# Polyketoenols and Chelates. An *N*-Methyl-2-pyridone Relative of the Xanthyrones: 4*H*-Quinolizone and 1,2-Dihydro-2-quinolone Formation and Chemistry

By **Leslie Crombie** and **Roderick V. Dove,** Department of Chemistry, University of Nottingham, Nottingham NG7 2RD

Methyl methoxymethylenecyanoacetate and methyl sodioacetoacetate condense to give a substituted 4*H*-quinolizone (7) which can also be made by sodium methoxide catalysed condensation of 3,5-bismethoxycarbonyl-6-methyl-2-pyridone with methyl methoxymethylenecyanoacetate. Employment of the *N*-methylated pyridones (14) and (20) in reactions with methyl methoxymethyleneacetoacetate gives substituted 1,2-dihydro-2-quinolinones, and this behaviour is compared with the 2-pyrone series where xanthyrones are isolated.

Methoxide-ion catalysed condensation of 3,5-bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20) with methyl methoxymethylenecyanoacetate gives an acidic *N*-methylpyridone analogue of the xanthyrone type (28), lacking the enolised terminus and having unsaturation at 2' rather than 1'. Boiling water converts it into an oxo-pyrano-2-pyridone (31), further degraded by methoxide ion into the pyridone (20). Again, there are significant structural and chemical contrasts with typical xanthyrones: these appear to arise from two sources; the lower reactivity of the pyridone ring, and steric compression between the *N*-methyl and the 2'-hydrogen of a 1'-unsaturated *trans*-side-chain.

Xᴀɴᴛʜʏʀᴏɴᴇ (1) can be prepared by ' melt assembly ' in which methyl sodioacetoacetate and methyl methoxymethyleneacetoacetate are heated together in the

(1)
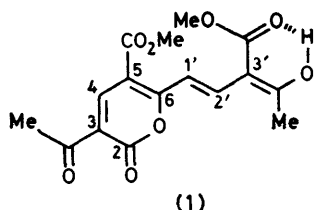
absence of a solvent.[1] In view of the chemistry described in the previous paper,[2] methyl methoxymethylenecyanoacetate (3 mol) and methyl sodioacetoacetate (1 mol) were heated together at 100 °C for 2.5 h to see if an analogue of the xanthyrone type, with a pyridone replacing the pyrone ring, could be obtained.

RESULTS AND DISCUSSION

The yellow crystalline product isolated, $C_{15}H_{14}N_2O_7$, was clearly not of the xanthyrone type (u.v. data) and showed three ester methyls in the n.m.r. spectrum along with a single olefinic proton at τ 1.00 and an AB quartet at 1.64 and 1.84, J 10 Hz. Two signals at −0.8br and −0.2br were assigned as the protons of a primary amine engaged in hydrogen-bonding, and a 4*H*-quinolizone formula (7) was entertained. It was supported by the finding that base-catalysed condensation of 3,5-bismethoxycarbonyl-6-methyl-2-pyridone (4) with methyl methoxymethylenecyanoacetate gave the same product. The mechanism of formation is summarised in Scheme 1. Pyridone (4) is considered to be formed as previously discussed:[2] the carbanion then undergoes Michael addition to a further 1 mol of (2). Intramolecular addition of the pyridone anion (5) to the nitrile leads, *via* the imine (6), to amine (7). An initial Michael
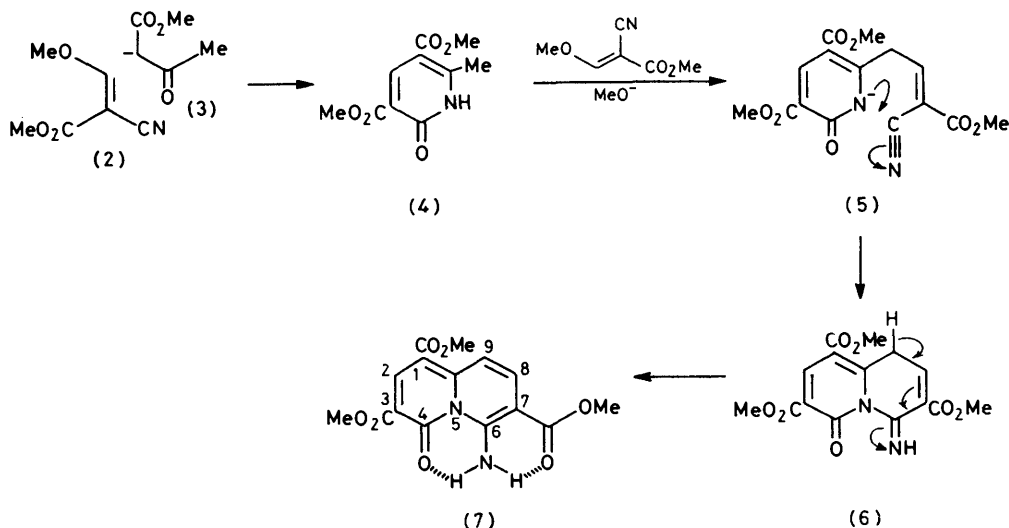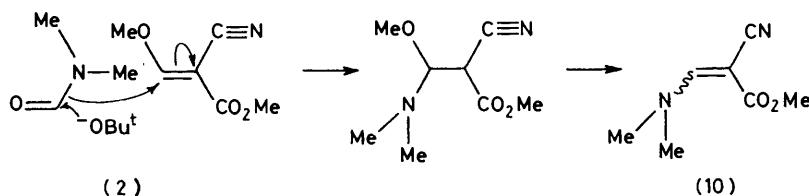

