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INTERNAL ROTATION IN CONJUGATED ETHYLENES

DYNAMIC NMR STUDY

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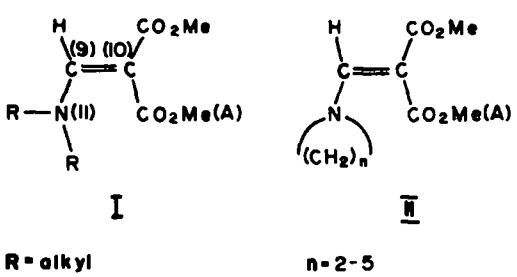
Abstract—The kinetic and activation parameters for the rotation about the C=C double bond and the C–N single bond in the compounds listed in Table 1 were determined by variable temperature NMR spectroscopy. Complete line shape analyses, using a computer REEP program, were carried out on several systems. The main objective of the present study is to determine the effect of the ring size in II on the two types of kinetic processes.

In our preceding publication[1] we presented the results of INDO studies of methyl - 2 - carbomethoxy - 3 - dimethylaminoacrylate and methyl - 2 - carbomethoxy - 3 - (1 - aziridino) - acrylate. The ground state and the transition state for the thermal isomerization about the C=C double bond and the C–N single bond in the above two compounds were calculated. Energies, charge distributions, dipole moments and bond orders were calculated for the minimum energy geometries of the various systems. The above study was performed in conjunction with dynamic NMR analyses of the rates and activation parameters of internal rotation in the above and related compounds. In the preceding report, the calculated barriers were compared with the experimental ones. The latter barriers, among others, were measured in the present work. The structural features which are most important in determining the ground and transition state energies were summarized in the concluding remarks of the preceding publication.[1] With this information at our disposal, we are ready to present and analyze the results of a dynamic NMR study of a series of related compounds.

In our previous studies,[2a–d], as well as in some other studies,[3] the rates of the two kinetic processes and their respective $\Delta G^{\ddagger}$ values in various compounds of the general structure I were determined at the coalescence temperatures of the two CO_2Me and NR_2 signals ($\Delta G_c^{\ddagger}$). Inasmuch as the entropy and enthalpy of activation cannot be determined from $\Delta G_c^{\ddagger}$ at a single temperature obviously such a technique is of limited value and the $\Delta G_c^{\ddagger}$ values at the various temperatures are not strictly comparable without introducing certain assumptions. The availability of all activation parameters for the two processes under consideration is therefore most desirable.[3]



The main objective of the present work is to determine the effect of the N substituents on the rates of rotation about the C=C double bond and the C–N single bond. More specifically, the N atom was incorporated into a ring structure II, and the ring size was varied from n = 2 to n = 5. The relevant rates for several model acyclic compounds of type I were also measured.

RESULTS

Variable temperature NMR spectra were recorded on a Varian HR-100 spectrometer equipped with a variable temperature controller, model V6040. Temperature calibrations were made with ethylene glycol and methanol samples using calibration curves supplied by Varian. The temperatures are believed to be accurate to ±1°. Solutions of 0.5 M conc. in the appropriate solvents were used. The spectrum obtained under the most homogeneous conditions was selected for rate computation.

The rate constants at each temperature were obtained by complete NMR line shape analysis (CLS) using a computer program REEP (Reduction of Error in the Estimation of Parameters), which is designed to solve nonlinear estimation problems. This program is a double precision FORTRAN IV coded routine combining the modified Marquardt method[4] and a gradient search technique[5] together with a projection method of Rosen.[6] By an iterative method it fits a theoretical NMR line to an experimentally observed line in the least square sense, by changing the following parameters: c—coefficient of intensity, τ—reciprocal of the rate constant and $\Delta\upsilon$—the chemical shift difference between the two exchanging sites at zero exchange. All measurements were performed below the coalescence temperature. To this program has been added a subroutine, which computes the standard errors in the parameters, the temperatures being equally weighed. It was found that the program was very good in estimating the parameters for large τ's, the error falling within the limits of 0.5–5%. However, as τ becomes smaller ($<10^{-4}$ sec) the error increases to nearly 100%. Nevertheless, all the rate constants so obtained were used to calculate the enthalpies and entropies of activation by a weighted least square computer program ACTENG[7] from the straight line of $1\,g\,(k/T) = f(1/T)$.

