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SYNTHESIS, CHEMICAL AND PHYSICAL PROPERTIES OF 2,3-DIAZA BICYCLO[3.2.0] HEPTADIENES

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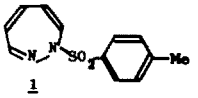
Abstract—A series of substituted (1H)-1,2-diazepines **2** undergo photoinduced isomerisation to the corresponding 2,3-diazabicyclo[3.2.0]-hepta-3,6-dienes **3** when irradiated in the near UV. 2-Ethoxycarbonyl derivatives **3** show restricted rotation around the N–CO bond of the urethane moiety which is analysed by variable temperature NMR technique, leading to the determination of the thermodynamic parameters. Thermally, bicyclic compounds **3** easily revert back to the parent diazepines **2** and open up to dienaminonitriles **15** and **16** under base catalysis.

Cycloheptatrienes, oxepines and [1-H]-azepines are known to undergo photoinduced electrocyclic isomerisation to the corresponding bicyclo[3.2.0] heptadienes,[1] 2-oxabicyclo [3.2.0] heptadienes[2] and 1-aza bicyclo [3.2.0] heptadienes[3] respectively. Arguing from analogy, we assumed the easily available 1,2-diazepines **2** to undergo similar photoisomerisation to the corresponding 2,3-diaza bicyclo [3.2.0] heptadienes **3** by a disrotatory electrocyclic ring closure.[4] Geometrical parameters, as computed from X-ray cristallographic data of 1-tosyl 1,2-diazepine **1**,[5] also were in favour of this working hypothesis since the butadiene moiety, although non planar, shows up as a slightly conjugated moiety. The remaining imine function in diazepine **1** is an isolated double bond and indeed behaves as such; as was shown by cycloaddition reactions with ketenes.[6]

Photoinduced isomerisation of 1,2-diazepines. All (1H)1,2-diazepines are orange to red coloured species in solution and present two absorption bands in the near UV spectrum (Table 1): a low energy absorption band shows up between λ_{max} 300 and 370 nm, which tails out in the visible region, whereas a high energy high intensity band appears between 215 and 230 nm.[7-9] It is the high-wavelengths absorption band which is responsible for the electrocyclic reaction (*vide infra*).

The first examples of photoinduced isomerisations of 1,2-diazepines **2** toward 2,3-diaza bicyclo[3.2.0] heptadienes **3** have been described simultaneously by Snieckus[10] and by our group.[11] In a typical run a 10^{-2} molar methylene chloride solution of 1-ethoxycarbonyl 1,2-diazepine **2b** is irradiated in a PYREX "immersion well" apparatus by means of a mercury high pressure lamp under N_2. Only the long-wavelength transition (λ_{max}: 362 nm) is induced under those conditions. After two days the starting material had disappeared and photodiazepine **3b** is isolated in 30% yield as a pale yellow oil [UV (EtOH) λ_{max} 249 nm (ϵ: 7100), 327 nm (ϵ: 290); IR ($CHCl_3$) ν (C=O) 1700 cm^{-1}, ν (C=N) 1580 cm^{-1}]. In the NMR spectrum the signals of the olefinic protons are assigned by double resonance spectroscopy and by analogy to the well established case of 2-oxa-bicyclo [3.2.0]hepta-3,6-diene **4** and of 2-aza 1-ethoxycarbonyl-bicyclo[3.2.0]-hepta-3,6-diene **5**, for which Paquette *et al.* have called attention to the anomalous vinyl and allyl couplings.[6,12] It can be seen, from the comparative coupling constants, indicated in Table 2, that within the cyclobutene ring the allylic couplings (J_{16} and J_{57}) are persistently higher than the vicinal couplings (J_{17} and J_{56}).[13] We shall deal later on with some additional NMR data which pertain to the restricted rotation of the urethane C–N bond.

