THE REACTIONS OF DIMETHYL 2,5-BIS(DIAZO)-3,4-DIKETOADIPATE WITH AROMATIC AND HETEROAROMATIC COMPOUNDS^a

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Abstract—Heating the title compound with benzene provides a mixture of dimethyl 1,3-dihydroxynaphthalene-2,4dicarboxylate and 3-carbomethoxy-4-hydroxy-5-phenylpyrone which rearranges on melting to the aforementioned naphthalene derivative. The initial substitution reaction appears to proceed through an intermediary pyronyl cation. The scope of this potential ring annelation reaction has been investigated for a range of aromatic and heteroaromatic compounds. Heating with basic substrates converts the bisdiazo compound into dimethyl 4-hydroxypyrazole-3,5dicarboxylate, while heating with isopropanol yields dimethyl 4,5-dihydroxypyridazine-3,6-dicarboxylate.

The present investigation arose out of our continuing search¹ for methods of generating bisketens. It had been reported previously² that photolysis of a methanolic solution of dimethyl 2,5-bis(diazo)-4,5-diketoadipate (1) provided tetramethyl ethane-1,1,2,2-tetracarboxylate (3), ostensibly by way of the bisketen (2). In the course of attempts to generate 2 we found that heating a benzene solution of the bisdiazo compound (1) provided a chromatographically separable mixture of two isomeric compounds with the composition $C_{14}H_{12}O_6$.

The first compound eluted was the minor product of the reaction. Its IR spectrum indicated the presence of H-bonded ester groups (1590, 1620 cm⁻¹) and OH groups (ca. 3,000 cm⁻¹). The NMR spectrum showed singlets at δ 4.05 (CO₂CH₃), δ 13.40 (OH) and δ 13.62 (OH) as well as a multiplet at δ 7.20–8.80 (ArH) with an integration ratio of 6:1:1:4. Consideration of the origin of this compound and the foregoing spectral data suggested that the compound is the naphthalene 4. The alternative structural isomers 8 and 9 would be expected, *inter alia*, to possess a single CO stretching frequency and a solitary singlet in the NMR for the OH protons. This supposition was confirmed in the case of 8, 1660 cm⁻¹ and δ 10.42 respectively, which was obtained from condensation of dimethyl phthalate

^a A preliminary account of part of this work has already appeared: C. W. Bird, C. K. Wong and D. Y. Wong, *Tetrahedron Letters* 4281 (1972).

with dimethyl succinate by analogy to the preparation³ of the diethyl ester.

The second compound eluted was the major product. The IR spectrum showed the presence of CO groups $(1760, 1620 \text{ cm}^{-1})$, one of which was H-bonded, and a OH group (2500-3500 cm⁻¹). The NMR spectrum showed singlets at $\delta 3.97$, 4.02 (OCH₃), $\delta 7.45$ (C₆H₃) and $\delta 14.60$ (OH) with an integration ratio of 3:3:5:1. Of the structures, 10-13, which might reasonably be considered for this compound the virtual singlet observed for the phenyl protons would appear to exclude formula 12. The UV spectra of 3-hydroxyfurans⁴ and 3-hydroxy-4pyrones⁵ undergo bathochromic shifts in alkaline solution, whereas 4-hydroxy-2-pyrones have been reported⁵ to exhibit a modest hypsochromic shift. As shown in the Table the UV spectrum of the present compound shows a very marked hypsochromic shift on basification, and the original spectrum is regenerated by subsequent acidification. In view of the limited basis on which the original generalisation⁵ was formulated some additional examples have been obtained and are included in Table 1. Thus we conclude that our compound is 3-carbomethoxy-4hydroxy-6-methoxy-5-phenylpyrone (10).

