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Ring Transformation of Furfural into an Unusual Bicyclic System: Characterisation and Dynamic Stereochemistry of 6,7-Diethoxycarbonyl-6,7-diaza-8-oxabicyclo[3,2,1]oct-3-en-2-one.

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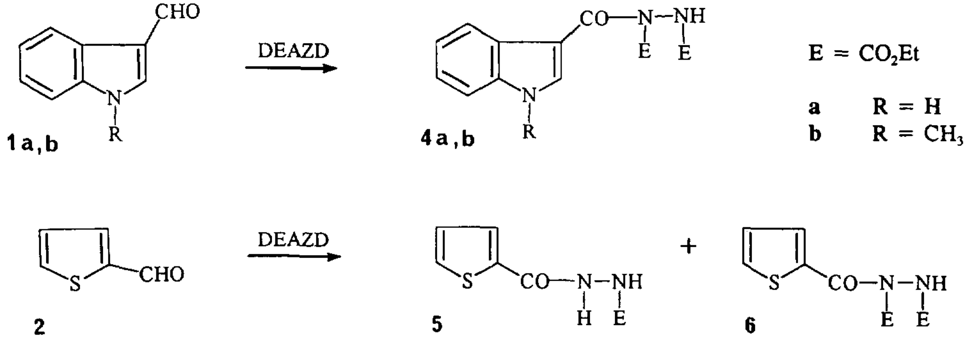
Abstract: 2-Formylthiophene and 3-formylindole react with diethyl azodicarboxylate to give simple products derived from reactions on the formyl group whereas 2-formylfuran reacts to give the unexpected bicyclic title compound. ^1H and ^{13}C NMR studies indicate that this compound undergoes a series of three dynamic conformational changes over the temperature range 50 to -90°C which are ascribed to slow rotation about the exocyclic carbamate bonds and hindered bridge inversion. © 1997 Elsevier Science Ltd.

In a previous paper [1] it was reported that N-substituted 2-formylpyrroles react with diethyl azodicarboxylate (DEAZD) to afford products derived from radical reactions on the formyl group [2] and Michael additions at C-5 of the pyrrole ring. [3] When this study was extended to 3-formylindoles **1a** and **1b** and 2-formylthiophene **2** the products obtained (**4a**, **4b**, **5** and **6**) were very similar to those derived from 2-formylpyrroles and involved reactions on the formyl group (Scheme 1). However when 2-formylfuran (furfural) **3** was reacted with DEAZD under similar conditions an unexpected adduct **7** was obtained (Scheme 2).

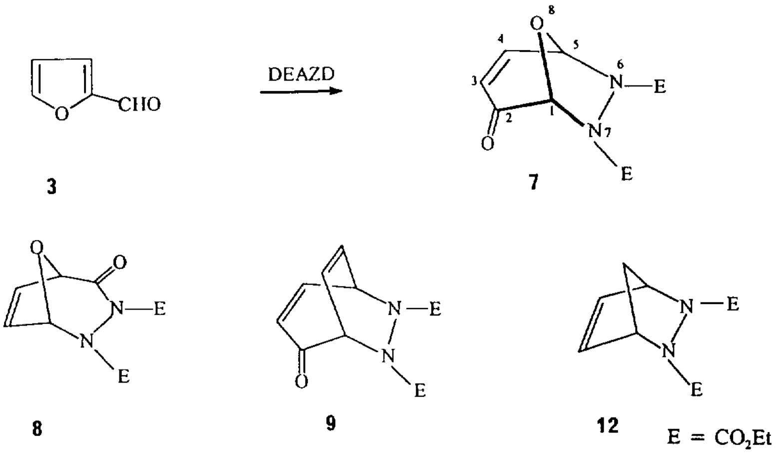


Scheme 1

RESULTS AND DISCUSSION

Isolation and identification of products

The products were purified by an initial column chromatography followed by Chromatotron purification. The N,N'-diethoxycarbonylhydrazine, which was always present as an impurity, crystallized out as a colourless solid during recrystallisation.



