound *VIIIa*. However, upon addition of a 25% NaOH solution, an instantaneous ring reclosure to the starting azepinone *IVa* was observed (Scheme 3).



SCHEME 3

The possibility of a Beckmann rearrangement through the *p*-toluenesulfonates *IX* and *X*, prepared by tosylation of oximes *IIa* and *IIIa* respectively, was also ex-

TABLE I

Physico-chemical data of azepinones *IVa*—*IVd*

Compound	M.p., °C	Formula M.w.	Calculated/Found		
			% C	% H	% N
IVa	196—198	$C_{14}H_{16}N_4O$	65·60	6·29	21·86
		256·3	65·51	6·23	21·96
IVb	240—241	$C_{15}H_{18}N_4O$	66·66	6·71	20·73
		270·3	66·65	6·83	20·70
IVc	174—176	$C_{14}H_{15}ClN_4O$	57·83	5·20	19·27
		290·8	58·01	5·22	18·99
IVd	151—152	$C_8H_{11}N_3O$	53·03	6·12	23·19
		181·2	52·88	6·12	23·31

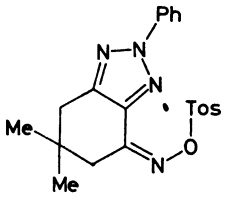
TABLE II

Spectral data of azepinones *IVa*—*IVd*

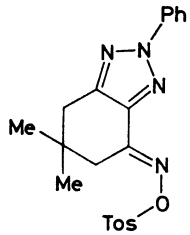
Compound	IR, cm^{-1}		^1H NMR ($CDCl_3$) δ, ppm					MS
	N–H	C=O	arom. H	6-CH_2[a]	8-CH_2	CMe_2	other H	*m/z* (% rel. intensity)
IVa	3 310 3 200	1 670	7·28—7·56 m 7·97—8·18 m	3·16 d[b]	2·93 s	1·14 s	—	256 (100, $M^{+\cdot}$), 241 (60), 228 (3), 213 (15)
IVb	3 310 3 190	1 665	7·35, 8·11 (AA'BB', J = 6 Hz)	3·21 d[b]	2·95 s	1·14 s	2·38 s (*p*-Me)	270 (100, $M^{+\cdot}$), 255 (53), 242 (5), 227 (13)
IVc	3 300 3 210	1 660	7·47, 8·12 (AA'BB', J = 6 Hz)	3·19 d[b]	2·93 s	1·15 s	—	292/290 (100, $M^{+\cdot}$), 287/285 (74), 264/262 (8), 249/247 (17)
IVd	3 260 3 200	1 670	—	3·08 d[b]	2·93 s	1·13 s	8·15 br (NH)	181 (54, $M^{+\cdot}$), 166 (16), 69 (100)

[a] J = 6 Hz. [b] Coinciding into a singlet by addition of D_2O.

amined[3,8], but after several attempts the starting sulfonates *IX* and *X* remained unchanged.

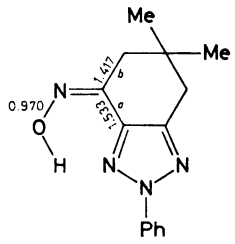


IX

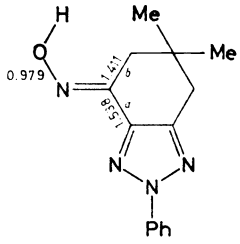


X

To examine the stability of oximes *II* and *III* and the strength of the bonds participating in Beckmann rearrangement, we have carried out CNDO/2 calculations (modified QCPE program 141) for the compounds *IIa*, *IId* and *IIIa*, *IIId*. It is noted that some simple (*Z*)- and (*E*)-oximes were recently examined by the MM force field method[9]. The geometry used for CNDO/2 calculations was based on