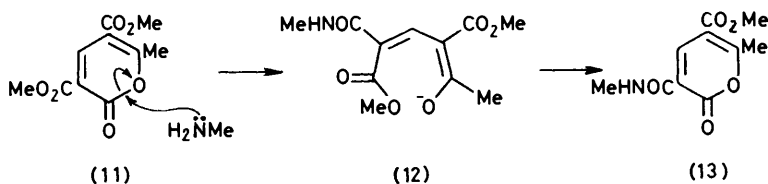Scʜᴇᴍᴇ 1   Formation of 6-amino-1,3,7-trismethoxycarbonyl-4-quinolizone

attack by the lactam anion would lead, on the other hand, via (8) to amine (9): the latter would not exhibit an AB quartet in the n.m.r. spectrum as required.


(8)   (9)
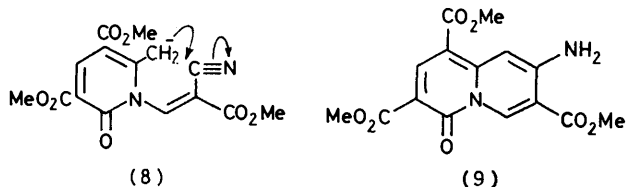
During examination of reaction conditions, methyl sodioacetoacetate and methoxymethylene compound (2) were treated with potassium t-butoxide in dimethyl-formamide and a product characterised as 2-cyano-3-

U.v. comparison of pyridones and N-methylpyridones.*

N-Methylpyridone (14)	213	277	340
	(14 300)	(13 600)	(8 300)
Pyridone (24)		274	327
		(12 400)	(7 000)
N-Methylpyridone (20)	209	262	333
	(19 000)	(14 700)	(8 500)
Pyridone (25)	204	260	329
	(19 800)	(17 100)	(8 400)

* $\lambda_{max.}$ (nm), $\varepsilon_{max.}$ in parentheses: solvent ethanol.

with dimethyl sulphate in dimethylformamide was therefore employed. Comparison of the u.v. spectra of pyridone (24) with N-methylpyridone (14), and (25) with (20), shows clear similarity (Table), supporting the occurrence of N- as opposed to O-methylation.

(2)   (10)

Scheme 2   Origins of 2-cyano-3-dimethylaminoacrylate

(11)   (12)   (13)

Scheme 3   Pyrone monomethylamide formation

(14)   (15)   (16)
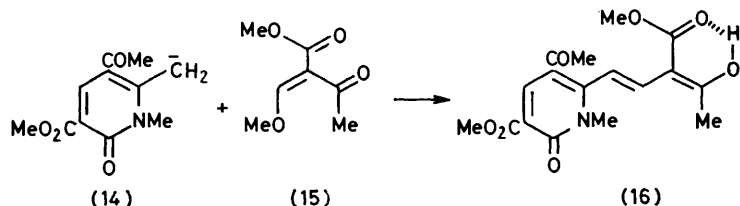
Scheme 4   N-Methylpyridone analogue of xanthyrone-forming reaction

dimethylaminoacrylate (10) [3] was isolated. N.m.r. data indicate that only one Z/E isomer is formed, but occurrence of two n.m.r. signals corresponding to the N-methyls suggests restricted rotation about the N–C bond. Presumably the compound is formed by reaction between (2) and the solvent as indicated in Scheme 2.