The rate constants k_{298}, $\Delta G_{298}^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for rotation about the C=C bond in compounds (1–7) are presented in Table 1. A CLS analysis was performed on

Table 1. NMR, rate constants and activation data for rotation about the C=C bond

Compd No.	X in X-CH=C(CO$_2$Me)$_2$	k_{298} (sec^{-1})	ΔH^* (kcal/mole)	ΔS^* (e.u.)	$\Delta G^{\ddagger}_{298}$ (kcal/mole)	$\overline{\Delta\nu}^c$ (cps)	Solvent	λ_{max}, (nm) (ϵ) (isooctane)
1		$<5\times10^{-5}$	>19	−13.4[b]	>23.2	6.4	C_4Cl_6	271(12,500)
2		$(5\pm0.3)\times10^{-2}$	15.2±0.5	−13.4±1.4	19.2±0.6	12.0	1-chloro naphthalene	291(14,800)
3		$(8.6\pm0.3)\times10^{-1}$	12.5±0.3	−17.1±0.9	17.5±0.4	5.2	C_6H_5Br	288(22,500)
4		$(1.2\pm0.1)\times10^{-2}$	9.4±0.4	−17.6±1.5	14.6±0.6	7.6	CH_2Cl_2	286(17,100)
5[d]	Me_2N-	16±1	8.3±0.3	−25.2±1.1	15.8±0.4	7.4	CH_2Cl_2	281(18,900)
6[e]	Et_2N-	70±5	7.4±0.8	−25.2[f]	14.3±0.6 (274°)	9.3	CH_2Cl_2	282(18,500)
7[e]	$(iPr)_2N$-	224±18	6.7±0.8	−25.2[f]	12.9±0.4 (246°)	7.3	CH_2Cl_2	283(18,700)

[a]Computed from $\Delta G^* = \Delta H^* - T\Delta S^*$. [b]Assumed to be as in 2. [c]Average values in the temperature range of the measurements. [d]The synthesis and properties of this compound are described in Ref. 2b. [e]The rate and activation parameters were calculated using the basic activation equations and $K_c = \Delta\nu \cdot \pi/\sqrt{2}$. The errors in k_{298}, ΔH^* and $\Delta G^{\ddagger}_c$ were computed using the following errors: ±0.5 Hz ($\Delta\nu$); ±1.5°(T_c); ±3 e.u. (ΔS). The value of −25.2 e.u. was used for ΔS^*. [f]Assumed to be as in 5.

compounds (2–5). For the acyclic analogs (6) and (7) only the rate constants at the coalescence temperatures of the CO_2Me signals ($k_C = \Delta\nu\ \pi/2$) were determined. The values of k_{298} and ΔH^* for these two compounds were evaluated assuming $\Delta S^* = -25.2$ e.u. found for the structurally similar 5. Since the NMR lineshape of 1 did not respond to temperature variations, only the limiting values of the various parameters were evaluated.

The relevant data for the rotation about the C–N bond are presented in Table 2. A CLS analysis was only carried out on the N-dimethylamino derivative (5). In treating the rest of the compounds, the coalescence techniques and calculations were employed. The values of k_{298}, and ΔH^* were evaluated assuming $\Delta S^* = 2.67 \pm 1.48$ e.u., which was found for 5. Since the species under consideration are essentially nonpolar in their transition state,[1] and since ΔS^* is low, we feel justified in applying the above entropy value to the rest of the structurally similar systems, also relying on the fact that it is the same process which is considered throughout the whole series.

DISCUSSION

The structural variations in the series under investigation are only centered around the vinylic N atom. It should be recalled that X-ray crystallographic analysis[8] is available for 5 and theoretical calculations were performed on the ground and transition states for both processes in 1 and 5.[1] For clarity, we shall separately analyze the data for each of the two processes (i.e. C=C and C–N rotations).

