days. On removal of the excess diazomethane and ether, a large amount of starting material was present. By repeated crystallization from pentane the starting material could be removed and 1.3 g (31%) of crude dione **23** (n = 6) was obtained, mp 63–69°. The analytical sample was prepared by sublimation, mp 74–75°. The dione **23** (n = 6) had the following spectral properties: ir ($CHCl_3$) 1725 (s), 1725 and 1784 cm^{-1} (sh); nmr ($CDCl_3$) δ 1.6 (broad absorption, 20 H, ring CH_2), and 2.63 ppm (s, 2 H, $CH_2C{=}O$).

Anal. Calcd for $C_{15}H_{20}O_2$: C, 76.88; H, 9.46. Found: C, 76.75; H, 9.70.

Registry No.—**2** (n = 5), 31934-25-5; **2** (n = 6), 22502-49-4; *cis*-**12**, 31934-27-7; *trans*-**12**, 31934-28-8; *cis*-**13** (n = 5), 31934-29-9; *trans*-**13** (n = 5), 31934-30-2; *cis*-**13** (n = 6), 31934-31-3; *trans*-**13** (n = 6), 31934-32-4; **15**, 31934-33-5; **16**, 31934-34-6; *cis*-**17**, 31934-35-7; *trans*-**17**, 31934-36-8; *cis*-**18** (n = 5), 31981-32-5; *trans*-**18** (n = 5), 31934-37-9; *cis*-**18** (n = 6), 31934-38-0; *trans*-**18** (n = 6), 31934-39-1; *cis*-**21**, 31934-40-4; *trans*-**21**, 31934-41-5; **22**, 31934-42-6; **23** (n = 4), 31934-43-7; **23** (n = 5), 31934-44-8; **23** (n = 6), 31934-45-9; diazomethane, 334-88-3.

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6-Acyl-5*H*-1-pyrindine-5,7(6*H*)-diones and Their Reaction with Hydrazine

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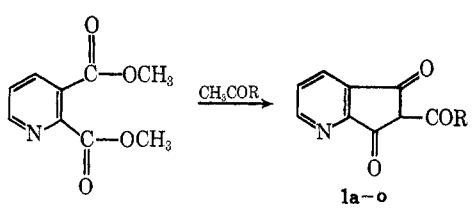
A series of 6-acyl-5*H*-1-pyrindine-5,7(6*H*)-diones (**1**) was prepared by condensing dimethyl 2,3-pyridinedicarboxylate with various methyl ketones. Depending upon the conditions, reaction of compounds **1** with hydrazine gave 3-substituted 1,4-dihydropyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridines (**6**), 3-substituted pyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-ones (**2**), or a mixture of the hydrazones of the two isomeric 3-substituted pyrazolo[3′,4′:3,4]cyclopentapyridin-4(1*H*)-ones (**4** and **5**).

Our interest in 2-acyl-1,3-indandiones and their reaction products with hydrazine[1-3] prompted us to prepare the structurally related compounds, the 6-acyl-5*H*-1-pyrindine-5,7(6*H*)-diones (**1a–o**) and to study their reaction with hydrazine. 6-Alkyl- and 6-aryl-5*H*-1-pyrindine-5,7(6*H*)-diones are reported in the literature[4,5] but no reference was found concerning the 6-acyl derivatives **1**.

The structural analogy with the 6-acyl-1,3-indandiones suggested the preparation of **1** by a method similar to that used to prepare the acylindandiones.[1] Yields varying from 8 to 69% were obtained by reacting dimethyl 2,3-pyridinedicarboxylate with the appropriate methyl ketone in the presence of sodium methoxide.

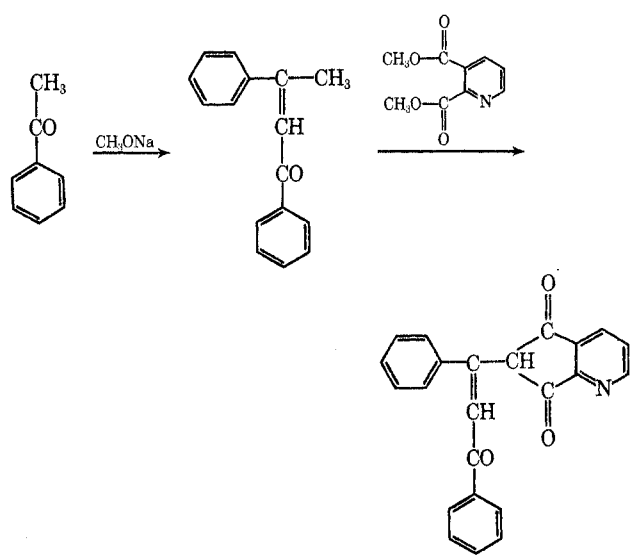


1a–o

When R is an aryl group instead of an alkyl, the reaction is slower and it is accompanied by side reactions. Thus, in the condensation of dimethyl 2,3-pyridinedicarboxylate with acetophenone to form compound **1m**, 6-(α-phenacylidenebenzyl)-5*H*-1-pyridine-5,7(6*H*)-dione was isolated as the by-product.

