Tetrahedron Vol. 36, pp. 81 to 85
Pergamon Press Ltd., 1980. Printed in Great Britain.

^{1}H NMR SPECTRA OF 1-ALKYL-1,2,3,4-TETRAHYDRO-2-OXO-3-AZOCINE-CARBOXYLIC ACID DERIVATIVES AND THEIR ANALOGUES

K. SOMEKAWA* and S. KUMAMOTO
Department of Applied Chemistry, Faculty of Engineering, Kagoshima University, Korimoto, Kagoshima 890, Japan

T. MATSUO
Department of Organic Synthesis, Faculty of Engineering, Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812, Japan

and

I. UEDA
College of General Education, Kyushu University, Ropponmatsu, Chuo-ku, Fukuoka 810, Japan

(*Received in Japan* 2 *April* 1979)

Abstract—^{1}H NMR spectra of 1-alkyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylates and -carbonitriles indicated that the geminal protons at the 1-α-position were located in nonequivalent magnetic environments. The difference in the chemical shifts amounted to as much as 0.73 ppm in the case of methyl 1-ethyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate at 26°, and the free energy of activation for the coalescence was estimated to be larger than 23 kcal/mol. The same type of nonequivalence and coalescence phenomena were also observed even with dimethyl protons at the 1-γ-position of 1-isobutyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate ($\Delta G_c^{\ddagger} = 19$ kcal/mol). The situation was hardly affected by the reduction of the C=C double bonds. The nonequivalence was not observed, however, if the substituent at the 3-position was absent. Therefore, these novel ^{1}H NMR spectra of 1-alkyl protons in the title compounds were concluded to be due to strong coupling between the restricted rotation around N(1)—C(α) bond and inversion of the 2-oxoazocine ring which required high energy of activation.

An X-ray diffraction study of the crystal structure of 1-methyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarbonitrile (**1a**) revealed that the molecule takes an extremely distorted boat conformation as shown in Fig. 1 and Table 1.[1] Several interesting features

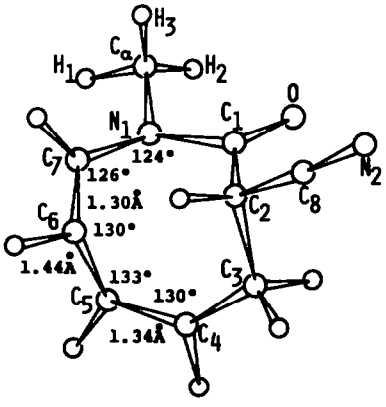


Fig. 1. Molecular structure of **1a** crystal.

Table 1. Torsion angles observed with members of the ring in **1a**.

N(1)	C(1)	C(2)	C(3)	101°
C(1)	C(2)	C(3)	C(4)	-112
C(4)	C(5)	C(6)	C(7)	-49
C(6)	C(7)	N(1)	C(1)	51

are noticed: (1) the essential single bond between C(5) and C(6) is fairly short (1.44 Å), while the dihedral angle concerning the bond is appreciably large (49°); (2) the bond angles of the C atoms in this part also show large values (*ca* 130°). These data indicate the presence of extremely large ring strain, and 1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylic acid derivatives (**1**) are expected to show fairly complex conformational behavior as it has been observed with unsaturated azacyclooctane derivatives.[2-4] In fact, extraordinary splitting patterns were observed with ^{1}H NMR signals of the alkyl groups substituted at the 1-position.[5] The NMR spectra, including the temperature-dependence, were investigated in detail and the conformational characteristics are discussed here.

The NMR signals show rather simple patterns and the unambiguous assignment can be made by the aid of decoupling techniques. An example of the spectra is given in Fig. 2, where it is clearly observed that the geminal protons of 1-α-methylene group of **1b** are found in magnetically nonequivalent environments ($J_{\alpha,\alpha'} = 14.0$, $J_{\alpha,\beta} = 7.0$ Hz). In addition to 1-homologues (**1b**, **1c**, **1d**, **1e** and **1f**), the partially reduced derivatives (**2** and **3**) were prepared and the spectra were measured at various temperatures. The chemical shifts of the alkyl group at the 1-position, as well as those of methoxycarbonyl group at the 3-position, are summarised in Table 2. Surprisingly large difference in the chemical shift ($\Delta\nu$) is observed with the geminal