Diazepines **2** having been obtained from the corres-



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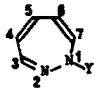


2

3

2a:	Y = $COCH_3$; Me-3; Me-7	**3a**:	Y = $COCH_3$; Me-1; Me-4
2b:	Y = CO_2Et	**3b**:	Y = CO_2Et
2c:	Y = CO_2iPr	**3c**:	Y = CO_2iPr
2d:	Y = CO_2Et; Me-4; Me-6	**3d**:	Y = CO_2Et; Me-5; Me-7
2e:	Y = CO_2Et; (CO_2Et)-4	**3e**:	Y = CO_2Et; (CO_2Et)-5
2f:	Y = CO_2Et; Me-5	**3f**:	Y = CO_2Et; Me-6
2g:	Y = CO_2Et; Me-4	**3g**:	Y = CO_2Et; Me-5

Table 1. UV absorption spectra of 1,2-diazepines measured in methanol solution

Diazepines	2a	2b	2c	2d	2e	2f	2g
λ_{max} (nm)	228	217	220	222	222	220	224
(ε_{max})	(8200)	(11200)	(11000)	(9000)	(9700)	(8000)	(8500)
λ_{max} (nm)	310	362	365	350	300	352	350
(ε_{max})	(640)	(280)	(270)	(330)	(900)	(270)	(260)

Table 2. NMR coupling constants (Hz) of cyclobutene protons in some heterobicyclo[3.2.0] - hepta - 3,6 - dienes (measured in $CDCl_3$ solutions)

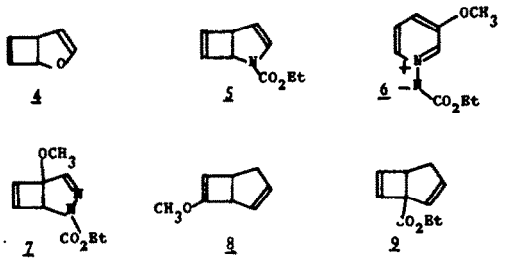
	J_{16}	J_{56}	J_{57}	J_{67}	J_{71}
4	2.8	0	1.5	2.8	0.0
5	2.6	0	0.4	2.6	0.0
3b	2.0	0.6	1.0	2.8	0.0

ponding 1-imino-pyridinium ylide by a photoinduced ring enlargement, it is of no surprise that one isolates in some instances the bicyclic isomers 3 along with their isomeric precursors 2, when the corresponding 1-iminopyridinium ylides are irradiated by UV light. In one case the 1,2-diazepines photoisomer could not even be isolated as was shown in a previous publication:[14] irradiation of 3-methoxy 1-ethoxycarbonyliminopyridinium ylide **6** leads directly to 2-ethoxycarbonyl 5-methoxy 2,3-diazabicyclo [3.2.0] hepta-3,6 diene **7** in 40% yield.

The irradiation time, which is required in order to consume all starting material, all other experimental conditions being kept constant, varies enormously as a function of the substituents (Experimental). No correlation could be drawn between site and nature of the substituent(s) on one hand, rate and regiospecificity of diazepine isomerisation on the other hand. We notice however that the electrondonating OMe group in the 4-position considerably accelerates the photoinduced electrocyclic process. One would of course assume electronic factors to play the dominant role in these reactions; Brember *et al.* postulated an interesting hypothesis for the substituent-dependent regiospecificity of cycloheptatriene ring transformations,[15] which is based on the polarisation of the two butadiene parts in the excited state. This hypothesis accounts well for the fact that 3-methoxycycloheptatriene leads to the 7-substituted bicyclic isomer **8**, whereas 3-ethoxycarbonyl-cycloheptatriene gives the 1-substituted isomer **9**. Unfortunately this hypothesis cannot be applied to our diaza-analogues, since electronwithdrawing - 4 - ethoxycarbonyl - diazepines as well as electrondonating 4-methoxydiazepines lead to the same type of bicyclic isomers, i.e. **3e** and **7** respectively, although the observed overall reaction rates are quite different (Table 3). All diazepines which have been investigated lead regiospecifically to 2,3-diazaisomers **3** and none to 1,2-diazaisomers. The chemical yields of bicyclic isomers are only moderate when compared to the excellent photoisomerisation (89% yield) obtained by Snieckus with triphenyldiazepines.[10] Furthermore 1-benzoyl and 1-tosyldiazepines, although slowly disappearing during UV irradiation, do not lead in our hands to any well defined photoproducts. Photoinduced decomposition of either the parent diazepines or the corresponding bicyclic photoisomers could account for these facts as well as for the only moderate yields of photoisomers 3.

