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NMR INVESTIGATION OF ROTATION ABOUT CARBON–CARBON DOUBLE-BOND

KINETIC AND THERMODYNAMIC ASPECTS OF ISOMERIZATION OF CONJUGATED KETENE-MERCAPTOAMINALS

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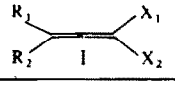
Abstract—The thermal isomerization rates of several conjugated ketene-mercaptoaminals involving rotation about a C=C double bond were found to be within the NMR time scale. Activation energies for the above process were determined from variable temperature NMR studies. The effects of various structural parameters on the energy barrier for isomerization were investigated and the contribution of the vinylic methylthio group to the above barrier was estimated. Internal H-bonding was found to have a pronounced effect on the rates of isomerization. Diastereomeric stabilities in suitably substituted systems were also determined.

INTRODUCTION

IN OLEFINS possessing low energy barriers for thermal isomerization, two types of systems have been investigated. The first constitutes conjugated eneamines such as Ia–Ic (Table 1) and similar compounds where R_2 represents various secondary amines.[1] An activation value for the thermal isomerization around the C=C double

TABLE 1. ACTIVATION ENERGIES FOR ROTATION ABOUT C–C BOND



	X_1	X_2	R_1	R_2	$\Delta G^{\ddagger}$ (kcal/mole)	Ref.
a	CO_2Me	CO_2Me	H	NMe_2	15·6	1
b	CO_2Me	CO_2Me	CH_3	NMe_2	<8·9	3
c	CO_2Me	CO_2Me	H	MeN(*p*-nitrophenyl)	22·1	1
d	CO_2Me	CO_2Me	H	OMe	27·7	2
e	CO_2Me	CO_2Me	t-But	OMe	18·3	2
f	NO_2	H	SMe	SMe	14·8	4
g	CN	CO_2Me	SMe	SMe	24·6	4

bond as low as 8·9 kcal/mole was determined for methyl 3-dimethylamino-2-carbomethoxycrotonate (Ib) from an NMR study. The second type constitutes conjugated enol ethers such as Id and Ie (Table 1) and other compounds where R_1 represents various alkyl groups.[2] The lowest activation value for the above process recorded for this type of compound is 18·3 kcal/mole for Ie, which was also determined by

NMR spectroscopy. Such isomerizations, which are of a degenerate nature in the compounds listed in Table 1, involve rotation about the C=C double bond. The rotational rates for the above-mentioned systems are too high to allow isolation of diastereomers (*cis-trans* isomers) at room temperature in similar non-degenerate exchange processes (excluding compound Id). On the other hand, the rates for this process are within the NMR time scale and thus can be quantitatively determined by a variable temperature NMR study. The energy barriers associated with the rotational process about the C=C bond were found to be very sensitive to various structural parameters. As a part of a more general study in which the relationship between structural parameters and energy barriers for isomerization of olefins is being investigated, it is of interest to examine the effect of a divalent vinylic sulphur on the above barrier. Such an effect can now be properly analysed in the light of our previous kinetic[1-3] and thermodynamic[3] data for the above process in systems such as Ia–Ie and the recently published[4] activation values for If and Ig (Table 1). In order to evaluate the contribution of the methylthio group to the activation energy of the isomerization process, the known conjugated enamines (Ia–Ic) were selected as comparison models. Consequently, it is of interest to examine the energy barriers of systems such as I, where R_1 and R_2 constitute substituted S and N atoms respectively. Comparison of these parameters with those of the above-mentioned models reveal the magnitude of the effect of a vinylic S atom on the energy barrier for isomerization. It is realized that such a comparative evaluation must be limited to the systems under consideration. The magnitude of the contribution of the methylthio group to the energy barrier depends on the nature of the system under consideration (this situation is analogous to the σ-ρ relationship in Hammet's function). Furthermore, the free energy of activation values for the various compounds were determined at different temperatures. In the absence of detailed kinetic studies, comparisons of such values are not strictly legitimate inasmuch as $\Delta G^{\ddagger}$ may depend on temperature. However, as long as the differences in the temperatures are not too large, and the difference in $\Delta G^{\ddagger}$ values are large (*vide infra*), the inaccuracies involved in such comparisons will be minimal.

SYNTHESIS

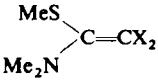
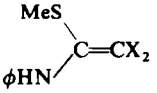
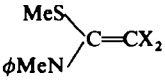
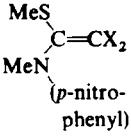
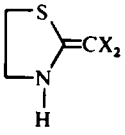
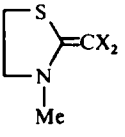
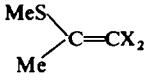
It was initially planned to affect the synthesis of the various ketene-mercaptoaminals, which are required for NMR studies (Tables 1 and 2), by exploiting the following reaction scheme.[5]

$$CS_2 + CH_2XY \xrightarrow[2.\ Me_2SO_4]{1.\ NaOMe} (MeS)_2C{=}CXY \xrightarrow{R_2NH} \begin{matrix} MeS \\ \diagdown \\ R_2N \end{matrix} \!\!>\!\! C = CXY$$

1a: X = CO_2Me; Y = CN
1b: X = Y = CO_2Me

In principle, such a scheme allows variations in X, Y and R in the final product and thus offers a simple route to the desired compounds. In addition to compounds **10**, **11**, and **15** listed in Table 3, which were previously prepared,[5] only **14** could be conveniently synthesized by direct replacement of the methylmercapto group by a secondary amine. Attempts to react N-methylaniline with **1a** under a variety of reaction conditions to obtain **12**, invariably led back to starting materials. It is difficult to

TABLE 2. NMR AND IR DATA

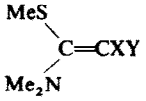
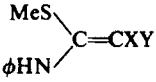
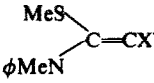
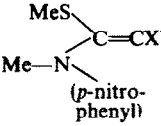
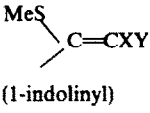
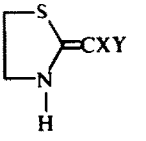
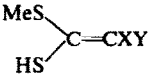
Compd No	Compound (X = CO_2Me)	NMR δ (ppm)[a]				IR ν cm^{-1} (CCl_4)	
		SMe	NMe	OMe	Other signals	C=O	Other bands
2		2·66	—	3·76		1752	
3		2·42	3·25	3·68		1689	1535 (C=C)
4		1·92	—	3·74	7·28 (φ) m* 10·63 (NH)	1731 1670	3165 (NH)
5		2·14	3·34	3·65	7·18 (φ)m*	1721 1702	
6		2·06	3·28	3·65	6·90 (φ) d* 8·13 (φ) d*	1717[b]	
7		—	—	3·95	3·14 (CH_2S) t* 3·90 (CH_2N) t 10·06 (NH)	1714 w* 1670 1633	1536 (C=C) 3150 (NH)
8		—	2·91	3·74	3·08 (CH_2S) t* 3·91 (CH_2N) t*	1719 1692	1542 (C=C)
9		2·40	2·33	3·91	2·33 (C–Me) 3·89	1734 1713	1555 (C=C)

[a] NMR Spectra were recorded on a Varian 100 Mc/s spectrometer, employing solns of 5–10% concentrations in $CDCl_3$ using TMS as internal standard.