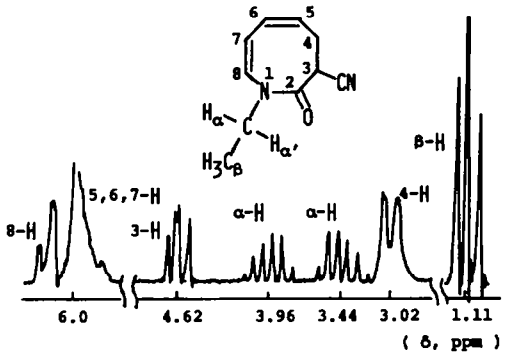
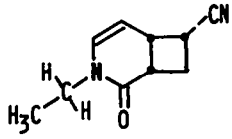


Fig. 2. ^{1}H NMR spectrum of **1b** at 160°.

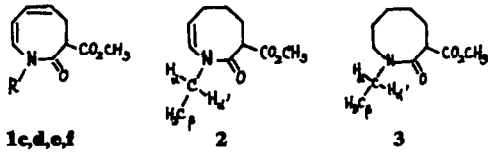
protons at the α-position of the alkyl group. As to **1b**, **1c** and **3**, the Δν-values are fairly large (80 ~ 90 Hz) at low temperatures. The value becomes as large as 120 Hz in the case of **1e** and **2**. At elevated temperature (~200°), the Δν-values are diminished to 40 ~ 50 Hz, but no coalescence is observed (Fig. 3). The same type of splittings are also observed with two Me groups at the 1-β-position in **1d**, as well as with those of the 1-γ-position in **1e** at ambient temperature. At low temperatures the Δν-values amount to 15 and 9 Hz for **1d** and **1e**, respectively, while coalescence of the signals is detected at high temperatures (140° for **1d** and 90° for **1e**). In the case of **4**, on the other hand, the coalescence temperature (Tc) of 3-α-methylene protons is 10° (J = 14.0 Hz), and the Δν-value is as small as 25 Hz at −70°. No splitting was observed with the 1-methyl peak of **1f** even at −90°.

Thus, proton signals of methylene group at 1-α-position of lactam appears to be split into multiplets when the geminal protons are located at nonequivalent positions due to the steric hindrance associated with bulky substituents. Me groups at 1-β- and 1-γ-positions are also in the similar situation as found in the case of **1d** and **1e**. The nonequivalence may partly come from restricted rotation about N(1)—C(α) bond. In addition, other conformational change must be also taken into consideration in order to explain the fact that the signal at the higher field (α–H) show much larger temperature-dependence than the counter part at the lower field (α–H') as summarised in Table 2.



(Compound (**4**))

Table 2. ^{1}H NMR data of **1b**, **1c**, **1d**, **1e**, **1f**, **2** and **3** at various temperatures (100 MHz).



1c,d,e,f **2** **3**

Comp. (R)	Solv.	Temp. (°C)	Chemical shifts, ν(δ, ppm) α-H'	α-H	$\Delta\nu_{\alpha,\alpha'}$	β-H	γ-H	OCH_3
1b	TB[a]	180	3.99	3.49	0.50	1.12		
	TB	26	3.84	3.09	0.75	1.00		
	MD[b]	-80	3.97	3.12	0.85	1.11		
1c	TB	200	4.0	3.5	0.5	1.15		3.90
($-CH_2CH_3$)	TB	26	3.84	3.07	0.77	1.00		3.60
	SD[c]	-79	3.74	2.91	0.83	1.02		3.54
1d	TB	140	4.80			1.17		3.70
($-CH(CH_3)_2$)	TB	40	4.8			1.13 0.98		3.63
1e	TB	200	3.73	3.28	0.45	2.05	0.85	3.81
($-CH_2CH(CH_3)_2$)	TB	90	3.68	2.99	0.69	1.88	0.83	3.68
	SD	-30	3.79	2.76	1.03	1.80	0.84 0.75	3.60
	SD	-90	3.8	2.6	1.2	1.74	0.8 0.7	3.6
1f	TB	180	3.04s					3.71
($-CH_3$)	SD	-90	3.06s					3.66
2	TB	180	3.98	3.5	0.48	1.12		3.81
	TB	26	3.86	2.99	0.87	1.01		3.61
	SD	-70	3.96	2.84	1.12	1.04		3.56
3	TB	180	3.80	3.37	0.43	1.18		3.87
	TB	26	3.61	3.01	0.60	1.03		3.62
	SD	-70	3.7	2.92	0.78	1.11		3.59

[a] 1,2,4-Trichlorobenzene. [b] Methanol-d_4. [c] CS_2·$CDCl_3$ (3:1).