Table 3. NMR spectrum of bicyclic compound **3g** at 37°C in acetone d-6; chemical shifts expressed in δ (ppm) and coupling constants in Hz

H-1	H-4	H-6	H-7	Me-5	CH_2	CH_3
4.45 d J_{16}=2.1	6.73 s	6.36 t J_{67}=2.6 J_{61}=2.1	5.90 d J_{76}=2.6	1.34 s	4.10 q J=7.0	1.22 t J=7.0



Restricted rotation around the N–CO *bonds in bicyclic compounds* 3. From the consideration of Dreiding models one would expect the roof-shaped heterobicyclic isomers **3** to have a rather rigid skeleton. Any restricted rotation of a side chain should therefore show up in the NMR spectra of compounds **3** when measured at variable temperature.

Such temperature dependent phenomena occur indeed with all heterocyclic photoisomers **3** and are probably due to restricted rotation around the N–CO bond of the built-in urethane functions. We shall restrict ourselves to the description of two cases, namely of bicyclic compounds **3g** and **3d**. The ^1H NMR spectrum of compound **3g**, measured in acetone d-6 at 37°C, is described in Table 3; when cooling the probe, the sharp singlet of H-4 broadens and splits into two singlets of different intensity below −30°; in a similar fashion the doublet of H-7 yields, below the coalescence temperature, two doublets at −70° (Fig. 1). One finds analogous results with the dimethyl-derivative **3d**: for example the sharp H-4 singlet measured at +37°C converts to two singlets at −50° (Fig. 1).

Lowering the temperature affects mostly protons H-4, H-1 and H-7 (or Me-7); coalescence occurs between −20° and −30° depending on the nature of the substituents. As stated above these phenomena are best explained by assuming the occurence of an equilibrium between type **A** and type **B** rotamers whose absorption bands can be resolved at −40° but not at room temperature on the NMR time scale. Intensities of the NMR absorption bands being not equivalent, the concentrations of the two rotamers are not equal either.

The reaction rate k_c of rotamer interconversion, at the coalescence temperature T_c,[16,17] permits to compute the free activation enthalpy ΔG_c^* from Eyring's Eqn.[18] From Table 4 it can be seen that ΔG_c^* values are similar for all diazabicyclic compounds **3**. The slightly higher potential barrier observed for the dimethyl derivative **3d**, as

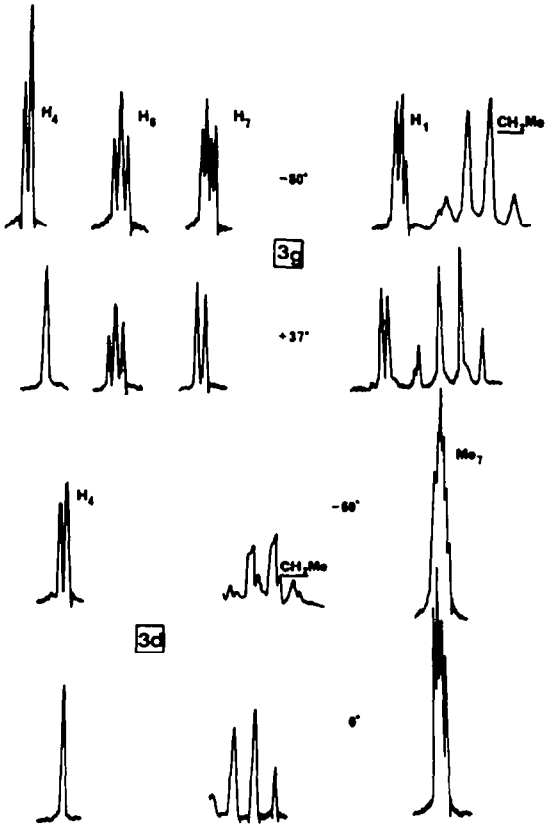


Fig. 1. Variable temperature NMR measurements of bicyclic compounds **3g** and **3d**.