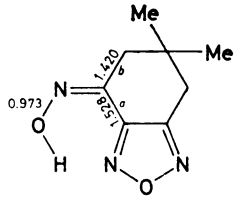
(*Z*)-*IIa*



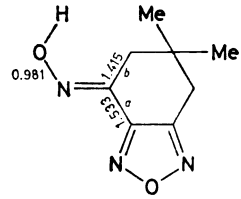
(*E*)-*IIIa*

$-E$(au) 177.0861

177.0626 $\Delta E_{[(Z)-(E)]}$ = 61.4 kJ/mol



(*Z*)-*IId*



(*E*)-*IIId*

$-E$(au) 137.3661

137.3423 $\Delta E_{[(Z)-(E)]}$ = 62.3 kJ/mol

The figure numbers refer to P_{AB} values

SCHEME 4

literature X-ray data for 2*H*-1,2,3-triazole[10] and 1,2,5-oxadiazole[11] rings as well as on standard values for the other bond lengths and angles[12], whereas the phenyl group in the compounds *IIa* and *IIIa* was taken in a coplanar conformation with respect to the triazole ring.

From the calculated energy values (E_{total}) given in Scheme 4 it can be seen that the (*Z*)-isomers *IIa*, *IId* are more stable than the corresponding (*E*)-isomers *IIIa*, *IIId* by c. 62 kJ/mol, most probably due to the possibility of intramolecular hydrogen bonding in the *Z* conformation. To evaluate the strength of the *a* or *b* bouns (Scheme 4) involved in Beckmann rearrangement we calculated the P_{AB} (bond overlap population) values for these bonds[13]. We have found that P_{AB} values for *a* bonds are always higher than the corresponding P_{AB} values for *b* bonds, in agreement with the experimental results, where Beckmann rearrangement of the weaker *b* bond is preferentialy observed. In addition, the P_{AB} value of the N—O bond is always slightly higher in the *E* conformation in agreement with the easier bond breaking during the rearrangement of the *Z* isomer. Similar results were also obtained for the strength of the bonds under consideration using some other parameters, like P_{AB} (electrons in bond) values[14]. All these data agree with the experimental results and could be considered as a good reasoning for the unsuccessful Beckmann rearrangement of the *E* isomer.

EXPERIMENTAL

Melting points are uncorrected and were obtained with a Kofler hot stage apparatus. IR spectra were measured on a Perkin–Elmer 297 spectrometer, wavenumbers are given in cm^{-1}. ^1H NMR spectra were recorded by a Varian Associates A-60A instrument with tetramethylsilane as internal standard, chemical shifts are given in ppm (δ-scale), coupling constants (J) in Hz. Mass spectra were measured with a Hitachi–Perkin–Elmer RMU-6L single focusing spectrometer and analyses were performed with a Perkin–Elmer Model 240B CHN Analyser. For thin layer chromatography (TLC) solvent system petroleum ether (60—80°C)–ethyl acetate 3 : 1 was used.

General Procedure for Preparation of 2-aryl-4,5,6,7-tetrahydro-6,6-dimethyl-2*H*-benzo[*d*]-[1,2,3]triazol-4-one Oximes (*IIa*—*IIc*) and (*IIIa*—*IIIc*), and 4,5,6,7-tetrahydro-6,6--dimethyl-benzo[*c*][1,2,5]oxadiazol-4-one Oximes (*IId*) and (*IIId*)

To a suspension of *I* (1 mmol) in a solution of $NH_2OH.HCl$ (174 mg, 2·5 mmol) and sodium acetate trihydrate (164 mg, 1·2 mmol) in water (15 ml), ethanol was added until a clear solution was formed. The mixture was refluxed for 3 h and then left at room temperature overnight, whereupon the faster moving component, the (*E*)-oxime *III* precipitated. By concentration of the filtrate the slower moving component, the (*Z*)-oxime *II* also precipitated. Oximes *III* were recrystallized from ethanol, and oximes *II* from ethanol containing a few drops of water.

4,5,6,7-Tetrahydro-6,6-dimethyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazol-4-one Oximes (*IIa*) and (*IIIa*)

(*Z*)-*Oxime* IIa. This isomer was obtained in 28% yield, m.p. 164—165°C (literature[1] m.p. 164—166°C). TLC: R_F 0·26.

(*E*)-*Oxime* IIIa. This isomer was obtained in 53% yield, m.p. 193–195°C (literature[1] m.p. 193–195°C). TLC: R_F 0·44.

4,5,6,7-Tetrahydro-6,6-dimethyl-2-(*p*-tolyl)-2*H*-benzo[*d*][1,2,3]triazol-4-one Oximes (*IIb*) and (*IIIb*)

(*Z*)-*Oxime* IIb. This isomer was obtained in 25% yield, m.p. 170–172°C (literature[1] m.p. 170–172°C). TLC: R_F 0·24.

