Reaction of Phthalic Anhydride with Ethyl Cyanoacetate: a Route to the 2*H*-Indeno[2,1-*c*]pyridine-1,9-dione, 2*H*-Indeno[2,1-*c*]pyridine-3,9-dione, 2*H*-Indeno[2,1-*c*]pyridazine-3,9-dione, and Indeno[2,1-*c*]pyran-1,9-dione Systems

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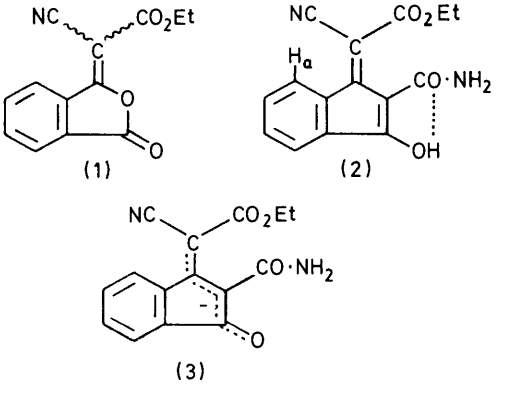
The Knoevenagel condensation of phthalic anhydride with ethyl cyanoacetate gives (*Z*)-ethyl 2-carbamoyl-8-cyano-3-hydroxybenzofulvene-8-carboxylate (2) in good yield. This compound provides a ready entry into the 2*H*-indeno[2,1-*c*]pyridine-1,9-dione, 2*H*-indeno[2,1-*c*]pyridine-3,9-dione, 2*H*-indeno[2,1-*c*]pyridazine-3,9-dione, and indeno[2,1-*c*]pyran-1,9-dione systems.

THE Knoevenagel condensation of phthalic anhydride with ethyl cyanoacetate has been reported [1] to furnish ethyl cyano(phthalidylidene)acetate (1), but neither the yield nor the stereochemistry were specified. Interest in compound (1) in connection with another project, led us to repeat this reaction under the same conditions, *i.e.* sodium as catalyst, in benzene for 4 h, but this afforded the desired product in only 9% yield.

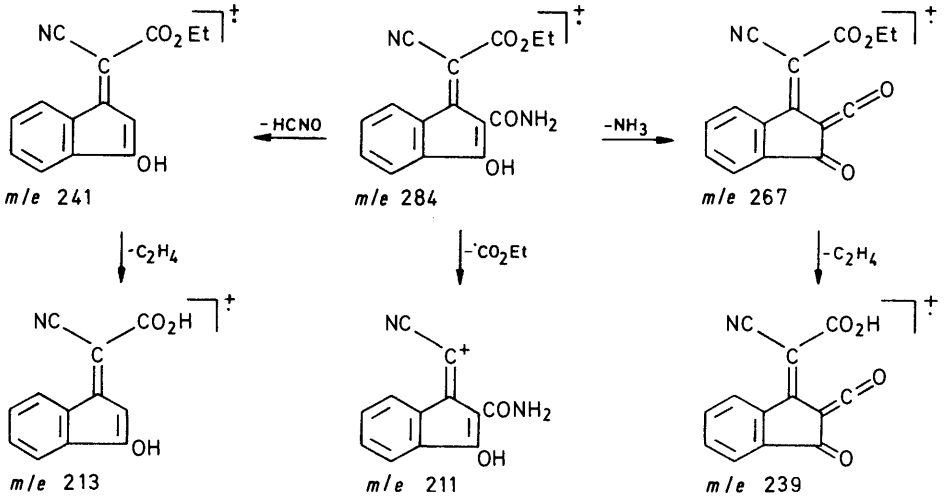
In an attempt to improve the productivity of this condensation, we used triethylamine as base, in toluene for 24 h (see Experimental section). Under these conditions a yellow colour was produced immediately, and upon refluxing an intense orange colour developed. On cooling, an orange oil, $\lambda_{max.}$ 482 nm, separated, which on acidification gave, in 64% yield, a white solid, identified as (*Z*)-ethyl 2-carbamoyl-8-cyano-3-hydroxybenzofulvene-8-carboxylate (2) on the basis of the following evidence.