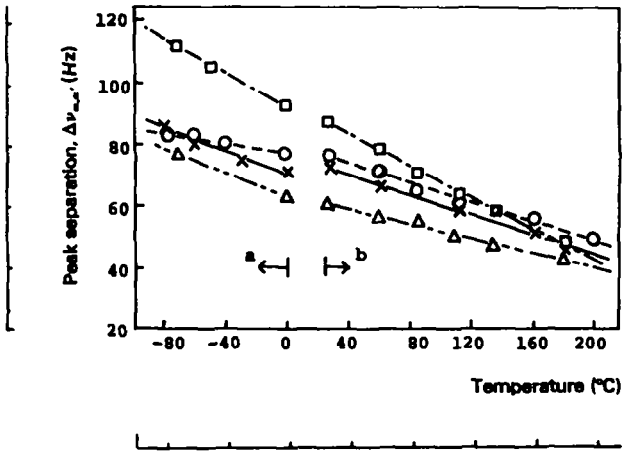


Fig. 3. Temperature-dependences of peak separations, $\nu_{\alpha,\alpha'}$, between 1-α-methylene protons in 1-alkyl-2-oxo-3-azocinecarboxylates. ×—×, **1b**; ○--○, **1c**; □-·□, 2; △-··△, 3. Measured with [a] the methanol-d_4 or $CS_2 \cdot CDCl_3$ (3:1) solution, or [b] the 1,2,4-trichlorobenzene solution.

As an aid for elucidating the cause for the non-equivalent environments surrounding the geminal protons, the difference in chemical shifts for 1-α-methylene protons in **1b** was estimated. The conformation of **1b** was assumed to be the same as that found in the crystal structure of **1a**, and the shielding effects of the following factors were evaluated at the positions of 1-methyl protons in **1a** as given in Fig. 1.

(1) *Magnetic anistropy effects.* Point-dipole approximations were applied under the assumption of the following anisotropy for each bond. $\Delta\chi_{C(1)-O} = \Delta\chi_{N(1)-C(1)} = 16.6$, $\Delta\chi_{C(6)-C(7)} = -10$, $\Delta\chi_{C(7)-N(1)} = 5.5$ in the units of 10^{30} cm^3 esu.[6] (Method A).

As an alternative, Jackman's graph[6] was used to evaluate the magnetic anisotropy effect of N(1)—C(1)—O group, where the susceptibility for N(1)—C(1) was assumed to be equal to that for CO group. (Method B).

(2) *Direct electrostatic effect.*[7] The dipole moment of the amide group, $\overset{+}{N}(1)=C(1)-\bar{O}$, was assumed to be 3.6 D.[8]

The long-range shielding effects as calculated by Method A are summarised in Table 3. It is clearly indicated that the proton closest to the CO group (H_2) is highly deshielded, and the estimated difference in the chemical shifts is approximately 0.4 ppm. Method B gives almost the same results:

Table 3. Calculated shielding effects due to magnetic anisotropy of various bonds in **1a**.

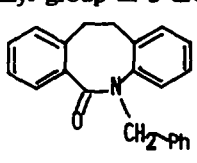
Bond	Shielding, Δσ (ppm)		
	H_1	H_2	H_3
C(1)-O	-0.13	-0.34	-0.10
N(1)-C(1)	-0.25	-0.42	-0.13
C(6)-C(7)	+0.004	-0.05	-0.07
C(7)-N(1)	+0.09	+0.09	-0.004
Total	-0.29	-0.72	-0.30

−0.4 (H_1), −1.1 (H_2) and −0.2 ppm (H_3). The predicated difference in the chemical shifts is somewhat larger than that obtained by Method A. The electrostatic effects, as calculated by Buckingham's equation[9] for the three protons were nearly equal to each other: −0.58 (H_1), −0.54 (H_2) and −0.55 ppm (H_3).