[b] Spectrum was recorded in chloroform.

* A doublet (d) of an AB quartet of the aromatic protons (J = 10 c/s). The Ph ring protons were recorded as a multiplet (m); t = triplet; w = weak intensity.

TABLE 3. NMR AND IR DATA

Compd No	Compound (X = CO_2Me; Y = CN)	NMR δ (ppm)[a] SMe	NMe	OMe	Other Signals	IR ν (cm^{-1})(CCl_4) C=O	Other Bands
10		2·62	3·27	3·68		1689	1534 (C=C)
11		2·22	—	3·80	7·37 (φ) m* 11·4 (NH)	1670	2201 (C≡N) 3100 (NH)
12		2·35	3·53	3·76	7·34 (φ) m*	1700	2191 (C≡N)
13		2·29	3·49	3·75	7·11 (φ) d* 8·17 (φ) d*	1714[b]	2192 (C≡N)
14		2·45	—	3·70	3·15 ($CH_2\phi$) t* 4·22 (CH_2N) t* 7·25 (φ) m*	1709	2193 (≡N)
15		--	—	3·73	3·40 (CH_2S) t* 4·03 (CH_2N) t* 9·18 (NH)	1673	1559 (C=C) 2200 (C≡N) 3240 (NH)
16		2·68	—	3·87	9·20 (SH)	1658 1712 (w) 1750 (w)	1533 (C=C) 2250 (SH)

[a] See footnote *a* in Table 2.

[b] The spectrum was recorded in chloroform.

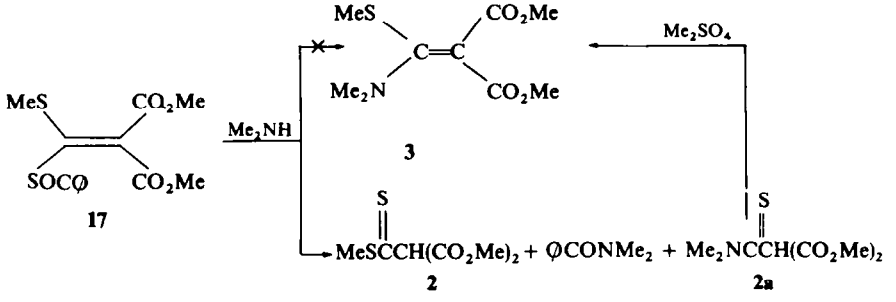
* See corresponding footnotes in Table 2.

rationalize this behaviour in view of the fact that upon refluxing a methonal solution of **1a** and indoline for 1 hr, compound **14** is produced in 77% yield, while **1a** fails to react with N-methylaniline, even in high boiling solvents (i.e. ethylene glycol) or upon heating without a solvent. On the other hand, aniline does react satisfactorily with **1a** to give **11**.

The desired N-methyl derivative (**12**) was subsequently prepared by methylation of **11** in a dimethylsulphate-potassium carbonate system. Since the delocalized anion of **11** has several sites available for methylation, it is important to ascertain the structure of the methylation product. The chemical shift of the newly appearing Me signal (3·53 ppm) in the NMR spectrum of **12** (Table 3) indicates that methylation has occurred on nitrogen.[6] A conceivable *C*-2 methylation product is expected to exhibit a Me resonance line at a higher magnetic field.[6] Furthermore, the CO stretching frequency in the IR spectrum of **12** (Table 3) unambiguously confirms the presence of conjugated ester groups. Besides, the presence of a band at 2191 cm^{-1} (C≡N stretching) in the IR spectrum of **12** (Table 3) rules out methylation of the nitrile N atom.

The N-methyl-*p*-nitro derivative (**13**) was prepared by nitration of **12**. The site of nitration can be readily verified from the AB pattern of the aromatic protons in the NMR spectrum of the product.

While **1a** still possesses partial reactivity towards nucleophilic attack at C-3, **1b** is essentially inert in the presence of amines under a variety of reaction conditions. These results imply that the rate determining step in these reactions is the formation of C-3-to-nitrogen bond, and therefore depends on the charge concentration on C-3. Thus, it would be desirable to construct a substrate with a diminished charge density on this C atom. Compound **17** seems, at first sight to be a reasonable choice. On one



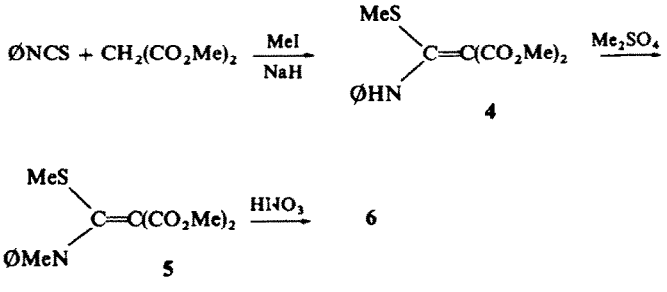
hand, the resonative interaction of the S atom with the benzoyl group increases its capacity to inductively withdraw electrons from C-3; on the other hand, the thiobenzoate anion is also a better leaving group than the methyl mercaptide anion in **1b**. However, compound **17** possesses now an additional electrophilic centre, the newly introduced CO group, which may compete with C-3 for nucleophiles. Unfortunately, the experimental findings indicate that the latter is far more reactive than the former, inasmuch as no trace of **3** could be detected in the products mixture. Analysis of the reaction products reveals the presence of N,N-dimethylbenzamide, methyl 1,1-dicarbomethoxy dithioacetate (**2**) and its dimethylamide derivative (**2a**). The formation of the first two compounds can indeed be rationalized by aminolysis of the thiol benzoate group followed by thioketonization of the resultant enethiol of **17**. However, the formation of the thioamide (**2a**) cannot be accounted for by the reaction of dimethylamine with **17**. Obviously, it must be the product of reaction of dimethylamine with **2**, both of which are present in the reaction mixture.