Elemental analysis agreed with the empirical formula $C_{15}H_{12}N_2O_4$, implying that two molecules of ethyl

[1] F. Sörm, J. Gut, and P. Kaňkovský, *Coll. Czech. Chem. Comm.*, 1950, **15**, 99.

cyanoacetate had reacted with one of phthalic anhydride. The mass spectrum showed a molecular ion at *m/e* 284 with abundant and characteristic ions at *m/e* 267, 241, 239, and 213 (Scheme 1). The initial loss of 17 mass units is structurally informative, as salicylamide displays a similar breakdown pattern.[2] The i.r. spectrum showed two strong carbonyl bands at 1 719 and 1 665 cm^{-1}, assigned respectively to conjugated ester and to the conjugated hydrogen-bonded amide groups. Three strong NH stretching vibrations at 3 415, 3 306, and



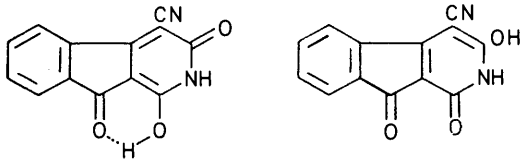
SCHEME 1 Principal mass spectral fragmentations of compound (2); structures are supported by metastable ions and by accurate mass measurements

3 192 cm^{-1} were in keeping with the presence of the primary amide function, and the presence of the conjugated nitrile system was supported by a weak band at 2 224 cm^{-1}. The ^1H n.m.r. spectrum showed a low-field distorted doublet at δ 8.7 assigned to H_a. Although this signal is of the type expected for a proton in this environment,[3] the degree of deshielding cannot be used reliably to assign the geometry about the exocyclic double bond.[4]

Compound (2) dissolved in basic reagents such as sodium carbonate solution, giving an orange solution ($\lambda_{max.}$ 482 nm), thought to contain the highly delocalised anion (3). This anion on heating underwent intramolecular cyclisation to give, in high yield, the 2*H*-indeno[2,1-*c*]pyridine-3,9-dione (4) as a yellow solid. This transformation was also effected thermally in refluxing monochlorobenzene. Accordingly, compound (2) is tentatively the *Z*-configuration as shown.

The cyclisation of compound (2), thermally or under basic conditions, afforded the tautomer (4) virtually exclusively. The solid-state i.r. spectrum of compound (4) showed carbonyl bands at 1 694 and 1 668 cm^{-1} (lactam and hydrogen-bonded five-membered ring ketone, respectively). Crystallisation of this tautomer from formic acid produced the other hydroxypyridone tautomer (5), again as a yellow solid. In this case the two carbonyl bands appeared at 1 736 and 1 694 cm^{-1}, the former being assigned to the five-membered ring ketone. The marked differences in the i.r. spectra of the two tautomers were used to show that each tautomer was isolated in not less than 98% tautomeric purity.

The tautomer (5), although stable in acidic media, was readily converted into the other tautomer in alkaline or in other polar non-acidic media. Hence the two hydroxypyridone forms of this unsymmetrically substituted 2,6-dihydroxypyridine derivative could be interconverted at will and isolated tautomerically pure.



2*H*-Indeno[2,1-*c*]pyridine-1,9-dione, the parent of the tautomer (5), has been prepared recently by conventional cyclisation of 3-cyano-4-phenyl-2(1*H*)-pyridone and used as an intermediate for a synthesis of the alkaloid perlolidine.[5]

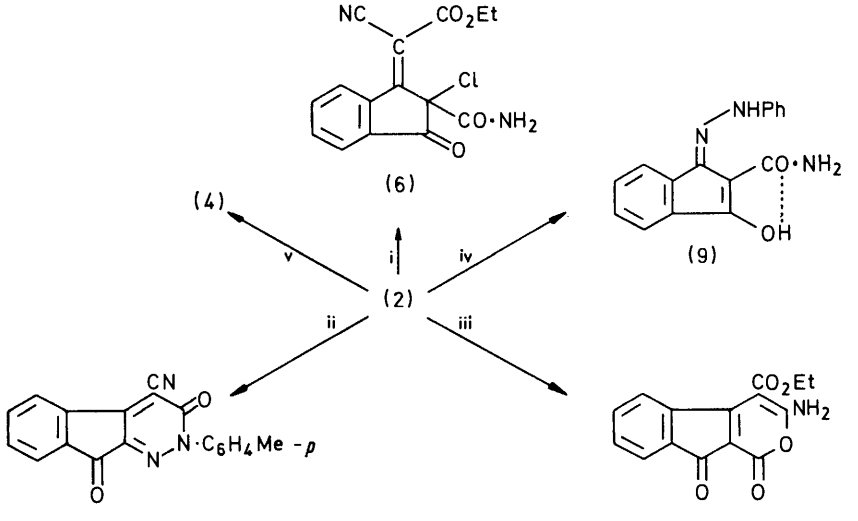
A number of further reactions of the benzofulvene derivative (2) were examined to confirm the structural assignment and to explore the chemistry of this potentially reactive molecule. Routes to a number of novel compounds not readily accessible by other means resulted (Scheme 2). Treatment with hypochlorous acid yielded the indanone derivative (6), $\nu_{max.}$ 1 748s

[2] 'Eight Peak Index of Mass Spectra,' Mass Spectrometry Data Centre, AWRE, Aldermaston, 1974, spectrum no. 03078.
[3] G. Jones and W. J. Rae, *Tetrahedron*, 1966, **22**, 3021.
[4] A. K. Bahl and W. Kemp, *J. Chem. Soc.* (*C*), 1971, 1583.
[5] J. C. Powers and I. Ponticello, *J. Amer. Chem. Soc.*, 1968, **90**, 7102.

