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NITRILE⇌KETENIMINE TAUTOMERISM IN SUBSTITUTED ALKYLIDENE MALONONITRILES AND ALKYLIDENE CYANOACETATES

A CHARACTERISTIC UV ABSORPTION BAND

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Abstract—Several alkylidene malononitriles (**1b**, **1d**, **1e**, **2b** and **4b**) and alkylidene cyanoacetates (**1a**, **2a** and **4a**) studied exhibit a long wavelength UV absorption band around 355 nm which shows a hyperchromic effect in the presence of ethanolic alkali. This band has been assigned to the ketenimine tautomer (**5**). Addition of water to **1b**, **1e** and **2b** gives the corresponding pyridine diols (**7a**, **7b** and **8a**) respectively. Similarly, addition of ethanol to **1e** and **2b** gave the corresponding ethoxypyridine derivatives (**7c** and **8b**). Mechanism of formation of these compounds is discussed. Structures, as well as mechanism of formation of **1c**, **7c** and **10** obtained from **1b**, **1e** and **2b** respectively on standing at room temperature are also discussed.

We have studied the UV absorption spectra of several 1,2-dicyano esters and 1,1,2-tricyano compounds with a view to demonstrate the presence of nitrile⇌ketenimine tautomerism.[1] Recently, we have synthesized several condensation products of β-keto esters with malononitrile and ethyl cyanoacetate in connection with the synthesis of heterocyclic compounds.[2] We now report the existence of a new characteristic long wavelength UV absorption band in some of the above-mentioned compounds and also discuss structures of a few of their transformation products.

The alkylidene malononitriles and cyano esters used in the present investigations were prepared by the Cope-Knoevenagel condensation[3] of the corresponding β-keto esters with malononitrile or ethyl cyanoacetate respectively in the presence of ammonium acetate and glacial acetic acid in benzene. All these compounds were characterised by IR, NMR and analytical data.

The UV spectral data of these compounds are given in Table 1. As seen from the Table, compounds **1a**, **1b**, **1d**, **1e**, **2a** and **2b** show a long wavelength absorption maxima around 355 nm with different extinction coefficients in addition to the expected band around 230 nm characteristic of substituted α,β-unsaturated esters and nitriles.[4] This long wavelength band is observed only in polar solvents like ethanol or methanol but not in non-hydroxylic solvents like heptane, cyclohexane or acetonitrile. This behaviour is similar to the one observed in the case of nitrile⇌ketenimine tautomerism in 1,2-dicyano esters and 1,1,2-tricyano compounds.[1,2] The λ_{max} is unaffected in presence of alkali, but its intensity is tremendously increased as seen from Table 1. This band is indicative of ex-

Table 1. UV spectral data of alkylidenemalononitriles and cyano acetates

Compound	EtOH λ_{max} nm	EtOH (ϵ)	EtOH-NaOH (0·1 M) λ_{max} nm	EtOH-NaOH (0·1 M) (ϵ)
1a	238	(11,800)	248	(9,400)
	356	(270)	356	(12,950)
1b	228	(13,700)	224	(24,700)
	356	(19,584)	356	(35,430)
1d	229	(8,000)	224	(16,200)
	355	(10,870)	356	(21,420)
1e	240	(13,200)	236	(15,635)
	356	(65)	356	(12,780)
1f	241	(7,370)	—	—
1g	236 (shoulder)	(1,740)	—	—
2a	236	(14,910)	246	(15,275)
	355	(7,205)	355	(38,970)
2b	232	(13,255)	229	(13,940)
	355	(34,800)	355	(41,530)
4a	300	(27,980)	256	(11,689)
	430	(61)	430	(25,510)
4b	300	(27,980)	236	(11,600)
	430	(4,430)	430	(30,430)