Scheme 2

The reaction of the indoles **1a** and **1b** with DEAZD afforded the diethoxycarbonyl hydrazides **4a** and **4b** respectively. However 2-formylthiophene gave the mono-ethoxycarbonyl hydrazide **5**, which had lost one CO_2Et group, in addition to the diethoxycarbonyl derivative **6** (Scheme 1). In the reaction of 2-formylfuran (**3**) with DEAZD the adduct **7** was isolated as a colourless solid (Scheme 2). The infrared spectrum showed a strong broad carbonyl band at 1700-1780 cm^{-1} and the mass spectrum indicated a parent ion at m/z 270.015 consistent with the molecular formula $C_{11}H_{14}N_2O_6$. The 60 MHz ^1H NMR spectrum recorded at ambient temperature in deuteriochloroform showed two ethoxy groups in slightly different environments and four other signals at δ 5.4 (singlet), 6.0 (doublet, J 10 Hz), 6.2 (doublet, J 4 Hz) and 7.0 (doublet of doublets, J 10 Hz and 4 Hz). High-field (300 MHz) spectra recorded at -10°C where the signals were sharper (see below) resolved the signal at δ 5.4 into a doublet with J 1.5 Hz.

The spectroscopic data are indicative of the diazabicyclic structure **7** (6,7-diethoxycarbonyl-6,7-diaza-8-oxabicyclo[3,2,1]oct-3-en-2-one). In particular the ^1H and ^{13}C chemical shifts and the $^3J_{H,H}$ spin coupling interactions are consistent with the proposed structure **7**. Thus the chemical shifts of H-3 (δ 6.0) and H-4 (δ 7.0) and their mutual 10 Hz coupling are indicative of a *cis*-enone moiety. The observed 4 Hz vicinal coupling between H-4 and the doublet signal at δ 6.2 enables the latter to be assigned to H-5, and the 1.5 Hz long range W-coupling between H-3 and H-1 at δ 5.4 is consistent with the proposed enone bridge structure. The assignments of H-1 (δ 5.4), H-3 (δ 6.0), H-4 (δ 7.0) and H-5 (δ 6.2) are supported by a 2D ^1H-^1H COSY spectrum which shows pronounced cross peaks confirming the H-1--H-3--H-4--H-5 spin interactions (Fig. 1).

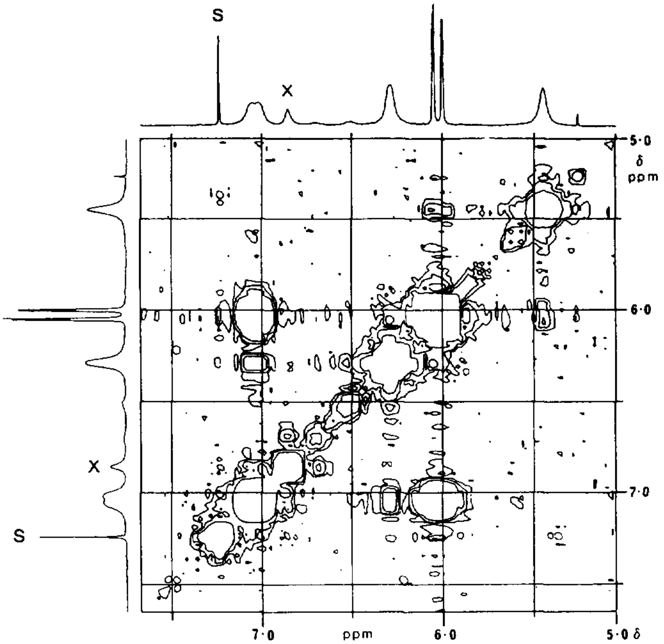


Figure 1: ^1H-^1H COSY spectrum of 7; s = $CHCl_3$ solvent, x = impurity

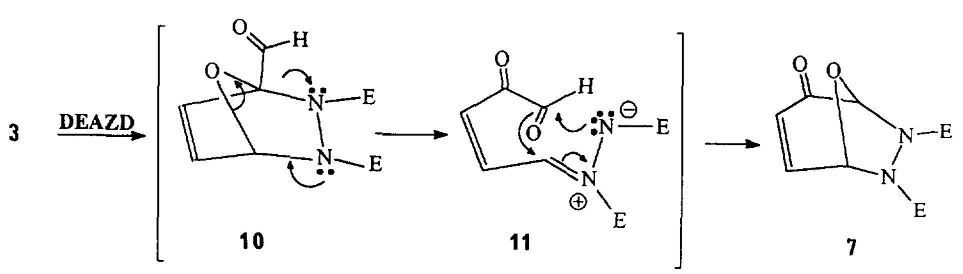
The ^{13}C NMR spectrum recorded in deuteriochloroform solution indicated the presence of two bridgehead alkyl carbons at δ 84.3 (C-5) and 87.7 (C-1), two alkene bridge carbons at δ 126.7 (C-3) and 141.6 (C-4), weak carbonyl signals at δ 154.2 and 156.4 (2 x CO_2) and 187.7 (C-2), two OCH_2 signals at δ 63.1 and 64.2 and a strong methyl signal (2 x CH_3) at δ 14.1. The above assignment of the C-1, C-3, C-4 and C-5 signals was achieved by selective ^1H decoupled ^{13}C NMR experiments on each of the corresponding proton signals.