Compound **2a**, which was obtained as a by-product in the above reaction, was exploited in a synthetic route for the preparation of **3**. It was indeed obtained by the

reaction of **2** with dimethylamine. Compound **2**, however, is now prepared by reacting CS_2 with sodium dimethylmalonate followed by monomethylation. In solution, compound **2** exists exclusively in the thione rather than in the enethiol form: (a) the IR stretching frequency of the esters' CO is at 1752 cm^{-1} (Table 2), thus clearly indicating the lack of unsaturation; (b) a one proton signal at 5·17 ppm in the NMR spectrum of **2** which is unaffected by addition of D_2O and must therefore be assigned to the C-2 hydrogen in the thione form rather than to the SH proton in the enethiol form.* Methylation of **2a**, which also exists exclusively in the thione form (one proton NMR signal at 5·02 ppm assigned to C-2 hydrogen), yields the desired compound **3**. In light of the spectral properties of **3**, it is conluded that methylation has occurred on S rather than on C-2; the two IR bands at 1689 and 1535 cm^{-1} must be related to the stretching frequencies of the conjugated esters and double bond respectively, in agreement with the structure assigned to **3** (Table 2). Furthermore, the chemical shift of the highest field Me signal in the NMR spectrum of **3** is 2·42 ppm (Table 2). This value can not be reconciled with a resonance line of a saturated C-Me in a conceivable C-2 methylated product.[6]

Compound **2** was further utilized as a precursor for the thiazolidine derivatives **7** and **8**. Reaction of **2** with aziridine yields **7**, probably by rearrangement of the primary adduct.[7] The structure of **7** was ascertained from its IR spectrum which exhibits low frequency stretching bands for the ester groups (Table 2), thus indicating the presence of conjugation in this molecule. Furthermore, both its IR and NMR spectra exhibit lines which must be assigned to a N–H group (Table 2).

The series of compounds (**4–6**) was prepared by a different method. Condensation of phenylisothicyanate with sodium dimethylmalonate, followed by addition of

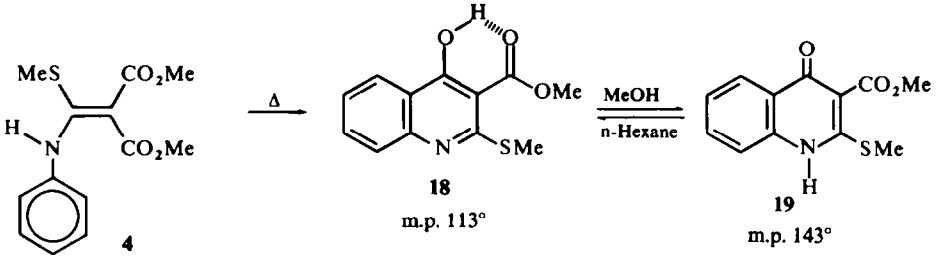


1 mole of methyl iodide, produces **4**. The presence of a low frequency NH stretching band in the IR spectrum of **4** (3165 cm^{-1}) coupled with the low frequency CO stretching band (1670 cm^{-1}) are indicative of intra-molecular H-bonding which in turn supports the structure assigned to **4**. The signal at 1·92 ppm (Table 2) in the NMR spectrum of **4** must be related to the SMe group. It is noted that this signal is shifted by 0·5 ppm with respect to the SMe resonance line in **3**. The significance of this shift will be discussed later. Additional chemical evidence in support of the structure assigned to **4** is its facile thermal cyclization (refluxing in decaline) to produce 2-methylthio-3-carbomethoxy-4-hydroxyquinoline (**18**). Stable enol **18** and keto **19**

* This is in contrast with the spectral properties of **16** (Table 3) which clearly demonstrate the predominance of the enethiol in solution.

forms of this compound could be isolated by selecting the proper solvent of crystallization.*

Methylation of **4** yields **5** and nitration of **5** produces **6** (Table 2). That methylation occurs on nitrogen could again be ascertained from the chemical shift of the newly appearing NMR signal—3·34 ppm. (Table 2). The site of nitration was deduced from the AB quartet of the aromatic protons in the NMR spectrum of **6**.



4 **18** m.p. 113° **19** m.p. 143°

KINETIC STUDIES

The mode of response of activation energies for rotation about a C=C bond to various structural parameters can be reconciled with a strongly polar transition state.[1–4] A positive charge is developed at C-3 and a negative charge at C-2 in the transition state for rotation. Such a transition state has the geometry where the two sp^2 C atoms and their substituents occupy orthogonal planes. The above conformation must be realized during the rotational process about the C=C bond and most probably corresponds to a state of maximum energy. The energy of such a polar transition state should be sensitive to structural variations. Thus, by changing the substituents on C-3 (S, O, N) a variable degree of stabilization of the positive charge in the transition state is anticipated. The σ_R values of the above substituted heteroatoms[9b,c] reflect their capacity of resonative interaction with the adjacent electron deprived centre (in the transition state) in a manner analogous to substituent effects on rates of electrophilic substitution reactions.[9b] A comparison of activation parameters with σ_R is presented in Table 5. Even though no quantiative relationship between the two is possible without additional kinetic data, it can be readily seen that the $\Delta G^{\ddagger}$ values are proportional to σ_R values of the vinylic substituent X. Consequently, the isomerization rate of methyl 3-methylmercapto-2-carbomethoxycrotonate (**9**) is too slow in comparison to NMR time scale. The two carbomethoxy

* The structure of the above two tautomeric forms were identified by their IR spectra in the solid phase. For the enol form, m.p. 113°, ν_{max}^{KBr} 1650 (H-bonded ester), 1614 cm^{-1} (double bond); for the keto form m.p. 143°; ν_{max}^{KBr} 1723 (conjugated ester), 1677 (conjugated ketone), 1610 cm^{-1} (double bond). In chloroform the enol form predominates, since the highest frequency CO stretching bond is at 1650 cm^{-1}. Stable keto and enol forms of such heterocyclic systems are rare. However, just recently this phenomenon was discovered in several analogous systems.[8] In fact the very same compound, among others, was prepared,[8] but the authors claim that only the quinolol form is stable in the solid state and report a m.p. of 98–100° for a product crystallized from light petroleum. They failed to obtain the quinolone form, when crystallization from methanol was attempted. In our hands the crystallization of the quinalol form from methanol yields the quinolone form, m.p. 143°.

signals did not coalesce at 200°, and a lower limit of activation was calculated (27·5 kcal/mole), taking Tc = 200° (Table 4).*

The activation data for the mercaptoaminals of Tables 2 and 3 are presented in Table 4. The NMR spectrum of 3 exhibits a singlet for the two carbomethoxy groups

TABLE 4. NMR AND ACTIVATION DATA[a]

Compd. No.	Signal Observed	Δν (c/s)	Tc (°C)	ΔG‡ (kcal/mole)[b]	Solvent
3	OMe	0	< −100	<9·4[c]	$(CD_3)_2CO$
					$C_6H_5CH_3$
					CH_2Cl_2
	NMe_2	27·4	−81·5	8·9	$(CD_3)_2CO$
4	OMe	7·2	−44·5	12·0	CH_2Cl_2
5	OMe	0	< −100	<8·5[d]	$(CD_3)_2CO$
6	OMe	26·2	−72·0	9·9	$(CD_3)_2CO$
7	OMe	1·8	123	22·3	$C_6H_5CH_3$
8	OMe	0	< −100	<9·4[c]	$(CD_3)_2CO$
					$C_6H_5CH_3$
					CH_2Cl_2
9	OMe	3·4	160		C_6H_5Br
	OMe	0·8	>200	>27·5[e]	C_2Cl_6
10	NMe_2	11·8	−59	11·0	CH_2Cl_2
13	SMe	8·4	−22·0	13·2	CH_2Cl_2

[a] Spectra were recorded on a Varian 100 Mc/s spectrometer with a variable temp probe. The chemical shift separations (Δν) are averages of at least three tracings and are accurate to 0·2 c/s. The temperature is accurate to 2°.