A report⁸ on the reversible ring opening-ring closure of 2-pyrones prompted an examination of the thermal stability of 10, which was found to be smoothly transformed into the naphthalene (4) on melting. This rearrangement entails electrocyclic ring opening of 10 to





the keten (15) which then undergoes cis-trans isomerisation via keto-enol tautomerism, prior to electrocyclic cyclisation to 4. An attempt to confirm the role of the 4-OH group in this process was thwarted when methylation of 10 gave an 0-methyl ether whose IR spectrum showed bands at 1750 and 1620 cm⁻¹ indicative of the 4-pyrone structure (16). Examples of analogous rearrangements are provided⁷ by the thermal conversion of 17 to 18.

Mixtures of the corresponding naphthalenes (5-7) and 2-pyrones (19-21) were obtained from reaction of the bisdiazo compound with anisole, toluene and chlorobenzene. A very low yield was obtained with chlorobenzene, and no comparable reaction was observed with benzonitrile or nitrobenzene. Mesitylene provided solely the pyrone (22). Examination of the NMR spectra of the pyrones obtained from anisole, toluene and chlorobenzene showed that only compounds resulting from attack at the *para* positions of the benzenoid substrates were obtained. In each case the pyrone underwent thermal rearrangement to the same naphthalene derivative as was obtained from the original reaction.

Our conclusion that these substitution reactions were electrophilic ones was strongly supported by the observation that the reaction of the bisdiazo compound with benzene was greatly accelerated by addition of a catalytic quantity of boron trifluoride etherate. Initially we viewed the reaction as proceeding as indicated in Scheme 1, however it seemed surprising that although 14 should be just as capable of forming an electrophile as 1 the potential products from its intramolecular cyclisation or reaction with excess substrate were not encountered. An alternative rationale is shown in Scheme 2. Following Wolff rearrangement of the bisdiazo compound, proton initiated cyclisation of the resulting keten (31) generates the pyrone diazonium cation (32) which can in turn provide the pyrone cation (33). Thus the initial products of these reactions would be the pyrones. Control experiments indicate that the rate of rearrangement of the pyrones to the corresponding naphthalenes under normal reaction conditions is sufficient to account for the amounts observed.

The reaction of an aromatic compound with the bisdiazo compound and subsequent thermal rearrangement of the resulting pyrone provides a single step ring

CO₂Me









and 37. While the pyrone (28) could be thermally converted into the dibenzofuran (37), the pyrone 29 obtained from 3-methylbenzofuran resisted all attempts to rearrange it into 39. Although such a cyclisation has a precedent⁹ in the interconversion of usnic acid (40) and the keten (41), in the present case the presence of an alternative site, the carbomethoxy group, for cyclisation in 38 precludes the formation of 39, which will have a less extensive aromatic conjugated system than the pyrone (29).

N-Carbethoxypyrrole and the bisdiazo compound gave



annelation procedure using essentially neutral reaction conditions, since the intermediary pyrone can be thermally rearranged without isolation. Hence a survey was made of the reactions of the bisdiazo compound with a range of aromatic and heteroaromatic compounds.

Although naphthalene gave only a very low yield of the l'-naphthyl pyrone (23) and phenanthrene provided an almost inseparable mixture of at least two pyrones, presumably the 2'- and 3'-phenanthryl-isomers, a satisfactory yield of 24 was obtained from the much more reactive pyrene. The position of substitution is assumed to be that found for other electrophilic substitution reactions of these hydrocarbons. The low reactivity towards naphthalene in particular may reflect the steric requirements of the electrophile (33).

The reaction of the bisdiazo compound with thiophen gave both 25 and 34. The NMR spectrum of 25, showing δ 7.21 H₃, 7.02 H₄ and 7.32 H₅ with observed coupling constants $J_{3,4} = 3.5$, $J_{3,5} = 1.3$ and $J_{4,5} = 5.2$ Hz, confirmed that substitution occurred at the 2-position of thiophen. The thermal rearrangement of 25 to the benzothiophen (34) established the orientation of the latter. 2,5-Dimethylthiophen provided only the pyrone (26). In keeping with the presumed electrocyclic mechanism of rearrangement no evidence could be obtained for the formation of the benzo[c]thiophen (35) even when the thermolysis of 26 was conducted in the presence of maleic anhydride, N-phenylmaleimide or dimethyl acetylenedicarboxylate. The bisdiazo compound converted benzo[b]thiophen into the pyrone (27) and the dibenzothiophen (36). Initial substitution at C-3 of benzothiophen is assumed by analogy with its behaviour towards other electrophiles.