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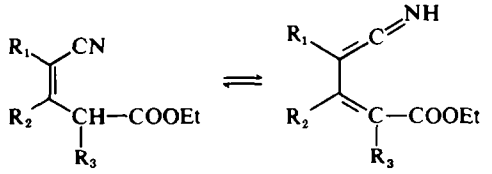
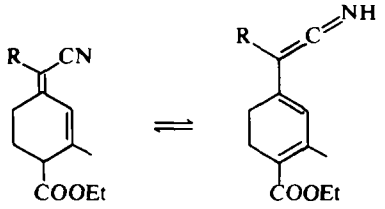
tended conjugation as in species **5** resulting from nitrile⇌ketenimine tautomerism, present to some extent in alcohol solution. The high intensity in alkaline solution is due to the increased concentration of this species.*



R_1 = COOEt or CN **5**

Compounds **4a** and **2b** show UV absorption maxima at 300 and 430 nm (Table 1). The latter band again shows only the hyperchromic effect in presence of alkali. The bathochromic shift of the two bands compared to those observed in compounds (**1a**, **1b**, **1d**, **1e**, **2a** and **2b**) could be expected because of the presence of an extra double bond extending conjugation. An additional double bond in the form of a homoannular diene system as in species **6** resulting from these two compounds is mainly responsible for the observed bathochromic shift of the 356 nm band. Such a bathochromic shift could be expected on the basis of Woodward rules.[5]



R_2 = COOEt or CN **6**

In order to confirm that the long wavelength band in these compounds is due to the presence of the tautomeric ketenimine species (**5** and **6**), the UV spectra of compounds **1f** and **1g** in which the absence of enolizable hydrogen does not permit the formation of the extended conjugated species (**5**) were studied. As expected, these compounds (**1f** and **1g**) do not show the long wavelength absorption band. Compound **1f** shows only a band at 241 nm corresponding to the alkylidene malononitrile moiety. Compound **1g** shows a band (shoulder) at 236 nm, the intensity of which is very low. This is due to the existence of this compound mainly in the form of **3**. Hence, this compound should be represented by structure **3** rather than **1g** proposed earlier.[7] This is also evident from its IR spectrum (neat) which shows a very weak C≡N absorption band at 2285 cm^{-1} characteristic of saturated nitriles and a weak band at 1590 cm^{-1} for C=C stretching. Structure **3** for this compound was further confirmed from its NMR spectrum which showed an olefinic proton (approximately 0·8 H) as a triplet (J = 4 Hz) at 6·25 δ.

The alkylidene malononitriles (**1b**, **1e** and **2b**) underwent facile addition of water on heating to give the respective pyridine diols† (**7a**, **7b** and **8a**). Structures of these compounds have been established by spectral data and comparison with authentic samples.[8-10] The formation of these pyridine diols by the addition of water can be rationalised as shown in Chart 1. The conversion of amides of the type **9** (**a** and **b**) to pyridine diols is well known.[8-10] The conversion of the nitrile to an amide under these mild conditions is the step which needs explanation. Alkylidene malononitrile (**1f**) and cyclohexylidene malononitrile are not hydrolysed by prolonged boiling with water. The facile formation of the pyridine diols in the present case *via* the amide‡ may be due to the participation of the carbethoxy group in the ketenimine tautomer as indicated in Chart 1 (Path A).

However, the formation of the pyridine diols can also be visualised by direct attack of water on the ketenimine species to give the amide (**9b**) followed by cyclisation (Chart 1, Path B). The former mechanism is preferred because a similar mechanism[11]§ (Chart 2 could explain the formation of ethoxypyridine derivatives (**7c** and **8b**) by heating the alkylidene malononitriles (**1e** and **2b**) respectively with ethanol. The structure of **8b** is based on its spectral data and also in analogy with the structure of **7c** established (chemical degradation) by Bickelhaupt and Van der Baan.[12,13]

The alkylidene malononitriles (**1b**, **1e** and **2b**) gave, in each case, a different product on standing at room temperature. The structures of all these compounds have been established on the basis of IR and NMR data discussed below.