[b] The ΔG‡ values were calculated from Eyring activation function taking the transmission coefficient as unity. The rates at Tc were calculated from the Gutomsky–Holm equation.[12]

[c] This value was calculated using Tc = −100° and Δν = 1·8 c/s as in the aliphatic di-ester compound 7.

[d] This value was calculated using Tc = 100° and Δν = 26·2 c/s as in the aromatic di-ester compound 6.

[e] This value was calculated using Tc = 200°.

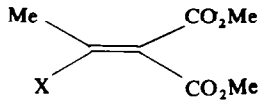
down to −95° (Table 4). This cannot be attributed to accidentally identical chemical shift of the two signals, since the spectrum was examined in a variety of solvents. It must therefore be concluded that the rotational rate about the C=C bond in 3 is high and out of the NMR time scale. An upper limit of ca 9 kcal/mole can be assigned to the rotational barrier (footnote *c* in Table 4). It is noted that the replacement of the vinylic hydrogen in Ia (Table 1) by either a Me group to give Ib (Table 1) or by a methylmercapto group to give 3 (Table 2) depresses the energy barrier below 8·9 and 9·4 kcal/mole respectively, and the finite values could not be measured by NMR. It follows that IIb and 3 must have similar activation values which is in accord with

* It has been found that the chemical shifts of the two carbomethoxy signals are strongly temperature dependent, but each to a different extent. Consequently, in C_2Cl_6 a temperature is reached where an apparent coalescence is observed, but further heating results in re-separation of the two sharp peaks. In fact, the differential chemical shift at high temperature is greater than at room temperature. Such behaviour may be ascribed to solvent–solute interactions.

the practically identical σ_R values of the two substituents ($\sigma_R^{Me} = -0{\cdot}13$; $\sigma_R^{SMe} = -0{\cdot}14$).[9b,c]

In the previously studied conjugated enamines, the replacement of a Me by Ph group on the N atom is accompanied by an increase of ca 3·8 kcal/mole in the activation energy for rotation about the C=C bond.[1,3] Accordingly, compound **5** was examined by NMR (Table 4). The two carbomethoxy groups again exhibit a singlet both at room temperature and down to −100° in a variety of solvents. This again must

TABLE 5. COMPARISON OF σ_R VALUES WITH ACTIVATION PARAMETERS

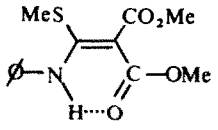


X	$\Delta G^{\ddagger}$ (kcal/mole)	σ_R^X
NMe_2	<8·9	−0·93
OMe	25·7	−0·52
SMe	>27·5	−0·14

indicate that even in this compound the rotational rate about the C=C bond is not within the NMR time scale and an upper limit of 8·5 kcal/mole can be assigned to the energy barrier (footnote *d* in Table 4). Since a measureable energy value is desired, the height of the barrier can be further increased by substituting the *para* position of the Ph group in **5** by a nitro group to give **6** (Table 2). From previous results such a substitution is accompanied by an increase of ca 2·7 kcal/mole in the barrier for rotation about the double bond.[1,3] Indeed, the $\Delta G^{\ddagger}$ value of **6** (9·9 kcal/mole) is now measurable by NMR as much as separation of the two carbomethoxy signals was observed below −72° (Table 4).* Given this value, and the previously mentioned contribution of the *p*-nitro group to $\Delta G^{\ddagger}$, the activation value of **5** can be estimated at 9·9–2·7 = 7·2 kcal/mole. In a similar way, knowing the contributions of N-Ph group to $\Delta G^{\ddagger}$, the activation value of **3** can be estimated at 7·2–3·8 = 3·4 kcal/mole. Inasmuch as the above two values are only of approximate nature, the corresponding rotational rates are definitely not within NMR time scale of measurement as indeed they could not be detected experimentally. Furthermore, the second value represents a strikingly low energy barrier for rotation about a C=C bond, and approaches the barrier for rotation about a σ bond in saturated compounds. The net contribution of the SMe group to the rotational barrier in the conjugated enamine systems under consideration can now be evaluated. The difference between the measurable activation parameters of Ic (Table 1) and **6** (Table 4) gives $\Delta G_{Ic}^{\ddagger} - \Delta G_{6}^{\ddagger} = 22{\cdot}1 - 9{\cdot}9 = 12{\cdot}2$ kcal/mole. In the light of the previous discussion and in the absence of additional data this value must be considered only as an approximation, albeit a useful one for estimation of energy barriers.

* The differential chemical shift of 26·2 c/s of the two carbomethoxy signals of **6** rules out an accidentally identical chemical shift of the corresponding signals in **5**.

Of the various mercaptoaminals listed in Table 4, compounds **4** and **7** deserve special consideration, since they reveal a unique phenomenon. It can be readily seen that their $\Delta G^{\ddagger}$ values (12·0 and 22·3 kcal/mole) are not in line with the rest of the series and are inconsistent with previous considerations. Indeed, these compounds differ structurally from the rest of the entries in Table 3 by possessing a secondary rather than a tertiary N atom. When the energy parameters of the above two compounds are compared with those of their N-Me analogues (**5** and **8**) it is apparent that the replacement of a Me by H on the N atom is accompanied by a substantial increase in $\Delta G^{\ddagger}$ values. In fact, the rotational rates of **5** and **8** are too high for NMR determination and only upper limits (ca. 9 kcal/mole) were assigned to the energy barriers (Table 4). Thus, the replacement of Me by H can be estimated as $\Delta G_4^{\ddagger} - \Delta G_5^{\ddagger} = 12{\cdot}0 - (<9) = >3$ kcal/mole, and $\Delta G_7^{\ddagger} - \Delta G_8^{\ddagger} = 22{\cdot}3 - (<9) = >13{\cdot}3$ kcal/mole. These pronounced differences certainly can not be attributed to electronic factors accompanying the replacement of a Me by H. We suggest that intra-molecular H-bonding is the factor responsible for the observed increments in the activation values. That such H-bonding, as depicted in the structure formulas **4** and **7**, is really operative, can be verified from the IR spectra in CCl_4 (Table 2). The NH stretching bands for **4** and **7**