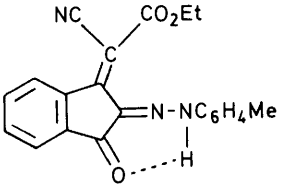
cm^{-1} (five-membered ring carbonyl). With the hydrogen bonding and conjugation removed from the amide carbonyl group the amide band had moved from 1 665 to 1 692 cm^{-1}. Bands at 2 225 and 1 728 cm^{-1} were consistent with the presence of conjugated nitrile and ester groups. That the exocyclic double bond was intact was confirmed by a low-field doublet at δ 8.8 in the ^1H n.m.r. spectrum, assigned to the *ortho* aromatic proton.

The susceptibility of the enol system of compound (2) to electrophilic attack was also demonstrated by the reaction with arenediazonium salts. Treatment with toluene-*p*-diazonium chloride in alkaline medium at low temperature furnished a pale yellow solid whose spectra were in accord with structure (7). The formation of this product is rationalised in terms of the normal Japp–Klingemann [6] mechanism, *i.e.* coupling followed by solvolysis and rearrangement to yield the expected hydrazone (10), which cyclises intramolecularly to give the 2*H*-indeno[2,1-*c*]pyridazine-3,9-dione (7). Cyclisation of the intermediate hydrazone could not be suppressed by the use of arenediazonium salts bearing strongly electron-attracting groups.

Attempted acid-catalysed hydrolysis of the benzofulvene derivative (2) in aqueous ethanol afforded a yellow solid, $C_{15}H_{11}NO_5$, which has been assigned structure (8). The mass spectrum showed a molecular ion at *m/e* 285 and accurate mass measurements confirmed the above formula. Hence the transformation of compound (2) ($C_{15}H_{12}N_2O_4 \longrightarrow C_{15}H_{11}NO_5$) suggested hydrolysis of the 2-carbamoyl group to a carboxy-group. However, the colour change from white to yellow and the



SCHEME 2 Reagents: i, HOCl; ii, *p*-$MeC_6H_4 \cdot N_2^+Cl^-$; iii, dil. HCl; iv, $PhNH \cdot NH_2$; v, Na_2CO_3



(10)

spectral data indicated that rearrangement had also taken place. Abundant mass spectral ions at *m/e* 257 $(M - C_2H_4)^+$ and 240 $(M - C_2H_5O)^+$ supported the presence of an ethyl ester group, and the *ortho* arrangement of the amino and ester functions was indicated by a peak at *m/e* 239 $(M - C_2H_5OH)^+$ (loss of ethanol is a feature of the fragmentation of ethyl anthranilate [7]). The spectrum also showed an abundant ion at *m/e* 241 $(M - 44)^+$. Since the mass spectra of α-pyrones are not characterised by the loss of CO_2 as a primary process,[8] the mass of the ion *m/e* 241 was accurately measured, and shown to correspond to $(M - C_2H_4O)^+$ and not $(M - CO_2)^+$.

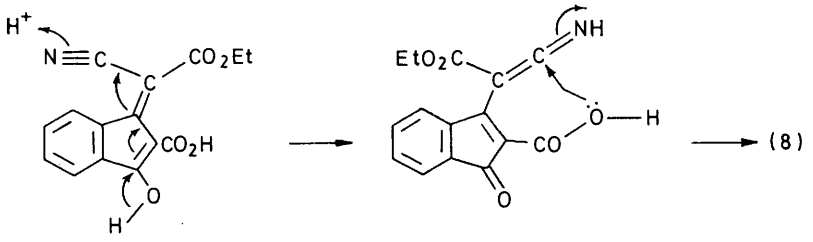
The ^1H n.m.r. spectrum of compound (8) showed the presence of an ethyl ester group, two labile protons, and four aromatic protons. One of the aromatic protons was more deshielded than the other three (δ 7.9), and is assigned to the proton *ortho* to the five-membered ring ketone. The i.r. spectrum showed strong carbonyl bands at 1 750, 1 700, and 1 690 cm^{-1}, assigned respectively to the conjugated δ-lactone,[9] ketone, and hydrogen-bonded ester. The strong NH stretching vibrations between 3 260 and 3 390 cm^{-1} and the preparation of an *N*-acetyl derivative supported the presence of a primary amino-group.

The formation of compound (8) can be rationalised in

[6] R. R. Phillips, *Org. Reactions*, 1959, **10**, 143.
[7] Ref. 2, spectrum No. V 78.
[8] H. Budzikiewicz, C. Djerassi, and D. H. Williams, 'Mass Spectrometry of Organic Compounds,' Holden–Day, San Francisco, 1967.
[9] R. N. Jones, C. L. Angell, T. Ito, and R. J. D. Smith, *Canad. J. Chem.*, 1959, **37**, 2007.