The alkylidene malononitrile (**1b**), on standing at room temperature, deposited needles, m.p. 148–9°. This analysed for $C_{11}H_{14}N_2O_3$ and showed UV maxima at 260 (ε, 15, 170) and 329 nm (21, 090). In the IR spectrum, it showed bands at 3500, 3280 (NH), 2220 (C≡N), 1720 (COOEt), 1705 ($CONH_2$) and 1603 (C=C) cm^{-1}. In the NMR spectrum ($CDCl_3$—drop of DMSO-d_6) it showed signals at 1,2(t, J = 7 Hz, 3H), 1·6–2·3(*m*, 4H), 2·78(*t*, J = 7 Hz, 2H), 4–4·3(*m*, 3H) and 6·7–7·2 δ(*b*, 2H). The spectral data fit in with the amide structure (**1c**). This structure was further confirmed by converting it to the already re-

*Weir *et al.*[6] have suggested the participation of ketenimine to explain the formation of a pyridine derivative from benzalmalononitrile in presence of ethanolic alkali.

†For the sake of convenience, we are representing these compounds as pyridine diols although IR evidence shows the presence of tautomeric pyridone forms also.

‡In one case the intermediate amide has been isolated and characterised (vide *infra*).

§Bickelhaupt and Van der Baan[11] have shown that similar cyclic intermediates are formed in these reactions. We are grateful to them for communicating their results to us in advance.