Rotation about the C=C double bond

Examination of the rate constants (Table 1) reveals a remarkable change (~10^7 fold) between the extreme ends of the series 1–7. We conclude that this process is highly

Table 2. NMR, Rate constants and activation data for rotation about the C–N bond in CH_2Cl_2 solutions

Compd	k_{298}[a] (sec^{-1})	$\Delta H^{\ddagger}$[a] (kcal/mole)	T_c(°K)	$\Delta G^{\ddagger}_c$[a] (kcal/mole)	$\Delta\nu$[b] (cps)
1	$>6\times10^7$	<7.6	<143	<7.3	10[c]
2	$(1.9\pm0.1)\times10^2$	15.1±0.6	281	14.4±0.2	16.6
3	$(1.8\pm0.1)\times10^2$	15.2±0.6	293	14.4±0.2	48.9
4	$(8.5\pm0.4)\times10^3$	12.9±0.5	247	12.2±0.2	34.4
5[d]	$(2.1\pm0.1)\times10^3$	13.7±0.4		12.9±0.2 (298°)	37.1
6	$(1.5\pm0.1)\times10^3$	13.9±0.5	257	13.2±0.2	13.8
7	$(1.6\pm0.1)\times10^3$	13.9±0.5	250	13.2±0.2	6.9

[a]The rates and activation parameters were calculated using the basic activation equation and $k_c = \Delta\nu \cdot \pi/\sqrt{2}$. The errors in k_{298}, ΔH^* and $\Delta G^{\ddagger}_{298}$ were computed using the following errors: ±0.5 Hz ($\Delta\nu$); ±1.5° (T_c); and ±2 e.u. (ΔS^*). The entropy value of 2.67±1.48 e.u., found for 5 in CLS analysis, was used throughout the rest of the calculations. [b]Chemical shift difference of protons α to N. The α protons were spin-decoupled during kinetic measurements. [c]Assumed for approximation of activation and kinetic parameters. [d]Data from complete line shape analysis.

sensitive to the structure of the amino moiety. Although solvent polarity does affect the rate of the process, care was taken to select solvents of low and similar polarities. Hence, we may compare the kinetic data in different solvents. It should be noted that the b.p. of the solvent and, therefore, the type of solvent which is used in dynamic NMR spectroscopy is dictated by the temperature range in which the dynamic spectral phenomena occur.

All four CLS analyses (compounds 2–5; Table 1) yield substantially large and negative entropy values. Considering the process to be an unimolecular one, this is taken as evidence for extensive charge separation and solvation in the transition state. This was indeed borne out by the calculations, which show electron transfer from N to CO_2Me via the π system in the transition state, and dipole moments of 4.30 and 6.03 D for the ground and transition state of **5** respectively.[1] It would be highly speculative to attribute physical significance to the relatively small changes in the ΔS^* values in Table 1. In the light of the large magnitude of the ΔS^* values, comparison of $\Delta G_C^{\ddagger}$ values where C is the variable NMR coalescence temperature, is meaningless.

The apparent reasons for large changes in ΔH^* in 1–7 (Table 1) is the geometry and size of the N-alkyl group, the only structural variable in the above series. Both X-ray analysis[8] and calculations[1] clearly indicate the nonplanarity of the CO_2CH_3(A) in **5**. The latter method yields a value of 2.35 kcal/mole as the energy gained by the above conformational twist with respect to an all-planar structure. This value is composed of two terms with opposite signs, i.e. the non-bonded interactions (NMe_2----CO_2Me) and the π interaction energy of the CO_2Me (A) group with the rest of the π system. The above non-bonded interaction is estimated at *ca* 3.75 kcal/mole.† This rather high value is not surprising in view of the highly congested nature of the all-planar conformation. Scale models indicate that in such a conformation, provided the N atom is planar (a feature borne out by the X-ray structure of **5**), the distance between the C atom of the N-Me group and the O atom of the ester carbonyl is 1.4 Å, i.e. prohibitively low. The conformation of the CO_2Me (A) group must therefore be quite sensitive to structural variations, and will consequently affect the rate of rotation about the C=C bond. This is clearly reflected by the low ΔH^* and $\Delta G^{\ddagger}_{298}$ values of the diethyl and diisopropyl amino, compounds **6** and **7** (Table 1). The ground state conformation of these two molecules is more energetic than **5**. Similar steric acceleration has been previously noted by us with similar molecules[9] but could not, at that time, be traced to a specific conformational situation.