The structures of the acylpyrindinediones **1a–o** are based upon the elemental analyses and are consistent with the infrared spectra.

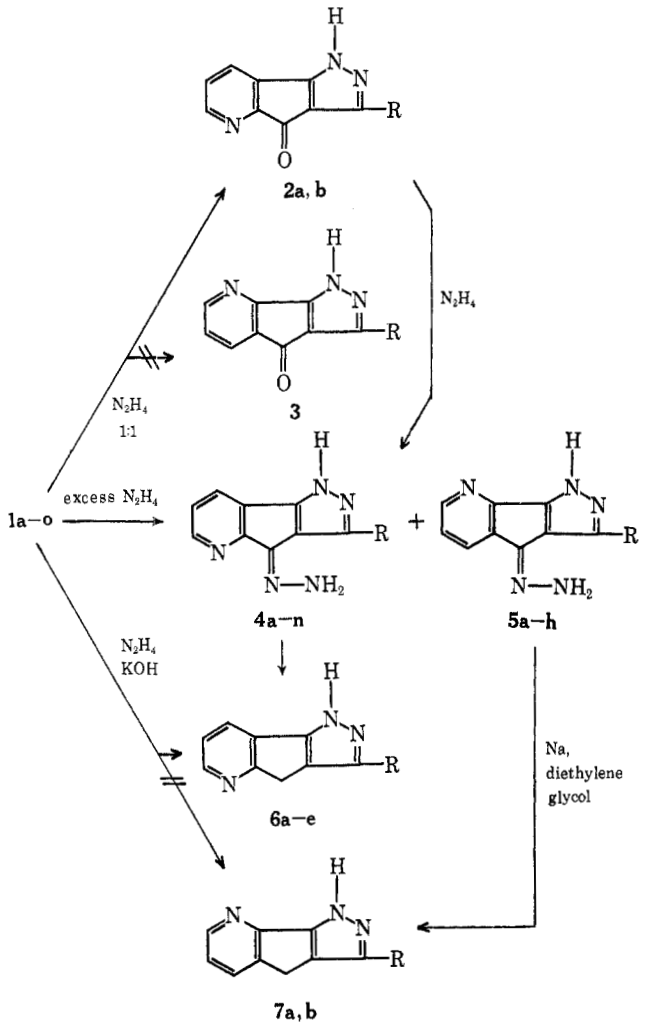
The addition of hydrazine to a hot solution of 6-acetyl-5*H*-1-pyrindine-5,7(6*H*)-dione (**1a**) in ethanol, followed by rapid cooling in ice, gave the corresponding monohydrazone with the hydrazono group on the side chain. This structural assignment was based on the similarities of the spectral and chemical properties of this hydrazone with those of the known α-hydrazone of 2-acetyl-1,3-indandione.[1] Several attempts to prepare the monohydrazones of other 6-acyl-5*H*-1-pyrindine-5,7(6*H*)-diones were unsuccessful. The products obtained were generally the ring-closed compounds **2**.



In the reaction of the acylpyrindinediones **1m** and **1n** with 1 equiv of hydrazine in refluxing ethanol, only one of the two possible isomers, 3-substituted pyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-one (**2**, Scheme I) or 3-substituted pyrazolo[3′,4′:3,4]-cyclopenta[2,1-*b*]pyridin-4(1*H*)-one (**3**), was isolated. Structure **2** was assigned to the isolated isomer, since the hydrazones of compounds **2** were found identical

(1) R. A. Braun and W. A. Mosher, *J. Amer. Chem. Soc.*, **80**, 2749 (1958).
(2) R. A. Braun and W. A. Mosher, *J. Org. Chem.*, **24**, 648 (1959).
(3) W. A. Mosher and W. E. Meier, *ibid.*, **35**, 3685 (1970).
(4) B. M. Bain and J. E. Saxton, *J. Chem. Soc.*, 5216 (1961).
(5) L. E. Neiland and G. Ya. Vanag, *Khim. Geterotsikl. Soedin.*, **1**, 114 (1967); *Chem. Abstr.*, **67**, 64269*k* (1967).

SCHEME I[a]



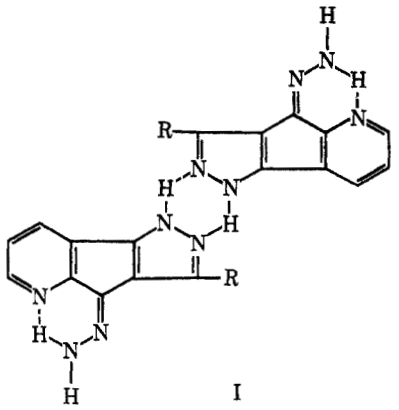
[a] For R see Tables I–III and Experimental Section.

with the hydrazones **4** prepared directly from compounds **1** as described below.