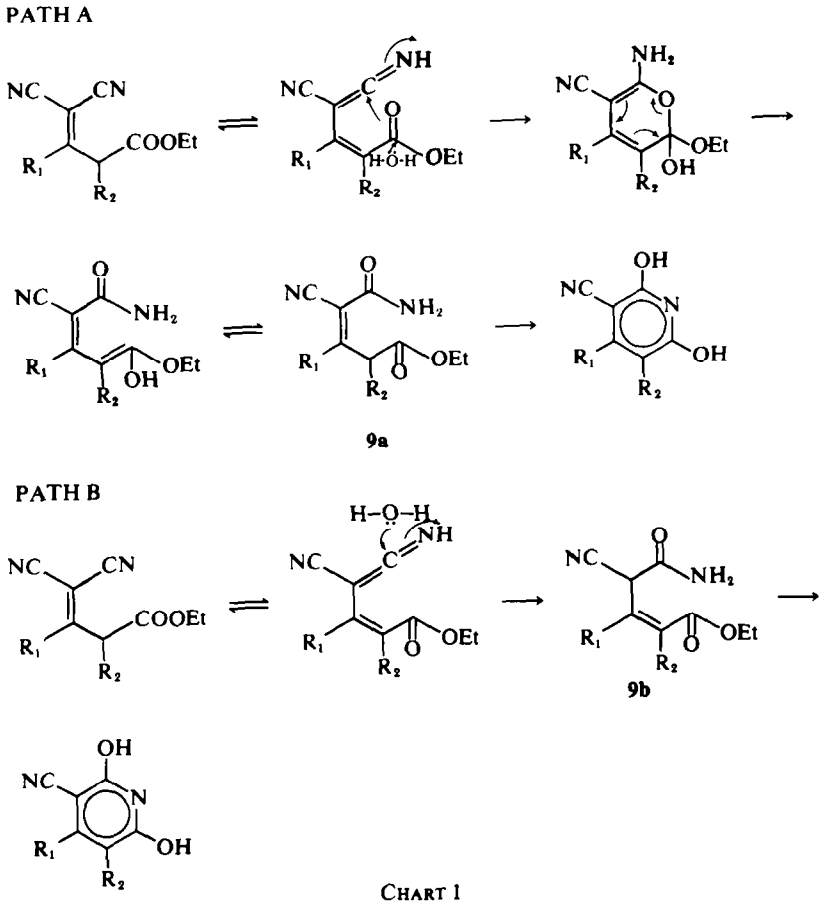


CHART 1

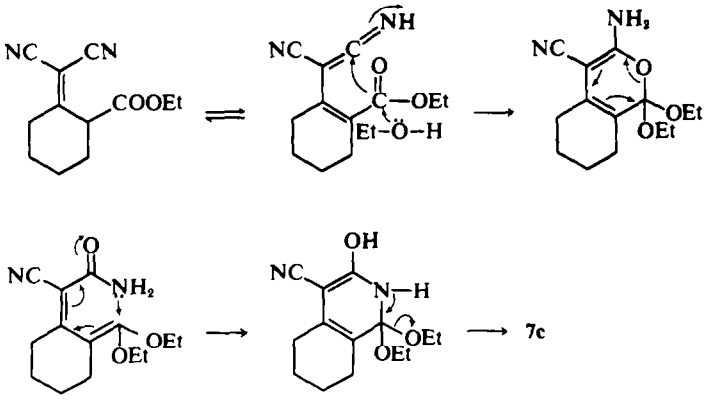


Chart 2

ported pyridine diol (**7a**) on boiling with water. The amide (**1c**) may be resulting by hydrolysis of the nitrile by atmospheric moisture as per mechanism indicated in Chart 1.

The alkylidene malononitrile (**1e**), on standing at room temperature, deposited a crystalline solid, m.p. 196–8° (M^+ 218). In the UV spectrum, it showed λ_{max} at 248 (ϵ, 11,960), 302 (10,790) and 329 (8690) nm. The presence in IR spectrum (nujol) of the bands at 3590 and 3200 cm^{-1} indicated NH or OH group. There was no band corresponding to carbonyl absorption. In the NMR spectrum, ($CDCl_3$—a few drops of DMSO—d_6) it showed signals at 1·40 (*t*, J = 7 Hz, 3H), 1·74 (*br.* singlet, 4H),

2·2–2·8 (*m*, 4H), 4·35 (*q*, J = 7 Hz, 2H) and 8·15 δ (*br.* singlet 1H). The signal at 8·15 δ disappeared on shaking with D_2O. On the basis of the above-mentioned spectral data and the mass spectral fragments (Experimental), two alternate structures (**7c** and **7d**) could be written for this compound. This solid was identical (TLC, IR and NMR) with the compound obtained by ethanol addition to 2-carbethoxycyclohexylidene malononitrile (**1a**) (*vide supra*) and also with the compound **7c** reported by Bickelhaupt *et al.*[13] The formation of this solid can be visualised as shown in Chart 3.

The alkylidene malononitrile (**1b**), on keeping at room temperature for a few days deposited crystalline solid, m.p. 164–5°, UV λ_{max} 237 (ε 26,200) and 325 nm (36,340). The presence of ester (1720 cm^{-1}), NH (3410, 3380), C≡N (2220) and double bond (1640) was inferred from its IR spectrum (nujol). The NMR spectrum ($CDCl_3$—drop of DMSO—d_6) showed signals at 1·27 (*t*, J = 7 Hz, 6H), 1·49 (*s*, 3H), 2·60 (*s*, 2H), 3·41 (*d*, J = 3 Hz, 2H), 4·13 (*q*, J = 7 Hz, 4H), 5·9 (*br*, S, 1H) and 7·50 δ (*br*, S, 2H). The signals at 5·9 and 7·5 δ disappeared on D_2O exchange. The signal at 5·9 δ can be assigned to the olefinic proton in **10** and this can get exchanged with D_2O presumably due to the presence of the tautomerism indicated below. The spectral data could be explained on the basis of the dimeric structure viz., 1-amino-2, 6, 6-tricyano-3, 5-bis(carbomethoxy-methyl)-5-methyl-cyclohexa-1,3-diene (**10**) for this compound. Similar dimers have been reported in literature.[14] Presumably, it is formed by a base catalysed (trace of impurities) Michael condensation followed by an intramolecular Thorpe cyclization.

In conclusion the UV spectral data and the chemical transformations discussed above support the nitrile⇌ketenimine tautomerism in these compounds.

EXPERIMENTAL

M.ps (hot stage) and b.ps reported herein are uncorrected. UV spectra were recorded in 95% EtOH on a UNICAM Sp 700A spectrophotometer. IR spectra were taken using Perkin Elmer Model 137B Infracord spectrometer. NMR spectra were taken either on a Varian A-60 or HA 100D spectrometer. Chemical shifts are quoted in δ values (ppm) relative to TMS as internal standard and coupling constants in Hz.