When proceeding along the series from **5** to **1** (Table 1), two important structural variations are anticipated.

(a) Contraction of the internal C–N–C angle of the rings.

(b) Since the calculations have demonstrated the presence of coplanar ester groups in the ground state of **1**, non-bonded interactions (R_2N----CO_2Me (A)) are gradually relaxed along the series **5–1**, due to the above mentioned contraction.

The interpretation and conclusions from the present data must be treated in conjunction with the results and conclusions presented in the preceding publication.[1] In the sense that the severe electronic requirements in the transition state to rotation about the C=C bond produce structurally similar transition states (starting from various compounds),[1] it is the structural changes in the ground state which give rise to the observed differences in the rates. The two most important energy factors which account for the differences in the rates (Table 1) are:

(a) The magnitude of the energy required to affect planarization of the N atom in the transition state, in order to provide for maximal stabilization, by the overlap of the N lone pair with the empty *p* orbital on C-9, which is generated in this state. Such a change will depend on the geometry of the N atom in the ground state.

(b) The magnitude of the non-bonded interaction energy (R_2N---CO_2Me (A)) liberated in the transition state, where the malonate moiety is coplanar.[1] This of course amounts of steric acceleration (or retardation) due to the particular ground state conformation of the CO_2Me (A) group.

The gradual decrease in ΔH^* in the acyclic series **5–7** reflects, as was mentioned previously, the steric acceleration effect due to increasingly larger non-bonded interactions (NR_2----CO_2Me (A)) in the ground state. The N atom in **6** and **7** is assumed to be planar as was found experimentally in **5**.[8] This is supported by the practically identical UV λ_{max} values of compounds **5–7** (Table 1). Therefore, the barriers in these three compounds are not affected by the configuration of the N atom, which is planar in both the ground and transition states.

The more interesting data concerns the set of cyclic compounds (**1–4**) where most of the rate change occurs. Furthermore, the restricted conformational freedom of the N-substituents, being locked in rings simplified the analysis.

While the experiment[8] has yielded a planar N atom in **5** and the calculations[1] indicate a pyrimidal N atom in **1**, we have no information regarding the configuration of the N-atom in **2–4**. However, an insight into this question may be gained by inspecting the UV spectra of these compounds (Table 1).

The hypsochromic shift of 10 nm between **5** and **1** is indicative of the known change in the configuration of the N atom. The partially pyrimidal geometry of the N atom in **1** diminishes the extent of electron delocalization in this compound. But on proceeding from **5** to **2** a gradual *bathochromic* shift totalling 10 nm was recorded (Table 1). Thus it will be unreasonable to invoke a pyrimidal (and also most probably partial pyrimidal) N atom in **2–4**. Instead, the gradual bathochromic shift is taken as an evidence for relaxation of the non-bonded interaction (NR_2----CO_2Me) due to the gradual ring contraction. Consequently the angle of twist of the CO_2Me (A) group diminishes along the series **5**→**2** allowing for more effective electron delocalization until it reaches zero in **1** where the N atom acquires partial pyrimidal nature (40°).[1] The gradual change in the IR stretching frequency of the C=C bond from 1614 cm^{-1} in **5** to 1558 cm^{-1} in **2** also supports the above structural concept.

It now remains to analyze the NMR kinetic data for the rotational process about the C=C double bond. Such a process must be intimately associated with the above

†This value was arrived at by the summation of 2.35 and 1.4 kcal/mole. The latter is the energy gained by coplanarization of the CO_2CH_3 (A) group in the transition state for C–N rotation in **5** and, therefore, constitutes a reasonable estimate of the $\pi - \pi$ interaction energy of the above group with the π systems.

mentioned ground state structural features. The outstandingly high barrier of 1 (Table 1) is the consequence of two important structural factors. Firstly, the pyrimidal (partial) N atom in 1 acquires a planar geometry in the transition state. Such a configurational change, which is unique for 1, is endothermic, requiring part of the rehybridization energy of aziridine (~20 kcal/mol; Table 3). Secondly the calculations[1] have indicated a substantial difference in the C(9)–C(10) bond orders in 5 and 1 (0.787 and 0.802 respectively). Obviously this must affect the barrier in the observed direction. It is not possible to estimate the relative contribution of these two factors.