Attempts to effect reaction of furan and 2-methylfuran with the bisdiazo compound were unsuccessful, but limited reaction did occur with benzofuran providing 28



the pyrone (30). The 5'-proton of the pyrrole ring was observed as an incompletely resolved double doublet at δ 7.6, while the 3'- and 4'-protons show a multiplet at $\delta 6.35-6.45$. Thermal rearrangement of 30 gave the indole (42) which was only formed in trace amounts in the original reaction. The structure 42 follows from the spectral data although the IR spectrum at first sight appears anomalous with three CO bands at 1750, 1720 and 1660 cm⁻¹. These features are due to the N-carbethoxy group preventing the coplanarity of the adjacent carbomethoxy group at position 7 with the benzene ring. This in turn precludes intramolecular H-bonding between the 6-OH and 7-carbomethoxy groups, hence the bands at 3400 and 1720 cm⁻¹. It is noteworthy that the chemical shifts of the Me protons of the carbomethoxy groups are appreciably different, δ 3.88 and 4.04, while in otherwise analogous compounds they are almost identical, $ca. 4.10\delta$.

A common product was obtained when the bisdiazo compound was heated with N-methylpyrrole, indole, thiazole or pyridine. Elemental analysis and mass spectroscopy showed it to have the composition

Table 1

4-Hydroxy-2-pyrone	λ_{\max}^{EtOH} (log ϵ)	$\lambda_{\max}^{Alk \ b}$ (log ϵ)	Shift
6-Me°	283 (3.78)	278 (3.84)	5 nm
3-Et-6-Me"	290 (3.92)	289 (3.98)	1
3,5-diPh-6-PhCH25	310 (4.07)	307 (4.05)	3
3-Ac-6-Me ^a	310 (4.05)	294 (3.91)	16
5-PhCO-6-Me ^d	272 (4.17)	265 (4-19)	7
3-CO2Me-5-Ph-6-MeO	315 (4.06)	273 sh (3.94)	42
3-CO2Me-5-p-MeC6H4		-	
-6-MeO	315 (4-12)	275 sh (4·00)	40
3-CO ₂ Me-5-(Me ₃ C ₆ H ₂) -6-MeO	313 (3.97)	276 (3-86)	37
3-CO ₂ Me-5-n-MeOC ₄ H	515 (5 71)	270 (5 00)	57
-6-MeO 3-CO-Me-5-p-CIC+H	315 (4-23)	276 sh (4·27)	39
-6-MeO	314 (4.01)	275 sh (3·98)	39

"From Ref. 5.

^bEthanol solution with a few drops of 2N NaOH.

^c Prepared according to Ref. 6.

^d Preparation, see Ref. 7.





precursor suggested that the compound was dimethyl 4hydroxypyrazole-3,5-dicarboxylate (45), and this was confirmed by comparison with an authentic¹⁰ specimen. In the course of the preparation of the bisdiazo compound it was noted that prolonged boiling with methanol during recrystallisation led to the formation of a high melting byproduct. Eventually it was found that a good yield of this compound could be obtained by refluxing an isopropanol solution of the bisdiazo compound. The molecular formula was established as C₈H₈N₂O₆ by elemental analysis and mass spectrometry. The IR spectrum revealed the presence of OH and/or imino groups (3350-2500 cm⁻¹) and CO groups (1740, 1590 cm⁻¹). Formulation of this compound as 46 or a tautomer received support from the results of its methylation with diazomethane. The dimethyl derivative (47) obtained exhibited IR bands at 1620 cm^{-1} (ring CO group), 1720 and 1750 cm⁻¹ (ester groups). The NMR spectrum consisted of four singlets at $\delta 3.92$, 2.97, 4.03 and 4.14 due to the four Me groups. The formation of both 45 and 46 can be envisaged as arising from a common intermediate, namely the diazaquinone (43). Direct reduction by isopropanol will yield the pyridazine (46) whereas a base catalysed benzilic acid rearrangement of 43 to 44 followed by decarboxylation provides the pyrazolone (45).