An alternative isomeric structure (**8**), which could conceivably have formed by an intramolecular conjugate addition of 1,2-diethoxycarbonyl-1-(2-furoyl)hydrazine at position 5 of the furan ring, can be excluded by the spectroscopic data. In particular the non-conjugated compound **8** would not be expected to show the observed strong UV absorption in the region 200-225 nm (see Experimental Section). Furthermore the observed vicinal H-C=C-H coupling of 10 Hz is too large for a *cis*-alkene group constrained in a five-membered ring where couplings of 4-6 Hz are expected.[4] Vicinal H-C=C-H couplings in the region of 10-12 Hz are indicative of a six or seven membered ring as found in structure 7. Specifically a three-bond enone HC=CH coupling of 11.1 Hz has been reported for the related Diels-Alder adducts **9** of tropone with DEAZD.[5] Compound **9** also shows a 2.4 Hz four-bond W-coupling between the bridgehead proton and the enone proton adjacent to the carbonyl group analogous to the observed 1.5 Hz W-coupling between H-1 and H-3 in compound 7.

The ^{13}C chemical shift of the isolated C-2 carbonyl signal (δ 187.7) is also more typical of an enone system (7) than an acylhydrazine (**8**) where a carbonyl resonance in the range δ 160-170 would have been expected. Further confirmation of the enone structure 7 is provided by ^1H coupled ^{13}C NMR spectra recorded at 100°C in deuterio-1,1,2,2-tetrachloroethane solution to remove residual exchange broadening effects. A clear doublet was observed for the C-2 carbonyl signal at δ 186.7 with $^3J_{C,H}$ 10.3 Hz. Previous work has established that a $^3J_{C,H}$ coupling constant of 10±0.5 Hz is characteristic of an enone system (^{1}H-C=C-^{13}C=O) where the vinyl proton is *trans* to the carbonyl group as in compound **7**.[6] The small couplings of C-5 (δ 83.5, doublet of triplets) and C-1 (δ 87.5, triplet) have the expected multiplicity for 2 x $^3J_{C,H}$ = 9.2 Hz plus 1 x $^2J_{C,H}$ = 4.8 Hz and 2 x $^3J_{C,H}$ = 4.0 Hz respectively.

The unexpected diazabicyclo[3,2,1] structure **7** may arise by rearrangement of the initial Diels-Alder adduct **10** from furfural and DEAZD. Conceivably **10** could undergo a 1,3-dipolar cycloreversion to the azomethine imine **11** followed by an intramolecular 1,3-dipolar cycloaddition of the azomethine imine moiety to the aldehyde carbonyl (Scheme 3), though other mechanisms are possible.

A detailed investigation of the NMR spectra of compound **7** over the temperature range 60 to -90°C indicated a series of dynamic changes. These changes are discussed in three sections:



Scheme 3

Dynamic process 1 (50 to 0°C)

An unusual aspect of the ^{1}H NMR spectra of compound **7** was the observation that when the spectrum was recorded at 270 or 300 MHz rather than 60 MHz the signals of H-1, H-4 and H-5 were broadened to the extent that their multiplet structure was not resolved (Fig. 2) though the H-3 signal was resolved into a sharp doublet of doublets ($^3J_{H,H}$ 10.0 and 1.6 Hz). Field dependent selective line broadening of this type is indicative of the existence of a dynamic exchange process above the coalescence temperature where the exchange broadening increases with the greater signal separation (in Hertz) present in a high-field spectrometer. This conclusion was confirmed by the observation that the signals assigned to H-1, H-4 and H-5 sharpened on warming the sample and resolved into the expected multiplets at *ca.* 80°C (in DMSO-d_6). Similarly on lowering the temperature to *ca.* -10°C (in CD_2Cl_2 or $CDCl_3$) well resolved signals were again observed for H-1 (δ 5.47, $^4J_{1,3}$ 1.5 Hz), H-3 (δ 6.06, $^3J_{3,4}$ 10.0 Hz), H-5 (δ 6.38, $^3J_{4,5}$ 4.1 Hz) and H-4 (δ 7.10, $^3J_{3,4}$ 9.7 Hz, $^3J_{4,5}$ 3.9 Hz) at -10°C in CD_2Cl_2.