We have previously argued on the basis of UV and IR spectra, that the non-bonded interactions (R_2N----CO_2Me (A)) are gradually relaxed (while the N atom is in planar geometry) in the series 5→2. At least part of the observed retardation in rotational rates in the above series (Table 1) is the kinetic consequence of this structural change. The magnitude of the total energy change is $\Delta H^*(5) - \Delta H^*(2) = 6.90$ kcal mol. This is a rather large value. Since the calculations[1] have indicated some decrease in the C(9)–N(11) bond length in the transition state for rotation about the C=C bond, it can be argued that along with the steric retardation effect, increasingly larger bending energy accompanies the transition states upon the decrease in C–N–C angle from 5 to 1.

An attempt to estimate the rate in 1 was made by examining isopropyl 1-carbomethoxy-3-(1-aziridino) acrylate. We planned to measure the rate of isomerization of this system by thermally perturbing the equilibrium between the energetically non-equivalent isomers. Unfortunately, this system exhibits $K_{298} \simeq 1$, which changes very little with temperature.

Rotation about the C–N *bond*

Inspection of the data of Table 2 reveals a striking insensitivity of both the rates and activation parameters toward the structural variations of the N substituents. Excluding compound 1, a rate factor of less than 50 is recorded between 2 and 7. These are the same compounds which produce a rate factor of more than 10^3 in the rotation about the C=C double bond. The CLS analysis of 5 indicates a small positive entropy of activation ($\Delta S^* = 2.67 \pm 1.48$ e.u.) and the calculation yields a transition state less polar than the ground state.[1] Furthermore, as shown by the calculations,[1] the rotational process about the C–N bond is accompanied by two important structural changes.

Table 3. Inversion barriers of amines[10]

Compound	ΔG* (kcal/mol)	T (°K)
	8.2	168
	19.2	333
	7.9	166
$(\emptyset CH_2)_2N$–CH_3	6.5	136

(A) The N atom relaxes to the more stable pyramidal configuration with a gain of 3.4 kcal/mole in the transition state (in 5).

(B) Coplanarization of the twisted CO_2Me group takes place with an energy gain of 1.4 kcal/mole (in 5).

The following energetic factors can be considered to affect the rotation about the C–N bond:

(a) The magnitude of the $p-\pi$ overlap of the N lone pair in the ground state, (this vanishes in the transition state).

(b) The energy associated with the conformation of the CO_2Me (A) group i.e. the magnitude of the non bonded interactions R_2N----CO_2Me (A).

(c) The energy gained by pyramidalization of the N atom in the transition state. Hybridization energies can be used to estimate the magnitude of this effect only in a relative sense, since the calculations indicate that only part of this value is actually being gained, i.e. 3.4 kcal/mole in the case of 5. The hybridization of dimethyl benzylamine, taken as a model system for the acyclic nitrogen compounds, requires 6.5 kcal/mol (Table 3).

It should be recalled that no major changes occur in the electronic charge distribution in the systems during this rotational process.[1] This may explain the general insensitivity of this process towards structural variations, in contrast to the previously described process. Furthermore, the major source of this rotational barrier lies in the magnitude of the $p-\pi$ conjugation of the N lone pair with the rest of the π system in the ground state.

Compounds 5–7 can be considered to have practically the same rotational barriers (Table 2) when analyzed either by the ΔH^* or the ΔG^* values. The amino compounds which correspond to the amino moieties in compounds 5–7 must also have practically equivalent hybridization energies. Furthermore, the $p-\pi$ overlap in the ground state of the above three compounds should be very similar, since the N atoms are planar and the N substituents do not form a geometrically strained configuration. Although the magnitude of the three factors mentioned above may fluctuate, the constancy of the barriers in 5–7 seems to indicate no drastic changes in these effects among the above three compounds. In particular the mild steric acceleration noted in the previously discussed process can not be observed in 5–7 (Table 2).

Compounds 2 and 3 have equivalent but distinctly higher barriers for C–N rotation as compared to the previous group 5–7. The fact that the barriers for these two compounds are the highest in the series 1–7 is somewhat surprising, especially when the very low barrier of 1 is considered (Table 2). However, the kinetic trend for the rotation about the C–N bond upon proceeding from 5 to 1 (Table 2) should be analyzed in terms of the three effects listed above.