On the basis of the above calculation, the low-field signal (defined as α–H' in Table 2) is suggested to be due to the proton at the position of H_2 in Fig. 1. Hence, the magnetic anisotropy of the amide group is considered to be the main factor in deciding the chemical shifts observed with the geminal protons. It is clear, however, some other factors should also be included to account for the unexpectedly large $\Delta\nu$-value (1.2 ppm) as obtained with **2**.

The activation parameters for coalescence of ^{1}H NMR signals under discussion afford another important information. The $\Delta G_c^{\neq}$-values were calculated by the use of T_c, $\Delta\nu$, J and Eyring's equation.[10] The data, as summarized in Table 4, indicate that the rate process is associated with extremely high barrier of activation. Highly restricted rotation involving tetrahedral carbon has been reported with 9-alkyl groups of 1,4-dimethoxy-9-alkyltriptycenes.[11,12] In the case of 9-ethyl homologue, however, $\Delta G_c^{\neq}$-value is as low as 14 kcal/mol. Since the steric environment around 1-alkyl protons in the title compounds is not so much crowded in comparison with those of 9-alkyl protons in the triptycene homologues, it is really surprising that the $\Delta G_c^{\neq}$-values for **1b**, **1c**, **2** and **3** exceed 22 kcal/mol.

As far as $\Delta\nu$-value is concerned, the geminal protons of benzyl group in **5** are found in almost



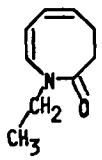
(Compound (5))

Table 4. Activation parameters for the coalescence of ^{1}H NMR spectra of the methylene and methyl groups in the alkyl substituent at the 1-position.

Comp.	Protons	T_c (°C)	$\Delta\nu$ (Hz)	J (Hz)	$\Delta G_c^{\ddagger}$ (kcal/mol)
1b	1-α-methylene	≳ 200	≳ 90	14.0	≳ 23.1
1c	1-α-methylene	≳ 200	≳ 90	14.0	≳ 23.1
1d	1-β-dimethyl	140	15	0	21.6
1e	1-α-methylene	≳ 200	≳ 120	14.0	≳ 22.8
	1-γ-dimethyl	90	9	0	19
2	1-α-methylene	≳ 200	≳ 120	14.0	≳ 22.8
3	1-α-methylene	≳ 200	≳ 90	14.0	≳ 23.1
4	3-α-methylene	10	30	14.0	14

the same situation as those of the title compounds. The coalescence of the signals has been reported to take place via ring inversion ($\Delta G_c^{\ddagger}$ = 21.4 kcal/mol).[10b] Then, the present situation might be explained by coupling between the restricted internal rotation N(1)—C(α) bond and inversion of 2-oxoazocine ring. Close examinations of the molecular structure of **1a** indicate that the cyano group at the axial position extends large steric hindrance to the conformational change via ring inversion.

On the basis of the above arguments, NMR spectra of **1b** homologue (**6**) without any substituent at the 3-position was examined. The 1-α-methylene protons of **6** gives clean quartet signals



(Compound (**6**))

(3.54 ppm in $CDCl_3$), which indicate the geminal protons are completely equivalent at ambient temperature. Then, the novel conformational behavior and the NMR spectra of the title compounds are concluded to be originated from the combination between the restricted rotation around the N(1)—C(α) bond and inversion of the 2-oxoazocine ring with a substituent at the 3-position.

EXPERIMENTAL

M.ps were measured on a Yanagimoto Mel-temp apparatus and are uncorrected. Spectral data were obtained with following spectrometers: JASCO Model A-3 (IR), JASCO Model JNM-MH-100 (100 MHz, ^{1}H NMR) and JEOL Model JMS-OLSG (MS). NMR spectra were recorded with TMS as an internal standard. The temp-dependence of ^{1}H NMR spectra were investigated by the use of a JEOL MH-100 spectrometer equipped with a variable temp prob. The concentration of the samples (**1b-1e**, **2**, **3** and **4**) were adjusted to 3–5% (w/v) in the stated solvents. Refluxing the mixture of 2-pyridone (0.15 mol), isobutyl iodide (0.15 mol) and potassium hydroxide (10 g) in dried ethanol (150 ml) for 2 hr afforded **7** (b.p. 137°/23 mm, 11% yield). **8** and **9** were similarly obtained by the reaction between 2-pyridone and the corresponding alkyl iodides.[13] The yields for **8** and **9** were 32 and 20%, respectively.