Table 4. Spectral parameters and ΔG_c^* values for rotamers of some bicyclic compounds 3

	$T_c \pm 3°K$	$\Delta\nu$ AB Hz	J_{45} Hz	kc s^{-1}	$\Delta G_c^* \pm 0.3$ Kcal/mole
3b	248	1.5	1.5	8.82	13.3
3c	248	2.8	1.5	10.26	13.3
3g	248	1.9	-	4.22	13.7
3d	253	2.8	-	6.22	13.8
3e	238	1.4	-	3.11	13.3

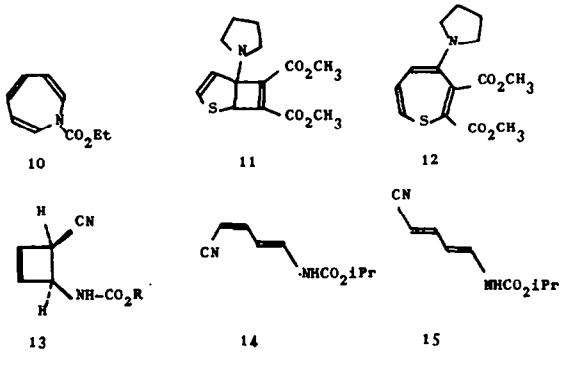
compared to **3b**, is probably due to some steric interactions. The ΔG_c^* value, for example of compound **3b** ($\Delta G_c^* = 13{\cdot}3$ kcal/mole) is similar to the one which has been obtained by Günther and Wenzl[19] for the restricted rotation observed for the iron tricarbonyl complex of 1-ethoxycarbonylazepine ($\Delta G_c^* = 13{\cdot}1$ kcal/mole). Anderson and Lehn found similar values for diurethanes.[20] Compared to amides, to formamides ($\Delta G_c^* = 19$–22 kcal/mole) and to simple carbamates ($\Delta G_c^* = 14$–16 kcal/mole), 2-ethoxycarbonyl bicyclic compounds 3 show slightly smaller potential barriers.

From the shape of the NMR spectra, observed at low temperature for compound **3d**, one may compute thermodynamic parameters for the kinetics of rotamer interconversion. We determined the exchange rate for this compound where one is dealing with two sites which are neither coupled nor equally populated. The expression $v = f(\omega)$,[22,23] obtained from Bloch's equations,[21] permits to compute and to draw the shape of the absorption bands. The computer traces out the curves $v = f(\omega)$, given different values of τi. By comparison, between the calculated and the at various temperatures observed spectra, one obtains the rate constant k, which permits, with the aid of Eyring's and Arrhenius's equation,[18] to attain the activation parameters pertaining to the restricted rotation around the N–CO bond. The graph log $k/T = f(1/T)$ leads to the enthalpy [$\Delta H^* = 15{\cdot}3 \pm 2{\cdot}5$ kcal/mole] and to the entropy of activation [$\Delta S^* = 5 \pm 7$ u.e.], whereas the graph ln $k = f$ (1/T) gives the activation energy ($E_a = 16{\cdot}9 \pm 2$ kcal/mole and ln $A = 35 \pm 4$].

Thermal cycloreversion of 2-alkoxycarbonyl-2,3-diazabicyclo [3.2.0] *heptadienes* **3** *to diazepines* **2**. Bicyclo [3.2.0]-6-heptenes and bicyclo[3.2.0]-2,6-heptadienes are known to undergo thermally induced cycloreversion to 1,3-cycloheptadienes and to cycloheptatrienes respectively.[24] These electrocyclic reactions occur at rather high temperatures (around 300°), a fact which is explained best by assuming that the orbital symmetry selection rules must be violated, since a concerted process for the opening of a cyclobutene should follow a conrotatory mode and lead to a cyclic cis-trans diene.[25]

It has been observed that the presence of an intracyclic heteroatom, attached to a bridgehead C atom in bicyclo [3.2.0]-2,6 heptadienes, greatly facilitates the thermal cyclo-reversion process: the bicyclic aza-compound **5** reverts back to the azepine **10** at 125°;[3] the thia-analogue **11**, which in addition to the S atom bears an exocyclic N atom attached to a bridgehead C atom, cannot even be isolated at room temperature and isomerises at −30° to thiepine **12**.[26]

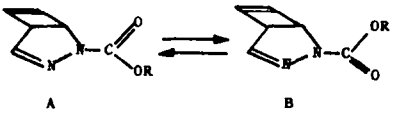
Whatever the precise reason for such low activation energy cycloreversions may be, and quite obviously such processes cannot be concerted ones, we observe similar behaviour with the 2-alkoxycarbonyl 2,3-diaza-bicyclo[3.2.0] hepta-3,6-dienes **3**. For example compounds **3b** and **3c** revert back to diazepine **2b** at 120° and to diazepine **2c** at 170° respectively, when heated in diphenylether.