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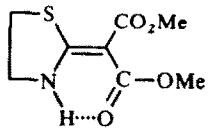


7

are found at frequencies of 3165 and 3150 cm^{-1} respectively, and their intensities are independent of concentration. These bands must therefore be assigned to the stretching of intramolecular H-bonded NH; no other NH stretching bands could be observed. Huisgen *et al.*[10] have noted that in *cis*-methyl 3-cyclohexylaminoacrylate the internally bonded NH absorbs IR light at 3312 cm^{-1} (CCl_4). The corresponding frequencies found for **4** and **7** are much lower than the above value and must indicate better bonding. The low frequency CO stretching bands of these compounds* also support the bonded structures depicted in **4** and **7** (Table 2). The increments in the activation values of the above two compounds with respect to their N-Me derivative represent the extra energy required to dissociate the intra-molecular H-bond.† This is true, provided that the esters interchange phenomenon which is observed by NMR is a consequence of rotation about the C=C bond. An alternative isomerization

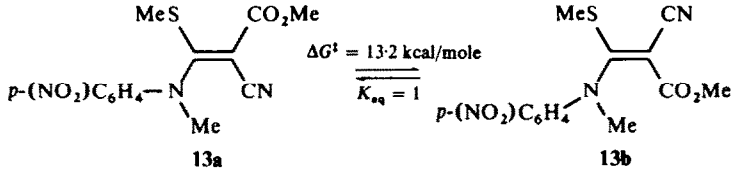
* Both **4** and **7** exhibit in their IR spectra a band at 1670 cm^{-1} (Table 2). Such a low frequency must be assigned to the stretching of the bonded crabonyls. However, the spectrum of **7** contains an additional low frequency intense line at 1633 cm^{-1} for which no definite assignment can be made at the present time. The C=C stretching bands of all the entries in Tables 2 and 3 are found in a narrow range of 1535–1559 cm^{-1} and are of intensities comparable to the CO bands (no assignments of this band were made for compounds containing a Ph group). Therefore, the unidentified line of **7** cannot be assigned to the C=C stretching mode for which an intense band at 1536 cm^{-1}, within the above-mentioned spectral range, was recorded. Furthermore, it cannot be related to NH bending mode which was assigned to a shoulder of medium intensity at 1523 cm^{-1}. This was verified[11] by deuteration of **7** which results in the disappearance of the above band and appearance of a new one at 1501 cm^{-1}, which must therefore be assigned to the N—D bending mode. The N—D stretching band was observed at 2385 cm^{-1}.

† In such an evaluation, changes in steric factors must also be considered.

route would constitute a prototropic shift from N to C-2. However, this amounts to an exchange process involving two isomers rather than two identical species, and is incompatable with the observed coalescence of two equal intensity lines in the NMR spectra of **4** and **7**. Since the activation values of **5** and **8**—the N-Me derivatives of **4** and **7**—could not be measured by NMR, it is impossible at present to quantitatively evaluate the H-bond energy (the various aspects of this phenomenon are being currently investigated).

From other investigations,[3] it has been established that the replacement of one ester group by a nitrile in several conjugated enamines such as Ia–Ic is accompanied by an increase in the energy for rotation about the C=C bond. This behaviour may be accounted for by the fact that σ_R of an ester[9a] (0·20) is larger than that of a nitrile[9a] (0·07). Consequently, an ester group can more effectively stabilize the adjacent negative charge in the transition state of rotation than a nitrile group. It is noted that the relationship between the total σ values[9a] ($\sigma_R + \sigma_I$) of the above two groups is inversed, namely σ (CN) > σ (CO_2Me). The above-mentioned behaviour of the activation parameters, in light of the electronic properties of the above two groups, strongly suggests that the magnitude of $\Delta G^{\ddagger}$ for rotation about the C=C bond is determined predominately by the energy level of the charged transition state rather than the ground state of the molecule. A series of 2-carbomethoxy-3-methylmercapto acrylonitrile derivatives, with variable substitution on C-3 (Table 3), were examined by NMR. It must be noted that while the rotational barriers of the di-esters of Table 2 are associated with identical species, those of the acrylonitrile compounds of Table 3 involve two diastereomers, which of course differ in their ground state energy. Therefore, the observation of only one signal in the NMR spectra of the latter class of compounds may, in principle, result from either one of the following situations: (a) Rotational rates are high and out of NMR time scale; (b) rotational rates are within the NMR time scale, but the difference in the diastereomeric stability precludes the detection of the less stable isomer due to its small population. It is estimated that the sensitivity limit of NMR measurement is at about 1% concentration. Thus, when $K_{eq} \leqslant 10^{-2}$, which results in free energy difference of 2·7 kcal/mole (at 25°) between the two exchanging diastereomers, only one signal would be observed by NMR; (c) the molecule is rigid and does not undergo the rotational process about the C=C bond. The thermodynamically controlled reaction yields only one isomer which is observed by NMR.

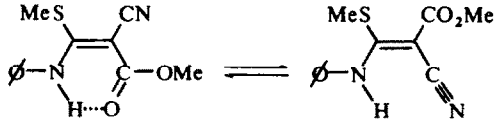
Situation (c) can be ruled out in view of the very low rotational barriers which were encountered with the diesters in Table 2, and on the basis of the anticipated results. We are, therefore, left with (a) and (b) or combination of these two situations. Of all the compounds listed in Table 3, only the NMR spectrum of the *p*-nitrophenyl derivative (**13**) exhibits doubling of all signals upon cooling. Inasmuch as all pairs of signals are of equal intensity, the ground state free energies of the two exchanging diastereomers (**13a**) and (**13b**) are identical. The activation energy for this exchange was found to be 13·2 kcal/mole (Table 4), and was calculated from the exchange rate at Tc; the latter was determined using Gutowsky–Holm relationship,[12] since the exchanging species are equally populated. Consideration of the magnitude of the above energy barrier, when related to a *p*-nitrophenyl derivative, readily indicates that the rotational barriers of all mercaptoaminals in Table 3 must be lower than 13·2 kcal/mole. Thus, regardless of the free energy difference between the two ex-



13a **13b**

changing diastereomers of **10** (Table 3), the rotational rates about the C=C bond must certainly be too high for NMR measurement. This follows from the previous finding[1] that replacement of a Me by *p*-nitrophenyl group on the N atom is accompanied by an increase of ca. 6·5 kcal/mole, yielding an estimated $\Delta G^{\ddagger}$ value of 13·2–6·5 = 6·7 kcal/mole for **10**. Similarly, using the previous value of 3·8 kcal/mole for the replacement of a Me by Ph group on the N atom,[1] the activation energy of **12** is estimated at 13·2–3·8 = 9·4 kcal/mole, just on the limit for NMR determination. The free energy difference between the two exchanging diastereomers of **12** is very probably identical with that of **13**, since the *p*-nitro group is expected to affect the rates but not the relative stability of the exchanging species. Thus the observation of only one set of signals in the NMR spectrum of **12** at low temperature must be the consequence of high rotational rates rather than a large difference in the diastereomeric stability of the two configurations.