1-Ethyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarbonitrile (**1b**) and *3-ethyl-2-oxo-3-azabicyclo*[4.2.0]*oct-4-en-7-carbonitrile* (**4**). A soln of **8** (20 mmol) and acrylonitrile (100 mmol) in 200 ml MeOH was irradiated for 30 hr with a 400W high-pressure mercury lamp. The solvent was removed by the use of a rotating evaporator and the residue was chromatographed on a silicagel column (diethyl ether, acetone). The material obtained from the first fraction was further purified by repeating column chromatography (silica gel, diethyl ether) to give **1b** (oil, 11% yield). The second fraction was treated in the same way to give **4** (oil, 34% yield).

Compound **1b**; IR (film): 2240, 1667–1640 cm^{-1}; NMR ($CDCl_3$): δ5.9 (br.d, 1, 8–H), 5.8–5.7 (m, 3, 5, 6, 7–H), 4.51 (dd, 1, 3–H), 2.94 (br.d, 2, 4–H), 3.89 (sex., 1, α–H'), 3.20 (sex., 1, α-H), 1.08 (t, 3, β–H) ppm, $J_{3,4}$ = 8, $J_{4,5}$ = 3, $J_{\alpha,\alpha'}$ = 14, $J_{\alpha,\beta}$ = 7.0 Hz; MS: *m/e* 176 (M^+, 100%). (Found: C, 67.80; H, 6.93; N, 15.80. Calc. for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90%).

Compound **4**; IR (film): 2240, 1667–1650 cm^{-1}; NMR ($CDCl_3$): δ6.20 (d, 1, 4–H), 5.04 (dd, 1, 5–H), 3.4 (m, 2, 1–H and 6–H), 3.28 (m, 1, 7–H), 2.74 (m, 2, 8–H), 3.50 (q, 2, α–H), 1.15 (t, 3, β–H) ppm, $J_{4,5}$ = 8.0, $J_{5,6}$ = 3, $J_{\alpha,\beta}$ = 7.0 Hz; MS: *m/e* 176 (M^+, 6%). (Found: C, 68.11; H, 6.96; N, 15.86. Calc. for $C_{10}H_{12}N_2O$: C, 68.16; H, 6.86; N, 15.90%).

Methyl 1-ethyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate (**1c**). After irradiation of **8** and methyl acrylate, the same usual work-up as described in **1b** gave **1c** (oil, 6% yield) from the initial fraction of the chromatography. IR (film): 1736, 1650 cm^{-1}; NMR ($CDCl_3$): δ5.88 (br.d, 1, 8–H), 5.8–5.7 (m, 3, 5, 6, 7–H), 4.34 (t, 1, 3–H), 2.84 (br. d, 2, 4–H), 3.90 (sex. 1, α–H'), 3.20 (sex., 1, α–H), 3.67 (s, 3, OCH_3), 1.08 (t, 3, β–H) ppm, $J_{3,4}$ = 8, $J_{\alpha,\alpha'}$ = 14 Hz; MS: 209 (M^+, 100%). (Found: C, 62.86; H, 7.14; N, 6.54. Calc. for $C_{11}H_{15}NO_3$: C, 63.16; H, 7.18; N, 6.70%).