General procedure for Cope-Knovenagal condensation. An equimolar mixture of β-keto ester and malononitrile (or ethyl cyanoacetate) was heated under reflux in dry benzene as solvent and ammonium acetate-glacial AcOH as catalyst with continuous water separation using a Dean-Stork water separator. After the water separation had ceased, the mixture was cooled, washed several times with water and once with brine, solvent removed and the residue fractionated under reduced pressure.

2-Carbethoxycyclopentylidene cyanoacetate (**1a**). This was prepared according to the reported procedure[15], b.p. 145–8°/1,5 mm.

2-Carbethoxycyclopentylidenemalononitrile (**1b**). Refluxing a mixture of 2-carbethoxycyclopentanone[16] (15·6 g), malononitrile (6·6 g), ammonium acetate (0·77 g), AcOH (1·3 ml) and benzene (50 ml) for 12 hr gave **1b** (10·5 g), b.p. 130–3°/2 mm; IR (Neat) ν_{max} 2240 (C≡N), 1725 (COOEt), and 1605 cm^{-1} (C=C); NMR (CCl_4), 1·32 (*t*, J = 7 Hz, 3H, CH_2-CH_3), 1·7–2·5 (*m*, 4H), 2·86 (*t*, J = 7 Hz, 2H, CH_2CH_2-), 3·8 (*m*, 1H, CH-COOEt) and 4·22 (*q*,

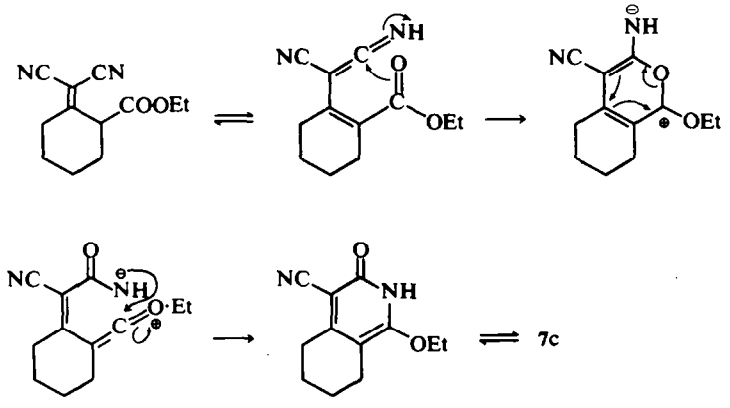
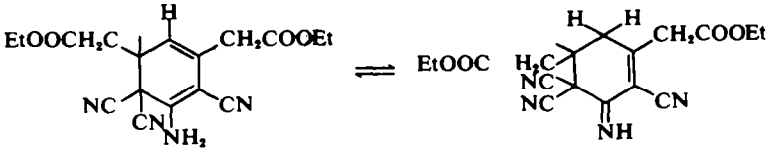


CHART 3



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J = 7 Hz, 2H, O-CH_2-CH_3) (Found: C, 64·42; H, 5·72; N, 13·46. $C_{11}H_{12}N_2O_2$ requires, C, 64·70; H, 5·88; N, 13·70%).

The distilled sample, on keeping for a few days at room temp, deposited crystalline solid (**1c**). This was filtered off and crystallised from benzene, m.p. 148–9° (found: C, 59·59; H, 6·67; N, 12·35. $C_{11}H_{14}N_2O_3$ requires: C, 59·46; H, 6·30; N, 12·61%).

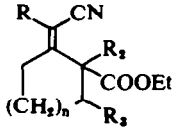
2,3-*Dicarbethoxycyclopentylidenemalononitrile* (**1d**). Starting from 2,3-dicarbethoxycyclopentanone[17] (4·5 g), malononitrile (1·3 g), ammonium acetate (0·2 g), AcOH (0·3 ml) and benzene (15 ml), **1d** was obtained after 8 hr refluxing (1·8 g), b.p. 170–5°/2–3 mm (short path distillation), IR (neat) ν_{max} 2235 (C≡N), 1725 (COOEt), and 1625 cm^{-1} (C=C) (Found: C, 67·82; H, 5·48; N, 9·80. $C_{14}H_{16}N_2O_4$ requires: C, 68·11; H, 5·8; N, 10·1%).