EXPERIMENTAL

 $C_7H_8N_2O_3$. The IR spectrum indicated the presence of OH and imino groups (3400 and 3200 cm⁻¹), as well as CO groups (1700 cm⁻¹). The NMR spectrum comprised a six proton singlet at $\delta 3.82$ and broad absorptions at $\delta 8.40-9.80$ and $\delta 14-15$ each integrating for one proton. Consideration of this information and the structure of its NMR spectra were either recorded at 100 MHz by the P.C.M.U., Harwell or at 60 MHz on a Perkin-Elmer R12E spectrometer for CDCl, solns with internal TMS. IR spectra were recorded for Nujol mulls on a Unicam SP 200 spectrophotomete: and UV spectra for ethanol solns on a Unicam SP 800 instrument Mass spectra were recorded either by the P.C.M.U., Harwell using an MS 9 instrument or by the U. of L. Mass Spectrometry Service at Q.E.C. on an MS 30. The reaction of dimethyl 2,5-bis(diazo)-3,4-diketoadipate with aromatic substrates

In the case of reactions with liquid substrates the bisdiazo compound subs. 11 (1.27 g) was heated with the substrate (10-20 ml) at 100-110° until all of the diazo compound had reacted, when the excess substrate was distilled off *in vacuo*. In the case of reactions with naphthalene, phenanthrene and pyrene the hydrocarbon (3 molar equivs) and the bisdiazo compound (1.27 g) were heated together in refluxing 1.2-dichloroethane (*ca.* 20 ml) until reaction was complete and the solvent distilled off. The products were isolated either by column chromatography on silica gel in benzene and benzene-EtOAc (17:3) or by preparative TLC using plates coated with silica gel and developing (\times 2) with benzene-EtOAc (7:3). The results with individual substrates were as follows:

(a) Benzene gave dimethyl 1,3-dihydroxynaphthalene-2,4dicarboxylate (4%) m.p. 147-48° from MeOH. (Found: C, 61·1; H, 4.5; M, 276. Calc. for C14H12O6: C, 60.9; H, 4.3%; M, 276). IR (Nujol) 1590, 1620 cm⁻¹; UV λ_{max} 253 (40960), 298 (7760), 310 (7330), 364 (5170) nm; NMR 84.05 (s, 6H, CH3O); 7.20-8.80 (m, 4H, ArH); 13.40 (s, OH); 13.62 (s, OH). It also gave 3carbomethoxy-4-hydroxy-6-methoxy-5-phenylpyrone (32%) m.p. 189-90 from MeOH. (Found: C, 61-1; H, 4-6; M, 276). IR (Nujol) 1760, 1620 cm 3 ; UV $\lambda_{\rm max}$ 237 (13350), 315 (11590); NMR $\delta 3^{.97},$ 4.02 $(2 \times s, 2 \times CH_3)$; 7.45 (s, C_6H_3) ; 14.60 (s, OH). The pyrone (0.6 g) was dissolved in MeOH (20 ml) and treated with an ethereal soln of a large excess of diazomethane. The cold soln was allowed to stand overnight and the oily residue obtained by evaporation chromatographed on silica gel in benzene which eluted 3carbomethoxy-2,6-dimethoxy-5-phenylpyrone (0.15g). This was finally evaporatively distilled in high vacuum and obtained as a colourless viscous liquid. IR (liquid film) 1750, 1620 cm⁻¹; NMR $(C_6D_6) \delta 3.24, 3.30, 3.52 (3 \times s, 3 \times CH_3); 7.32 (s, C_6H_5).$

