The Synthesis of 2,4-Diaryl-5*H*-indeno- and 2,4-Diaryl-5*H*-pyridocyclopenta[1,2-*d*]pyrimidin-5-ones

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A series of 2,4-diaryl-5*H*-indeno[1,2-*d*]pyrimidin-5-ones (**4a–f**) was prepared by condensing 2-(para-substituted benzylidene)-1,3-indandiones (**1a–f**) with benzamidine in the presence of sodium methoxide. The reaction of compound **4a** with hydrazine yielded the corresponding hydrazone **6**, the azine **7**, 2,4-diphenyl-5*H*-indeno[1,2-*d*]pyrimidin-5-ol (**5a**), or 2,4-diphenyl-5*H*-indeno[1,2-*d*]pyrimidine (**8a**), depending upon the conditions. 6-(Para-substituted benzylidene)-5*H*-1-pyrindine-5,7(6*H*)-diones (**9a–e**) reacted with benzamidine to yield mixtures of two isomeric 2,4-diaryl-5*H*-pyridocyclopenta[1,2-*d*]pyrimidin-5-ones (**10a–e** and **11a–e**).

The condensation of 2-benzylidene-1,3-indandione (**1a**) with guanidine to form 2-amino-4-phenyl-5*H*-indeno[1,2-*d*]pyrimidin-5-one was reported by this laboratory.[1] Continuation of work on the cyclization reactions of **1a** led us to investigate the reaction of a number of 2-(para-substituted benzylidene)-1,3-indandiones (**1a–f**) and of their aza analogs, the 6-(para-substituted benzylidene)-5*H*-1-pyrindine-5,7-(6*H*)-diones (**9a–e**), with benzamidine (**2**).

The reaction of α,β-unsaturated ketones with benzamidine to form substituted pyrimidines has been reported by Dodson and Seyler in 1951.[2] Since then this synthesis has not been further explored.[3]

We found that when 2 equiv of the benzylidene-indandiones **1a–f** were allowed to react with 1 equiv of benzamidine in the presence of 4 equiv of sodium methoxide 2,4-diaryl-5*H*-indeno[1,2-*d*]pyrimidin-5-ones (**4a–f**) were formed in maximum yields of 32%. Evidence for the structures of compounds **4** is provided by elemental analyses, spectral data, and the formation of derivatives as described below.

A possible mechanism for the formation of the indenopyrimidinones **4** is shown in Scheme I. It consists of a Michael addition of **2** to the activated double bond of **1**, followed by ring closure, dehydration to dihydroindenopyrimidinone, and dehydrogenation to **4** by base-catalyzed air oxidation. The role played by the air in this step was not completely investigated. The Michael adduct **3** was isolated in 34% yield when equivalent amounts of **1a**, the hydrochloride of **2**, and sodium methoxide were heated at reflux for 1 hr. This adduct was then cyclized to **4a** by heating at reflux in methanol with sodium methoxide. In this step, beside the formation of **4a**, a reverse Michael reaction took place simultaneously regenerating **1a**. When acetic acid was used in place of sodium methoxide in the cyclization of **3**, none of compound **4a** was formed and only **1a** was isolated from the reaction mixture.

The diarylindenopyrimidinones **4** reacted with hydrazine to give compounds **5**, **6**, **7**, or **8** (Scheme II) depending upon the conditions. Addition of indenopyrimidinones (**4a** and **4c**) to ethanolic solutions of hydrazine containing catalytic amounts of acetic acid, followed by heating the mixtures at reflux for 10 hr gave the corresponding carbinol derivatives **5a** and **5b** in 70–80% yields. The structures of these compounds are supported by elemental analyses and ir and nmr spectra. The probable mechanism for the formation of the carbinols involves the oxidation of hydrazine to diimide,[4–6] which then reduces the carbonyl group.[7,8] This reaction mechanism is postulated to proceed through a cis addition by means of a cyclic transition state.[9,10]