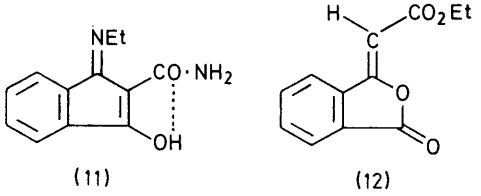
terms of hydrolysis of the 2-carbamoyl group of compound (2) with acid-catalysed isomerisation and cyclisation (Scheme 3).

As already mentioned, compound (2) cyclised on treatment with base to give the 2*H*-indeno[2,1-*c*]pyridine-3,9-dione (4). Bases such as sodium hydroxide, sodium carbonate, ammonia, pyridine, and ethylamine catalysed



SCHEME 3

this reaction. Treatment with phenylhydrazine, on the other hand, gave the hydrazone (9), identical with an authentic sample prepared from 1,3-dioxoindane-2-carboxamide [10] and phenylhydrazine. This reaction is



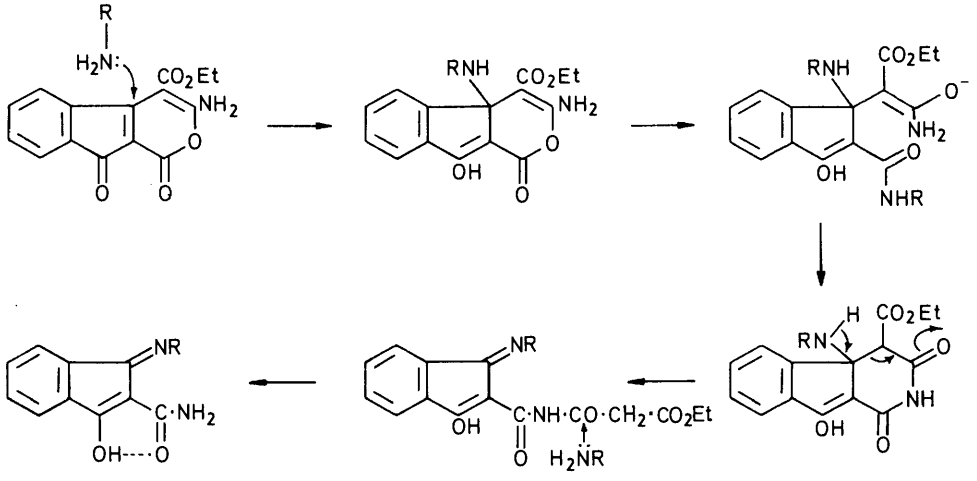
(11) (12)

believed to proceed by nucleophilic attack of phenylhydrazine at the 3-position of compound (2), followed by elimination of ethyl cyanoacetate.

2*H*-indeno[2,1-*c*]pyridine-1,9-dione derivative of type (5). Heating compound (8) with ethylamine solution unexpectedly gave the indenylideneamine (11) as an orange solid. Moreover use of phenylhydrazine in place of ethylamine in this reaction resulted in the hydrazone (9). The mechanism in Scheme 4 is suggested for both these reactions.

Other reactive methylene compounds, *e.g.* cyanoacetamide, malononitrile, diethyl malonate, and *p*-tolylsulphonylacetonitrile, have been treated with phthalic anhydride under the conditions described for the preparation of compound (2), but no related product has been isolated. In the case of diethyl malonate, (*Z*)-ethyl phthalidylideneacetate (12) [12] was obtained in low yield.

The formation of the benzofulvene derivative (2) is believed to proceed as shown in Scheme 5. Initially ethyl cyano(phthalidylidene)acetate (1) is produced, and this reacts further with ethyl cyanoacetate, either conjugatively to give the substituted glutarate (13) or directly at the lactone carbonyl group to give the diketone (14). Products of type (13) are not uncommon



SCHEME 4

Further confirmation of structure (8) was sought by attempted conversion of the pyrone [11] derivative into a in Knoevenagel reactions.[13] The intermediacy of compound (1) was supported by its successful use in the reaction in place of phthalic anhydride. An internal