(b) Anisole gave dimethyl 2,4-dihydroxy-6-methoxynaphthalene-1,3-dicarboxylate (3%) m.p. 155–57° from MeOH. (Found: M, 306·0733. Calc. for $C_{15}H_{14}O_7$: M, 306·0740). IR (Nujol) 1645, 1610 cm ¹; UV λ_{max} 242 (45590), 269 sh (29980), 279 sh (25090), 298 (11320), 380 (5810) nm. Also formed was 3-carbomethoxy-4-hydroxy-6-methoxy-5-(*p*-methoxyphenyl)pyrone (28%) m.p. 132–35° from MeOH. (Found: C, 58·8; H, 4·8; M, 306. Calc. for $C_{15}H_{14}O_7$: C, 58·8; H, 4·6%: M, 306); IR (Nujol) 1760, 1610 cm ⁻¹; UV λ_{max} 254 (20000), 315 (16940) nm; NMR δ 3·82, 3·96, 4·02 (3 × s, 3 × CH₃); 6·97 (d) and 7·28. (d) J_{obt} = 8·4 Hz (4H, ArH); 14·40 (OH).

(c) Toluene yielded dimethyl 2,4-dihydroxy-6methylnaphthalene-1,3-dicarboxylate (3%) m.p. 173-75° from MeOH. (Found: C, 62.0; H, 5.1; M, 290. Calc. for C15H14O6: C, 62·0; H, 4·8%; M, 290); IR (Nujol) 1650, 1630 cm⁻¹; UV λ_{max} 253 (39730), 299 (8700), 311 (7540), 369 (5220) nm; NMR δ2-49 (s, CH₃); 4·14 (s, 2×CH₃); 7·50-7·80 (m, 3H, ArH); 13·78 (s, OH), 13.90 (s, OH). Also isolated was 3-carbomethoxy-4-hydroxy-6methoxy-5-(p-methylphenyl)pyrone (17%) m.p. 188-91° from MeOH. (Found: C, 61-9; H, 4-8%; M, 290); IR (Nujol) 1760, 1620 cm $^{3};~\rm UV~\lambda_{max}$ 242 (13990), 315 (13230) nm; NMR $\delta2{\cdot}38,$ 4.00, 4.07 (3 \times s, 3 \times CH₃); 7.18 (d) and 7.28 (d) J_{obs} 6Hz (4H, ArH); 14-45 (s, OH).

(d) Chlorobenzene provided dimethyl 6-chloro-2,4dihydroxynaphthalene (<1%) m.p. 140 – 41° from MeOH. (Found: M, 310·0250. Calc. for $C_{14}H_{11}$ ³⁵ClO₆: M, 310·0245); IR (Nujol) 1640, 1620 cm⁻¹; UV λ_{max} 257 (28090), 297 (7750), 309 (6000), 354 (5230) nm. The accompanying product was 3-carbomethoxy-5-(*p*chlorophenyl)-4-hydroxy-6-methoxypyrone (3%) m.p. 178 – 80° from MeOH. (Found: C, 53·9; H, 3·6; M, 310, 312. Calc. for $C_{14}H_{11}$ ClO₆: C, 54·2; H, 3·5%; M, 310, 312); IR (Nujol) 1760, 1620 cm⁻¹; UV λ_{max} 246 (13140), 314 (10160) nm; NMR δ 3·97, 4·03 (2×s, 2×CH₃); 7·27 (d) and 7·46 (d) J_{obx} 8·1 Hz (4H, ArH); 14-60 (s, OH).

(e) Mesitylene gave 3-carbomethoxy-4-hydroxy-6-methoxy-5-(2', 4', 6'-trimethylphenyl)pyrone (4%) m.p. 167 – 68° from MeOH. (Found: M, 318·1068. Calc. for $C_{17}H_{18}O_6$: M, 318·1103); IR (Nujol) 1760, 1620 cm⁻¹; UV λ_{max} 221 (18280), 313 (9310) nm; NMR δ 2·10, 2·31, 2·38, 4·00, 4·03 (5×s, 5×CH₃); 7·49 (s, 2H, ArH); 14·40 (s, OH).