Base induced rearrangement of 2-alkoxycarbonyl 2,3-diaza bicyclo[3.2.0] *heptadienes* **3** *toward 1-cyano-4-carbamidobutadienes*. Since 1,2-diazepines, which bear slightly acidic H atoms at the C-3 position, open up and lead to 1-cyano 4-carbamido butadienes when treated with a base,[11] it was believed that the pyrazoline moiety of bicyclic compounds **3** would undergo a similar base catalysed ring cleavage and give 3,4-disubstituted erythro cyclobutenes **13**.

Treatment at 6° of bicyclic compound **3c** with sodium isopropylate in isopropanol leads specifically to the known nitrile isomer **14** having Z–E configuration;[11] no substituted cyclobutene could be isolated. Formation of the butadiene derivative **14** is best explained by assuming,

first a base induced cleavage of the pyrazoline ring leading to cyclobutene **13** (R = i-Pr), followed by a fast conrotatory ring opening. The same base catalysed reaction, when performed at room temperature, gives a mixture of the Z–E butadiene **14** and its Z–Z isomer **15**.[11] In a third experiment isomer **14** is treated with base at room temperature; a mixture of both isomers **14** and **15** is obtained, a fact which demonstrates that the Z–E isomer is formed in the first step. In addition some 2-aminopyridine forms, which is best explained by assuming base catalysed ring closure of the cis-cis dienaminonitrile isomer, followed by saponification of the urethane moiety.



A B

EXPERIMENTAL

Microanalyses were performed by the Service Central de Microanalyse du CNRS at Lyon and Strasbourg; m'ps were measured on a LEITZ apparatus and are uncorrected. IR and UV spectra were determined with BECKMAN IR-20-A and DB spectrophotometers respectively. ^{1}H NMR spectra were obtained with Varian A-60-A, T-60 and HA-100 spectrometers in deuterated solvents using TMS as an internal standard (*s*, singlet; *d*, doublet; *t*, triplet; *q*, quadruplet; *m*, multiplet). Mass spectroscopic determinations were performed with an LKB-9000-S apparatus. Column, thin and thick layer chromatographies were carried out with silicic acid from Merck (Darmstadt). Solvents are reagent grade and were distilled before use. Photochemical reactions were conducted by a Pyrex vessel and cooled internally to 10–20° by a doublewalled Pyrex finger.

Photoinduced isomerisation of 1,2-*diazepines* **2** *to* 2,3-*diazabicyclo* [3.2.0]-4,6-*heptadienes* **3**

Standard procedure. A given amount (mg) of **2** is dissolved in 200 ml methylene chloride such as to obtain roughly a 10^{-2} molar soln. UV irradiation of such a soln is performed under N_2 by means of a mercury high pressure lamp (Philips HPK 125W) through PYREX glass until all starting material disappeared. The reaction is followed by UV spectroscopy and by TLC. After evaporation of methylene chloride *in vacuo* the remaining yellow oil is chromatographed over silicic acid with a 1/1 v/v cyclohexane/ethyl acetate mixture. The resulting bicyclic photoisomer **3** is further purified through distillation under reduced pressure.