The NMR spectra of **11** and **15** exhibit singlets for all the groups even at −100°. These compounds possess a secondary rather than tertiary N atom, and from IR studies it is concluded that as in the corresponding di-esters (**4** and **7**) the NH in **11** and **15** is also internally bonded. Thus, the low frequencies of both NH and C=O stretching bands in the IR spectra of these two compounds (Table 3) support such H-bonded species (the intensity of the NH band was independent of concentration). These results can be reconciled only with the configuration depicted in **11a** as the exclusively predominating specie, since the linear nitrile group in **11b** is not in the



11a **11b**

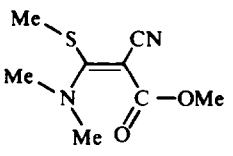
appropriate geometrical disposition for internal H-bonding. It must be realized that should both configurations be significantly populated, their simultaneous detection by IR would be possible due to significant differences in their spectral properties. Specifically, the two carbonyls in **11a** and **11b** are expected to absorb IR light of different frequencies. Thus as has already been noted, the di-ester (**4**) exhibits two C=O stretching bands at 1670 and 1731 cm^{-1} (Table 2). The former band, which must be assigned to the H-bonded CO, is at identical frequency as the corresponding band in **11** (Table 3). The 1731 cm^{-1} band, which necessarily must be assigned to the non-bonded CO, is appropriately missing in the IR spectrum of **11**. In conclusion, regardless of the energy required for the interconversion **11a** ⇌ **11b**, the concentration of the latter is beyond the sensitivity limit of NMR measurement. The isomer (**11a**) owes its stability over **11b** to the internal H-bond. Thus, while in the di-esters (**4** and **7**) the internal H-bond affects the kinetics of these systems, in compound **11** only its thermodynamic consequences are observed. The above considerations are also true of com-

pound **15**. It must be realized, however, that even though only one isomer of **11** and **15** was detected by NMR and IR spectra, they must be in a dynamic equilibrium with the corresponding undetected isomers. The rotational rates for the above two compounds are most probably within the NMR time scale, as has been found for **4** and **7**.

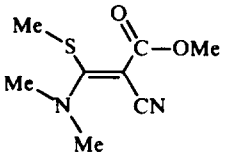
Finally, the data already presented allows us to analyze some kinetic and thermodynamic aspects of the rotation process about the nitrogen-to-sp^2 C bond (nitrogen rotation). This process is analogous to rotation about amide bond, and in the minimum energy conformation the molecule most probably assumes an essentially all planar geometry. In such a conformation the disposition of the nitrogen lone pair with respect to the adjacent π system allows maximum electron delocalization. When, during the nitrogen rotational process, the C=C π system and the nitrogen p orbital reach orthogonality, electron delocalization is minimal and therefore such a conformation may be regarded as the transition state for the above mentioned process.

From all the ketene-mercaptoaminals which were investigated, only compounds **3** and **10** (Tables 2 and 3) exhibit signals multiplicity which is attributed to the nitrogen rotational process. Thus upon cooling, the singlets of the NMe_2 group, which were observed in the NMR spectra of **3** and **10**, split into equal intensity doublets. It is of interest to consider the structural implications of the $\Delta G^{\ddagger}$ relationship between **3** and **10** (8·9 and 11 kcal/mole respectively, Table 2).

It is apparent that the replacement of CO_2Me by CN results in an increase of 2·1 kcal/mole in the free energy of activation for the nitrogen rotational process. This change in energy could be accounted for by variation in steric interactions which accompany the above structural modification. Thus, the replacement of the trigonal CO_2Me group by the linear CN relieves steric interactions with the NMe_2 group in the



10a



10b

planar ground state, which operates to increase the energy barrier under consideration. However, such a situation requires that configuration **10b** will be significantly populated. It has already been stated that the exchange process **10a** $\rightleftharpoons$ **10b** is too fast for NMR measurement. From chemical shifts considerations it can be argued that **10a** is the predominating configuration in equilibrium with **10b**. Thus, inspection of the chemical shift data for compounds **3** and **10** in Tables 2 and 3 respectively reveals that the replacement of CO_2Me by CN virtually does not affect the chemical shift of the NMe_2 signal (0·02 ppm shielding), but significant de-shielding (0·2 ppm) of the SMe signal is noted. An analogous deshielding of the SMe group is also observed with the pair **4** and **11** (Tables 2, 3) where it has been rigorously established that the exclusively predominating configuration of **11** is the H-bonded **11a**. It follows that **10a** predominates in the equilibrium system **10a** $\rightleftharpoons$ **10b**. Thus the steric argument which has been suggested in order to account for the $\Delta G^{\ddagger}$ relationship between **3** and **10** (nitrogen rotation), which requires predominance of configuration **10b**, can no longer be invoked. It must be concluded that the entire difference in the activation energy for the nitrogen rotation between **3** and **10** is due to electronic effects associated

with the above structural modification. As has already been stated, previous investigation[3] revealed pronounced increments in $\Delta G^{\ddagger}$ values for rotation about the C=C bond upon replacement of CO_2Me by CN. In fact, this has also been confirmed in the present investigation as can be readily verified by comparing the energy parameters of compounds **6** and **13** (Table 4). This phenomenon was interpreted on the basis of a heteropolar transition state for rotation about the C=C bond which is resonatively stabilized to a larger extent by a CO_2Me (σ_R = 0·20) than by a CN group (σ_R = 0·07).[9a] In variance with the above process, the nitrogen rotation does not in any stage involve charge separation. Consequently, a resonative mechanism of stabilization does not play a prominent role inasmuch as both the ground and transition states for nitrogen rotation are essentially neutral. The activation energy for this process (less steric energy term) can be considered as the resonance energy of the nitrogen *p* electrons with the rest of the π system. It is maximum in the essentially planar ground state and zero in the orthogonal transition state. It follows that the difference between $\Delta G^{\ddagger}$ values (nitrogen rotation) of **3** and **10** reflects changes in resonance energy in the ground state of these molecules. Consequently, the replacement of CO_2Me by CN augments electron delocalization. Necessarily, such an effect must operate mainly by an inductive mechanism since $\sigma_I(CN) > \sigma_I(CO_2Me)$.[9a] This is in agreement with the experimental results which require greater electron delocalization in **10** ($\Delta G^{\ddagger}$ = 11·0 kcal/mole) than in **3** ($\Delta G^{\ddagger}$ = 8·9 kcal/mole). It should be noted that the predominance of a resonative mechanism in the ground state of these two molecules would lead to the opposite relationship between the activation energies of these two compounds, since $\sigma_R(CN) < \sigma_R(CO_2Me)$.[9a]