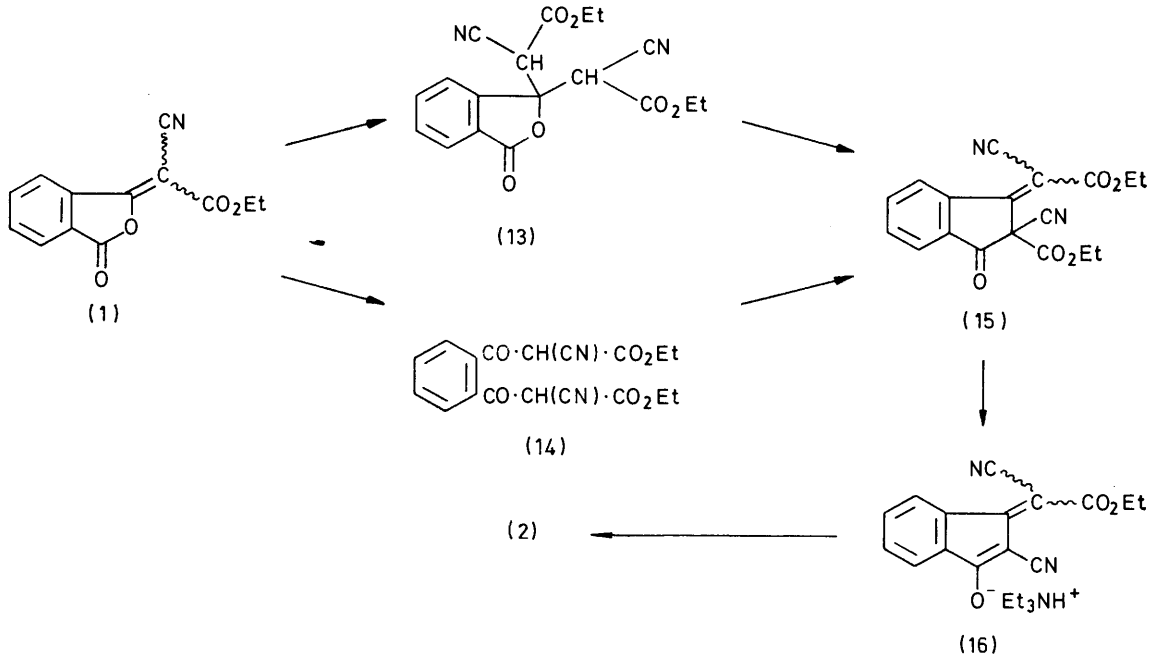
[10] R. L. Horton and K. C. Murdock, *J. Org. Chem.*, 1960, **25**, 938.

[11] N. P. Shusherina, N. D. Dmitrieva, E. A. Luk'yanets, and R. Ya Levina, *Russ. Chem. Rev.*, 1967, **36**, 175.

[12] C. E. Castro, E. J. Gaughan, and D. C. Owsley, *J. Org. Chem.* 1966, **31**, 4071.

[13] G. Jones, *Org. Reactions*, 1967, **15**, 204.

Knoevenagel reaction of either compound (13) or (14) leads to the indanone derivative (15), which on base-induced de-ethoxycarbonylation gives the orange oil (16). Although carbon dioxide is evolved during the reaction, hydrolysis and decarboxylation of compound (15) is not believed to be the major pathway, as propyl acetate can be used as solvent without inhibiting the reaction and a negligible amount of CO_2 is evolved if the lactone (1) is used in place of phthalic anhydride. Finally, acid-catalysed hydrolysis of the 2-cyano-group



SCHEME 5

of the orange oil (16) during work-up yields compound (2).

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 177 spectrophotometer, n.m.r. spectra with a Varian HA 100 spectrometer, u.v. spectra with a Unicam SP 800 spectrometer, and mass spectra with an A.E.I. MS9 spectrophotometer. Coupling constants are expressed in Hz.

Ethyl Cyano(phthalidylidene)acetate (1).—Ethyl cyanoacetate (29 g), sodium (4.7 g), and toluene (150 ml) were heated together on a steam-bath for 1 h, then stirred at room temperature overnight. Phthalic anhydride (25 g) was added and the mixture was stirred at 80—85 °C for 4 h, cooled, and finally added to ice (500 g). The aqueous layer was acidified and extracted with ether, and the combined organic layers were washed with water, dried (Na_2SO_4), and distilled to *ca.* 50 ml. After 24 h the white solid was collected and dried to give the product (3.9 g), contaminated with phthalic anhydride. Crystallisation from toluene gave ethyl cyano(phthalidylidene)acetate (1.9 g, 9%) as white plates, m.p. 206 °C (lit.,[1] 200—202 °C); $\nu_{max.}$ (Nujol) 2 224 (C≡N), 1 825, 1 809 (lactone), and 1 730 cm^{-1} (ester C=O); δ ($CDCl_3$) 1.4 (3 H, t, *J* 7, CH_3), 4.5 (2 H, q, *J* 7, CH_2), 7.8—8.2 (3 H, m, ArH), and 8.6 (1 H, dd, ArH *ortho* to exocyclic C:C) (Found: C, 64.3; H, 3.6; N, 5.6%; M^+, 243. Calc. for $C_{13}H_9NO_4$: C, 64.2; H, 3.7; N, 5.6%; *M*, 243); *m/e* 243, 215, 199, and 171 [*M** 190, (243 ⟶ 215), 163 (243 ⟶ 199), and 136 (215 ⟶ 171)].