Broadening and resharpening behaviour of this type is indicative of slowing exchange with a minor (sometimes hidden) component.[7] Inspection of spectra recorded at -10 and -20°C revealed the appearance of a new singlet signal at δ 6.03 close to the H-3 signal of the main component (Fig. 2). The signal at δ 6.03, estimated to be *ca.* 10% relative intensity, is assigned to H-1 in the minor component. The assignment was confirmed by the observation that low power irradiation of the minor signal at δ 6.03 induced a 50% reduction in the intensity of the main H-1 doublet signal by saturation transfer between exchanging partners. The minor exchanging partners of H-4 and H-5 were more difficult to assign due to the onset of a second dynamic

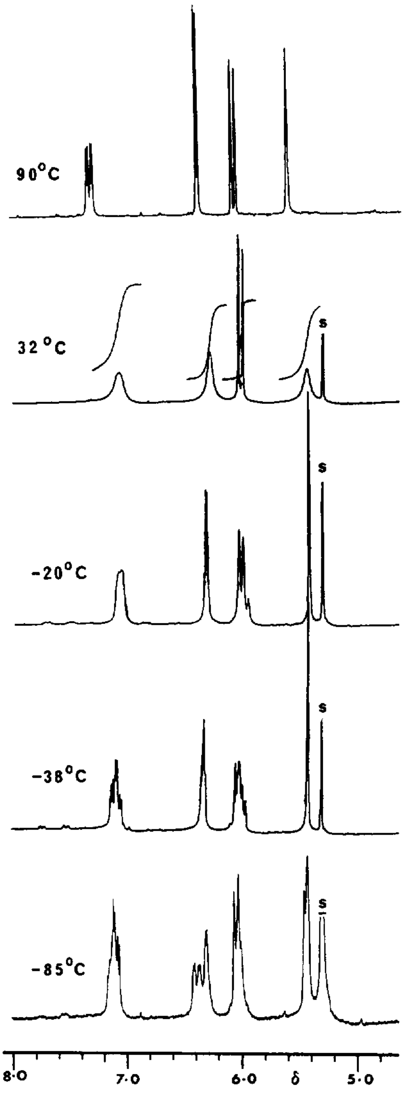


Figure 2. ^{1}H NMR spectra of 7 at various temperatures. Spectrum at 90°C recorded in DMSO-d_6, all other spectra in CD_2Cl_2 ($s = CH_2Cl_2$)

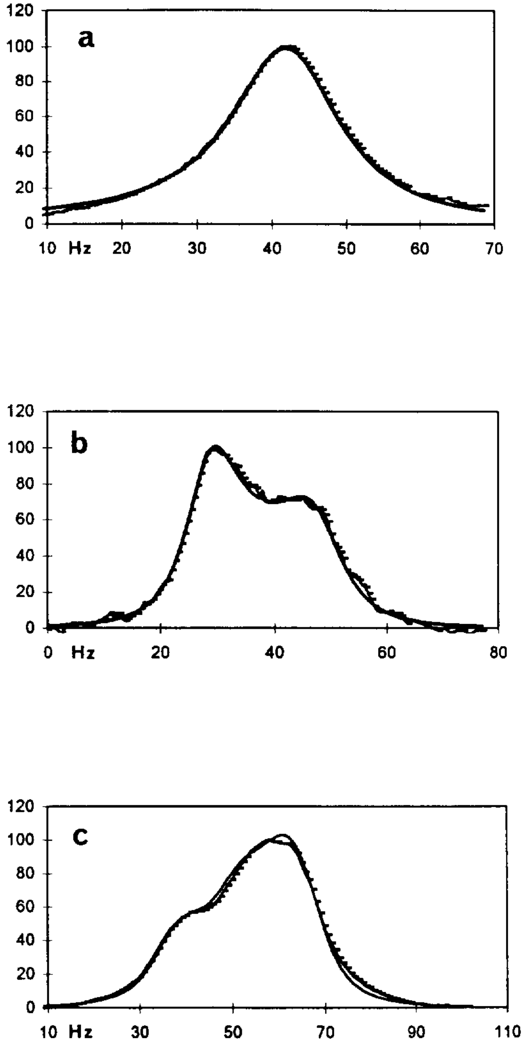


Figure 3. Experimental (points) and best fit calculated (solid lines) bandshapes for: **a** the H-1 signal at 32.1 °C, **b** the C-4 signal at -19.9°C, and **c** the H-5 signal at -73.1°C

process in the minor component at *ca.* -10°C. The minor H-4 signal is assigned to a broad signal centred at δ 7.7 (-10°C) which splits further at -30°C into two very small doublet of doublet signals at δ 7.75 and 7.78, each *ca.* 5% intensity relative to the main component. The H-5 signal from the minor component is presumed to be either further broadened by a second dynamic process or hidden under another signal.