Addition of acetic acid to a refluxing propanolic solution of indenopyrimidinone **4a** and hydrazine with continued refluxing for 1 hr gave the hydrazone **6** in 40% yield. Elemental analyses and spectral data support this structure. Tlc shows that the carbinol **5a** and the indenopyrimidine **8a** are also formed as by-products in this reaction. When the above mixture was heated at reflux for 3 days, instead of 1 hr, no hydrazone was found and the reaction proceeded to the formation of the indenopyrimidine **8a** (63% yield), which was identical with an authentic sample prepared from 2-benzylidene-1-indanone and benzamidine. This unusual reaction, in which the alkaline catalyst used in the Wolff–Kishner reduction is omitted, has been previously observed in a few cases.[11–13] It is believed, however, that this is the first reported instance of a cyclic carbonyl compound being reduced to a hydrocarbon by hydrazine at refluxing propanol temperature and in the presence of acetic acid.

In the presence of potassium hydroxide, indenopyrimidinone **4a** reacted with hydrazine to give in refluxing propanol azine **7** in 90% yield and in diethylene glycol at 200°, as in the standard Wolff–Kishner reduction, compound **8a** in 64% yield.

Several attempts have been made to prepare 2-methyl-4-phenyl-5*H*-indeno[1,2-*d*]pyrimidin-5-one from **1a** and acetamidine hydrochloride. The only product isolated was the Michael 1:1 adduct (40% yield), which by treatment with acidic or basic catalysts regenerated compound **1a** with evolution of ammonia.

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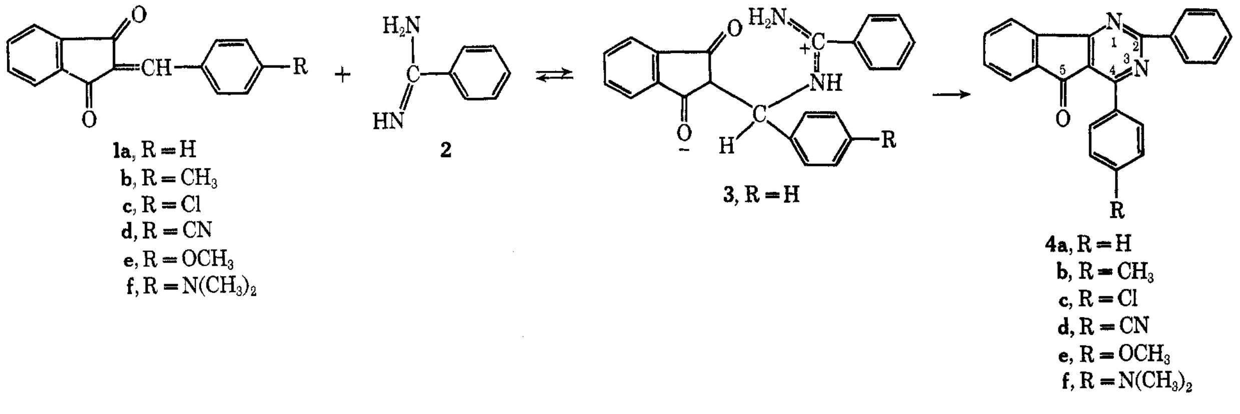
SCHEME I