(Z)-*Ethyl 2-Carbamoyl-8-cyano-3-hydroxybenzofulvene-8-carboxylate* (2).—Phthalic anhydride (44.4 g, 0.3 mol), ethyl cyanoacetate (22.6 g, 0.2 mol), and toluene (300 ml) were stirred together, and triethylamine (30 ml) was added. The resultant yellow suspension was stirred at 90 °C for 24 h and then allowed to cool. The toluene solution, together with the orange oil which had separated, was extracted with water (3 × 1 l), and the aqueous extract was added, with stirring, to ice (500 g) and concentrated hydrochloric acid (40 ml). The solid which separated was collected, washed with water (200 ml), and dried ($CaCl_2$) to give a bluish-grey solid (18.2 g, 64%). Crystallisation from methanol gave white *needles*, m.p. 194 °C; $\nu_{max.}$ (Nujol) 3 415, 3 306, 3 192 (NH_2), 2 224 (C≡N), 1 719 (conjugated ester C=O), and 1 665 cm^{-1} (conjugated H-bonded amide C=O); $\lambda_{max.}$ (pyridine) 482 nm; δ [$(CD_3)_2SO$] 1.3 (3 H, t, *J* 7, CH_3), 4.3 (2 H, q, *J* 7, CH_2), 7.3—8.1 (5 H, m, ArH and $CONH_2$), and 8.74 (1 H, d, *J* 7, H_a) (Found: C, 63.3; H, 4.3; N, 9.8%; M^+, 284.079 1. $C_{15}H_{12}N_2O_4$ requires C, 63.4; H, 4.3; N, 9.9%; *M*, 284.079 7).

4-Cyano-1-hydroxy-2H-indeno[2,1-c]pyridine-3,9-dione (4).—(a) The benzofulvene (2) (25 g) was added slowly, with stirring, to N-sodium carbonate (800 ml) at 85 °C. The initial orange solution was rapidly converted into a yellow suspension. Stirring was continued for 1 h, then the mixture was cooled to room temperature and acidified with hydrochloric acid; the solid was collected, washed with water, and dried to give the product (20.3 g, 97%). Crystallisation from aqueous dimethylformamide gave yellow *needles*, m.p. >300 °C; $\nu_{max.}$ (Nujol) 3 140 (NH), 2 230 (C≡N), 1 695 (pyridone C=O), and 1 668 cm^{-1} (five-membered ring C=O); $\lambda_{max.}$ (water–cellosolve, 1 : 1) 249,

295, 306, 340sh, and 430 nm (log ε 4.4, 4.3, 4.3, 3.5, and 3.7); δ [$(CD_3)_2SO$] 7.44—7.67 (3 H, m, ArH), 7.90—8.11 (1 H, m, aromatic H, *ortho* to CO), and 10.23 (1 H, s, NH) (Found: C, 65.6; H, 2.3; N, 11.2%; M^+, 238. $C_{13}H_6N_2O_3$ requires C, 65.6; H, 2.5; N, 11.8%; *M*, 238); *m/e* 238, 220, 195, 192, and 167 [*m** 203.4 (238 ⟶ 220), 167.5 (220 ⟶ 192), 159.8 (238 ⟶ 195), and 143 (195 ⟶ 167)].

(*b*) The benzofulvene (2) (1 g) and chlorobenzene (50 ml) were heated under reflux for 1 h. The yellow solid which separated was filtered off, washed with a little ethanol, and dried to give the product (0.55 g, 66%), identical with the material prepared in sodium carbonate solution.

4-*Cyano*-3-*hydroxy*-2H-*indeno*[2,1-c]*pyridine*-1,9-*dione* (5).—The tautomer (4) (1 g) was dissolved in boiling formic acid (100 ml); the solution was filtered and then set aside at room temperature for 20 h. The solid was filtered off, washed with a little formic acid, and oven-dried to give the product (0.7 g, 70%), m.p. >300 °C; $\nu_{max.}$ (Nujol) 3 120 (NH), 2 235 (C≡N), 1 736 (five-membered ring C=O), and 1 695 cm^{-1} (pyridone C=O); electronic (in aqueous cellosolve) and ^1H n.m.r. [$(CD_3)_2SO$] spectra were identical with those of the tautomer (4) (Found: C, 65.4; H, 2.4; N, 11.4. $C_{13}H_6N_2O_3$ requires C, 65.6; H, 2.5; N, 11.8%).