Methyl 1-isopropyl-1,2,3,4-tetrahydro-2-oxo-3-azocinecarboxylate (**1d**). The irradiated soln containing **9** and methyl acrylate was treated in the same manner as the above to obtain **1d** (m.p 98–100°, 1% yield) from the initial fraction of the chromatography. IR (KBr): 1726, 1636 cm^{-1}; NMR ($CDCl_3$): δ5.92–5.7 (m, 4, 5, 6, 7, 8–H), 4.34 (t, 1, 3–H), 2.83 (br.d, 2, 4–H), 4.83 (sev., 1, α–H), 3.69 (s, 3, OCH_3), 1.24 (d, 3, β–H'), 1.05 (d, 3, β–H) ppm, $J_{\alpha,\beta}$ = 7 Hz; MS: *m/e* 213 (M^+, 100%). (Found: C, 64.62; H, 7.81; N, 6.22. Calc. for $C_{12}H_{17}NO_3$: C, 64.56; H, 7.67; N, 6.27%).

Methyl 1-*isobutyl*-1,2,3,4-*tetrahydro*-2-*oxo*-3-*azocine-carboxylate* (**1e**). The irradiated soln containing **7** and methyl acrylate was treated in the same manner as the above to obtain **1e** (oil, 4% yield) from the initial fraction of the chromatography. IR (film): 1740, 1651 cm^{-1}; NMR ($CDCl_3$): δ5.9–5.7 (m, 4, 5, 6, 7, 8–H), 4.40(dd, 1, 3–H), 2.86 (br.d, 2, 4–H), 3.70 (s, 3, OCH_3), 3.84 (dd, 1, α–H'). 2.98 (dd, 1, α–H), 1.80 (m, 1, β–H), 0.88 (d, 3, γ–H'), 0.84 (d, 3, γ–H) ppm, $J_{\alpha,\alpha'}$ = 14, $J_{\alpha,\beta}$ = 7 Hz; MS: *m/e* 237 (M^+, 100%). (Found: C, 66.13; H, 8.00; N, 6.06. Calc. for $C_{13}H_{19}NO_3$: C, 66.10; N, 7.63; N, 5.93%).

Methyl 1-*ethyl*-1,2,3,4,5,6-*hexahydro*-2-*oxo*-3-*azocine-carboxylate* (**2**) and *methyl* 1-*ethyl*-*perhydro*-2-*oxo*-3-*azocinecarboxylate* (**3**). H was introduced to a stirred suspension of **1e** (0.77 mmol) and PtO_2 (25 mg) in 5 ml of *MeOH* at room temp. After recognising the disappearance of **1e** by gc and removal of the catalysis and the solvent stepwise, the residue was chromatographed on silica gel to give **2** (oil, 43% yield) as the initial fraction (diethyl ether) and **3** (m.p 120–124°, 36% yield) as the second fraction (diethyl ether-acetone).

Compound **2**; IR (film): 1748, 1660–1635 cm^{-1}; NMR ($CDCl_3$): δ5.91 (d, 1, 8–H), 5.48 (q, 1, 7–H), 3.75 (dd, 1, 3–H), 2.1–1.4 (m, 6, 4, 5, 6–H), 3.64 (s, 3, OCH_3), 3.89 (m, 1, α–H'), 3.12 (sex., 1, α–H), 1.13 (s, β–H) ppm, $J_{3,4}$ = 4 and 8, $J_{6,7}$ = 8, $J_{7,8}$ = 8, $J_{\alpha,\alpha'}$ = 14, $J_{\alpha,\beta}$ = 7 Hz; MS: *m/e* 211 (M^+, 39%). (Found: C, 62.33; H, 8.05; N, 6.70. Calc. for $C_{11}H_{17}NO_3$: C, 62.54; H, 8.11; N, 6.63%).

Compound **3**; IR (KBr): 1743, 1637 cm^{-1}; NMR ($CDCl_3$): δ3.35 (m, 2, 8–H), 3.75 (t, 1, 3–H), 2.0 (m, 2, 4–H), 1.7–1.5 (br, 6, 5, 6, 7–H), 3.67 (s, 3, OCH_3), 3.70 (m, 1, α–H'), 3.11 (sex., 1, α–H), 1.14 (t, 3, β–H) ppm, $J_{3,4}$ = 7, $J_{\alpha,\alpha'}$ = 14, $J_{\alpha,\beta}$ = 7 Hz; MS: *m/e* 213 (M^+, 13%). (Found: C, 61.78; H, 8.71; N, 6.69. Calc. for $C_{11}H_{19}NO_3$:C, 61.95; H, 8.98; N, 6.57%).