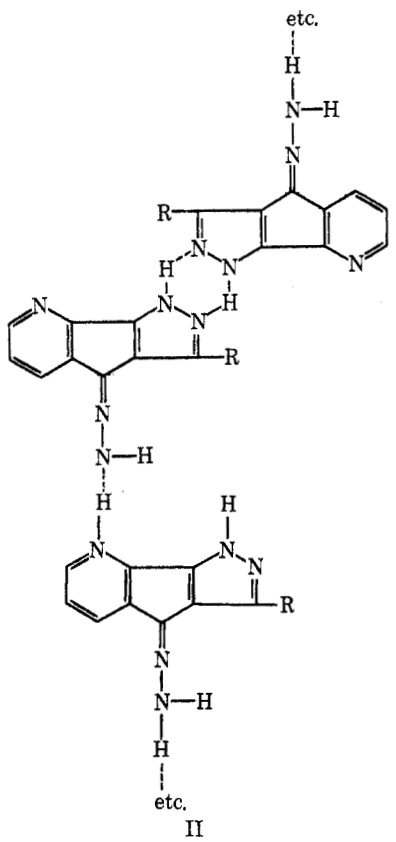
Considering the similarity of this reaction with that between 2-acetyl-4-nitro-1,3-indandione and hydrazine, in which 3-methyl-8-nitroindeno[1,2-*c*]pyrazol-4(1*H*)-one was obtained,[3] one would predict that isomer **3** would be formed preferentially. However, none of this isomer was found. The structure of the tautomer 3-substituted pyrazolo[3′,4′:3,4]cyclopenta-[1,2-*b*]-pyridin-4(2*H*)-one was also considered. The similarity of the infrared spectra of compounds **2** with those of the known 3-substituted indeno[1,2-*c*]-pyrazol-4(1*H*)-ones[2] favors structure **2** and we will use this structure in subsequent discussion without excluding the possibility of the tautomeric structure.

The reaction of the acylpyrindinediones **1** with a large excess of hydrazine in refluxing ethanol yielded in most cases a mixture of two isomeric hydrazones. These compounds were easily separated by means of their different solubilities in benzene. The soluble isomer constitutes the main fraction and shows a lower melting point than the insoluble isomer. When only one isomer was found, it was the benzene-soluble one.

The infrared spectra and the physical properties of these two isomers suggest structure **4** for the benzene-soluble isomer and structure **5** for the benzene-insoluble isomer. Several types of intra- and intermolecular hydrogen bonds are possible in these isomers. Some are shown in structures I and II.



I



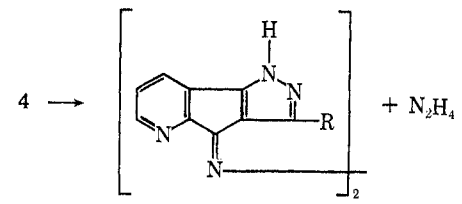
II

The infrared spectra of the benzene-soluble compounds show a broad and weak band at 3360 cm^{-1}, which is tentatively assigned to an intramolecular hydrogen-bonded NH_2 group, and very broad and weak bands at 3150 and 3050 cm^{-1}, which may be assigned to an intermolecular hydrogen-bonded NH group, as represented in I. This structure also shows the type of intermolecular hydrogen bonding which can lead to a dimer, and this accounts for the relatively low melting points of the isomers **4** in comparison with isomers **5** and for their solubility in nonpolar solvents.

The infrared spectra of the benzene-insoluble compounds show a sharp band at 3350 cm^{-1}, which is tentatively assigned to free NH_2 groups (from terminal hydrazono group), and bands at 3220 and 3160 cm^{-1}, which may be assigned to associated NH_2 and NH groups, respectively. These associated bands are not quite so broad as those shown by the benzene-soluble compounds. Structure II shows the type of intermolecular hydrogen bonding which can lead to

polymers, and this accounts for the higher melting points of isomers **5** and for their very low solubilities in nonpolar solvents.

Hydrazones **4** decomposed when heated at about 250° to give the corresponding azines and hydrazine. This



disproportionation reaction can proceed at a lower temperature in the presence of hydrochloric acid. An alternate route to these azines is based on the reaction of the pyrindinediones **1** with excess hydrazine in acetic acid.

The Wolff–Kishner reduction of hydrazones **4** by the Huang-Minlon modification gave the corresponding 3-substituted 1,4-dihydropyrazolo[3′,4′:3,4]-cyclopenta[1,2-*b*]pyridines (**6a–e**). These compounds were also obtained directly from the acylpyrindinediones **1** by using the Wolff–Kishner reduction. In the latter reaction the other possible isomer, the 3-substituted 1,4-dihydropyrazolo[3′,4′:3,4]-cyclopenta-[2,1-*b*]pyridine (**7**), was not found. Compounds **7** instead were obtained when the hydrazones **5** were heated at 210° with sodium in diethylene glycol.

The nmr spectra of compounds **6** and **7** show that the methylene group in **6** is slightly more deshielded than in **7**, indicating the proximity of the nitrogen atom to the methylene group in the former compounds. These results give further evidence for the structures assigned to compounds **4** and **5** from which **6** and **7**, respectively, are derived.