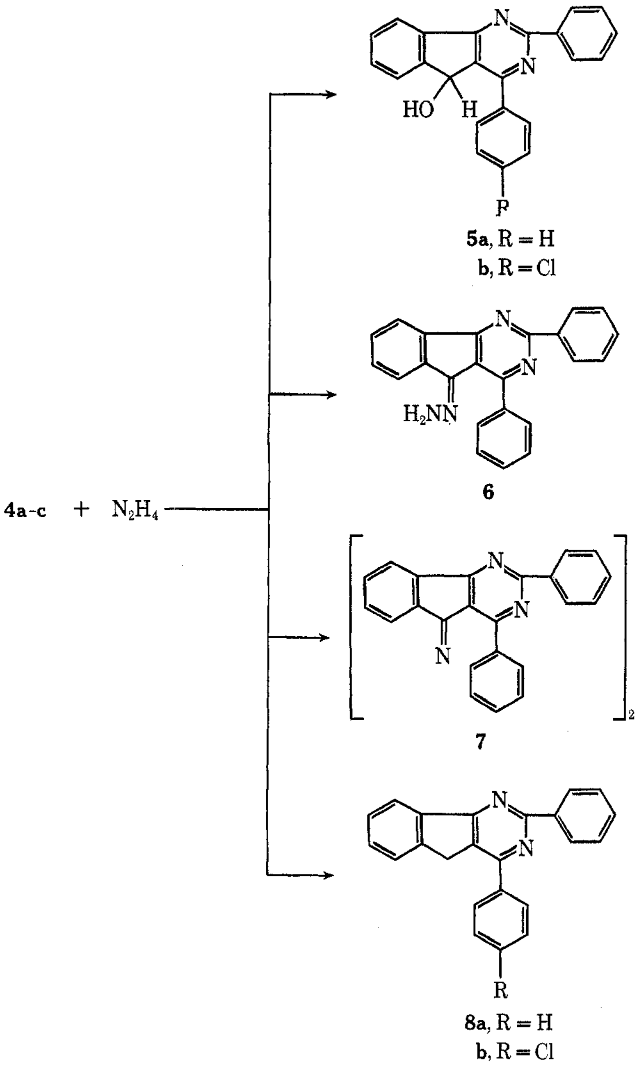
1a, R = H
b, R = CH_3
c, R = Cl
d, R = CN
e, R = OCH_3
f, R = $N(CH_3)_2$

2

3, R = H

4a, R = H
b, R = CH_3
c, R = Cl
d, R = CN
e, R = OCH_3
f, R = $N(CH_3)_2$

SCHEME II



4a-c + N_2H_4

5a, R = H
b, R = Cl

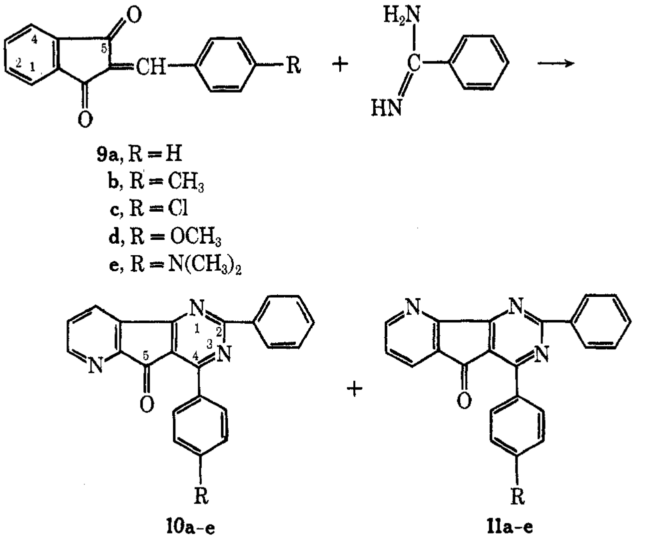
6

7

8a, R = H
b, R = Cl

The condensation of 6-(para-substituted benzylidene)-5*H*-1-pyrindine-5,7(6*H*)-diones (**9a–e**) with benzamidine in the presence of sodium methoxide, as in the method for preparing the indenopyrimidinones **4**, gave mixtures of the isomers **10** and **11** in 35% yield. Attempts to separate these two isomeric components were unsuccessful. The spectral properties of these mixtures were similar to those of compounds **4** and were in agreement with the assigned structures.