In order to block step (5)→(6) leading to 4H-quinolizone synthesis, the use of N-methylated pyridones was examined. Attempts to prepare (20) by treatment of the pyrone (11) with methylamine gave only the mono-methylamide (13), probably via (12) (Scheme 3). Direct methylation of 5-acetyl-3-methoxycarbonyl-6-methyl-2-pyridone (24) by alternate additions of sodium methoxide and dimethyl sulphate was successful, but less so in the case of 3,5-bismethoxycarbonyl-6-methyl-2-pyridone (20). As a general method, isolation of the dry sodium salt of the pyridone, followed by treatment
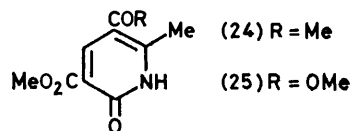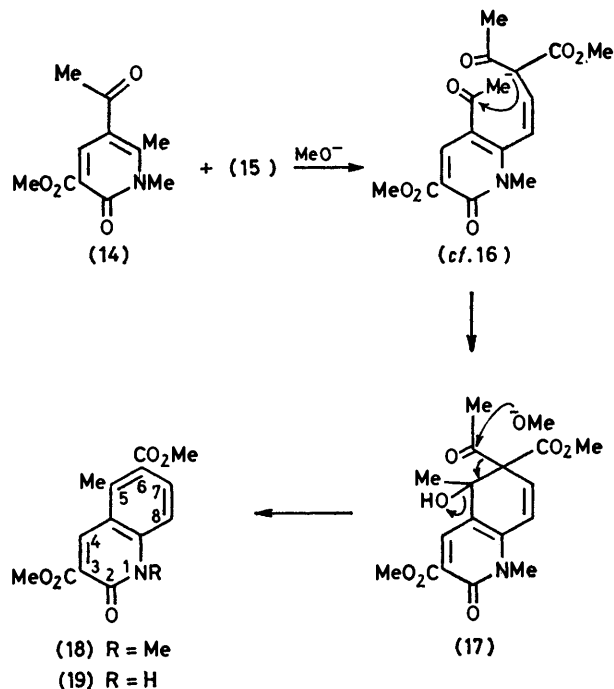
If base-catalysed reaction of 5-acetyl-1,6-dimethyl-3-methoxycarbonyl-2-pyridone with methyl methoxy-methyleneaceoacetate is to follow the pattern of xanthy-rone formation,[1] product (16) is to be expected (Scheme 4). Instead, two crystalline compounds, the 1,2-dihydro-2-quinolinone (18) and its demethylated product

(24) R = Me
(25) R = OMe

(19) were isolated when 1 mol of sodium methoxide was used as catalyst. Separate experiments showed that (18) is demethylated to (19) by boiling methanolic sodium methoxide, and the former is envisaged as being formed by Michael addition to give (16) which cyclises,
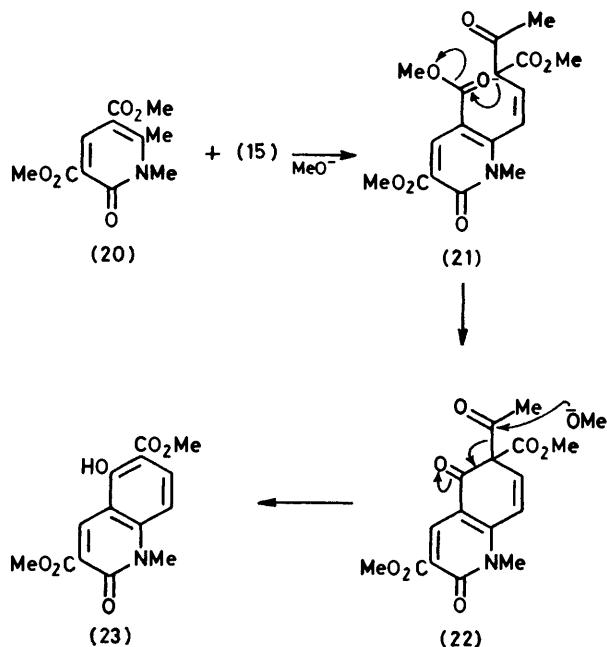
in the $Z(cis)$ form of the anion, by aldol condensation. Base-catalysed deacetylative dehydroxylation, with aromatisation, gives (18) (Scheme 5). The n.m.r. spectrum of the dihydroquinolinone (18) showed two ester methyls (τ 6.07 and 6.03), an N-Me (τ 6.25), an aromatic methyl (τ 7.14), a single aromatic proton (τ 1.19), and an aromatic AB quartet (τ 1.87 and 2.75; J 10 Hz). In a similar fashion, treatment of 3,5-bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20) with methyl methoxy-methyleneacetoacetate (15) in the presence of sodium methoxide (1 mol) gave 3,6-bismethoxycarbonyl-5-hydroxy-1-methyl-1,2-dihydroquinolinone (23) (Scheme 6).

Scheme 6   Formation of 3,6-bismethoxycarbonyl-5-hydroxy-1-methylquinolone

(18) R = Me
(19) R = H

Scheme 5   Formation of 3,6-bismethoxycarbonyl-5-methyl-quinolones

The behaviour of the N-methylpyridones thus contrasts with that of the pyrone series. In the latter, a compound such as dimethylxanthophanic enol (1) is readily intercepted when 1 mol of sodium methoxide is used in the condensation. Further treatment with sodium methoxide (>1 mol) leads to attack on the pyrone ring to give, in the case cited, (26) or an ionised tautomer which follows cyclisation by an aldol pathway to (27) (Scheme 7). Because of the relative stability of the N-methylpyridone ring towards methoxide cleavage, the alternative course of cyclisation of the side-chain, followed by aromatisation, is preferred. A factor which assists the latter cyclisation and appears to account for the non-isolation of a ' pyridono-xanthyrone ' (16), is steric compression between the N-Me (or alternatively the CO_2Me) and the 2′-olefinic hydrogen of the $E(trans)$ side-chain when it lies coplanar with the ring: this destabilisation is not present in a xanthyrone such as (1).