Experimental Section[6]

6-Acyl-5*H*-1-pyridine-5,7(6*H*)-diones (1a–o).—The following general procedure was used. A mixture of dimethyl 2,3-pyridinedicarboxylate (0.0256 mol) and the appropriate methyl ketone (0.0259 mol) in dry benzene (80 ml) was added to a stirred suspension of sodium methoxide (0.13 mol) in dry benzene (100 ml). The mixture was stirred at 40° for 6 hr, then at reflux for 3–4 days. A yellow to brown solid mass adhered to the walls of the flask. The reaction mass was cooled to room temperature and the solvent was decanted into a separatory funnel and washed twice with water. The aqueous washings were added to the solid residue in the reaction flask, boiled with Darco, and filtered hot; the filtrate was cooled in ice. The precipitate was collected by filtration, dissolved in water (50 ml), and acidified with 50% hydrochloric acid. The yellow solid was collected, dried, and recrystallized from petroleum ether (bp 75–90°), unless otherwise indicated (Table I).

The sodium salts of some acylpyrindinediones are very soluble in water and do not crystallize out on cooling. In these cases the alkaline solution, after boiling with Darco, was filtered, cooled, and acidified with 50% hydrochloric acid and the acylpyrindinedione was separated by extraction with ether.

The sodium salt of **1k** is almost insoluble in water. In this case, after the benzene layer was separated, water was added to the solid reaction mass and the mixture was heated on a steam bath. The yellow sodium salt was collected by filtration, washed with water, and suspended in water, and the slurry was made acid to litmus by adding 50% hydrochloric acid under strong agitation. After 3 hr of stirring the solid was collected and crystallized from petroleum ether.

6-Benzoyl-5*H*-1-pyrindine-5,7(6*H*)-dione (1m) was prepared as in the general procedure described above, except that, after the reaction mixture was refluxed for 4 days, 0.5 *N* sodium hydroxide solution (150 ml) was added at room temperature and the benzene layer was separated. The alkaline solution was washed once with ether, boiled with Darco, filtered, acidified with 50% hydrochloric acid, and cooled in ice overnight to give **1m**, as green-yellow crystals.

In another experiment for preparing **1m**, after separation of the benzene layer, the alkaline solution was acidified to pH 5 with 50% hydrochloric acid and the resulting deep red solution was extracted with ether. Removal of the ether and crystallization of the residue from ethanol gave 1.0 g of the by-product, 6-(α-phenacylidenebenzyl)-5*H*-1-pyrindine-5,7(6*H*)-dione as dark violet crystals: mp 158°; ir 1700, 1660, and 1600 cm^{-1}.

Anal. Calcd for $C_{23}H_{15}NO_3$: C, 78.17; H, 4.28; N, 3.96. Found: C, 78.39; H, 4.50; N, 4.06.

Controlled ozonolysis of this compound in dichloromethane gave **1m** as shown by mixture melting point and comparison of the ir spectra.

The yields, melting points, and elemental analyses of compounds **1a–o** are recorded in Table I. The infrared spectra of compounds **1a** show absorption bands at 2950, 1680, 1650, and 1600 cm^{-1}; **1j** at 2950, 1720, 1650 and 1600 cm^{-1}; **1k** (Nujol) at 3000, 1710, 1680, 1650, and 1570 cm^{-1}; **1m** at 3000, 1680, 1650, and 1580 cm^{-1}.

6-Acetyl-5*H*-1-pyrindine-5,7(6*H*)-dione α-Hydrazone.—Hydrazine (0.2 g, 0.00625 mol) was added to a hot solution of **1a** (0.5 g, 0.00265 mol) in ethanol (50 ml). The mixture was quickly chilled in ice and the precipitate was recrystallized from ethanol, giving 0.3 g (55%) of the hydrazone of **1a** as dark orange crystals: mp 265° dec; ir 3350, 3275, 3200, 2950, 1680, 1640, 1580, and 1570 cm^{-1}.

Anal. Calcd. for $C_{10}H_9N_3O_2$: C, 59.10; H, 4.46; N, 20.65. Found: C, 59.18; H, 4.67; N, 21.00.

This hydrazone gives a positive Tollens test and dissolves rapidly in 10% aqueous sodium hydroxide, giving a bright red solution. This behavior is characteristic of 2-acyl-1,3-indandione hydrazones with the hydrazono group on the side chain.[1] The hydrazone of **1a** when treated with dilute hydrochloric acid gives **1a** (ir and mixture melting point).

3-Phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-b]pyridin-4(1*H*)-one (2a).—To a suspension of **1m** (6.0 g, 0.0239 mol) in anhydrous ethanol (150 ml) was added 95% hydrazine (0.76 g, 0.0239 mol). The red solution was heated at reflux for 12 hr and then cooled to room temperature. The solid was collected by filtration and recrystallized from ethanol to give **2a** in 84% yield as colorless needles: mp 311°; ir 3400, 3100, 2700, 1700 cm^{-1}.

Anal. Calcd. for $C_{15}H_9N_3O$: C, 72.86; H, 3.67; N, 17.00. Found: C, 72.86; H, 3.85; N, 17.27.

Na Salt of 2a.—A mixture of **2a** (1.2 g, 0.00486 mol) and 10% aqueous sodium hydroxide solution (200 ml) was refluxed until a yellow solution was obtained. A little amount of insoluble material was filtered off through a sintered-glass funnel and the filtrate was cooled overnight to give 1 g (77%) of yellow needles: mp >360°; ir 1680, 1640, and 1600 cm^{-1}. No bands appeared in the region between 3500 and 2900 cm^{-1}.