2-*Carbethoxycyclohexylidenemalononitrile* (**1e**). Starting from 2-carbethoxycyclohexanone[18] (13 g), malononitrile (5·05 g), ammonium acetate (1 g), AcOH (1·4 ml) and benzene (40 ml) **1e** was obtained after 8 hr refluxing, (9 g), b.p. 143–5°/2·5 mm (reported[13] b.p. 110°/0·5 mm), IR (neat) ν_{max} 2235 (C≡N), 1725 (COOEt) and 1620 cm^{-1} (C=C); NMR (CCl_4), 1·28 (*t*, J = 7 Hz, 3H,-CH_2-CH_3), 1·5–2·0 (*m*, 2H), 2–3·3 (*m*, 4H), 3·9 (*br*, 1H,-C-C*H*-COOEt) and 4·21 (*q*, J = 7 Hz, 2H,-O-CH_2-CH_3). By continuing reflux for 24 hr, **7c** is obtained in about 60% yield.

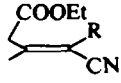
The condensation product **1e** on standing at room temp for several days deposited a solid (**7c**) which was filtered off, washed with benzene and crystallised from benzene, m.p. 196–8° (reported[13] 196°). Mass spectral fragments: (*m/e*) 218, 203 (M-CH_3), 190 (M-C_2H_4 or CO; m* 165·5), 189 (M-C_2H_5), 175 (190-CH_3) and 162 (190-CO or C_2H_4).

2- *Carbethoxy-2- methyl-cyclohexylidenemalononitrile* (**1f**). Refluxing a mixture of 2-methyl-2-carbethoxycyclohexanone[19] (20·4 g), malononitrile (7·4 g), ammonium acetate (1·72 g), acetic acid (2 ml) and benzene (100 ml) for 7·5 hr, gave **1f** (7 g), b.p. 167–70°/6 mm as a colorless oil. A forerun of the starting material (14·5 g, b.p. 95–100°) was recovered. IR (neat) ν_{max} 2265 (C≡N), 1735 (COOEt) and 1590 (C=C) cm^{-1}, NMR (CCl_4), 1·28 (*t*, J = 7 Hz, -CH_2-CH_3), 1·58 (*s*, 3H, CH_3), 2·4–2·9 (*m*, 2H, allylic CH_2) and 4·2 (*q*, J = 7 Hz, -O-CH_2-CH_3) (Found: N, 12·36; $C_{13}H_{16}N_2O_2$ requires N, 12·07%).

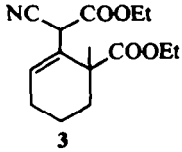
Ethyl 6-methyl-6-carbethoxycyclohexenyl cyanoacetate (**1g**). This compound was prepared as reported in literature[7], b.p. 180–2°/4 mm; IR (neat) ν_{max} 2285 (*w*, C≡N), 1725, 1735 (COOEt) and 1590 cm^{-1} (*w*, C=C); NMR (CCl_4



1a: $n = 1$; R_1 = COOEt; $R_2 = R_3$ = H
b: $n = 1$; R_1 = CN; $R_2 = R_3$ = H
c: $n = 1$; R_1 = $CONH_2$; $R_2 = R_3$ = H
d: $n = 1$; R_1 = CN; R_2 = H; R_3 = COOEt
e: $n = 2$; R_1 = CN; $R_2 = R_3$ = H
f: $n = 2$; R_1 = CN; R_2 = Me; R_3 = H
g: $n = 2$; R_1 = COOEt; R_2 = Me; R_3 = H