1-*Ethyl*-1,2,3,4-*tetrahydroazocin*-2-*one* (**6**) and 1-*ethyl*-1,2,3,4-*tetrahydro*-2-*oxo*-3-*azocinecarboxylic acid* (**10**). The soln of **1b** (1.1 mmol) in 3 ml EtOH was mixed wth 20% NaOHaq (1 ml). After refluxing for 2 hr the soln was concentrated at reduced pressure and acidified with 6 N HCl. The ppt was collected, washed with water and dried to give acid, **10** (*m.p* 168–170°, 75% yield). **10** (0.5 mmol) was sealed in glass tube and heated for 2 hr at 170°. The residue was chromatographed on silica gel (diethyl ether) to give **6** (oil, 53% yield).

Compound **6**; IR (film): 1660–1630 cm^{-1}; NMR ($CDCl_3$): δ5.95–5.75 (br, 4, 5, 6, 7, 8–H), 3.54 (q, 2, α–H), 2.64 (br, 4, 3, 4–H), 1.08 (t, 3, β–H) ppm, $J_{3,4}$ ≈ 6 and 12 (by Eu(dpm)$_3$), $J_{\alpha,\beta}$ = 7 Hz; MS: *m/e* 151 (M^+, 8%). (Found: C, 71.13; H, 8.65; N, 9.01. Calc. for $C_9H_{13}NO$: C, 71.49; H, 8.67; N, 9.26%).

Compound **10**; IR (KBr): 2800–2400, 1747, 1640–1610 cm^{-1}; NMR ($C_6D_5NO_2$): δ10.1 (br, 1, COOH), 5.9–5.8 (br, 4, 5, 6, 7, 8–H), 4.35 (dd, 1, 3–H), 2.90 (m, 2, 4–H), 3.99 (sex., 1, α–H'), 3.23 (sex., 1, α–H), 1.07 (t, 3, β–H) ppm, $J_{3,4}$ = 6 and 10, $J_{\alpha,\alpha'}$ = 14, $J_{\alpha,\beta}$ = 7 Hz; MS: *m/e* 195 (M^+, 30%). (Found: C, 61.32; H, 6.69; N, 7.10. Calc. for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.17%).

REFERENCES

[1]I. Ueda, K. Somekawa, S. Kumamoto and T. Matsuo, *Acta Cryst.* **B35**, 778 (1979).

[2]L. A. Paquette and L. D. Wise, *J. Am. Chem. Soc.* **87**, 1561 (1965).

[3]H. L. Yale, F. A. Sowinski and E. R. Spitzmiller, *J. Heterocyclic Chem.* **9**, 899 (1972).

[4]R. Crossley, A. P. Downing, M. Nógrádi, A. B. de Oliveira, W. D. Ollis and I. O. Sutherland, *J. Chem. Soc. Perkin I*, 205 (1973).

[5]S. Kumamoto, K. Somekawa and N. Nomiyama, 36*th National Meeting of the Chemical Society of Japan*, Abstr. II, p. 870. Osaka, April (1977).

[6]L. M. Jackman and S. Sternhell, *Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry* p. 88, Pergamon Press, London (1969).

[7]N. Nakagawa, *Analysis of NMR Spectra* p. 45, Kyoritsu Shuppan, Tokyo (1966).

[8]R. C. Weast, *Handbook of Chemistry and Physics* E-66, CRC Press, Cleveland (1976).

[9]A. D. Buckingham, *Canad. J. Chem.* **38**, 300 (1960).

[10a]Y. Kitahara, M. Oda and S. Miyakoshi, *Tetrahedron Letters* 4141 (1975); [b]W. D. Ollis and J. F. Stoddart, *Chem. Commun.* 571 (1973).

$$k = \pi\sqrt{\Delta\nu^2 + 6J^2}/\sqrt{2}, \quad k = RT/Nh \cdot e^{(-\Delta G^{\neq}/RT)}$$

[11]M. Nakamura, M. Oki, H. Nakanishi and O. Yamamoto, *Bull. Chem. Soc. Japan* **47**, 2415 (1974).

[12]H. Nakanishi and O. Yamamoto, *Ibid.* **51**, 1777 (1978).

[13]C. Räth, *Liebigs Ann.* **486**, 71 (1931).