Apart from compounds **3** and **10**, in all other mercaptoaminals the N atom is nonsymmetrically substituted. Therefore, the nitrogen rotational process results in the exchange of two diastereomeric conformations. Consequently, the detection of separate signals from the individual conformers is conditioned by both the magnitude of the rotational rates and the free energy difference between the two exchanging species. For all of these compounds, no separate NMR signals from the individual conformers, which result from nitrogen rotation, could be observed at low temperature. The most stable conformation of these systems can be identified from chemical shifts considerations. In proceeding from **3** to **4** (Table 2) and from **10** to **11** (Table 3), the SMe signals are being shifted upfield by 0·5 and and 0·4 ppm respectively. It has already been demonstrated that the most stable conformations of **4** and **11** are H-bonded as depicted in structures **4** and **11a**. Since all the spectral data indicate their exclusive predominance in solution, it necessarily follows that the Ph ring in these two compounds is in a s-*trans* disposition with respect to the double bond. The pronounced shift of the SMe group must therefore result from its proximity to the Ph ring. Furthermore, the direction of the shift (shielding) implies that the SMe group is being subjected to the diamagnetic field of the Ph ring. This in turn requires that the Ph ring plan be twisted with respect to the plan of the double bond and its substituents (model consideration indeed indicates considerable congestion in an all planar conformation). Such large effects experienced by the SMe groups and manifested by the pronounced upfield shifts of their NMR signals cannot be inticipated from a remote s-*cis* Ph group. A conceivable s-*cis* conformation would rather affect the chemical shift of the *cis* CO_2Me group[3] which is found however to differ only by 0·06 ppm in proceeding from **3** to **4**. It follows therefore that the SMe group can serve as a probe for the con-

formational preference with respect to the nitrogen rotation. Indeed, it can readily be seen that the SMe signals of **5** and **6** are also shielded with respect to **3** (Table 2), and furthermore those of **12** and **13** are shielded with respect to **10** (Table 3). It may therefore be concluded that regardless of the rate of rotation about the nitrogen-to-sp^2 carbon bond in the above mentioned set of compounds, the predominating conformations must be those in which the Ph ring is in an s-*trans* disposition with respect to the double bond.

EXPERIMENTAL

All m.p.s were determined on a Fisher–Johns apparatus and are uncorrected. UV spectra were measured with a Cary recording spectrometer Model 14.

Methyl 1,1-*dicarbomethoxy-dithioacetate* (**2**). This compound was prepared according to the procedure given by Gompper and Töpel[5a] using dimethyl malonate, with the following modification: after dilution of the reaction mixture with water, the soln was washed with ether, acidified with HCl, and the separated oil was extracted with ether. Removal of the ether left an unstable red-yellow oil (ca. 74%), that although containing a small amount of dimethyl malonate was pure enough for further reactions. An analytical sample was obtained by a low-pressure distillation, b.p. 124°/0·01 mm. (Found: C, 38·01; H, 4·54; S, 28·72; $C_7H_{10}O_4S$ requires: C, 37·82; H, 4·52; S, 28·85%); λ_{max}^{MeOH} 315 (5700), 334 (7900) mμ(ε).

1,1-*Dicarbomethoxy*-N,N-*dimethylthioacetamide* (**2a**). Dimethylamine (excess) in MeOH was added to a soln of **2** (2·22 g, 0·01 mole) in MeOH (15 ml), and the reaction mixture was refluxed for 5 hr. Removal of the methanol and excess of dimethylamine left 1·23 g (56%) of product, m.p. 119° after recrystallization from MeOH. (Found: C, 44·02; H, 5·98; N, 6·31; $C_8H_{13}NO_4S$ requires: C, 43·83; H, 5·98; N, 6·39%).

Methyl 3-*dimethylamino*-3-*methylmercapto*-2-*carbomethoxyacrylate* (**3**). Me_2SO_4 (1·89 g, 0·015 mole) was added to a stirred soln of **2a** (3·3 g, 0·015 mole) in dry acetone (40 ml), containing K_2CO_3 (2·07 g, 0·015 mole), and the mixture was refluxed for 6 hr. Removal of the carbonate and the acetone left an oil which was distilled at low-press, b.p. 115°/0·1 mm. The product, 2·1 g (60%) solidified after distillation m.p. 75°. (Found: C, 46·29; H, 6·67; N, 5·80; $C_9H_{15}NO_4S$ requires: C, 46·35; H, 6·48; N, 6·10%); λ_{max}^{MeOH} 247 (16,600) 338 (7000) mμ (ε).

Methyl 3-*anilino*-3-*methylmercapto*-2-*carbomethoxyacrylate* (**4**). NaH (0·1 mole, 4·8 g of 50% oil dispersion) was added to a stirred soln of dimethyl malonate (13·2 g, 0·1 mole) in dimethylacetamide (90 ml). The soln was cooled to 0°, and phenylisothiocyanate (13·5 g, 0·1 mole) was added dropwise. Stirring was continued for 1·5 hr at room temp, and then the soln was cooled again to 0°, and MeI (14·5 g, 0·1 mole) was added dropwise. After stirring for 4 hr at room temp, ether and water were added, the layers separated, and the ethereal layer was washed with water and dried over $MgSO_4$. Removal of the ether left an oil, 22·2 g (79%) which solidified upon addition of light petroleum and cooling, m.p. 65° after recrystallization from light petroleum. (Found: C, 55·71; H, 5·20; N, 4·96; $C_{13}H_{15}NO_4S$ requires: C, 55·51; H, 5·38; N, 4·98%); λ_{max}^{MeOH} 316 (14,500) mμ (ε).

Methyl 3-(N-*methylanilino*)-3-*methylmercapto*-2-*carbomethoxyacrylate* (**5**). Me_2SO_4 (2·52 g, 0·02 mole) was added to a stirred soln of **4** (5·6 g, 0·02 mole) in dry acetone (30 ml) containing K_2CO_3 (5·5 g, 0·04 mole), and the mixture was refluxed for 20 hr. Removal of the carbonate and the acetone left an oil which solidified upon addition of light petroleum, yielding 5·8 g (98%) of product, m.p. 84° after recrystallization from $CHCl_3$ light petroleum. (Found: C, 57·22; H, 5·90; N, 4·52; $C_{14}H_{17}NO_4S$ requires: C, 56·94; H, 5·80; N, 4·74%); λ_{max}^{MeOH} 238 (9700), 294 (7600), 339 (8900) mμ (ε).