2a: R = COOEt
b: R = CN



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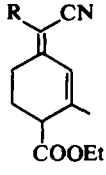
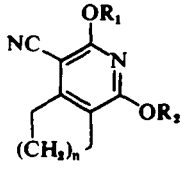
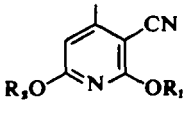


4a: R = COOEt
b: R = CN



7a: $n = 1$; $R_1 = R_2$ = H
b: $n = 2$; $R_1 = R_2$ = H
c: $n = 2$; R_1 = H; R_2 = Et
d: $n = 2$; R_1 = Et; R_2 = H



8a: $R_1 = R_2$ = H
b: R_1 = H; R_2 = Et

10

1·1–1·5 (*m*, 9H), 4·0–4·4 (*m*, 5H) and 6·25 (*t*, J = 4 Hz, 1H).

Ethyl 1-cyano-2- methylglutaconate (**2a**). This was prepared according to the reported method of Dutta *et al.*[20], b.p. 135–9°/2 mm; NMR ($CDCl_3$), 1·15–1·5 (overlapping triplets, 6H), 2·35 (*s*, 2H), 2·44 (*s*, 1H), 3·61 (*s*, 0·7H), 3·88 (*s*, 0·3H) and 3·95–4·50 (overlapping quartets, 4H).

The NMR spectrum of this compound indicates the presence of geometrical isomers *E* and *Z* in the ratio of 1:2 respectively. The sharp singlets at 2·35 (2H) and 3·88 (1·3H) corresponding to the methyl and methylene (CH_2-$COOC_2H_5$) could be assigned to the *Z* isomer on the basis of the NMR of the corresponding malononitrile compound (**2b**).

Ethyl 3-dicyanomethylenebutyrate (**2b**). Refluxing a mixture of ethyl acetoacetate (20 g), malononitrile (10·4 g), ammonium acetate (1·2 g), AcOH (1·5 ml) and benzene (75 ml) for 6 hr gave **2b** (22 g) as yellow oil, b.p. 126–7°/5 mm; IR (neat) ν_{max} 2230 (C≡N), 1735 (COOEt) and 1605 cm^{-1} (C=C); NMR ($CDCl_3$) 1·28 (*t*, J = 7 Hz, 3H, CH_2-CH_3), 2·38 (*s*, 3H, CH_3), 3·6(*s*, 2H, CH_2-COOEt) and 4·24 (*q*, J = 7 Hz, 2H, O-CH_2-CH_3) (Found: C, 60·26; H, 5·33; N, 15·72. $C_9H_{10}N_2O_2$, requires: C, 60·66; H, 5·66; N, 15·72%). This compound has been reported by Urishibara,[21] but no physical data has been given.

The distilled sample (**2b**) on standing at room temp for several days, deposited a solid which could be crystallised from benzene, m.p. 164–5°, IR (nujol) ν_{max} 3410, 3380 (NH), 2220 (C≡N), 1720 (COOEt), 1680 and 1640 cm^{-1} (Found: C, 60·59; H, 5·91; N, 16·18. $C_{18}H_{20}N_4O_4$ requires: C, 60·66; H, 5·66; N, 15·72%).

6-Carbethoxy-3- (1-carbethoxy-1-cyanomethylene)-1-methylcyclohexene (**4a**). Refluxing a mixture of 4-carbethoxy-3-methyl-cyclohex-2-enone[22] (18·2 g), ethyl cyanoacetate (11·3 g), ammonium acetate (1 g), AcOH (1·2 ml) and benzene (60 ml) for 10 hr gave **4a** (17·5 g), b.p. 200–8°/5 mm, IR (neat) ν_{max} 2235 (C≡N), 1730 (COOEt) and 1630 cm^{-1} (C=C) (Found: C, 64·72; H, 6·5; N, 5·23. $C_{13}H_{19}NO_4$ requires: C, 64·99; H, 6·8; N, 5·05%).