1-Ethyl-3-phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-b]pyridin-4-one.—A mixture of the sodium salt of **2a** (0.3 g, 0.0012 mol) and a large excess of ethyl bromide in ethanol (25 ml) was refluxed for 5 hr. A little amount of white solid was filtered off and the filtrate was evaporated to dryness. The residue, recrystallized from methanol, gave 0.2 g (65.4%) of yellow, silky needles, mp 168°. The infrared spectrum showed no bands in the 3400–2900-cm^{-1} region.

Anal. Calcd. for $C_{17}H_{13}N_3O$: C, 74.16; H, 4.76; N, 15.26. Found: C, 73.99; H, 4.64; N, 15.36.

3-(*p*-Methoxyphenyl)pyrazolo[3′,4′:3,4]cyclopenta[1,2-b]pyridin-4(1*H*)-one (2b). was obtained as yellow needles, mp 325°, in

(6) Melting points were determined with a Fisher–Johns melting point apparatus, unless otherwise indicated, and are uncorrected. For high melting point compounds a sealed capillary tube in a silicon bath was used. The infrared spectra were recorded on a Baird Model B recording spectrophotometer and on an Infracord spectrophotometer Model 137, using potassium bromide pellets. For the study of the structures of compounds **4** and **5**, the infrared spectra were obtained on Perkin-Elmer Models 221 G and 421 spectrophotometers (potassium bromide pellets). The insolubilities of these compounds in carbon tetrachloride, carbon disulfide, or chloroform made this study very difficult as the intermolecular hydrogen bonding could not be overcome by dilution. Nuclear magnetic resonance spectra were obtained on a Varian A-60A spectrometer, DMSO-d_6 being used as a solvent and TMS as an internal standard. Elemental analyses were performed by Dr. A. Bernhardt, Mikroanalytisches Laboratorium, Max Planck Institute für Kohlenforschung, Mülheim (Ruhr), West Germany.

TABLE I

6-ACYL-5*H*-1-PYRINDINE-5,7(6*H*)-DIONES (1a–o)

Compd	R	Yield, %	Mp, °C	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
1a	CH_3	37.2	148	$C_{10}H_7NO_3$	63.49	3.73	7.41	63.72	3.92	7.15
1b	C_2H_5	39.4	149	$C_{11}H_9NO_3$	65.02	4.46	6.89	64.93	4.73	6.61
1c	C_3H_7	32.4	89	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.40	5.10	6.36
1d	*i*-C_3H_7	36.0	92	$C_{12}H_{11}NO_3$	66.35	5.10	6.45	66.58	5.29	6.48
1e	C_4H_9	64.2	88	$C_{13}H_{13}NO_3$	67.52	5.67	6.06	67.52	5.63	6.10
1f	*i*-C_4H_9	45.7	101	$C_{13}H_{13}NO_3$	67.52	5.67	6.06	67.62	5.74	6.00
1g	*sec*-C_4H_9	27.2	77	$C_{13}H_{13}NO_3$	67.52	5.67	6.06	67.67	5.57	6.14
1h	C_5H_{11}	50.0	98[a]	$C_{14}H_{15}NO_3$	68.55	6.16	5.71	68.77	6.05	5.72
1i	C_6H_{13}	20.0	88	$C_{15}H_{17}NO_3$	69.48	6.61	5.40	69.33	6.30	5.44
1j	$CH_2C_6H_5$	18.7	139	$C_{16}H_{11}NO_3$	72.44	4.18	5.28	72.47	4.28	5.49
1k	$CH(C_6H_5)_2$	69.0	170	$C_{22}H_{15}NO_3$	77.40	4.43	4.10	77.29	4.43	3.94
1l	C_3H_5[b]	49.0	177	$C_{12}H_9NO_3$	66.97	4.22	6.51	66.96	4.40	6.51
1m	C_6H_5	38.3	188[c,d]	$C_{15}H_9NO_3$	71.71	3.61	5.57	71.53	3.60	5.54
1n	*p*-$OCH_3C_6H_4$[e]	8.4	161[d]	$C_{16}H_{11}NO_4$						
1o	$C_{10}H_7$(1-)	21.6	110	$C_{19}H_{11}NO_3$	75.74	3.68	4.65	76.15	3.69	4.63

[a] Recrystallized from petroleum ether (bp 30–60°). [b] Cyclopropyl group. [c] Recrystallized from methanol. [d] A sealed capillary tube in a silicon bath was used. [e] This compound was not easily purified for analysis. However, the product of the reaction of **1n** with hydrazine, **2b**, gave good analyses.