(a) From previous argument, the $p-\pi$ *overlap* in the ground state intensifies in proceeding from 4→2. This would contribute toward the *increase* in the barrier. However, as indicated by a change of 20 nm in the λ_{max} values of 2 and 1 (Table 1), the $p-\pi$ overlap in 1 must be perturbed, and consequently should contribute towards decreasing of the rotational barrier in this particular compound.

(b) A gradual relaxation of the *non-bonded interactions* (R_2N----CO_2Me (A)) has been previously argued to occur along the series 5→1 (which was considered to

be responsible for the change in the $p-\pi$ overlap). Such a trend is anticipated to stabilize the conformational ground state along the above series and consequently should contribute toward the *increasing* in the barrier for C–N rotation (steric retardation).

(c) It is well known (Table 3) that the inversion barrier, or *hybridization energies* of the N atom, increases with the decrease in the ring size. Since part of the hybridization energy is gained in the transition state, it follows that the barrier should *decrease* in proceeding to smaller ring compounds, i.e. **5**→**1**.

Actually, the kinetic trend for the series in Table 2 can be rationalized in terms of the sum of the above three energy effects provided a "contribution factor" is assigned to each one of the three effects. However, it is noted that the $p-\pi$ overlap effect can by itself account for the entire kinetic trend under discussion. Alternatively we may conclude that this is the most important structural factor which govern the energetics of the process under consideration. According to the previous argument, it is associated with the conformation of the CO_2Me (A) group which in turn determines the magnitude of the non-bonded interactions, which augments the first effect along the series **5**→**1**. It is concluded that the above two effects outweigh the hybridization energy effect. Although these energies are substantial (Table 3), it should be recalled that only part of them are being gained in the transition state.

Finally, we believe that the current analysis of the rate and activation parameters for the two processes discussed above, which was based on the combination of theoretical calculations and several physical methods, provides a rational basis for analysis of the many other structurally similar systems which were examined by us[2] and others.[3]

EXPERIMENTAL

Methyl 2-carbomethoxy-3-chloroacrylate. The K salt of dimethyl formylmalonate, 198 g (1 mole), prepared from KOMe and dimethyl formylmalonate in MeOH, was suspended in 500 ml CH_2Cl_2. PCl_5 208.5 g (1 mole) was added in small portions with cooling to the above suspension. The mixture was stirred and refluxed for 4 hr, then cooled and filtered. The CH_2Cl_2 was evaporated and the residual yellow oil was distilled, b.p. 109°/20 mm (135 g, 76%). (Invariably the substance was contaminated with HCl), ν_{max} (neat) 3053, 1742, 1725 and 1614 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 3.80 (3H, s), 3.87 (3H, s), 7.50 (1H, s).

Methyl 3-(1-aziridino)-2-carbomethoxyacrylate (**1**). To a soln of methyl 2-carbomethoxy-3-chloroacrylate, 4.35 g (0.025 mole) in dry ether (25 ml), a soln was added, dropwise with stirring, of aziridine 1.18 g (0.0275 mol) and triethylamine 2.77 g (0.027 mol) in dry ether (15 ml). The temp. was kept at 0–5° during the addition. The mixture was allowed to warm to room temp., the solids were filtered, the solvent evaporated and the residue distilled, b.p. 86°/7 × 10^{-3} mm, 1.63 g (35%); UV max (isooctane) 271 nm (ϵ 12,500); ν_{max} (CCl_4) 1720, 1692 and 1608 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 2.22 (4H, s), 3.72 (3H, s), 3.80 (3H, s), and 7.65 (1H, s). (Found: C, 51.70; H, 5.81; N, 7.72. Calc. for $C_8H_{11}NO_4$: C, 51.89; H, 5.99; N, 7.56%).