Table 1: Dynamic ^{1}H and ^{13}C NMR Data for the Three Stereodynamic Processes in Bicyclic Hydrazide **7** [a]

Process	Signal	Ratio [b]	$\Delta\nu$/Hz	J/Hz	Temp/°C [c]	k/s^{-1} [d]	$\Delta G^‡$/kcal mol^{-1} [d]
1	H-1	1.0:0.12	145	1.6	32.1	80.9, 675	15.2, 13.9
1	H-4	1.0:0.12	146	4.1,9.9	32.1	87.8, 732	15.2, 13.9
1	C-5	1.0:0.12	182	-	31.2	84.3, 703	15.1, 13.9
1	C-1	1.0:0.12	172	-	31.2	82.7, 689	15.2, 13.9
2	H-4	1.0:0.82	11.7	4.1,9.9	-19.9	29.5, 36.0	13.0, 12.9
2	C-5	1.0:0.82	22.6	-	-19.9	30.8, 37.5	13.0, 12.9
2	C-4	1.0:0.82	23.4	-	-19.9	34.2, 41.8	13.0, 12.9
3	H-5	1.0:1.0	29.9,18.7	4.1	-73.1	37.9	10.1
3	C-2	1.0:1.0	117	-	-85.0	260	10.0

[a] Determined in CD_2Cl_2 solution at 270.0 MHz (^{1}H) or 67.8 MHz (^{13}C). [b] Measured from low temperature spectra and adjusted slightly to optimise the fit between calculated and experimental spectra. [c] Temperature at which k was determined (at or close to the coalescence temperature). [d] First value is for the major → minor process and second value is for the minor → major process (1 cal mol^{-1} = 4.184 J mol^{-1}).

^{13}C NMR spectra of compound **7** also provides evidence of the dynamic behaviour. Thus close inspection of the ambient temperature spectra (recorded in CD_2Cl_2) indicated selective broadening of the C-1 and C-5 bridgehead signals at δ 88.3 and 84.9, both OCH_2 signals (δ 63.5 and 64.7) and the vinylic C-4 signal at δ 142.2. These signals sharpened on cooling and at -10°C a number of small signals from the minor component had appeared (*ca.* 10% relative intensity).

Computer aided analysis of the H-1 signal at 32.1°C, where the exchange broadening was at a maximum gave a good fit between the calculated and the experimental lineshape (Fig. 3). The lineshapes of the exchange broadened H-4, C-1 and C-5 signals were also analysed to give the exchange rates (Table 1). There is good agreement between the barriers determined from the four different sets of coalescing signals with the mean $\Delta G^‡$ = 15.2 kcal mol^{-1} (major → minor) and 13.9 kcal mol^{-1} (minor → major).

(c) Dynamic process 2 (-10 to -40°C)

On lowering the temperature below -10°C (in CD_2Cl_2) the signals of H-3 (δ 6.06) and H-4 (δ 7.10) began to broaden again, and by -40°C each had split into two partly overlapping multiplet signals (Fig. 2) of unequal intensity (*ca.* 0.8:1.0). In the same temperature range the OCH_2 multiplet signals at δ 4.15 and 4.32 and the higher field methyl triplet at δ 1.26 also collapsed and separated into two partly overlapping multiplets. The small signal separation combined with the multiplet nature of these signals made an accurate determination of the exchange rate difficult, but the exchange broadened H-4 signal at -20°C was analysed as an 8-site coalescence of two doublet of doublets, relative intensity 0.82:1.0 (Table 1).

The ^{13}C NMR spectra recorded in this temperature range were more simple to analyse due to the absence of coupling. Thus the C-5 bridgehead signal at δ 84.8 (CD_2Cl_2) broadened selectively below -10°C and at -36°C it had clearly split into two components at δ 84.77 and 85.13 with an intensity ratio of 1.0:0.82 respectively. Similarly by -36°C the bridge C-4 signal had separated into two components at δ 142.51 and 142.82, intensity ratio 0.82: 1.0 respectively. Computational analysis of these signals (Fig. 3) at the coalescence temperature (-20°C) gave $\Delta G^{\ddagger}$ 13.0 and 12.9 kcal mol^{-1} respectively (major→minor) in good agreement with the barrier determined from the ^1H NMR analysis of the H-4 signal at the same temperature (Table 1).