The substituted benzylidenepyrindinediones **9a–e** were prepared in very good yields from 6-(methoxycarbonyl)-5*H*-1-pyrindine-5,7-(6*H*)-dione and the appropriate aromatic aldehyde following the method developed by Neiland and Vanags for preparing compound **9a**.[14]



9a, R = H
b, R = CH_3
c, R = Cl
d, R = OCH_3
e, R = $N(CH_3)_2$

10a-e

11a-e

Experimental Section[15]

2-(Para-substituted benzylidene)-1,3-indandiones (1a–f) were obtained in 80–98% yield by condensing 1,3-indandione with the appropriate aldehyde according to the procedure of Ionescu.[16] **2-(*p*-Cyanobenzylidene)-1,3-indandione (1d)** is not reported in the literature. It was obtained in 90% yield, from 1,3-indandione and *p*-cyanobenzaldehyde, as yellow needles: mp 232–233° (benzene); ir 2240–2230 (C≡N), 1735 and 1700 (C=O), 1640–1580 (C=C and C=N), and 847–738 cm^{-1} (aromatic bending).

Anal. Calcd for $C_{17}H_9NO_2$: C, 78.76; H, 3.48; N, 5.40. Found: C, 79.05; H, 3.48; N, 5.22.

2,4-Diaryl-5*H*-indeno[1,2-*d*]pyrimidin-5-ones (4a–f).—The following general procedure was used. To a stirred solution of sodium methoxide prepared from sodium (0.23 g, 0.01 g-atom) and anhydrous methanol (20 ml) were added benzamidine hydro-

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[14] L. E. Neiland and G. Vanags, *Latv. PSR Zinat. Akad. Vestis*, **1**, 74 (1963); *Chem. Abstr.*, **60**, 4102*f* (1964).

[15] Melting points were taken on a Fisher-Johns melting point apparatus between circular cover plates and are corrected. The infrared spectra were determined on a Perkin-Elmer Model 137 spectrophotometer as potassium bromide pellets. Ultraviolet spectra were taken on a Perkin-Elmer spectrophotometer Model 202, using chloroform as the solvent. Nuclear magnetic resonance spectra were obtained on a Varian Associates spectrometer, Model A-60A, deuterated chloroform, unless otherwise noted, being used as the solvent. Chemical shifts are reported as δ values (parts per million) relative to tetramethylsilane as an internal standard. Elemental analyses were performed by the Micro Analysis, Inc., Marshallton, Del., and by the M-H-W Laboratories, Garden City, Mich.

[16] M. V. Ionescu, *Bull. Soc. Chim. Fr.*, **47**, 210 (1930).

Table I

2,4-Diaryl-5H-indeno[1,2-d]pyrimidin-5-ones (4a-f)

Compd	R	Mp, °C[a]	Yield, %	Formula	% C Calcd	% C Found	% H Calcd	% H Found	% N Calcd	% N Found
4a	H	194–195	29	$C_{23}H_{14}N_2O$	82.67	82.83	4.19	4.34	8.38	8.44
4b	CH_3	218–220[b]	24	$C_{24}H_{16}N_2O$	82.76	82.83	4.60	4.70	8.05	7.92
4c	Cl	233–235	32	$C_{23}H_{13}ClN_2O$	74.90	74.82	3.53	3.51	7.60	7.51
4d	CN	272–274	6.6	$C_{24}H_{13}N_3O$	80.22	80.44	3.62	3.66	11.70	11.73
4e	OCH_3	204–205[b]	15	$C_{24}H_{16}N_2O_2$	79.12	79.16	4.40	4.23	7.69	7.38
4f	$N(CH_3)_2$	240–243[b]	26	$C_{25}H_{19}N_3O$	79.57	79.55	5.04	4.92	11.14	11.20

[a] Crystallization solvent, benzene–ethanol mixture. [b] Isolated by chromatography on alumina (benzene as eluent).

chloride dihydrate (0.48 g, 0.0025 mol) and the appropriate 2-(para-substituted benzylidene)-1,3-indandione (0.005 mol) at room temperature. The mixture was heated at reflux for 24 hr (ammonia evolution) and cooled overnight. The precipitate was collected, washed several times with methanol and with water, and dried to give compounds **4** as yellow needles.