Further attempts to make a ' pyridono-xanthyrone '

involved condensation of 3,5-bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20) with methyl methoxymethyl-enecyanoacetate in the presence of sodium methoxide. A new colourless, crystalline compound, $C_{16}H_{16}N_2O_7$ was isolated which showed a singlet in the n.m.r. at τ 1.28, assigned to the pyridone ring proton, together with a two proton doublet (τ 5.39), an olefinic triplet (τ 2.42), and the expected ester and N-Me resonances. Vibrations assigned to a nitrile (2 220), esters (1 705—1 735), and a pyridone carbonyl (1 655 cm^{-1}) were present. The compound, formulated as (28), is thus of the general xanthyrone type but it lacks the typical enolised terminus of (1). An interesting feature is that the n.m.r. data show that the double bond, in solution, is conjugated to the nitrile and ester, rather than to the N-methyl-
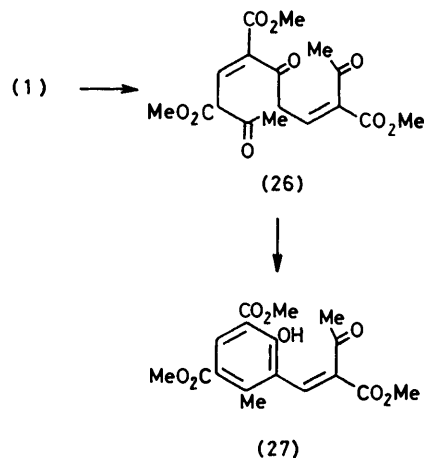

Scheme 7   Sodium methoxide-catalysed reaction of dimethyl xanthophanic enol

pyridone (no AB system). As mentioned above, a planar 1'-olefin encounters steric hindrance from the ' di-*ortho-* ' substituents of the pyridone ring. A methylene at 1' and a double bond at 2' break the chromophore into two parts, whilst allowing relief of unfavourable interactions by rotation at C-1'. In acid solution the ' pyridono-xanthyrone ' had $\lambda_{max.}$ 213 (ε 21 700), 264
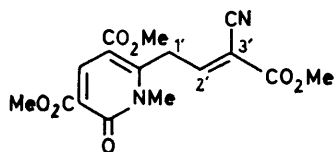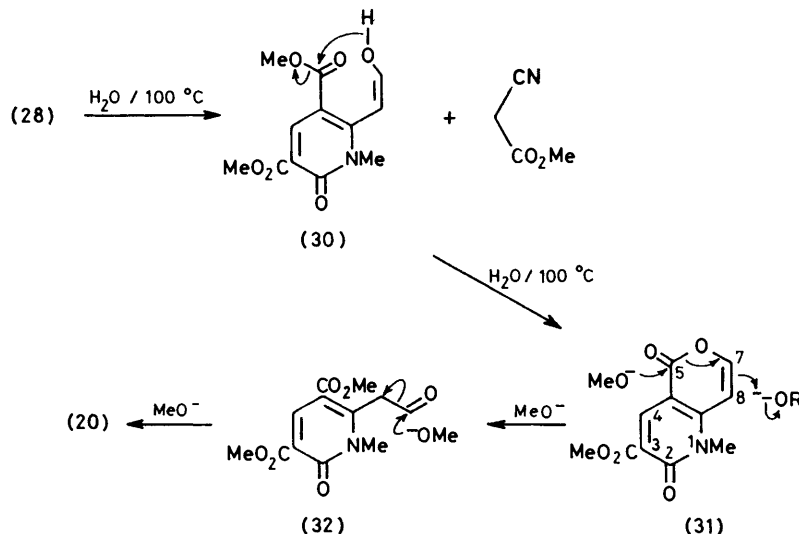

(28)

(10 900), and 336 nm (8 120), but in neutral solution it showed some ionisation; $\lambda_{max.}$ 213 (ε 21 800), 262 (11 100), 336 (7 100), and 491 nm (3 600). In base, strong absorption developed in the visible, $\lambda_{max.}$ 255 (ε 17 800), 322 (4 300), and 488 nm (65 500): a highly delocalised version of the ion represented as (29) accounts for the long-wavelength absorption.
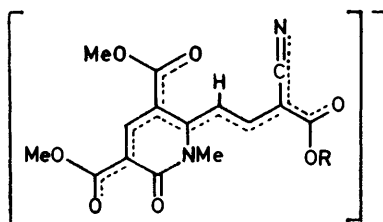
(29)