Dynamic Process 3 (-60 to - 90°C)

In the temperature range -40 to -60°C the ^1H NMR signals were relatively sharp multiplets. However, on cooling below -60°C the H-5 signal at δ 6.45 broadened and at -85°C it had split into three partly overlapping doublet signals at δ 6.43, 6.48 and 6.53 with intensity ratio approximately 2:1:1 (Fig. 2). The more intense higher field signal (δ 6.43) was considered to be an accidental coincidence of two doublet signals. These four signals result from splitting of the H-5 signal first by process 2 and then by process 3. Computer assisted analysis of the H-5 signal at -73.1°C gave the best fit between experimental and calculated lineshape (Fig. 3) for exchange of both the downfield signals (δ 6.48 and 6.53) with the coincident upfield signals at δ 6.43, and an intensity ratio of 1.82:0.82:1.0 for the signals at δ 6.43, 6.48 and 6.53 respectively. The doublet splitting of these four component H-5 signals (4.1 Hz) was included in the lineshape analysis giving an eight line coalescence overall (Table 1). Broadening of the OCH_2 multiplet signals was also observed in this temperature range but the signals were too complicated to analyse.

In the ^{13}C NMR spectra recorded at -60°C selective broadening was observed for both OCH_2 signals (δ 85 and 87) and some of the carbamate ester carbonyl signals (δ 155-160). The splitting of the OCH_2 signals at -85°C was too small for a satisfactory analysis, but one of the carbamate carbonyl signals (δ 157.5) had split into two widely separated components of approximately equal intensity at δ 156.7 and 158.4. Coalescence of these signals occurred at -60°C, but the poor signal to noise ratio for these weak carbonyl signals prevented a meaningful lineshape analysis. However a manual analysis for the coalescence of these well separated singlet signals gave $\Delta G^{\ddagger}$ 10.0 kcal mol^{-1} at -60°C in excellent agreement with the barrier determined by analysis of the H-5 signal (Table 1).

Discussion of the conformational changes

In principle seven possible conformational changes can be envisaged for the bicyclic hydrazine **7**. These are pyramidal inversion at each of the nonequivalent nitrogen atoms, rotation about the two nonequivalent exocyclic $N-CO_2Et$ bonds, rotation about the two CO−OEt bonds, and inversion of the N-N- bridge (involving torsion about the N−N bond).

Slow rotation about the CO−OEt bonds is not considered very likely since such processes are normally rapid on the NMR time-scale down to -100°C. Similarly, nitrogen inversion can almost certainly be discounted as an observable process in NMR spectra of this type of compound in the temperature range -100 to 50°C. Monocyclic and bicyclic N-alkylhydrazines do show significant barriers to nitrogen inversion (8 - 14 kcal mol^{-1}), but these barriers are known to be greatly reduced, or eliminated altogether, in N-acyl or N-carboalkoxy derivatives due to amide type conjugation between the nitrogen lone pair and the adjacent carbonyl group.[8]

The three conformational changes cannot be assigned *a priori* from the observed spectral changes, hence assignments must rely on comparisons with related hydrazide systems. Previous ^{1}H NMR studies on several mono- and bicyclic N,N′-dicarboalkoxyhydrazines indicate barriers to rotation about N-CO_2R bonds in the range 12.6 - 14.8 kcal mol^{-1}.[8] Thus for example the bicyclic hydrazide **12** has a N-CO_2Me rotation barrier ($\Delta G^{\ddagger}$) of 13.7 kcal mol^{-1}.[9] Somewhat higher barriers (16.2 kcal mol^{-1}) have been reported in acyclic hydrazides.[8]

On this basis the barrier of 10.1 kcal mol^{-1} for the lowest temperature process 3 in compound **7** would seem to be too low to be assigned to rotation about an N-CO_2Et bond, particularly as the electronic and steric environment of the N-CO_2Et groups in hydrazide **7** appears to be comparable with that in compound **12**. Accordingly the higher temperature processes 1 and 2 in hydrazide **7**, with $\Delta G^{\ddagger}$ 13.9/15.2 and 12.9/13.0 kcal mol^{-1} respectively, are probably due to rotational isomerism about the two nonequivalent N-CO_2Et bonds. The observation that process 1 is associated with large splitting of the H-4, H-5, C-4 and C-5 signals might indicate that the higher barrier (13.9/15.2 kcal mol^{-1}) arises from rotation about the N(6)-CO_2Et bond, and that process 2 is associated with rotation about the N(7)-CO_2Et bond.