(*E*)-*Oxime* IIIb. This isomer was obtained in 65% yield, m.p. 211–212°C. TLC: R_F 0·40. IR spectrum (Nujol): 3 170 (NOH). ^{1}H NMR spectrum ($CDCl_3$): 8·06 and 7·32, 4 H (AA'BB', J = 8·5, ArH); 2·77 s, 4 H (2 × CH_2); 2·41 s, 3 H (*p*-Me); 1·15 s, 6 H (2 × Me). ^{1}H NMR spectrum (CD_3SOCD_3): 11·40 s, 1 H (NOH); 7·93, 7·39, 4 H (AA'BB', J = 8·5, ArH); 2·72 s, (7-CH_2); 2·62 s, 2 H (5-CH_2); 2·37 s, 3 H (*p*-Me); 1·04 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 270 (100), 255 (24), 238 (11). For $C_{15}H_{18}N_4O$ (270·3) calculated: 66·65% C, 6·71% H, 20·72% N; found: 66·63% C, 6·64% H, 20·90% N.

2-(*p*-Chlorophenyl)-4,5,6,7-tetrahydro-6,6-dimethyl-2*H*-benzo-[*d*][1,2,3]triazol-4-one Oximes (*IIc*) and (*IIIc*)

(*Z*)-*Oxime* IIc. This isomer was obtained in 27% yield, m.p. 157–159°C (literature[1] m.p. 157–159°C). TLC: R_F 0·27.

(*E*)-*Oxime* IIIc. This isomer was obtained in 65% yield, m.p. 222–225°C, TLC: R_F 0·48. IR spectrum (Nujol): 3 140 (NOH). ^{1}H NMR spectrum ($CDCl_3$): 7·45, 8·06, 4 H (AA'BB', J = 9, ArH); 2·74 s, 4 H (2 × CH_2); 1·13 s, 6 H (2 × Me). ^{1}H NMR spectrum (CD_3SOCD_3): 11·43 s, 1 H (NOH); 8·03, 7·64, 4 H (AA'BB', J = 9, ArH); 2·73 s, 2 H (7-CH_2); 2·62 s, 2 H (5-CH_2); 1·06 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 292/290 (100), 277/275 (25), 260/258 (18). For $C_{14}H_{15}ClN_4O$ (290·8) calculated: 57·83% C, 5·20% H, 19·27% N; found: 57·88% C, 5·33% H, 19·22% N.

4,5,6,7-Tetrahydro-6,6-dimethyl-benzo[*c*][1,2,5]oxadiazol-4-one Oximes (*IId*) and (*IIId*)

(*Z*)-*Oxime* IId. This isomer was obtained in 23% yield, m.p. 155–157°C. TLC: R_F 0·20. IR spectrum (Nujol): 3 280 (NOH). ^{1}H NMR spectrum ($CDCl_3$): 9·88 br s, 1 H (NOH); 2·81 s, 2 H (7-CH_2); 2·58 s, 2 H (5-CH_2); 1·08 s, 6 H (2 × Me). ^{1}H NMR spectrum (CD_3SOCD_3): 12·33 s, 1 H (NOH); 2·83 s, 2 H (7-CH_2); 0·99 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 181 (100), 166 (21), 149 (22). For $C_8H_{11}N_3O_2$ (181·2) calculated: 53·03% C, 6·12% H, 23·19% N; found: 53·33% C, 6·10% H, 22·93% N.

(*E*)-*Oxime* IIId. This isomer was obtained in 64% yield, m.p. 205–207°C, TLC: R_F 0·39. IR spectrum (Nujol): 3 250 (NOH). ^{1}H NMR spectrum ($CDCl_3$): 8·15 br s, 1 H (NOH); 2·83 s, 2 H (7-CH_2); 2·73 s, 2 H (5-CH_2); 1·11 s, 6 H (2 × Me). ^{1}H NMR spectrum (CD_3SOCD_3): 12·27 s, 1 H (NOH); 2·87 s, 2 H (7-CH_2); 2·69 s, 2 H (5-CH_2); 1·02 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 181 (100), 166 (33), 149 (42). For $C_8H_{11}N_3O_2$ (181·2) calculated 53·03% C, 6·12% H, 23·19% N; found: 53·28% C, 6·18% H, 22·98% N.