(f) Naphthalene gave 3-carbomethoxy-4-hydroxy-6-methoxy-5-

(1'-naphthyl)pyrone (4%) m.p. $167 - 68^{\circ}$ from MeOH. (Found: C, 65·8; H, 4·7; M, 326. Calc. for C₁₆H₁₄O₆: C, 66·2; H, 4·3%; M, 326); IR (Nujol) 1760, 1620 cm⁻¹; UV λ_{max} 246 (28630), 315 (13320), nm; λ_{max}^{alk} 278 (19270) nm; NMR δ 3·98, 4·05 (2 × s, 2 × CH₃); 7·31–8·01 (m, 7H, ArH); 14·58 (s, OH).

(g) Phenanthrene yielded a mixture of 3-carbomethoxy-4hydroxy-6-methoxy-5-phenanthrylpyrones (10%) which were only partially separable by TLC. The mass spectrum showed the anticipated molecular ion(s) at m/e 376 and the IR spectrum the characteristic CO bands at 1780 and 1630 cm⁻¹.

(h) Pyrene gave 3-carbomethoxy-4-hydroxy-6-methoxy-5-(1'pyrenyl)pyrone (22%) m.p. $211 - 13^{\circ}$ from EtOAc. (Found: C, 71·7; H, 4·2. Calc. for C₂₄H₁₆O₆: C, 72·0; H, 4·0%); IR (Nujol) 1760, 1620 cm⁻¹; UV λ_{max} 241 (92800), 265 (47200), 275 (69600), 324 (40000), 239 (50400) nm; NMR δ 3·93, 3·97 (2×s, 2×CH₃); 7·76-8·24 (m, 9H, ArH); 14·36 (s, OH).

(i) Thiophen provided dimethyl 4,6-dihydroxybenzo(b)thiophen-5,7-dicarboxylate (2%) m.p. $150-52^{\circ}$ from MeOH. (Found: C, 51-0; H, 3·8; M, 282. Calc. for $C_{12}H_{10}O_6S$: C, 51-0; H, 3·5%; M, 282); IR (Nujol) 1645 cm⁻¹; UV λ_{max} 252 (39480), 260 sh (31820), 269 sh (26990), 294 (9870), 302 (9870), 341 (6240); NMR $\delta 4\cdot 06$. 4·10 (2×s, 2×CH₃); 7·72 (d, H2) and 7·96 (d, H3) $J_{2,3} = 5\cdot 4$ Hz, 13·30 (s, OH); 14·20 (s, OH). It also gave 3carbomethoxy-4-hydroxy-6-methoxy-5-(2'-thienyl)pyrone (14%) m.p. 147 - 48° from MeOH. (Found: C, 51·3; H, 3·9%; M, 282); IR (Nujol) 1760, 1610 cm⁻¹; UV λ_{max} 239 (6580), 267 (6460), 315 (3990); λ_{mx}^{the} 274 (7280) nm; NMR $\delta 4\cdot 00$, 4·16 (2×s, 2×CH₃); 7·02 (dd, H4'); 7·21 (dd, H3'); 7·32 (dd, H5'), $J_{3,4} = 3\cdot5$; $J_{3,5} = 1\cdot3$ and $J_{4,5} = 5\cdot2$ Hz; 15·02 (s, OH).

(j) 2,5-Dimethylthiophen gave 3-carbomethoxy-4-hydroxy-6methoxy-5-(2',5'-dimethyl-3'-thienyl)pyrone (33%) m.p. 149 – 50° from MeOH. (Found: C, 54·1; H, 4·8; M, 310. Calc. for $C_{14}H_{14}O_6S$: C, 54·2; H, 4·5%; M, 310); IR (Nujol) 1770, 1620 cm⁻¹; UV λ_{max} 238 (18050), 316 (12400) nm; λ_{max}^{abc} 278 (9840) nm; NMR δ 2·21, 2·42, 4·00, 4·08 (4×s, 4×CH₃); 6·64 (s, Het-H); 14·78 (s, OH).