The ' pyridono-xanthyrone ' (28) is a reactive compound: thus refluxing with neutral distilled water gave the 2'-oxopyrano-2-pyridone (31). In $(CD_3)_2SO$, the n.m.r. spectrum showed that one methyl ester (τ 6.11) one *N*-Me (τ 6.24), a pyridone ring proton (τ 1.59), and an AB quartet due to the pyrone protons (τ 3.03 and 1.99; J 8 Hz) were present. The oxo-pyrano-pyridone

is envisaged as being formed by a retro-aldol reaction eliminating methyl cyanoacetate, the resulting hydroxy-methylene compound cyclising in a Claisen manner (Scheme 8). This behaviour again contrasts with typical xanthyrones where boiling with water releases, by pyrone decarboxylation, a reactive chain. This undergoes cyclisation and aromatisation either intact, or after further retro-aldol cleavage.[4,5]

The oxopyrano-pyridone (31) had the same u.v. spectrum in neutral and acidic medium, $\lambda_{max.}$ 220 (ε 25 100), 260 (10 600), 266infl. (10 100), 286 (5 600), 297 (4 800), and 356 nm (10 600), but under basic conditions rapid changes in absorption occurred. The compound was therefore set aside with methanolic sodium methoxide (6 mol) for 12 h at 20 °C and found to be degraded to 3,5-bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20) *via* ring opening [*cf.* (31)] and deformylation (32) (Scheme 8).

EXPERIMENTAL

Unless stated otherwise, u.v. data refer to ethanol solutions and n.m.r. data are given as τ values ($CDCl_3$) unless stated otherwise.

Reaction between Methyl Sodioacetoacetate and Methyl Methoxymethylenecyanoacetate (Melt Conditions).—Methyl sodioacetoacetate (2.0 g) and methyl methoxymethylene-cyanoacetate (6.6 g) were heated on steam for 2.5 h. Water (15 ml) and aqueous acetic acid (1 : 1) were added and the mixture was filtered. The dried solid was stirred with chloroform (50 ml), and purified by chromatography on Florisil, eluting with ether–methanol to give 6-*amino-1,3,7-trismethoxycarbonyl-4-quinolizone* (7), m.p. 211 °C from methanol–chloroform, yellow needles (200 mg) (Found: C, 54.3; H, 4.0; N, 7.7%; M^+ 334. $C_{15}H_{14}N_2O_7$ requires C, 53.9; H, 4.2; N, 8.4%), $\nu_{max.}$ (mull) 3 300, 3 210, 1 715 (ester CO), 1 705 (ester CO), 1 690 (ester CO), 1 660 (quinol-izone CO), and 1 615 cm^{-1}; $\lambda_{max.}$ (ethanolic hydrochloric acid) 210 (ε 27 200), 231infl. (10 300), 255 (5 620), 293 (8 740), 338infl. (5 300), 365 (9 050), and 465 (27 800) nm; $\lambda_{max.}$ (ethanol) 210 (ε 29 400), 231infl. (11 550), 255 (6 550), 293 (9 420), 338 (5 940), 265 (9 360), and 465 (30 400) nm;

SCHEME 8 Degradation of ' pyridono-xanthyrone ' (28) by boiling water and by sodium methoxide

$\lambda_{max.}$ (ethanolic sodium hydroxide) 224 (ε 10 900), 243 (9 650), 266infl. (8 030), 293 (6 870), 338 (14 500), and 435 (18 400) nm; τ -0.80 (br, 1 H, NH), -0.2(br, 1 H, NH), 1.00 (1 H, s; 2-H), 1.64 (1 H, d; 9-H; J 10 Hz), 1.84 (1 H, d; 8-H; J 10 Hz), 6.05 (6 H, s; 2 × OCH$_3$), and 6.09 (3 H, s; OCH$_3$).

Reaction of 3,5-Bismethoxycarbonyl-6-methyl-2-pyridone (4) and Methyl Methoxymethylenecyanoacetate in the Presence of Sodium Methoxide.—The pyridone (4) (2.0 g) and methyl methoxymethylenecyanoacetate (1.25 g) were added to a solution of sodium methoxide [from sodium (0.2 g) and methanol (20 ml)] and refluxed (6 h). Work-up gave unchanged pyridone (0.74 g) and the quinolizone (7) (20 mg), yellow needles from acetone, m.p. 205 °C, identical (spectral data) with the specimen above.