General Procedure for Beckmann Rearrangement of Oximes *IIa*–*IId* and *IIIa*–*IIId*

A stirred solution of an oxime isomer in dry ether was cooled in an ice bath. Excess of phosphorus pentachloride (molar ratio oxime/PCl_5 1 : 2) was added to the cold solution, which was then allowed to warm to room temperature. The reaction mixture was stirred at room tempe-

rature for 2 h and was then poured onto a crushed ice. The product was extracted with dichloromethane, the extracts were dried, the solvent was evaporated and the remainder was chromatographed on a silica gel column using as eluent – light petroleum–ethyl acetate mixture (5 : 1) and with increasing the amount of ethyl acetate up to 1 : 2, to give in elution order the starting ketone *Ia*—*Id*, unreacted oxime, and the azepinone *IVa*—*IVd*. The analytical and spectral data of azepinones *IVa*—*IVd* are given in Table I and Table II.

Beckmann Rearrangement of Oxime *IIa*

As described above the following compounds were isolated: 4,5,6,7-tetrahydro-6,6-dimethyl-2--phenyl-2*H*-benzo[*d*][1,2,3]triazol-4-one (*Ia*) in 5% yield, m.p. 116—118°C (literature[1] m.p, 116—118°C), 2% of unreacted oxime *IIa*, and 5,6,7,8-tetrahydro-7,7-dimethyl-2-phenyl-1,2,3--triazol[4,5-*c*]azepin-4-one (*IVa*), 59% yield, m.p. 196—198°C.

Beckmann Rearrangement of Oxime *IIIa*

The following compounds were isolated: *Ia* in 6% yield, 8% of unreacted oxime *IIIa* and the azepinone *IVa* in 11% yield. A considerable amount of unidentified polymeric material was also formed.

Beckmann Rearrangement of Oxime *IIb*

The following compounds were isolated: 4,5,6,7-tetrahydro-6,6-dimethyl-2-(*p*-tolyl)-2*H*-benzo-[*d*][1,2,3]triazol-4-one (*Ib*), 4% yield, m.p. 153—155°C (literature[15] m.p. 153—155°C), 3% of unreacted oxime *IIb*, and 5,6,7,8-tetrahydro-7,7-dimethyl-2-(*p*-tolyl)-1,2,3-triazol[4,5-*c*]-azepin--4-one (*IVb*), 33% yield, m.p. 240—241°C.

Beckmann Rearrangement of Oxime *IIIb*

The following compounds were isolated: *Ib* in 4% yield, 7% of unreacted oxime *IIIb*, and the azepinone *IVb* in 8% yield. A considerable amount of unidentified polymeric material was also formed.

Beckmann Rearrangement of Oxime *IIc*

The following compounds were isolated: 2-(*p*-chlorophenyl)-4,5,6,7-tetrahydro-6,6-dimethyl-2*H*--benzo[*d*][1,2,3]triazol-4-one (*Ic*), 5% yield, m.p. 155—156°C (literature[15] m.p. 155—156°C), 2% of unreacted starting material and 2-(*p*-chlorophenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-1,2,3--triazol[4,5-*c*]azepin-4-one (*IVc*), 22% yield, m.p. 174—176°C.

Beckmann Rearrangement of Oxime *IIIc*

The following compounds were isolated: *Ic* in 3% yield, 4% unreacted *IIIc*, and *IVc* in 12% yield. A considerable amount of unidentified polymeric material was also formed.

Beckmann Rearrangement of Oxime *IId*

The following compounds were isolated: 6,7-dihydro-6,6-dimethyl-benzofurazan-4(5*H*)-one (*Id*), 5% yield, m.p. 66—69°C (literature[16] m.p. 66—68°C), 3% of unreacted starting material and 5,6,7,8-tetrahydro-7,7-dimethyl-1,2,5-oxadiazol[3,4-*c*]azepin-4-one (*IVd*), 29% yield, m.p. 151 to 152°C.