(k) Benzo(b)thiophen yielded dimethyl 2.4dihydroxydibenzothiophen-1,3-dicarboxylate (3%) m.p. 216-18° from MeOH. (Found: C, 58.0; H, 3.8; M, 332. Calc. for C10H12O6S: C, 57·8; H, 3·6%; M, 332); IR (Nujol) 1645, 1610 cm⁻¹; UV λ_{max} 258 (23580), 272 (19920), 286 (18170), 308 (13970), 378 (3660), 396 (3490) nm; NMR 84.01 (s, 6H, CH3); 7.47-8.26 (m, 4H, ArH); 10.58 (s, OH); 11.19 (s, OH). Also formed was 5-(3'-benzo(b)thienyl)-3-carbomethoxy-4-hydroxy-6methoxypyrone (13%) m.p. 202-203° from MeOH. (Found: C, 57-8; H, 3-9%; M, 332); IR (Nujol) 1760, 1620 cm⁻¹, UV λ_{max} 225 (30980), 268 (8920), 292 (8850), 300 (9400), 315 (7190) nm; λ_{max}^{hk} 273 (11060) nm; NMR 83.97, 4.00 (2×s, 6H, CH₃); 7.30-8.02 (m, 5H, ArH): 14.60 (s. OH).

(1) Benzofuran gave dimethyl 1,3-dihydroxydibenzofuran-2,4dicarboxylate (0-4%) m.p. 154 – 55° from MeOH. (Found: M, 316·0578. Calc. for $C_{16}H_{12}O_7$: M, 316·0583); IR (Nujol) 1640, 1620 cm⁻¹; UV λ_{max} 256 (22750), 316 (6000), 327 sh (5056), 380 (3160) nm; It also yielded 5-(2'-benzofuryl)-3-carbomethoxy-4hydroxy-6-methoxypyrone (4%) m.p. 170 – 71° from MeOH. (Found: C, 60·6; H, 4·1; M, 316. Calc. for $C_{16}H_{12}O_7$: C, 60·7; H, 3-8%; M, 316); IR (Nujol) 1750, 1620 cm⁻¹; UV λ_{max} 246 (18530), 312 (6520) nm; NMR 84·04, 4·10 (2×s, 2×CH₃); 6·70–7-80 (m, 5H, ArH); 14·52 (s, OH).

(m) 3-Methylbenzofuran provided 3-carbomethoxy-4-hydroxy-6-methoxy-5-(3'-methyl-2'-benzofuryl)pyrone (6%) m.p. 156 – 57° from MeOH. (Found: C, 62·3; H, 4·5; M, 330. Calc. for $C_{17}H_{14}O_7$: C, 61·8; H, 4·2%; M, 330); IR (Nujol) 1780, 1610 cm⁻¹; UV λ_{max} 263 (26400), 280 sh (22000), 285 sh (20540) nm; NMR δ 2-2, 4·06, 4·21 (3 × s, 3 × CH₃); 7·15–7·85 (m, 4H, ArH); 14·50 (s, OH).

(n) N-Carbethoxypyrrole gave 5-(N-carbethoxy-2'-pyrrolyl)-3carbomethoxy-4-hydroxy-6-methoxypyrone (20%) m.p. 135 – 36° from MeOH. (Found: C, 53·0; H, 4·8; N, 4·1; M, 337. Calc. for $C_{15}H_{15}NO_8$: C, 53·4; H, 4·4; N, 4·1%; M, 337); IR (Nujol) 1760, 1630 cm⁻¹; UV λ_{max} 221 (26960), 248 sh (12580), 312 (10780) nm; λ_{max}^{ath} 268 (14160) nm; NMR δ 1·30 (t, CH₃C); 4·00 (s, CH₃O); 4·07 (s, CH₃O), 4·37 (q, CH₂); 6·40 (m, H3' and H4'); 7·52 (m, H5'); 14·27 (s, OH). Heating this compound to 200° provided dimethyl N-carbethoxy-4,6-dihydroxyindole-5,7-dicarboxylate m.p. 148 – 50° from MeOH, which was only formed in trace amounts in the preceding reaction. (Found: C, 52.9; H, 4.5; N, 4.5%; M, 337); IR (Nujol) 3400, 1750, 1720, 1660 cm⁻¹; UV λ_{max} 253 (38400), 341 (3260); λ_{max}^{ubs} 257 (29700), 279 (29700), 305 sh (23200), 354 (5790) nm; NMR δ 1.38 (t, CH₃, J = 6 Hz), 3.88 (s, CH₃); 4.04 (s, CH₃); 4.39 (q, CH₂); 6.70 (d, IH) and 7.33 (d, IH) J = 4 Hz; 10.82 (s, OH); 11.52 (s, OH).