The melting points, yields, and analytical data of compounds **4a–f** are listed in Table I. The ir spectra showed a single C=O band at 1750–1710 cm^{-1}, C=C and C=N absorptions at 1625–1530 cm^{-1}, consisting of several bands, and aromatic absorptions in the intervals of 760–755 and 690–683 cm^{-1}; in addition, bands at 2220–2210 cm^{-1} for compound **4d**, at 1235–1185 cm^{-1} for compound **4e**, and at 1365–1360 cm^{-1} for compound **4f**; uv λ_{max} at 250–260 mμ (ϵ 23,000–36,000) and 300–307 (34,000–44,000); nmr showed a singlet at 2.45 and an aromatic multiplet at 7.25–8.94 for compound **4b** and a singlet at 3.95 and an aromatic multiplet at 6.95–8.9 for compound **4e**, integration 3:13 for compounds **4b** and **4e**.

Hydrazone of 4a (6).—A mixture of **4a** (0.34 g, 0.001 mol), 1-propanol (30 ml), and 95% hydrazine (0.2 ml) was heated at reflux for 1 hr. Acetic acid (0.05 ml) was added, and the mixture was refluxed for an additional hour and then cooled in ice overnight. Filtration and washing of the cake with methanol and then with water gave 0.14 g (40%) of **6** as pale yellow crystals: mp 198–199° (ethanol); ir 3300 and 3200 (N—H), 1580–1530 (C=C and C=N) and 745–690 cm^{-1} (aromatic bending); nmr (DMSO-d_6) showed a singlet (broad) at 3.40 (2, NH) and an aromatic multiplet at 7.35–8.80 (14 protons).

Anal. Calcd for $C_{23}H_{16}N_4$: C, 79.31; H, 4.59; N, 16.10. Found: C, 79.59; H, 4.56; N, 15.95.

In an attempt to obtain additional hydrazone **6**, the reaction filtrate was evaporated to dryness under reduced pressure. The residue was found to be a mixture of compounds **4a**, **5a**, **6**, and **8a** by thin layer chromatography under uv.

The 2,4-dinitrophenylhydrazone of 4a was prepared by adding a solution consisting of 0.20 g (0.001 mol) of 2,4-dinitrophenylhydrazine, 1 ml of concentrated sulfuric acid, 1.5 ml of water, and 5 ml of ethanol to a solution of 0.25 g (0.75 mmol) of **4a** in 20 ml of a boiling 1:1 chloroform–ethanol mixture and continuing refluxing for 0.5 hr. A 76% yield of orange crystals, mp 275° dec, was obtained. The ir spectrum showed a characteristic nitro absorption in the interval 1550–1500 cm^{-1} and no carbonyl band.

Anal. Calcd for $C_{29}H_{18}N_6O_4$: C, 67.70; H, 3.50; N, 16.34. Found: C, 67.70; H, 3.35; N, 16.34.

The 2,4-dinitrophenylhydrazone of 4e was obtained by following the procedure above described for the dinitrophenylhydrazone of **4a**. Bright orange crystals, mp 300°, were obtained.

Anal. Calcd for $C_{30}H_{20}N_6O_5$: C, 66.18; H, 3.67. Found: C, 66.47; H, 3.69.

2-Benzylidene-1,3-indandione–Benzamidine 1:1 Adduct (3).—To a solution of sodium methoxide prepared from sodium (0.12 g, 0.005 g-atom) and anhydrous methanol (20 ml) were added 0.96 g (0.005 mol) of benzamidine hydrochloride dihydrate and 1.17 g (0.005 mol) of **1a** at room temperature. The mixture was refluxed for 1 hr and cooled in ice for 1 day. Filtration, washing, and drying gave 0.59 g (34%) of **3** as bright orange needles: mp 168° dec; insoluble in most organic solvents and slightly soluble in cold water; ir spectrum showed a strong and broad band at 3200–2900 cm^{-1} ($\gg N^+H$, $=N^+H_2$, and aromatic CH stretching vibrations),[17] and absorptions at 1680–1675 and 1550–1500 cm^{-1} (enolate anion vibrations).[18] The strong C=N$^+$ absorption in benzamidine hydrochloride[19] (1700–1675 cm^{-1}) was shifted to 1620–1600 cm^{-1} in compound **3**; nmr (DMSO-d_6) showed a singlet at 6.02 (assigned to the methine proton)[20] and an aromatic multiplet at 7.00–8.20 in the ratio 1:17. The amidinium protons were shown to be contained in the aromatic multiplet, since the ratio of the above signals was 1:14 after D_2O exchange. No enolic protons were observed.