Beckmann Rearrangement of Oxime *IIId*

By addition of ethanol to the reaction mixture an unidentified, polymeric compound was isolated in 76% yield, m.p. 205–206°C (ethanol). The remainder was subjected to column chromatography as above to give: *Id* in 4% yield, 6% of unreacted *IIId*, and *IVd* in 5% yield.

4,6,7,8-Tetrahydro-7,7-dimethyl-2-phenyl-5*H*-1,2,3-triazol[4,5-*c*]azepine (*VIa*)

Azepinone *IVa* (100 mg) was added portionwise to a suspension of lithium aluminium hydride (100 mg) in tetrahydrofuran (20 ml). The mixture was stirred and heated under reflux for 3 h. Water was then added followed by addition of a few drops of 20% sodium hydroxide solution. After filtration the organic layer was concentrated, the residue was extracted with dichloromethane, the dichloromethane extract was dried with $MgSO_4$ and the solvent was evaporated. The residue crystallized after mixing with light petroleum; 86 mg (91%), m.p. 68–70°C (light petroleum). IR spectrum (Nujol): 3 260 (NH). ^{1}H NMR spectrum ($CDCl_3$): 8·13–7·90 m, 2 H (2 × ArH); 7·55–7·18 m, 3 H (3 × Ar-H); 3·95 s, 2 H (4-CH_2); 2·84 s, 2 H (8-CH_2); 2·72 s, 2 H (6-CH_2); 2·10 br s, 1 H (NH); 0·92 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 242 (100), 227 (63), 210 (100), 200 (15). For $C_{14}H_{18}N_4$ (242·3) calculated: 69·39% C, 7·49% H, 23·12% N; found: 69·50% C, 7·38% H, 23·16% N.

5-Acetyl-5,6,7,8-tetrahydro-7,7-dimethyl-2-phenyl-1,2,3-triazol-[4,5-*c*]azepin-4-one (*VIIa*)

Azepinone *IVa* (50 mg) was added to a suspension of sodium hydride (115 mg) in toluene (10 ml) at room temperature. The mixture was stirred for 3 h and then acetyl chloride (0·7 ml) dissolved in toluene (2 ml) was added dropwise. Stirring was continued for 24 h. Further amount of acetyl chloride (0·7 ml) and sodium hydride (150 mg) were added and the reaction mixture was heated at 80°C for 12 h. Filtration and evaporation of the solvent afforded an oil which crystallized by treatment with ether–light petroleum mixture; 45 mg (74%), m.p. 116–118°C (ether–light petroleum). IR spectrum (Nujol): 1 700 (CO). ^{1}H NMR spectrum ($CDCl_3$): 8·38 to 8·00 m, 2 H (2 × ArH); 7·70–7·30 m, 3 H (3 × ArH); 3·71 s, 2 H (6-CH_2); 2·85 s, 2 H (8-CH_2); 2·65 s, 3 H ($COCH_3$); 1·11 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 298 (62), 283 (3), 270 (13), 256 (82), 77 (100). For $C_{16}H_{18}N_4O_2$ (298·3) calculated: 64·41% C, 6·08% H, 18·78% N; found: 64·61% C, 6·01% H, 18·90% N.

5-Acetyl-5,6,7,8-tetrahydro-7,7-dimethyl-1,2,5-oxadiazol[3,4-*c*]azepin-4-one (*VIId*)

This compound was prepared as above by acetylation of azepinone *IVd* in 67% yield, m.p 85–86°C (ether–light petroleum). IR spectrum (Nujol): 1 710 (CO). ^{1}H NMR spectrum ($CDCl_3$): 3·55 s, 2 H (6-CH_2); 2·83 s, 2 H (8-CH_2); 2·60 s, 3 H ($COCH_3$); 1·04 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 223 (13), 205 (3), 195 (10), 181 (100). For $C_{10}H_{13}N_3O_3$ (223·2) calculated: 53·81% C, 5·87% H, 18·82% N; found: 54·09% C, 5·69% H, 18·74% N.