Treatment of 3,5-Bismethoxycarbonyl-6-methyl-2-pyridone with Methyl Methoxymethylenecyanoacetate and Potassium t-Butoxide in Dimethylformamide.—The pyridone (1.0 g) and the methyl methoxymethylenecyanoacetate (0.61 g) in dimethylformamide (15 ml), and potassium t-butoxide (1.0 g) were heated to 100 °C with stirring (90 min). Evaporation and work-up followed by chromatography on Florisil, eluting with ether, gave methyl 2-cyano-3-dimethyl-aminoacrylate (10) (100 mg), crystallised from cyclo-hexane–chloroform as needles, m.p. 98 °C (lit.,[3] m.p. 97—100 °C) (Found: C, 54.45; H, 6.40; N, 17.75%; M^+ 154. C$_7$H$_{10}$N$_2$O$_2$ requires C, 54.55; H, 6.55; N, 18.15%); $\nu_{max.}$ (KBr) 2 220 (nitrile), 1 685 (ester CO), and 1 620 cm^{-1} (olefin); τ 2.29 (1 H, s; =CH–), 6.28 (3 H, s; OCH$_3$), 6.64 (3 H, s; NCH$_3$), and 6.80 (3 H, s; NCH$_3$).

Treatment of 3,5-Bismethoxycarbonyl-6-methyl-2-pyrone (11) with Methylamine.—The pyrone (3.0 g) in methanol (30 ml) at 0 °C was treated with 33% methylamine in ethanol (1.25 g): an exothermic reaction occurred. After 5 min, work-up gave 5-methoxycarbonyl-6-methyl-3-methylcarbox-amido-2-pyrone (13), m.p. 223 °C (from chloroform) (Found: C, 53.3; H, 4.95; N, 6.65%; M^+ 225. C$_{10}$H$_{14}$NO$_5$ requires C, 53.35; H, 4.90; N, 6.20%); $\nu_{max.}$ (KBr) 1 730 (pyrone CO), 1 710 (ester CO), 1 625 (amide CO), and 1 545 cm^{-1}; $\lambda_{max.}$ (ethanol) 208 (ε 16 160), 258 (11 980), and 330 (8 560) nm; $\lambda_{max.}$ (ethanolic hydrochloric acid) showed no change; $\lambda_{max.}$ (ethanolic sodium hydroxide) 266 (ε 12 820) and 348 (7 480) nm; τ(CF$_3$CO$_2$H) 0.69 (1 H, s; =CH–), 5.88 (3 H, s; OCH$_3$), 5.96 (3 H, s; NCH$_3$), and 6.89 (3 H, s; CH$_3$).

Methylation of 5-Acetyl-3-methoxycarbonyl-6-methyl-2-pyridone (24) with Dimethyl Sulphate.—The pyridone (1.5 g) was added to excess of sodium methoxide in methanol (50 ml), and the mixture was heated to reflux. Dimethyl sulphate and sodium methoxide solution were added alter-nately, so that the solution remained alkaline, until the conversion of the pyridone to its *N*-methyl analogue appeared to be complete (t.l.c.). Work-up gave 5-acetyl-1,6-dimethyl-3-methoxycarbonyl-2-pyridone (14) (1.1 g, 69%), crystallised from benzene, m.p. 119 °C (Found: C, 59.2; H, 5.55; N, 6.2%; M^+ 223. C$_{11}$H$_{13}$NO$_4$ requires C, 59.2; H, 5.85; N, 6.3%); $\nu_{max.}$ (KBr) 1 705 (ester CO), 1 685 (acetyl CO), 1 655 (pyridone CO), and 1 590 cm^{-1}; $\lambda_{max.}$ (ethanol) 213 (ε 14 290), 277 (13 590), and 340 (8 340) nm; $\lambda_{max.}$ (ethanolic sodium hydroxide) and $\lambda_{max.}$ (ethanolic hydrochloric acid) showed no change; τ(CDCl$_3$) 1.42 (1 H, s; =CH–), 6.10 (3 H, s; OCH$_3$), 6.38 (3 H, s; NCH$_3$), 7.50 (3 H s; COCH$_3$), and 7.25 (3 H, s; CH$_3$).

Methylation of 3,5-Bismethoxycarbonyl-6-methyl-2-pyridone (25) with Dimethyl Sulphate in Dimethylformamide.—The pyridone (2.0 g), methanol, and sodium methoxide [from

sodium (0.24 g) and methanol (15 ml)] gave the sodium salt which was dried *in vacuo* and added to dimethylformamide (20 ml) and dimethyl sulphate (1.05 g). After reflux (10 min), work-up gave 3,5-*bismethoxycarbonyl-1,6-dimethyl-2-pyridone* (20) (1.37 g, 69%), m.p. 142 °C (from chloroform–cyclohexane) (Found: C, 55.6; H, 5.6; N, 5.6%; M^+ 239. C$_{11}$H$_{13}$NO$_5$ requires C, 55.2; H, 5.5; N, 5.9%), $\nu_{max.}$ (KBr) 1 735 (ester CO), 1 710 (ester CO), 1 660 (pyridone CO), and 1 540 cm^{-1}; $\lambda_{max.}$ (ethanolic hydrochloric acid) 210 (ε 19 900), 262 (15 210), and 332 (8 990) nm; $\lambda_{max.}$ (ethanol) 209 (ε 19 030), 262 (14 650), and 333 (8 500) nm; $\lambda_{max.}$ (ethanolic sodium hydroxide) 262 (ε 14 780) and 332 (9 110) nm; τ(CDCl$_3$) 1.30 (1 H, s; =CH–), 6.11 (3 H, s; OCH$_3$), 6.14 (3 H, s; OCH$_3$), 6.36 (3 H, s; NCH$_3$), and 7.15 (3 H, s; CH$_3$).