3-*Amino*-4-*ethoxycarbonylindeno*[2,1-c]*pyran*-1,9-*dione* (8).—The benzofulvene (2) (10 g), water (150 ml), ethanol (150 ml), and concentrated hydrochloric acid (5 ml) were heated, under reflux, for 1 h. During this period a yellow solid separated. The suspension was chilled in ice and the solid collected, washed with ethanol (100 ml) and water (200 ml), and dried to give the product (6.6 g, 66%). Crystallisation from ethanol gave yellow *needles*, m.p. 207 °C; $\nu_{max.}$ (KBr) 3 390, 3 260 (NH_2), 1 750 (pyrone C=O), 1 700 (five-membered ring C=O), and 1 690 cm^{-1} (H-bonded ester C=O); δ [$(CD_3)_2SO$] 1.3 (3 H, t, *J* 7, CH_3), 4.4 (2 H, q, *J* 7, CH_2), 7.5—7.7 (3 H, m, ArH), 7.9 (1 H, m, ArH *ortho* to CO), and 8.7br (2 H, s, NH_2) (Found: C, 63.2; H, 3.7; N, 4.9%; M^+, 285.064 3. $C_{15}H_{11}NO_5$ requires C, 63.2; H, 3.9, N, 4.9%; *M*, 285.063 7); *m/e* 285, 257, 241, and 213 [*m** 231.8 (285 ⟶ 257), 203.8 (285 ⟶ 241), and 188.3 (241 ⟶ 213)]; *acetate*, m.p. 186 °C (from ethyl acetate) (Found: C, 62.6; H, 3.9; N, 4.3. $C_{17}H_{13}NO_6$ requires C, 62.4; H, 4.0; N, 4.3%).

(Z)-*Ethyl* 2-*Carbamoyl*-2-*chloro*-3-*oxoindan*-1-*ylidene*-(*cyano*)*acetate* (6).—The benzofulvene (2) (2 g), glacial acetic acid (40 ml), ethanol (10 ml), and water (10 ml) were heated with stirring to 80 °C. Sodium hypochlorite solution (15%; 3 ml) was added dropwise, and stirring was continued at 80 °C for a further 3 min. The suspension was filtered and the filtrate cooled to crystallise the product (1.3 g, 58%). Recrystallisation from ethanol gave white *plates*, m.p. 190 °C; $\nu_{max.}$ (Nujol) 3 418, 3 290, 3 210 (NH), 2 225 (C≡N), 1 748 (five-membered ring C=O), 1 728 (αβ-unsaturated ester C=O), and 1 692 cm^{-1} (amide C=O); δ [$(CD_3)_2SO$] 1.3 (3 H, t, *J* 7, CH_3), 4.3 (2 H, q, *J* 7, CH_2), 7.9—8.3 (5 H, m, ArH and NH_2), and 8.8 (1 H, d, ArH *ortho* to exocyclic double bond) (Found: C, 56.1; H, 3.3; Cl, 11.2; N, 8.4%; M^+, 318. $C_{15}H_{11}ClN_2O_4$ requires C, 56.5; H, 3.5; Cl, 11.1; N, 8.8%; *M*, 318).

4-*Cyano*-2-p-*tolyl*-2H-*indeno*[2,1-c]*pyridazine*-3,9-*dione* (7).—*p*-Toluidine (2.14 g) was dissolved in 2N-hydrochloric acid (40 ml); the solution was chilled in ice and 2N-sodium nitrite (10 ml) was added dropwise, with stirring. After 5 min the excess of nitrite was destroyed with the minimum of sulphamic acid, the solution filtered, and the filtrate added dropwise over 0.75 h to a suspension of the benzofulvene (2) (5.68 g) in water (600 ml) containing 2N-sodium carbonate solution (60 ml), at 5 °C. The solid was filtered off, washed with water, and dried (yield 5.0 g, 80%). Crystallisation from cellosolve gave pale yellow *needles*, m.p. 258 °C; $\nu_{max.}$ (Nujol) 2 227 (C≡N), 1 732 (five-membered ring C=O), and 1 689 cm^{-1} (lactam C=O); δ [$(CD_3)_2SO$] 2.4 (3 H, s, Me), 7.3—7.6 (4 H, dd, MeC_6H_4), and 7.8—8.4 (4 H, m, ArH) (Found: C, 72.7; H, 3.2; N, 13.2%; M^+, 313. $C_{19}H_{11}N_3O_2$ requires C, 72.8; H, 3.5; N, 13.4%; *M*, 313); *m/e* 313, 298, 285, and 270 [*m** 283.7 (313 ⟶ 298), 259.5 (313 ⟶ 285), and 255.7 (285 ⟶ 270)].