6 - Carbethoxy - 3 - dicyanomethylene - 1 - methylcyclohexene (**4b**). Condensation of 4 - carbethoxy - 3 - methyl - cyclohex - 2 - enone (13·6 g), malononitrile (4·9 g), ammonium acetate (0·75 g), AcOH (0·8 ml) in refluxing benzene (50 ml) gave after 10 hr **4b**, (10·2 g), b.p. 193–5°/5 mm (reported[23] 200–1°/9 mm); IR (neat) ν_{max} 2230 (C≡N) and 1730 cm^{-1} (COOEt); NMR ($CDCl_3$) 1·3 (*t*, J = 7 Hz, 3H, -CH_2-CH_3), 2·12 (*s*, 3H, CH_3), 2·7–3·0 (*m*, 2H), 3·189–3·4 (*m*, 1H, *CH*-COOEt), 4·23 (*q*, J = 7 Hz, O-CH_2-CH_3) and 6·7 (1H, $J_{allylic}$ = 1·5 Hz, H_3C—C=C*H*—).

3-Cyano-2,6-dihydroxy-4,5-trimethylenepyridine (**7a**). (a) A mixture of **1c** (100 mg) and water (5 ml) was boiled for 2 hr, cooled and filtered. The solid was recrystallised from EtOH to give **7a** (30 mg), m.p. 282–5° (reported[8] 276–8° in vacuum), UV λ_{max} 261 (ε 13,570) and 329 nm (20,530); IR (nujol) ν_{max} 3450 (*br.*), 2240 (C≡N), 1690 and 1610 cm^{-1}; NMR (DMSO-d_6) 1·8–3·0 (*m*, 6H) and 8·9–9·9 (*br.*, 2H) (Found: C, 61·50; H, 4·94; N, 15·96. $C_9H_8N_2O_2$ requires: C, 61·36; H, 4·54; N, 15·90%).

(b) Refluxing a mixture of **1b** (0·5 g) with water (20 ml) for 24 hr gave **7a** (0·2 g), m.p. 282–5°.

4-Cyano-2, 6-dihydroxy-5, 6, 7, 8-tetrahydroisoquinoline (**7b**). Refluxing a mixture of **1e** (1 g) and water 30 ml) for 24 hr gave a solid which was filtered and dried (0·5 g). This was crystallised from aqueous EtOH, m.p. 280–3° (reported[9a, b] 278°, 280–2°).

4-Cyano-1-ethoxy-3-hydroxy-5, 6, 7, 8-tetrahydroisoquinoline (**7c**). Refluxing a mixture of **1e** (1 g), with EtOH (20 ml) for 24 hr gave on cooling and removal of most of the EtOH, **7c** (0·2 g), m.p. 196-8° (crystallised from benzene) (reported[13] m.p. 196°).

3-Cyano-2,6-dihydroxy-4-methylpyridine (**8a**). A mixture of **2b** (1·5 g) and water (30 ml) was refluxed for 24 hr, cooled and filtered to give **8a** (0·13 g) on recrystallisation from EtOH, m.p. 314–5° (d) (reported m.p. 315–20° (d); NMR (DMSO-d_6), 2·17 (*s*, 3H, CH_3), 5·43 (*br. s*, 1H) and 9·7 (*br. s*, 2H). The latter two signals disappeared on D_2O exchange.

6-Ethoxy-2-hydroxy-4-methyl-pyridine (**8b**). A mixture of **2b** (2 g) was refluxed with EtOH (40 ml) for 24 hr. Solvent was removed *in vacuo* and benzene added to the residue. The solid, thus precipitated, was recrystallised from EtOH to yield, **8b** (0·2 g), m.p. 233–4°; NMR ($CDCl_3$- few drops DMSO-d_6), 1·53 (*t*, J = 7 Hz, CH_2-CH_3), 2·37 (*s*, 3H, CH_3), 4·27 (*q*, J = 7 Hz, O-CH_2-CH_3) and 5·95 (*s*, 1H, olefinic) (Found: C, 60·38; H, 5·58; N, 15·53. $C_9H_{10}N_2O_2$ requires: C, 60·67; H, 5·61; N, 15·72%.)

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