TABLE II

3-SUBSTITUTED PYRAZOLO[3′,4′:3,4]CYCLOPENTA[1,2-*b*]PYRIDIN-4-(1*H*)-ONE HYDRAZONES (4a–n)

Compd	R	Yield, %	Mp, °C[a]	Ratio of isomers 4:5	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
4a	CH_3	68.0	265[b]	8:1	$C_{10}H_9N_5$	60.29	4.55	35.16	60.20	4.71	34.97
4b	C_2H_5	38.0	225[c]	4:1	$C_{11}H_{11}N_5$	61.95	5.20	32.85	62.20	5.22	32.78
4c	C_3H_7	83.5	182[d]	1:0	$C_{12}H_{13}N_5$	63.42	5.77	30.82	63.62	5.63	30.75
4d	*i*-C_3H_7	50.0	200[d]	3:1	$C_{12}H_{13}N_5$	63.42	5.77	30.82	63.70	5.93	30.45
4e	C_4H_9	32.0	164[c]	10:3	$C_{13}H_{15}N_5$	64.71	6.27	29.03	64.85	6.20	28.95
4f	*i*-C_4H_9	36.0	144[c]	3:2	$C_{13}H_{15}N_5$	64.71	6.27	29.03	64.74	5.91	29.05
4g	*sec*-C_4H_9	40.0	185[c]	2:1	$C_{13}H_{15}N_5$	64.71	6.27	29.03	65.00	6.40	28.85
4h	C_5H_{11}	96.0	186[d]	1:0	$C_{14}H_{17}N_5$	65.86	6.71	27.43	66.00	6.61	27.33
4i	C_6H_{13}	48.3	148[d]	1:0	$C_{15}H_{19}N_5$	66.89	7.11	26.00	66.89	7.04	25.94
4j	$CH_2C_6H_5$	48.0	188[d]	4:1	$C_{16}H_{13}N_5$	69.80	4.76	25.44	69.58	5.10	25.61
4k	$CH(C_6H_5)_2$	58.0	193[d]	1:0	$C_{22}H_{17}N_5$	75.19	4.88	19.93	75.35	5.16	19.80
4l	C_3H_5[e]	47.7	210[c]	5:1	$C_{12}H_{11}N_5$	63.98	4.92	31.09	63.66	5.19	30.92
4m	C_6H_5	96.0	240[f]	1:0	$C_{15}H_{11}N_5$	68.95	4.24	26.81	68.71	4.37	25.76[g]
4n	*p*-$OCH_3C_6H_4$	71.0	238[b]	1:0	$C_{16}H_{13}N_5O$	65.97	4.50	24.04	66.20	4.59	23.81

[a] Samples for melting point determinations were heated rapidly, as slow heating causes disproportionation to form the symmetrical azines and hydrazine. [b] Recrystallization solvent: ethanol. [c] Recrystallization solvent: benzene. [d] Recrystallization solvent: benzene–petroluem ether (bp 30–60°). [e] Cyclopropyl group. [f] Recrystallization solvent: ethanol–water. [g] This compound was not easily purified for analysis. However, the Wolff–Kishner reduction of this compound gave a product, **6e**, of good analysis.

90% yield from **1n** and hydrazine following the procedure above described for **2a**. Its infrared spectrum is similar to that of **2a**.

Anal. Calcd for $C_{16}H_{11}N_3O_2$: C, 69.30; H, 4.00; N, 15.16. Found: C, 69.29; H, 4.12; N, 14.94.

3-Substituted Pyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4-(1*H*)-one Hydrazones (4a–n) and 3-Substituted Pyrazolo[3′,4′:3,4]cyclopenta[2,1-*b*]pyridin-4-(1*H*)-one Hydrazones (5a–h). From Compounds 1.—The general procedure was as follows. To a mixture of the appropriate 6-acyl-5(*H*)-1-pyrindine-5,7(6*H*)-dione (1) (0.00493 mol) and anhydrous ethanol (100 ml) was added 95% hydrazine (0.63 g, 0.0197 mole) and the resulting yellow solution was refluxed for 48 hr. The solvent was evaporated on a steam bath under reduced pressure, the residue was extracted at the boil with benzene, and the suspension was filtered. The filtrate was concentrated and cooled and the precipitated solid was recrystallized from a suitable solvent (see Table II) to give **4a–n** as yellow crystals.

The product, insoluble in benzene, was recrystallized from ethanol or ethanol–water mixtures to give **5a–h** as colorless crystals. In the case of compounds **4a** and **5a** the residue, after evaporation of the solvent, was chromatographed on neutral alumina (elution with chloroform) to give starting material **1a**, compound **4a**, and compound **5a**, in the order indicated. The ir spectra of compounds **4** show bands at 3360, 3150, and 3050 cm^{-1} and those of compounds **5** at 3350, 3220, and 3160 cm^{-1}.

The yields, melting points, and elemental analyses of the hydrazones **4a–n** and **5a–h**, prepared from compounds **1**, are listed in Tables II and III, respectively.

3-Phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridine-4(1*H*)-one Hydrazone (4m). From Compound 2a.—A mixture of **2a** (2.48 g, 0.01 mol), 95% hydrazine (0.34 ml), and absolute ethanol (50 ml) was stirred at reflux for 48 hr. The solvent was evaporated under reduced pressure and the yellow residue, completely soluble in hot benzene, was chromatographed on neutral alumina (chloroform as the eluent) to give 2.12 g (81%) of **4m**. The identity of this compound with that obtained directly from **1m** with excess of hydrazine was established by mixture melting point determination and by comparison of the ir spectra. Further elution of the alumina column yielded none of the isomer **5**.