Reaction between 5-Acetyl-1,6-dimethyl-3-methoxycarbonyl-2-pyridone (14) and Methyl Methoxymethyleneacetoacetate in the Presence of Sodium Methoxide (1.0 mol).—The pyridone (2.0 g) was added to sodium methoxide [from sodium (0.21 g) and methanol (20 ml)]. Methyl methoxymethylene-acetoacetate (1.42 g) was added, and the mixture was refluxed for 2.5 h. Work-up gave 3,6-*bismethoxycarbonyl-5-methyl-2-quinolone* (19) (1.5 g, 62%), m.p. 202 °C (from chloroform–cyclohexane) (Found: C, 60.8; H, 4.7; N, 5.1%; M^+ 275. C$_{14}$H$_{13}$NO$_5$ requires C, 61.1; H, 4.75; N, 5.1%), $\nu_{max.}$ (KBr) 1 730 (ester CO), 1 715 (ester CO), 1 625 (quinolone CO), and 1 570 cm^{-1}; $\lambda_{max.}$ (ethanol) 211 (ε 16 100), 256 (37 200), 306infl. (7 850), 314 (8 440), and 358 (5 320) nm; $\lambda_{max.}$ (ethanolic hydrochloric acid) no change; $\lambda_{max.}$ (ethanolic sodium hydroxide) 258 (ε 44 600), 290infl. (8 100), 300infl. (7 150), and 342 (6 990) nm; τ(CDCl$_3$) -4.36(br, NH), 0.69 (1 H, s; =CH–), 1.75 (1 H, d; 8-H; J 9 Hz), 2.56 (1 H, d; 7-H; J 9 Hz), 6.05 (3 H, s; OCH$_3$), 6.12 (3 H, s; OCH$_3$), and 7.09 (3 H, s; CH$_3$).

The mother liquors, gave, after chromatography on silica, eluting with chloroform, and crystallisation from cyclohexane–chloroform, 3,6-*bismethoxycarbonyl-1,5-dimeth-yl-2-quinolone* (18) (0.16 g, 6%), m.p. 180 °C (Found: C, 62.3; H, 5.2; N, 4.5%; M^+ 289. C$_{15}$H$_{15}$NO$_5$ requires C, 62.3; H, 5.2; N, 4.8%); $\nu_{max.}$ (KBr) 1 715 (ester CO), 1 655 (quinolone CO), and 1 570 cm^{-1}; $\lambda_{max.}$ (ethanol) 212 (17 320), 260 (45 700), 303 (6 700), and 359 (5 350) nm; $\lambda_{max.}$ (ethanolic hydrochloric acid) and $\lambda_{max.}$ (ethanolic sodium hydroxide) showed no change; τ(CDCl$_3$) 1.19 (1 H, s; 4-H), 1.87 (1 H, d; 8-H; J 10 Hz), 2.75 (1 H, d; 7-H; J 10 Hz), 6.03 (3 H, s; OCH$_3$), 6.07 (3 H, s; OCH$_3$), 6.25 (3 H, s; NCH$_3$), and 7.14 (3 H, s; CH$_3$).

Reaction between 3,5-Bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20) and Methyl Methoxymethyleneacetoacetate in the Presence of Sodium Methoxide (1.0 mol).—The pyridone (1.0 g) was added to sodium methoxide [from sodium (0.1 g) and methanol (25 ml)], followed by methyl methoxymethyl-eneacetoacetate (0.66 g); the mixture was refluxed (1 h). Work-up gave 3,6-*bismethoxycarbonyl-5-hydroxy-1-methyl-2-quinolone* (23) (0.65 g, 53%), m.p. 207 °C (from benzene) (Found: C, 58.1; H, 4.5; N, 4.4%; M^+ 291. C$_{14}$H$_{13}$NO$_6$ requires C, 57.8; H, 4.5; N, 4.8%); $\nu_{max.}$ (KBr) 1 705 (ester CO), 1 665 (chelated ester CO), 1 625 (quinolone CO), and 1 585 cm^{-1}; $\lambda_{max.}$ (ethanolic hydrochloric acid) 208 (ε 17 700), 267 (41 600), 282infl. (22 800), and 327 (10 400) nm; $\lambda_{max.}$ (ethanol) 208 (ε 16 100), 267 (39 800), 282infl. (21 800), and 328 (9 560) nm; $\lambda_{max.}$ (ethanolic sodium hydroxide) 235 (ε 32 600), 262 (26 300), 310 (20 400), 351 (6 010), and 422 (12 500) nm; τ(CDCl$_3$) -1.88 (1 H, s; OH, removed by D$_2$O exchange), 1.09 (1 H, s; 4-H), 1.98