Methyl 3-(N-*methyl*-p-*nitroanilino*)-3-*methylmercapto*-2-*carbomethoxyacrylate* (**6**). HNO_3 (0·82 g, *d*·1·5, 0·013 mole) in AcOH (10 ml) was added dropwise at room temp to a soln of **5** (2·95 g, 0·01 mole) in AcOH (40 ml). After stirring for 24 hr at room temp, the soln was poured into ice-cold water, ether was added, the layers were separated and the ethereal layer was washed with water and dried over $MgSO_4$. Removal of the ether, and addition of MeOH yielded 1·2 g (38%) of product, m.p. 105° after recrystallization from MeOH. (Found: C, 49·33; H, 4·61; N, 7·70; $C_{14}H_{16}N_2O_6S$ requires: C, 49·42; H, 4·74; N, 8·32%); λ_{max}^{MeOH} 301 (15,300), 372 (21,000) mμ (ε).

2-(*Bis-carbomethoxy*)-*methylenethiazolidine* (**7**). Ethyleneimine (3 ml, excess) in EtOH (10 ml) was added dropwise at room temp to a stirred soln of **2** (4·44 g, 0·02 mole) in EtOH (20 ml). After stirring at room temp for 2 hr, the soln was refluxed for 24 hr, cooled and light petroleum was added. The product, 2·2 g (51%) separated after cooling for several hr, m.p. 102° after recrystallization from MeOH. (Found: C,

44·19; H, 5·04; N, 6·64; $C_8H_{11}NO_4S$ requires: C, 44·24; H, 5·11; N, 6·45%); λ_{max}^{MeOH} 227 (13,500), 283 (23,300) mμ (ε).

2-(*Bis-carbomethoxy*)-*methylene*-N-*methylthiazolidine* (**8**). Me_2SO_4 (2·52 g, 0·02 mole) was added to a stirred soln of **7** (4·34 g, 0·02 mole) in dry acetone (40 ml), containing K_2CO_3 (2·76 g, 0·02 mole). After reflux and stirring for 20 hr, the carbonate and the acetone were removed and the remaining oil solidified upon treatment with cold EtOH, yielding 3·79 g (86%) of product, m.p. 106° after recrystallization from MeOH. (Found: C, 46·92; H, 5·97; N, 6·13; $C_9H_{13}NO_4S$ requires: C, 46·74; H, 5·67; N, 6·06%); λ_{max}^{MeOH} 249 (6800), 295 (15,200) mμ (ε).

Methyl 3-*methylmercapto*-2-*carbomethoxycrotonate* (**9**). Dimethyl thioacetylmalonate was prepared by passing H_2S for 10 hr through an ice-cooled soln of dimethyl acetylmalonate in abs ether–EtOH (40 : 10, V/V), saturated with HCl,[13] yield 80%, b.p. 65°/1 mm. (Found: C, 44·47; H, 5·17; S, 16·57; $C_7H_{10}O_4S$ requires: C, 44·20; H, 5·30; S, 16·86%).

The above compound (3·8 g, 0·02 mole) in ether (30 ml), was methylated with diazomethane at 0°. Removal of the ether left an oil which solidified upon cooling, yielding 3·9 g (95%) of product, m.p. 46° after recrystallization from EtOAc–light petroleum. (Found: C, 47·42; H, 5·78; S, 16·09; $C_8H_{12}O_4S$ requires: C, 47·04; H, 5·92; S, 15·70%); λ_{max}^{MeOH} 294 (13,100) mμ (ε).

Methyl 3-(N-*methylanilino*)-3-*methylmercapto*-2-*cyanoacrylate* (**12**). This compound was prepared in 85% yield by methylation of methyl 3-anilino-3-methylmercapto-2-cyanoacrylate[5b] with Me_2SO_4, according to the procedure given for **5**, m.p. 84° after recrystallization from ether–light petroleum. (Found: C, 59·68; H, 5·40; N, 10·54; $C_{13}H_{14}N_2O_2S$ requires: C, 59·53; H, 5·38; N, 10·68%); λ_{max}^{MeOH} 328 (15,000) mμ (ε).

Methyl 3-(N-*methyl*-p-*nitroanilino*)-3-*methylmercapto*-2-*cyanoacrylate* (**13**). This compound was prepared in 78% yield by nitration of **12** according to the procedure given for **6**; m.p. 143° after recrystallization from EtOH. (Found: C, 50·58; H, 4·54; N, 13·15; $C_{13}H_{13}N_3O_4S$ requires: C, 50·81; H, 4·26; N, 13·68%); λ_{max}^{MeOH} 318 (17,100), 377 (16,200) mμ (ε).

Methyl 3-(1-*indolino*)-3-*methylmercapto*-2-*cyanoacrylate* (**14**). Indoline (1·19 g, 0·01 mole) was added to a soln of methyl 3,3-bis-methylmercapto-2-cyanoacrylate[5a] (2·03 g, 0·01 mole) in MeOH (20 ml) and the reaction mixture was refluxed for 1 hr and then left at room temp overnight. Ether was added and the soln was cooled in ice-salt bath. A crystalline product was obtained, yield 2·1 g (77%), m.p. 118° after recrystallization from ether–light petroleum. (Found: C, 61·08; H, 5·08; N, 9·92; $C_{14}H_{14}N_2O_2S$ requires: C, 61·31; H, 5·15; N, 10·21%), λ_{max}^{MeOH} 240 (7500), 305 (9100), 364 (17,400) mμ (ε).

Methyl 3-*benzoylmercapto*-3-*methylmercapto*-2-*carbomethoxyacrylate*. Dimethyl malonate (26·4 g, 0·02 mole) was added dropwise to a stirred soln of NaOMe prepared frrom Na (8·05 g, 0·35 mole) in MeOH (100 ml). The soln was cooled to 5°, and CS_2 (13·4 g, 0·175 mole) was added dropwise. After 0·5 hr stirring, Me_2SO_4 (22 g, 0·175 mole) was added dropwise, and 1 hr later benzoyl chloride (24·5 g, 0·175 mole) was added dropwise. After stirring at room temp overnight, ether and water were added, the layers were separated, the ethereal layer washed with water and dried over $MgSO_4$. Removal of the ether left an oil from which 12 g (21%) of a solid product was obtained upon addition of ether–light petroleum and cooling at −70°, m.p. 99° after crystallization from MeOH. (Found: C, 51·77; H, 4·52; $C_{14}H_{14}O_5S$ requires: C, 51·54; H, 4·33%); λ_{max}^{MeOH} 249 (18,400), 317 (10,200), mμ (ε).

2-*Methylmercapto*-3-*carbomethoxy*-4-*hydroxyquinoline*. A soln of **4** (1·4 g, 0·005 mole) in decaline (15 ml) was refluxed for 2 hr. On cooling and addition of light petroleum 0·87 g (70%) of product was obtained. The product melts at 113° on recrystallization from light petroleum. (Found: C, 57·84; H, 4·66; S, 12·80; $C_{12}H_{11}NO_3S$ requires: C, 57·82; H, 4·45; S, 12·86%); λ_{max}^{MeOH} 228 (16,700), 264 (24,600), 320 (s) (7900), 332 (s) (1500) mμ (ε). (For additional chemical and physical properties, see text.)

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