3-(*p*-Methoxyphenyl)pyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-one Hydrazone (4n). From Compound 2b.—It was obtained in 88% yield as yellow crystals, following the procedure above described for **4m**. This compound was found identical (mixture melting point and ir) with the compound obtained directly from **1n** and excess hydrazine, as described above.

3-*n*-Amylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridine-4(1*H*)-one azine was obtained in 42.8% yield by heating **4h** in a silicon oil bath at 250° for 15 min. The dark brown mass was recrystallized twice from ethanol to give yellow needles, mp 311° (sealed tube in an oil bath).

Anal. Calcd. for $C_{28}H_{30}N_8$: C, 70.27; H, 6.32; N, 23.42. Found: C, 70.22; H, 6.45; N, 23.21.

3-Phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)-one azine was obtained by refluxing for 2 hr a mixture of **4m** (0.5 g, 0.0019 mol) and 25% aqueous hydrochloric acid (15 ml). The resulting red solid (0.35 g, 74.8%) recrystallized from a mixture

TABLE III

3-SUBSTITUTED PYRAZOLO[3′,4′:3,4]CYCLOPENTA[2,1-*b*]PYRIDIN-4(1*H*)-ONE HYDRAZONES (5a–h)

Compd	R	Yield, %	Mp, °C[a]	Empirical Formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
5a	CH_3	8.5	281	$C_{10}H_9N_5$	60.29	4.55	35.16	60.07	4.59	35.02
5b	C_2H_5	9.5	250	$C_{11}H_{11}N_5$	61.95	5.20	32.85	61.77	5.15	32.88
5c	*i*-C_3H_7	17.0	233	$C_{12}H_{13}N_5$	63.42	5.77	30.82	63.68	6.10	30.61
5d	C_4H_9	9.6	197	$C_{13}H_{15}N_5$	64.71	6.27	29.03	64.87	6.11	28.82
5e	*i*-C_4H_9	24.0	214	$C_{13}H_{15}N_5$	64.71	6.27	29.03	65.11	6.31	29.00
5f	*sec*-C_4H_9	20.0	196	$C_{13}H_{15}N_5$	64.71	6.27	29.03	64.50	6.28	28.89
5g	$CH_2C_6H_5$	12.0	238	$C_{16}H_{13}N_5$	69.80	4.76	25.44	69.77	5.05	25.41
5h	C_3H_5[b]	9.6	244	$C_{12}H_{11}N_5$	63.98	4.92	31.09	64.13	5.04	30.81

[a] Samples for melting point determinations were heated rapidly, as slow heating causes disproportionation to form the symmetrical azines and hydrazine. [b] Cyclopropyl group.

TABLE IV

3-SUBSTITUTED 1,4-DIHYDROPYRAZOLO[3′,4′:3,4]CYCLOPENTA[1,2-*b*]PYRIDINES (6a–e)

Compd	R	Mp, °C	Empirical formula	Calcd, % C	Calcd, % H	Calcd, % N	Found, % C	Found, % H	Found, % N
6a	*i*-C_3H_7	162[a]	$C_{12}H_{13}N_3$	72.33	6.57	21.09	72.39	6.65	20.78
6b	*sec*-C_4H_9	171[a]	$C_{13}H_{15}N_3$	73.27	7.05	19.78	72.94	6.84	19.93
6c	*n*-C_5H_{11}	155[a]	$C_{14}H_{17}N_3$	74.00	7.54	18.49	74.10	7.60	18.49
6d	$CH(C_6H_5)_2$	272[b,c]	$C_{22}H_{17}N_3$	81.71	5.30	13.00	81.93	5.54	12.80
6e	C_6H_5	300[c,d]	$C_{15}H_{11}N_3$	77.27	4.75	18.02	77.07	4.69	17.89

[a] Recrystallization solvent: benzene–petroleum ether (bp 30–60°). [b] Recrystallization solvent: benzene–methanol. [c] A sealed capillary tube in a silicon bath was used. [d] Recrystallization solvent: acetone.

of benzene and dimethylformamide did not melt up to 360°; ir 3400–3200 and 1620 cm^{-1}.

Anal. Calcd. for $C_{36}H_{18}N_8$: C, 73.45; H, 3.70; N, 22.85. Found: C, 73.32; H, 3.89; N, 22.59.

This azine was also obtained (80% yield) by refluxing for 3 hr a mixture of **1m** and 3 equiv of hydrazine in acetic acid. The identity of this azine with that above described was established by ir spectra comparison.

3-Substituted 1,4-Dihydropyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]-pyridines (6a–e). Procedure A. From Pyrindinediones 1.—A mixture of the appropriate pyrindinedione **1** (0.0088 mol), 95% hydrazine (2.0 ml), and diethylene glycol (40 ml) was heated in an open flask over a 1-hr period to 140°. To the resulting clear yellow solution was added a solution of potassium hydroxide (5.0 g) in diethylene glycol (20 ml), the temperature was raised slowly to 200°, and the mixture was kept at this temperature for 1 hr. The dark red solution was cooled and added with stirring to ice water (200 ml). The precipitate was collected by filtration, washed, and recrystallized from suitable solvent (see Table IV) to give **6a–e** as yellow crystals (**6d** is colorless) in 55–65% yields. In the case of **6a** and **6c**, after heating at 200°, the cold mixture was poured into water and extracted with ether. The solvent was evaporated and the residue was recrystallized.