(1) 2 - Acetyl - 1,4 - dimethyl - 2,3 - diazabicyclo[3.2.0] hepta - 3,6 - diene **3a**. Compound **2a** (500 mg) was irradiated according to the standard procedure, the Philips lamp being replaced by a Hg high pressure Hanovia 450W lamp. Bicyclic isomer **3a** was obtained in 54% yield after 40 hr as a yellow oil: IR ($CHCl_3$) 1655 cm^{-1} (C=O), 1645 cm^{-1} (C=N) and 1615 cm^{-1} (C=C); UV (EtOH) λ_{max} 252 nm (ϵ 8000) and 300 nm (ϵ 130); NMR ($CDCl_3$) δ 6·33 (q, 1, J = 2·9, 0·7 Hz, H_7), δ 6·25 (q, 1, J = 2·9, 0·6 Hz, H_6), δ 3·45 (m, 1, J = 0·7, 0·7 and 0·6 Hz, H_5), δ 1·98 (d, 3, J = 0·7 Hz, Me_4) and δ 1·79 (s, 3, Me_1); MS *m/e* 164 (M^+). (Found: C, 65·5; H, 7·6; N, 16·9; Calcd. for $C_9H_{12}ON_2$: C, 65·83; H, 7·37; N, 17·06%).

(2) 2 - *Ethoxycarbonyl* - 2,3 - *diazabicyclo*[3.2.0] *hepta* - 3,6 - *diene* **3b**. Compound **2b** (332 mg) was irradiated according to the standard procedure. Bicyclic isomer **3b** was obtained in 30% yield after 55 hr as a pale yellow oil: IR ($CHCl_3$) 1700 cm^{-1} (C=O) and 1580 cm^{-1} (C=N); UV (EtOH) λ_{max} 249 nm (ϵ 7100) and 327 nm (ϵ 300); NMR ($CDCl_3$) δ 6·87 (d, 1, J = 1·5 Hz, H_4), δ 6·3 (m, 1, J = 2·8, 2·0, 0·6 Hz, H_6), δ 6·03 (q, 1, J = 2·8, 1·0 Hz, H_7) δ 5·0 (q, 1, J = 4·2; 2·0, H_1), δ 4·08 (m, 1, J = 4·2, 1·5, 1·0, 0·6 Hz, H_5); MS *m/e* 166 (M^+). Found: C, 57·5; H, 6·2; N, 16·9. Calcd. for $C_8H_{10}O_2N_2$; C, 57·82; H, 6·07; N, 16·86%).

(3) 2 - *Isopropoxycarbonyl* - 2,3 - *diazabicyclo* [3.2.0] *hepta* - 3,6 - *diene* **3c**. The synthesis of bicyclic isomer **3c** has already been described.[11]

(4) 2 - *Ethoxycarbonyl* - 5,7 - *dimethyl* - 2,3 - *diazabicyclo* [3.2.0] 3,6 - *heptadiene* **3d**. Compound **2d** (388 mg) was irradiated according to the standard procedure. Bicyclic isomer **3d** was obtained in 55% yield after 8 hr as a pale yellow oil: IR ($CHCl_3$) 1700 cm^{-1} (C=O), 1635 cm^{-1} (C=N) and 1585 cm^{-1} (C=C; UV (EtOH) λ_{max} 250 nm (ϵ: 5500); NMR (acetone-d-6) δ 6·71 (s, 1, H_4), δ 6·0 (m, 1, J = 2·3 and 1·7 Hz, H_6), δ 4·32 (m, 1, J = 2·3 and 0·7 Hz, H_1), δ 1·67 (q, 3, J = 0·7 Hz, Me_7) and δ 1·30 (s, 3, Me_5); MS *m/e* 194 (M^+). (Found: C, 61·8; H, 7·3; N, 14·4. Calcd. for $C_{10}H_{14}O_2N_2$: C, 61·83; H, 7·27; N, 14·42%).

(5) 2,5 - *Diethoxycarbonyl* - 2,3 - *diazabicyclo*[3.2.0]*hepta* - 3,6 - *diene* **3e**. Compound **2e** (476 mg) was irradiated according to the standard procedure. Bicyclic isomer **3e** was obtained in 48% yield after 23 hr as an orange oil: IR ($CHCl_3$) 1710 and 1730 cm^{-1} (C=O), 1580 cm^{-1} (C=C); UV (CH_2Cl_2) λ_{max} 253 (ϵ 6000); NMR (acetone-d-6) δ 7·03 (s, 1, H_4), δ 6·50 (q, 1, J = 2·8, 2·0 Hz, H_6), δ 6·17 (d, 1, J = 2·8 Hz) and δ 5·07 (1, d, J = 2·0 Hz, H_1); MS *m/e* (238 (M^+). (Found: C, 55·2; H, 6·0; N, 11·8. Calcd. for $C_{11}H_{14}O_4N_2$, C, 55·45; H, 5·92; N, 11·76%).