(1 H, d; 8-H; J 10 Hz), 3.18 (1 H, d; 7-H; J, 10 Hz), 6.01 (3 H, s; OCH$_3$), 6.05 (3 H, s; OCH$_3$), and 6.30 (3 H, s; NCH$_3$).

Reaction between 3,5-Bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20) *and Methyl Methoxymethylenecyanoacetate catalysed by Sodium Methoxide* (1.0 *mol*).—The pyridone (2.0 g) was added to sodium methoxide [from sodium (0.2 g) and methanol (60 ml)], followed by methyl methoxymethylenecyanoacetate (1.18 g), and the mixture was refluxed (1 h). Methanol was removed under reduced pressure, and the residue was dissolved in chloroform (100 ml). This solution was treated with 2N hydrochloric acid, washed with water, dried (MgSO$_4$), and the chloroform removed. Crystallisation from cyclohexane–chloroform gave 3,5-*bismethoxycarbonyl-1-methyl-6-(3-cyano-3-methoxycarbonyl-prop-2-enyl)-2-pyridone* (28) (1.8 g, 89%), m.p. 116 °C, as slightly pink needles (Found: C, 55.4; H, 4.4; N, 7.9%; M^+ 348. C$_{16}$H$_{16}$N$_2$O$_7$ requires C, 55.15; H, 4.6; N, 8.05%); $v_{max.}$ (KBr) 2 220 (nitrile), 1 735 (ester), 1 700 (ester), 1 655 (pyridone CO), and 1 620 cm^{-1}; $\lambda_{max.}$ (ethanolic hydrochloric acid) 213 (ε 21 700), 264 (10 900), and 336 (8 125) nm; $\lambda_{max.}$ (ethanol) 213 (21 800), 262 (11 080), 336 (7 050), and 491 (3 570) nm; $\lambda_{max.}$ (ethanolic sodium hydroxide) 255 (17 770), 322 (4 310), and 488 (65 500) nm; τ(CDCl$_3$) 1.28 (1 H, s; 4-H), 2.42 (1 H, t; 2'-H; J 7 Hz), 5.39 (2 H, d; 1'-H, J, 7 Hz), 6.11 (9 H, s; 3 × OCH$_3$), and 6.37 (3 H, s; NCH$_3$).

Reaction of 3,5-Bismethoxycarbonyl-1-methyl-6-(3-cyano-3-methoxycarbonylprop-2-enyl)-2-pyridone (28) *with Water*.—The pyridone (1.0 g) was refluxed for 3 h with distilled water (75 ml) and then extracted with chloroform. Methyl cyanoacetate was formed (t.l.c. on silica) and the

crystalline material was recrystallised from methanol to give 3-*methoxycarbonyl-1-methyl-5-oxopyrano*[4,3-b]*pyridin-2-one* (31), (0.35 g, 52%), m.p. 231 °C (decomp.) (Found: C, 56.05; H, 3.95; N, 5.65%; M^+ 235. C$_{11}$H$_9$NO$_5$ requires C, 56.15; H, 3.85; N, 5.95%), $v_{max.}$ (KBr) 1 725 (ester and pyrone CO), 1 655 (pyridone CO), and 1 630 cm^{-1}; $\lambda_{max.}$ (ethanol) 220 (ε 25 100), 260 (10 570), 266infl. (10 140), 286 (5 590), 297 (4 820), and 356 (10 630) nm; $\lambda_{max.}$ (ethanolic hydrochloric acid) no change; τ(DMSO) 1.59 (1 H, s; 4-H), 1.99 (1 H, d; 7-H; J, 8 Hz), 3.03 (1 H, d; 8-H; J, 8 Hz), 6.11 (3 H, s; OCH$_3$), and 6.24 (3 H, s; NCH$_3$).

Reaction of 3-Methoxycarbonyl-1-methyl-5-oxopyrano-[4,3-b]*pyridin-2-one* (31) *with Sodium Methoxide* (6.0 *mol*).— The pyranopyridone (31) (0.55 g) was added to sodium methoxide solution [from sodium (0.3 g) and methanol, (60 ml)] at <10 °C. The mixture was set aside at 20 °C for 12 h. Work-up gave 3,5-bismethoxycarbonyl-1,6-dimethyl-2-pyridone (20), (0.4 g, 72%), m.p. and mixed m.p. 140 °C, confirmed by i.r. and n.m.r. data.

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