Procedure B. From Hydrazones 4.—A mixture of the appropriate hydrazone **4** (0.00383 mol), potassium hydroxide (2.0 g), and diethylene glycol (25 ml) was heated in an open flask over a 2-hr period to 200°. The resulting brown solution was cooled and poured into ice water (100 ml) and the precipitate was recrystallized from suitable solvent (see Table IV) to give **6a–e** in 50–60% yields. In the case of **6a** and **6c**, after heating at 200°, the cold mixture was worked up as described above under A. In the preparation of compound **6b**, sodium was used in place of potassium hydroxide and the mixture was heated at 210° for 12 hr, then cooled, acidified with dilute hydrochloric acid, and extracted with benzene. The solvent was removed under reduced pressure and the residue was recrystallized from benzene–petroleum ether.

The melting points and elemental analyses of compounds **6** are recorded in Table IV. The ir spectra show absorption bands in the 3200–2900-, 1600–1580-, 1470–1450-, 1420–1410-, and 1090–1070-cm^{-1} regions. The nmr spectra of **6a** and **6b** show peaks at δ 3.5 (s, 2 protons) and at δ 8.2, 7.7, and 7.1 ppm. (m, aromatic protons). The compounds prepared according to procedure A were identical with those prepared according to procedure B as shown by mixture melting point determinations and by comparison of the infrared spectra.

1,4-Dihydro-3-isopropylpyrazolo[3′,4′:3,4]cyclopenta[2,1-*b*]-pyridine (7a).—A mixture of hydrazone **5c** (2.0 g), sodium (2.0 g), and diethylene glycol (70 ml) was heated at 210° for 12 hr, then cooled, acidified with dilute hydrochloric acid, and extracted with benzene. Removal of benzene under reduced pressure and crystallization of the residue from benzene–petroleum ether gave **7a** (45% yield) as yellow crystals, mp 167°; nmr shows peaks at δ 3.3 (s, 2 protons) and at δ 8.2, 7.7, and 7.1 ppm (m, aromatic protons).

Anal. Calcd for $C_{12}H_{13}N_3$: C, 72.33; H, 6.57; N, 21.10. Found: C, 72.00; H, 6.67; N, 20.97.

3-*sec*-Butyl-1,4-dihydropyrazolo[3′,4′:3,4]cyclopenta[2,1-*b*]-pyridine (7b) was obtained in 48% yield from hydrazone **5f**, following the above procedure for **7a**, as yellow crystals, mp 178°; the nmr spectrum is similar to that of compound **7a**.

Anal. Calcd. for $C_{13}H_{15}N_3$: C, 73.27; H, 7.05; N, 19.78. Found: C, 73.06; H, 6.90; N, 19.64.

Registry No.—**1a**, 32121-10-1; **1b**, 32121-11-2; **1c**, 32121-12-3; **1d**, 32121-13-4; **1e**, 32121-14-5; **1f**, 32121-15-6; **1g**, 32121-16-7; **1h**, 32121-17-8; **1i**, 32111-61-8; **1j**, 32111-62-9; **1k**, 32111-63-0; **1l**, 32111-64-1; **1m**, 32111-65-2; **1n**, 322207-46-8; **1o**, 32111-66-3; **2a**, 32111-67-4; **2a** Na salt, 32111-68-5; **2b**, 32111-69-6; **4a**, 32111-70-9; **4b**, 32111-35-6; **4c**, 32111-36-7; **4d**, 32111-37-8; **4e**, 32111-38-9; **4f**, 32207-33-3; **4g**, 32207-34-4; **4h**, 32111-39-0; **4i**, 32111-40-3; **4j**, 32111-41-4; **4k**, 32111-42-5; **4l**, 32111-43-6; **4m**, 32111-44-7; **4n**, 32111-45-8; **5a**, 32111-46-9; **5b**, 32207-35-5; **5c**, 32110-91-1; **5d**, 32110-92-2; **5e**, 32110-93-3; **5f**, 32110-94-4; **5g**, 32110-95-5; **5h**, 32110-96-6; **6a**, 32110-97-7; **6b**, 32110-98-8; **6c**, 32110-99-9; **6d**, 32111-00-5; **6e**, 32111-01-6; **7a**, 32111-02-7; **7b**, 32111-03-8; hydrazine, 302-01-2; 6-acetyl-5*H*-1-pyrindine-5,7(6*H*)-dione α-hydrazone, 32120-78-8; 1-ethyl-3-phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4-one, 32120-79-9; 3-*n*-amylpyrazolo[3′4′:3,4]-cyclopenta[1,2-*b*]pyridin-4(1*H*)-one azine, 32256-03-4; 3-phenylpyrazolo[3′,4′:3,4]cyclopenta[1,2-*b*]pyridin-4(1*H*)one azine, 32120-80-2.

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