Anal. Calcd for $C_{23}H_{18}N_2O_2$: C, 77.97; H, 5.08; N, 7.91. Found: 78.07; H, 5.08; N, 7.65.

Cyclization of 3.—To a solution of sodium methoxide prepared from sodium (0.023 g, 0.001 g-atom) and anhydrous methanol (10 ml) was added **3** (0.35 g, 0.001 mol) at room temperature. The mixture was refluxed for 24 hr (ammonia evolution) and cooled in ice overnight. The crude mixture recrystallized from a 1:1 ethanol–benzene mixture gave 0.07 g (30%) of **4a** as yellow crystals, mp 194–195°. Mixture melting point with a sample of **4a** prepared as above showed no depression.

Acidification of the reaction filtrate with 6 *N* hydrochloric acid and purification of the precipitate by fractional crystallization or column chromatography (chloroform–hexane mixture as eluent) resulted in the formation of **1a**, as shown by mixture melting point with an authentic sample.

2-Benzylidene-1,3-indandione–Acetamidine 1:1 Adduct.—It was prepared following the procedure above described for compound **3**, except that 0.48 g (0.005 mol) of acetamidine hydrochloride was used in place of benzamidine hydrochloride. A 40% yield of yellow orange needles, mp 181° dec, was obtained. The ir spectrum was similar to that of **3**; nmr (DMSO-d_6) showed a singlet at 2.20, a singlet at 5.68, and an aromatic multiplet at 6.90–7.60 in the ratio of 3:1:12, respectively. The amidinium protons were shown to be contained in the aromatic multiplet, since the ratio of the above signals after D_2O exchange was 3:1:9. No enolic protons were found.

Anal. Calcd for $C_{18}H_{16}N_2O_2$: C, 73.97; H, 5.48; N, 9.59. Found: C, 73.85; H, 5.61; N, 9.52.

2,4-Diphenyl-5*H*-indeno[1,2-*d*]pyrimidin-5-ol (5a).—A hot solution of **4a** (0.34 g, 0.001 mol) in an anhydrous benzene–ethanol mixture (35 ml) was added dropwise to a stirred solution of 95% hydrazine (0.25 ml), anhydrous ethanol (5 ml), and glacial acetic acid (0.025 ml). The reaction mixture was heated at reflux for 10 hr and then evaporated to dryness under reduced pressure. The residue was washed with methanol and with water and dried to give 0.28 g (83%) of **5a** as pale yellow crystals: mp 259–261° (methanol–benzene); ir 3200–3150 (OH), 1575–1545 (C=C and C=N), 1040 (CO stretching), and 750, 690 cm^{-1} (aromatic bending); nmr (DMSO-d_6) showed a singlet at 3.42 (1, OH), a singlet at 6.05 (1, CH), and an aromatic multiplet at 7.0–8.9 (14 protons). The position of the hydroxyl proton was determined by D_2O exchange.

Anal. Calcd for $C_{23}H_{16}N_2O$: C, 82.13; H, 4.76; N, 8.33. Found: C, 82.11; H, 4.81; N, 8.36.

4-(*p*-Chlorophenyl)-2-phenyl-5*H*-indeno[1,2-*d*]pyrimidin-5-ol (5b).—A suspension of 0.37 g (0.001 mol) of **4c**, 20 ml of anhydrous ethanol, 1 ml of 95% hydrazine, and 0.05 ml of acetic acid, prepared as for compound **5a**, was heated at reflux for 10 hr and then cooled in ice for several hours. The precipitate was collected, washed with methanol and water, and dried to give 0.26 g (70%) of **5b** as pale yellow crystals, mp 257–259° (ethanol). The ir and nmr spectra were similar to those of compound **5a**.