(6) 2 - *Ethoxycarbonyl* - 6 - *methyl* - 2,3 - *diazabicyclo*[3.2.0] - *hepta* - 3,6 - *diene* **3f**.

Compound **2f** (360 mg) was irradiated according to the standard procedure. Bicyclic isomer **3f** was obtained in 18% yield only after 95 hr as a pale yellow oil: IR ($CHCl_3$) 1720 cm^{-1} (C=O), 1640 cm^{-1} (C=N) and 1585 cm^{-1} (C=C); UV (CH_2Cl_2) λ_{max} 251 nm (ϵ 5300); NMR ($CDCl_3$) δ 6·96 (d, 1, J = 4 Hz, H_4), δ 5·84 (m, 1, H_7), δ 4·88 (m, 1, H_1), δ 4·10 (m, 1, H_5), δ 1·80 (m, 3, J = 1·5 and 1·0 Hz); MS *m/e* 180 (M^+). Compound **3f** being unstable, no elemental analyses have been determined.

(7) 2 - *Ethoxycarbonyl* - 5 - *methyl* - 2,3 - *diazabicyclo*[3.2.0]*hepta* - 2,3 - *diene* **3g**. Compound **2g** (360 mg) was irradiated according to the standard procedure. Bicyclic isomer **3g** was obtained in 45% yield after 20 hr as a pale yellow oil: IR ($CHCl_3$) 1700 cm^{-1} (C=O) and 1585 cm^{-1} (C=C); UV (EtOH) λ_{max} 252 nm (ϵ 4900) and 294 nm (ϵ 2000); NMR (acetone-d-6), δ 6·73 (s, 1, H_4), δ 6·36 (t, 1, J = 2·6, 2·1 Hz, H_6), δ 5·90 (d, 1, J = 2·6 Hz, H_7), δ 4·45 (d, 1, J = 2·1 Hz, H_1), δ 1·34 (s, 3, Me_5); MS *m/e* 180 (M^+). (Found: C, 59·4; H, 6·7; N, 15·3. Calcd. for $C_9H_{12}O_2N_2$: C, 59·98; H, 6·71; N, 15·55%).

Photoinduced synthesis of 2 - *ethoxycarbonyl* - 5 - *methoxy* - 2,3 - *diazabicyclo*[3.2.0] - *hepta* - 3,6 - *dienes* **7**

A soln of **6** (1·0) g in 1·8 l benzene was irradiated by means of a Philips HPK 125 W Hg high pressure lamp through Pyrex glass. After 10 hr the starting material had disappeared; *in vacuo* evaporation of benzene followed by chromatography of the mixture over silicic acid with a 6/4 v/v cyclohexane-ethyl acetate mixture led to the isolation of isomer **7** in 40% yield as a yellow oil: IR ($CHCl_3$) 1700 cm^{-1} (C=O); UV (C_6H_6) λ_{max} 255 nm (ϵ 4500) and 300 nm (ϵ 45); NMR ($CDCl_3$) δ 7·0 (s, 1, H_4), δ 6·51 (q, 1, J = 2·8, 1·2 Hz, H_6), δ 5·95 (d, 1, J = 2·8 Hz, H_7), δ 4·90 (d, 1, J = 1·2 Hz, H_1) and δ 3·38 (s, 3, MeO); MS m/e 196 (M^+). Compound **7** being unstable, no elemental analyses have been performed.