The lowest temperature process 3 may be assigned to inversion of the C(1)-N(7)-N(6)-C(5) bridge. Large barriers, $\Delta G^{\ddagger}$ 16.4 - 19.7 kcal mol^{-1}, have been reported for -N-N- bridge inversion in mono- and bi-cyclic hydrazides where the N—N bond is contained in a six-membered ring.[8] The preferred ground-state conformation of these hydrazide systems involves twisting around the N—N bond to minimise stereoelectronic repulsion between the adjacent nitrogen lone pairs and unfavourable steric interactions between the vicinal CO_2R groups. Compound **12** does not apparently shown a high barrier to bridge inversion due to the limited flexibility of the diazabicyclo[2,2,1]heptene system which restricts bridge twisting. The somewhat more flexible diazabicyclo[3,2,1]octene structure of **7** may allow sufficient twisting about the N—N bond to cause a modest barrier (10.1 kcal mol^{-1}) for inversion about the C(1)-N(7)-N(6)-C(5) bridge. However the possibility that process 3 is associated with slow rotation about one of the C(O)-OEt bonds cannot be excluded.

EXPERIMENTAL

General — Mps were determined with a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer-843 spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on Perkin Elmer R-24, Bruker AC-200, Bruker AC-250, Jeol GSX-270 and Varian Gemini-300 spectrometers. Mass spectra were obtained on a Hewlett-Packard 5930A spectrometer and high-resolution mass spectra were obtained using a VG Autospec, TRIO 1000 (Fisons) instrument. The ionization mode used in mass spectra was electron impact (EI) at 70 ev or fast atom bombardment (FAB). Microanalyses were performed at "Centro de Investigacion" CSIC, Barcelona.

General Procedure — A solution of the corresponding aldehydes (0.017 mol) and DEAZD (0.053 mol) in dichloromethane (20 ml) was heated in a sealed tube in the conditions indicated in each particular case. The crude mixtures were chromatographed on a silica gel column with increasing ratios of ethyl acetate:hexane as eluent.

1,2-Diethoxycarbonyl-1-(3-indolylcarbonyl)hydrazine (**4a**) — The title compound was obtained from the aldehyde **1a** after 18 h at 150°C (1.7 g, 34%); mp 122-123°C (from dichlorometane/hexane); (Found: M^+, 319.1166. $C_{15}H_{17}N_3O_5$ requires *M*, 319.1168); ν_{max}(mineral oil) 3300, 1740 and 1680 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 0.96-1.10 (6H, m), 4.03-4.15 (4H, m), 7.02-7.20 (2H, m), 7.23-7.44 (1H, m), 7.84 (1H, m), 7.96 (1H, s), 8.04 (1H, m) and 10.0 (1H, s); δ_C(62.9 MHz; $CDCl_3$) 13.5 (q), 13.9 (q), 62.5 (t), 63.6 (t), 109.7 (s), 112.2 (d), 120.9 (d), 122.3 (d), 123.2 (d), 126.5 (s), 133.7 (d), 136.2 (s), 154.5 (s), 156.6 (s) and 166.1 (s); m/z 319 (M^+, 8%), 144 (100), 116 (12), 89 (8) and 63 (3).

1,2-Diethoxycarbonyl-1-[3-(1-methylindolylcarbonyl)]hydrazine (**4b**) — A solution of 1-methylindole-3-carboxaldehyde **1b** (0.017 mol) and DEAZD (0.053 mol) was heated 10 h at reflux temperature. After this time, the mixture was chromatographed on a silica gel column with increasing ratios of ethyl acetate:hexane affording the title compound (0.6 g, 22%); (Found: M^+, 333.1324. $C_{16}H_{19}N_3O_5$ requires *M*, 333.1324); ν_{max}(mineral oil) 3330, 1730 and 1660 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.14 (3H, t, *J* 7 Hz), 1.21 (3H, t, *J* 5 Hz), 3.70 (3H, s), 4.18 (4H, q, *J* 7 Hz), 7.23 (3H, m), 7.49 (1H, s) and 8.08 (1H, m); δ_C(62.9 MHz; $CDCl_3$) 14.0 (q), 14.3 (q), 33.4 (q), 62.3 (t), 63.5 (t), 108.8 (s), 109.8 (d), 121.4 (d), 122.3 (d), 123.0 (d), 127.1 (s), 130.5 (s), 136.8 (d), 154.2 (s), 156.0 (s) and 165.0 (s); m/z 333 (M^+, 47%), 287 (9), 215 (22), 200 (12), 158 (100), 130 (37), 103 (32), 89 (8) and 77 (27).