Methyl 3 - (1 - azetidino) - 2 - carbomethoxyacrylate (**2**). This compound was prepared as described for the synthesis of **1** using the above mentioned molar quantities, solid, cryst. from ether (78%) m.p. 61–62°; UV max (isooctane) 291 (ϵ 14,800), 221 nm (ϵ 5290); ν_{max}(CCl_4) 1703, 1678 and 1588 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 2.42 (2H, qt; J = 8.2 Hz), 3.73 (3H, s), 3.75 (3H, s), 4.29 (4H, t; J = 8.2 Hz) and 7.59 (1H, s). (Found: C, 54.39; H, 6.67; N, 6.92. Calc. for $C_9H_{13}NO_4$: C, 54.26; H, 6.58; N, 7.03%).

Methyl 2 - carbomethoxy - 3 - (1 - pyrrolidino) acrylate (**3**). A soln of methyl 2 - carbomethoxy - 3 - methoxy acrylate,[11] 4.35 g (0.025 mol) and azetidine, 1.59 g (0.0275 mol) in ether (25 ml) was refluxed for 24 hr. The solvent was evaporated and the residue distilled, b.p. 120°/5 × 10^{-5} mm, 2.5 g (50%); UV max (isooctane) 288 (ϵ 22,500), 225 nm (ϵ 5280); ν_{max}(CCl_4) 1695 and 1598 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 1.94 (4H, m), 3.40 (4H, m), 3.68 (3H, s), 3.75 (3H, s) and 7.75 (1H, s). (Found: C, 56.45; H, 7.26; N, 6.74. Calc. for $C_{10}H_{15}NO_4$: C, 56.33; H, 7.09; N, 6.57%).

Methyl 2 - carbomethoxy - 3 - (1 - piperidino) acrylate (**4**). This compound was prepared as described for the synthesis of **3** replacing pyrrolidine with piperidine. Solid was obtained, 82% m.p. 53–54° (ether-pet ether); UV max (isooctane) 286 (ϵ 17,100), 224 nm (ϵ 4100); ν_{max}(CCl_4) 1683 and 1601 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 1.66 (6H, m), 3.29 (4H, m), 3.71 (6H, s), and 7.52 (1H, s). (Found: C, 58.11; H, 7.61; N, 6.35. Calc. for $C_{11}H_{17}NO_4$: C, 58.14; H, 7.54; N, 6.16%).

Methyl 2 - carbomethoxy - 3 - diethylaminoacrylate (**6**). This compound was prepared as described for the synthesis of **3** using diethylamine. Oil was obtained, b.p. 109°/5 × 10^{-5} mm (60%); UV max (isooctane) 282 (ϵ 18,500), 227 nm (ϵ 3620); ν_{max} (CCl_4) 1700 and 1605 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 1.18 (6H, t; J = 7.0 Hz), 3.27 (q, 4H; J = 7.0 Hz), 3.70 (6H, s) and 7.48 (1H, s). (Found: C, 55.86; H, 8.06; N, 6.63. Calc for $C_{10}H_{17}NO_4$: C, 55.80; H, 7.96; N, 6.51%).

Methyl 2 - carbomethoxy - 3 - diisopropylaminoacrylate (**7**). This compound was prepared as described for the synthesis of **3** using diisopropylamine. A solid was obtained, 78% m.p. 92° (Et–Ac-pet ether); UV max (isooctane) 284 (ϵ 18,700), 235 nm (ϵ 3700); ν_{max}(CCl_4) 1715, 1693 and 1593 cm^{-1}; NMR ($CDCl_3$–Me_4Si) δ 1.30 (12H, d; J = 7.0 Hz), 3.72 (2H, sept.; J = 7.0 Hz), 3.77 (6H, s) and 7.63 (1H, s). (Found: C, 59.09; H, 8.53; N, 5.81. Calc. for $C_{12}H_{21}NO_4$: C, 59.24; H, 8.70; N, 5.76%).

Iso - propyl - 3 - (1 - aziridino) - 2 - methoxyacrylate. This compound was prepared (36%) by the method described for the synthesis of **1**, b.p. 92°/3 × 10^{-3} mm. ν_{max}(CCl_4) 1720 and 1605 cm^{-1}; NMR ($CDCl_3$ + Me_4Si), two isomers ~1:1, δ 1.20 and 1.28 (6H, d; J = 7 Hz); 2.17 and 2.20 (4H; multiplet), 3.69 and 3.78 (3H; s), 5.04 (1H; sept.; J = 7 Hz), 7.62 and 7.64 (1H; s).

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