4-Carboethoxyl-2-phenyl-5-(2,2-dimethyl)propylamino-1,2,3-triazole Hydrochloride (*VIIIa*)

To 77 mg (0·3 mmol) of azepinone *IVa* ethanol (3·6 ml) and hydrochloric acid (0·5 ml) were added and the mixture was refluxed for 7 h. Then another hydrochloric acid (0·2 ml) were added and the reaction mixture was refluxed for 2 h until all the azepinone was hydrolyzed as indicated by TLC. The ethanol was evaporated under a reduced pressure and the product was filtered off; yield 95 mg (93%), m.p. 240–244°C. IR spectrum (Nujol): 3 120 (NH_2.HCl); 1 705 (CO). ^{1}H NMR spectrum ($CDCl_3$): 8·60 br s 2 H (NH_2); 8·31–7·97 m, 2 H (2 × ArH); 7·63–7·16 m,

3 H (3 × ArH); 4·42 q, 2 H (CH_2, $J = 7$); 3·16 s, 2 H (CH_2NH_2); 2·94 s, 2 H (CH_2); 1·39 t, 3 H (CH_3, $J = 7$); 1·15 s, 6 H (2 × Me). Mass spectrum *m/z*, (%): (M^+-HCl) 302 (33), 273 (100), 258 (33), 256 (35), 227 (81).

All affords to isolate the free amine failed, because by addition of water and a small amount of 25% NaOH solution an instantaneous ring reclosure to the starting azepinone *IVa* was observed.

(*Z*)-4,5,6,7-Tetrahydro-6,6-dimethyl-2-phenyl-2*H*-benzo[*d*][1,2,3]-triazol-4-one Oxime *p*-Toluenesulfonate (*IX*)

A stirred solution of oxime *IIa* (2 mmol) in acetone (40 ml) was cooled in an ice bath and treated with equimolar quantities of 8% NaOH solution and *p*-toluenesulfonyl chloride. The reaction mixture was stirred for 30 min, evaporated to dryness, and the remainder was chromatographed on a column of alumina (Brockmann activity I) using as eluant light petroleum whereupon the unreacted *p*-toluenesulfonyl chloride was removed. Elution with benzene gave the *p*-toluenesulfonate *IX* in 87% yield, m.p. 182—184°C (ethanol). IR spectrum (Nujol): 1 630 (C=N). ^{1}H NMR spectrum ($CDCl_3$): 8·22—8·02 m, 2 H (2 × ArH); 7·90 and 7·25 AA'BB' system, 4 H, (4 × ArH, $J = 9$); 7·60—7·16 m, 3 H (3 × ArH); 2·71 s, 2 H (7-CH_2); 2·48 s, 2 H, (5-CH_2); 2·39 s, 3 H (*p*-Me); 1·01 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 410 (3), 255 (6), 240 (22), 225 (20), 78 (100). For $C_{21}H_{22}N_4O_3S$ (410·5) calculated: 61·45% C, 5·40% H, 13·65% N; found: 61·45% C, 5·40% H, 13·67% N.

(*E*)-4,5,6,7-Tetrahydro-6,6-dimethyl-2-phenyl-2*H*-benzo[*d*][1,2,3]-triazol-4-one Oxime *p*-Toluenesulfonate (*X*)

The *p*-toluenesulfonate *X* was obtained from the oxime *IIIa* in a 76% yield by the procedure described above. M.p. 171—173°C (ethanol). ^{1}H NMR spectrum ($CDCl_3$): 8·20—8·87 m, 4 H (4 × ArH); 7·59—7·20 m, 5 H (5 × ArH); 2·71 s, 2 H (7-CH_2); 2·69 s, 2 H (5-CH_2); 2·39 s 3 H (*p*-Me); 1·03 s, 6 H (2 × Me). Mass spectrum, *m/z* (%): M^+ 410 (14), 255 (15), 240 (100). 225 (73). For $C_{21}H_{22}N_4O_3S$ (410·5) calculated: 61·45% C, 5·40% H, 13·65% N; found: 61·28% C, 5·32% H, 13·59% N.

Attempted Beckmann Rearrangements of (*Z*)- and (*E*)-4,5,6,7-tetrahydro--6,6-dimethyl-2-phenyl-2*H*-benzo[*d*][1,2,3]triazol-4-one Oxime *p*-Toluenesulfonates (*IX*) and (*X*)

The Beckmann rearrangment was attempted with both *p*-toluenesulfonate *IX* and *X* on an alumina column[3,2] and also with potassium carbonate solution[17], but in all cases the starting compounds were recovered unchanged.

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