1-Ethoxycarbonyl-2-(2-thenoyl)hydrazine (**5**) — The title compound was obtained from the aldehyde **2** after 12 h at 140°C (0.8 g, 20%); mp 123-126 °C (from dichloromethane/hexane); (Found: M^+, 214.0410. $C_8H_{10}N_2O$ requires *M*, 214.0412); ν_{max}(mineral oil) 3200, 1700 and 1640 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.24 (3H, t, *J* 7.3 Hz); 4.15 (2H, q, *J* 7.3 Hz), 7.03 (1H, dd, *J* 5.1 and 3.6 Hz), 7.11 (NH, bs), 7.45 (1H, dd, *J* 5.1 and 1.1 Hz) and 7.64 (1H, d, *J* 3.6 Hz); δ_C(62.9 MHz; $CDCl_3$) 14.3 (q), 62.5 (t), 127.8 (d), 129.6 (d), 131.3 (d), 135.3 (s), 157.2 (s) and 162 (s); m/z 214 (M^+, 10%), 168 (20), 124 (20), 111.0 (100) and 83 (6).

1,2-Diethoxycarbonyl-1-(2-thenoyl)hydrazine (**6**) — The title compound was obtained from the aldehyde **2** after 12 h at 140 °C (1.2 g, 40%); (Found: M^{+1}, 287.0703. $C_{11}H_{14}N_2O_5S$ requires M^{+1}, 287.0701); ν_{max}(mineral oil)/cm^{-1} 3290, 1730 and 1680 cm^{-1}; δ_H(250 MHz; $CDCl_3$) 1.33 (6H, m); 4.33 (4H, m), 7.11 (1H, dd, *J* 4.8 and 4 Hz), 7.64 (1H, dd, *J* 4.8 and 1.3 Hz) and 7.93 (1H, dd, *J* 4 and 1.3 Hz); δ_C(62.9 MHz; $CDCl_3$) 14.0 (q), 14.3 (q), 62.8 (t), 64.2 (t), 127.2 (d), 133.8 (d), 134.4 (s), 135.6 (d), 155.2 (s), 155.7 (s) and 162.5 (s); m/z 242 (4%), 214 (8.6), 168 (5), 111 (100) and 83 (6); m/z (FAB) 288 M^{+2}.

6,7-Diethoxycarbonyl-6,7-diaza-8-oxabicyclo[3,2,1]oct-3-en-2-one (**7**) — The title compound was obtained from furfural **3** after 24 h at 100 °C (1.4 g, 40%); (Found: M^+, 270.0151. $C_{11}H_{14}N_2O_6$ requires *M*, 270.0164); ν_{max}(mineral oil) 1700-1780 cm^{-1}; λ_{max}(H_2O)/nm 200 (ϵ/dm^3 mol^{-1} cm^{-1} 6310), 224 sh, (4200), 352 (120). δ_H(250 MHz; $CDCl_3$) 1.16 (3H, t, *J* 7.1 Hz), 1.26 (3H, t, *J* 7.1 Hz), 4.14 (2H, q, *J* 7 Hz), 4.23

(2H, q, *J* 7 Hz), 5.41 (1H, br s), 6.0 (1H, dd, *J* 10 and 1.3 Hz), 6.26 (1H, br s) and 7.0 (1H, br s); δ_C(62.9 MHz; $CDCl_3$) 14.0 (q), 14.1 (q), 63.1 (t), 64.1 (t), 84.1 (d), 87.7 (d), 126.7 (d), 141.6 (d), 154.2 (s), 156.4 (s) and 187.7 (s); m/z 270 (M^+, 90%), 227 (23), 199 (50), 169 (50), 97 (100) and 82 (53).

Dynamic NMR Studies - Variable temperature ^1H and ^{13}C NMR spectra were recorded on a Jeol GSX-270 spectrometer operating at 270 and 67.8 MHz respectively. Probe temperatures were calibrated to ±0.1°C using a Comark Model C9001 digital thermometer equipped with a copper-constantan fine-gauge thermocouple lead inserted in a non-spinning sample tube containing 0.7 ml of solvent. Exchange broadened spectra were analysed on a pentium computer using a PC version of the iterative multisite exchange program INMR.[10] Component lines of first-order spin coupled multiplets were treated as separate sites with the appropriate relative intensity.

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