(o) N.-Methylpyrrole, indole and thiazole gave dimethyl 4hydroxypyrazole-3,5-dicarboxylate (19, 36 and 12% respectively) m.p. 241 – 43° from H₂O identical with an authentic sample.¹⁰ (Found: C, 42·4; H, 4·4; N, 14·1; M, 200. Calc. for C₇H₈N₂O₅: C, 42·0; H, 4·0; N, 14·0%; M, 200); IR (Nujol) 3400, 3200, 1700, 1675 cm⁻¹; UV λ_{max} 275 (13840) nm; NMR (d₆-DMSO) δ 3·82 (s, 2 × CH₃); 8·40–9·80 (br, NH); 14·00–15·00 (br, OH).

Dimethyl 1,4-dihydroxynapthalene-2,3-dicarboxylate

Dimethyl phthalate and dimethyl succinate were reacted together in methanolic NaOMe following the procedure³ used for synthesising the diethyl ester. The product (6%) had m.p. 112 – 13° from MeOH. (Found: C, 60.4; H, 4.5; M, 276. Calc. for $C_{14}H_{12}O_{s}$: C, 60.8; H, 4.3%; M, 276); IR (Nujol) 1660 cm⁻¹; UV λ_{max} 220 (98570), 264 (69980), 364 (24640) nm; NMR δ 3.86 (s, 2 × CH₃); 7:60–7:80 (m, 2H, ArH); 8·10–8·30 (m, 2H, ArH); 10·42 (s, 2 × OH).

Reaction of dimethyl 2,5-bis(diazo)-3,4-diketoadipate with isopropanol

The bisdiazo compound (2 g) in freshly distilled isopropanol was heated under reflux for 24 hr. The solution was evaporated *in* vacuo, and the residual solid recrystallised from MeOH to give dimethyl 4,5-dihydroxypyridazine-3,6-dicarboxylate (0·43 g) m.p. 218 – 19°. (Found: C, 41-8; H, 3·4; N, 12·2; M, 228. Calc. for C₈H₈N₂O₆: C, 42·1; H, 3·5; N, 12·2%; M, 228); IR (Nujol) 3350 – 2500, 1740, 1590 cm⁻¹; UV λ_{max} 318 (12370) nm; NMR (d₆-DMSO) δ 2·84 (s, 2×CH₃); 8·60–12·20 (br, 2H, NH&/OH).

The pyridazine (0.5 g) in dry DMF (30 ml) was treated with an ethereal soln of diazomethane (from 20 g N-nitrosomethylurea).

After standing for 2 days at room temp the soln was evaporated *in vacuo*. Preparative TLC of the sticky brown residue on silica gel with CHCl₃-MeOH (1:1) gave dimethyl 5-methoxy-N-methylpyridaz-4-one-3,6-decarboxylate (82 mg) m.p. 98-99° from EtOH-60/80 petroleum ether. (Found: C, 46-8; H, 4-8; N, 10-9; M, 256. Calc. for $C_{10}H_{12}N_2O_6$: C, 46-8; H, 4-7; N, 10-9%; M, 256); IR (Nujol) 1750, 1720, 1620 cm⁻¹; UV λ_{max} 292 (13930) nm; NMR δ 3-92, 3-97, 4-03, 4-14 (4×s, 4×CH₃).

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