3-*Hydroxy*-1-*phenylhydrazonoindene*-2-*carboxamide* (9).—(*a*) 1,3-Dioxoindane-2-carboxamide [10] (189 mg), phenylhydrazine (216 mg), ethanol (25 ml), water (0.5 ml), and concentrated hydrochloric acid (1 drop) were heated under reflux until a solution was obtained. The mixture was then cooled to room temperature and after 48 h a yellow solid had separated. The crystals were collected, washed with a little ethanol, and dried (yield 40 mg, 14%). Recrystallisation from ethanol gave orange *needles*, m.p. 217 °C; $\nu_{max.}$ (Nujol) 3 420, 3 210, 3 145 (NH_2), and 1 672 cm^{-1} (H-bonded amide C=O); $\lambda_{max.}$ (EtOH) 265, 275, 303, and 420 nm (log ε 4.4, 4.4, 3.8, and 4.0) (Found: C, 69.0; H, 4.6; N, 15.0%; M^+, 279. $C_{16}H_{13}N_3O_2$ requires C, 68.8; H, 4.7; N, 15.0%; *M*, 279); *m/e* 279, 262, and 234 [*m** 246 (279 ⟶ 262) and 209 (262 ⟶ 234)].

(*b*) The benzofulvene (2) (2.84 g), phenylhydrazine (1.5 g), and ethanol (150 ml) were heated under reflux for 15 min then cooled. The solid was filtered off, washed with ethanol and water, and dried (yield 1 g, 36%). Crystallisation from ethanol gave yellow *needles*, m.p. 217 °C, identical with the above hydrazone (9).

(*c*) The indenopyrandione (8) (2.85 g), phenylhydrazine (2.5 g), and ethanol (150 ml) were heated under reflux for 0.5 h, then cooled. The solid was collected, washed with ethanol, and dried (yield 2 g, 72%; m.p. 217 °C). The product was identical with the hydrazone (9).

1-*Ethylimino*-3-*hydroxyindene*-2-*carboxamide* (11).—To the indenopyrandione (8) (2 g) suspended in hot ethanol (100 ml) was added aqueous ethylamine solution (*ca.* 30%; 5 ml). A reddish solution resulted initially, which gradually turned orange. On chilling in ice, orange crystals separated which were filtered off, washed with a little ethanol, and oven-dried to give the product (0.8 g, 52%), m.p. 206 °C; $\nu_{max.}$ (Nujol) 3 405, 3 350, 3 290, and 3 180 (NH_2), and 1 630 cm^{-1} (H-bonded amide C=O); $\lambda_{max.}$ (EtOH) 223, 227, 269, 280, and 420nm (log ε 4.4, 4.4, 4.6, 4.6, and 3.4); δ ($CDCl_3$) 1.4 (3 H, t, *J* 7, CH_3), 3.9 (2 H, q, *J* 7, CH_2), 5.4br (1 H, s, NH), 7.4—7.7 (4 H, m, ArH), 7.9br (1 H, s, NH), and 11.5br (1 H, s, OH) (Found: C, 66.9; H, 5.7; N, 12.8%; M^+, 216. $C_{12}H_{12}N_2O_2$ requires C, 66.7; H, 5.6; N, 13.0%; *M*, 216).

(Z)-*Ethyl Phthalidylideneacetate* (12).—Phthalic anhydride (29.6 g), diethyl malonate (32 g), and toluene (150 ml) were stirred together and triethylamine (20 ml) was added. The mixture was heated at 100 °C for 24 h, the solvent was removed by distillation, and the oil so obtained was chilled in ice. The solid was filtered off, washed with a little methanol, dried (6 g), and purified by dissolving in hot ethanol and heating under reflux for 0.75 h. On cooling, a white solid crystallised which was isolated in the usual manner to give the product (2.8 g, 13%), m.p. 130 °C (lit.,[9] 134—135 °C); $\nu_{max.}$ (Nujol) 1 790 (lactone C=O), and

1 718 cm^{-1} (conjugated ester C=O); δ ($CDCl_3$) 1.3 (3 H, t, *J* 7, CH_3), 4.2 (2 H, q, *J* 7, CH_2), 5.8 (1 H, s, CH=), and 7.6—8.1 (4 H, m, ArH) (Found: C, 65.9; H, 4.7%; M^+, 218. Calc. for $C_{12}H_{10}O_4$: C, 66.1; H, 4.6%; *M*, 218).

Reaction of Ethyl Cyano(phthalidylidene)acetate with Ethyl Cyanoacetate.—Ethyl cyano(phthalidylidene)acetate (0.49 g), ethyl cyanoacetate (0.11 g), triethylamine (0.5 g), and toluene (20 ml) were stirred at 90 °C under nitrogen for 16 h; the effluent gases were bubbled through lime water. At the end of the reaction the lime water was only faintly turbid. The mixture was cooled and extracted with water (100 ml), and the extract was acidified to pH *ca.* 1 with dilute hydrochloric acid. The pale orange solid so formed, isolated in the usual way (0.22 g, 77%), was identical with the benzofulvene (2).

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