Determination of restricted rotation around N–CO bonds in bicyclic compounds **3** *by NMR*

NMR spectra were determined with a Varian A-60-A spectrophotometer equipped with a variable temp probe. Recorded temps are accurate within ±3° limits. Lifetimes τ_i were determined using the Gutowski-Holm equations[22] which permit to compute and to plot the curve $v = f(\Delta\omega)$. This equation was put on a computer-program; given various τ values the curves were traced out as a function of $\Delta\omega = \omega - (\omega_A + \omega_B)/2$ where ω_A and ω_B represent the abscissa of the A and B absorption bands pertaining to proton H-4 of the two rotamers. Comparison of experimental with calculated spectra yielded the correct τ value from which one obtained the rate constant k (Table 5). Errors upon ΔH^* and ΔS^* were estimated from the maximum and minimum slopes of the (log k/T = f 1/T) straightlines. The same applied for E_a and ln A. ALCAL computer program was used with a 9820 A Hewlett-Packard calculator equipped with a xy plotter.

Thermal isomerisation of 2 - *isopropoxycarbonyl* - 2,3 - *diazabicyclo* [3.2.0] *hepta* - 3,6 - *diene* **3c**. A soln of **3c** (50 mg) in

Table 5. Calculated values for τ and k parameters as a function of temperature

t (°C)	T (°K)	$\frac{10^3}{T}$	τ (s)	$k = \frac{1}{2\tau}$	$\log \frac{k}{T}$	ln k
- 7,5	265,5	3,766	0,028	17,86	- 1,172	2,883
- 13	260	3,846	0,055	9,091	- 1,456	2,207
- 15,5	257,5	3,883	0,075	6,667	- 1,587	1,897
- 18,5	254,5	3,929	0,105	4,762	- 1,728	1,561
- 21	252	3,968	0,130	3,846	- 1,816	1,347
- 22,5	250,5	3,992	0,200	2,500	- 2,001	0,916
- 26,5	246,5	4,057	0,360	1,389	- 2,249	0,329
- 29,5	243,5	4,107	0,630	0,794	- 2,487	-0,231

diphenyl ether (10 ml) was heated to 135° for 18 hr under N_2; no reaction occured. At 170° **3c** isomerised quantitatively within 2 hr, as monitored by ^{1}H NMR, and gave **2c**: m.p. 56°; IR, UV and NMR spectra of an authentic sample identical.

Thermal isomerisation of 2 - *ethoxycarbonyl* - 2,3 - *diazabicyclo*[3.2.0]*hepta* - 3,6 - *diene* **3b**. A soln of **3b** (50 mg) in diphenyl ether (10 ml) was heated to 120° for 20 hr under N_2. Quantitative conversion to **2b** was observed, as monitored by ^{1}H NMR: identical IR, UV and NMR spectra with an authentic sample of **2b**.

Base induced isomerisation of 2 - *isopropoxycarbonyl* - 2,3 - *diazabicyclo*[3.2.0]*hepta* - 3,6 - *diene* **3c**. (1) *At* 6°. A soln of **3c** (500 mg) and i-RoNa (65 mg Na added) in i-PrOH (20 ml) was maintained for 14 hr at 6°. Water was added and the mixture was extracted several times with ether. The resulting ethereal soln was dried over Na_2SO_4 and evaporated to dryness in *vacuo*. Column-chromatography over silic acid with a 6/1 v/v cyclohexane-ethyl acetate mixture gave the starting material **3c** (180 mg) and **14** (300 mg): m.p. 94–95°, IR, UV and NMR spectra identical with an authentic sample.[11]

(2) *At* 23°. The same procedure was repeated at room temp over a 24 hr period. Careful chromatography of the mixture yielded three products: starting material **3c** (80 mg), *cis/trans*-**14** (200 mg, m.p. 94–95°, and its *trans/trans* isomer **15** (110 mg), m.p. 115° (11) which was identical with an authentic sample (IR, UV and NMR spectra).

Base catalysed interconversion of cis/trans *to* trans/trans *dienaminonitriles* **14**. A soln of *cis–trans*-**14** (300 mg) and i-PrONa (50 mg Na added) in i-PrOH (20 ml) was refluxed for 5 days under N_2. Addition of water, followed by ether extraction and chromatography over silicic acid with a 7/3 v/v cyclohexane/ethyl acetate mixture, gave three compounds: *cis-trans*-**14**, m.p. 95° (90 mg); its *trans-trans* isomer **15**, m.p. 115° (50 mg); and 2-aminopyridine (30 mg) where spectral data (IR, UV, NMR) were identical with those of a commercial sample.

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