Anal. Calcd for $C_{23}H_{15}ClN_2O$: C, 74.45; H, 4.05; N, 7.56. Found: C, 74.57; H, 4.01; N, 7.47.

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(19) Sadtler Standard Spectra, IR 18879 (1961).

(20) C. L. Stevens, R. C. Freeman, and K. Noll, *J. Org. Chem.*, **30**, 3719 (1965).

TABLE II

6-(PARA-SUBSTITUTED BENZYLIDENE)-5*H*-1-PYRINDINE-5,7-(6*H*)-DIONES (**9a–e**)

Compd	R	Mp, °C[a]	Yield, %	Formula	% C		% H		% N	
					Calcd	Found	Calcd	Found	Calcd	Found
9a	H	175–176[b]	68	$C_{15}H_9NO_2$	76.60	76.48	3.83	3.88	5.96	5.98
9b	CH_3	222–223	70	$C_{16}H_{11}NO_2$	77.11	77.05	4.42	4.54	5.62	5.42
9c	Cl	241–242	83	$C_{15}H_8ClNO_2$	66.77	66.73	2.97	2.99	5.19	5.12
9d	OCH_3	204–205	87	$C_{16}H_{11}NO_3$	72.45	72.68	4.15	4.38	5.28	5.18
9e	$N(CH_3)_2$	240–242	95	$C_{17}H_{14}N_2O_2$	73.38	72.99	5.04	5.12	10.07	9.91

[a] Recrystallization solvent, dioxane or dioxane–water mixture. [b] Reference 12.

TABLE III

MIXED 2,4-DIARYL-5*H*-PYRIDOCYCLOPENTA[1,2-*d*]PYRIMIDIN-5-ONES (**10a–e** + **11a–e**)

Compd	R	Mp, °C	Yield, %	Formula	% C		% H		% N	
					Calcd	Found	Calcd	Found	Calcd	Found
10a + **11a**	H	225–236	36	$C_{22}H_{13}N_3O$	78.80	78.52	3.88	3.97	12.53	12.33
10b + **11b**	CH_3	234–246	35	$C_{23}H_{15}N_3O$	79.08	79.04	4.30	4.30	12.04	11.95
10c + **11c**	Cl	260–275	38	$C_{22}H_{12}ClN_3O$	71.69	71.69	3.25	3.57	11.37	11.51
10d + **11d**	OCH_3	220–232	34	$C_{23}H_{15}N_3O_2$	75.62	75.67	4.11	4.29	11.50	11.27
10e + **11e**	$N(CH_3)_2$	272–288	37	$C_{24}H_{18}N_4O$	76.19	76.46	4.76	4.65	14.82	14.85

2,4-Diphenyl-5*H*-indeno[1,2-*d*]pyrimidin-5-one Azine (7).—A mixture of **4a** (0.34 g, 0.001 mol), 1-propanol (30 ml), 95% hydrazine (0.2 ml), and potassium hydroxide (0.056 g, 0.001 mol) was refluxed for 2.5 hr and then cooled in ice for several hours. The orange brown solid was collected by filtration and washed with water and with methanol to give 0.29 g (90%) of **7**: mp 300°; ir 1580–1540 (C=C and C=N absorption), 750 and 690 cm^{-1} (aromatic bending).

Anal. Calcd for $C_{46}H_{28}N_6$: C, 83.13; H, 4.22; N, 12.65. Found: C, 83.00; H, 4.31; N, 12.55.

2,4-Diphenyl-5*H*-indeno[1,2-*d*]pyrimidine (8a). A. From 2-Benzylidene-1-indanone.—It was obtained by the procedure above described for preparing compound **4a**, except that 2-benzylidene-1-indanone[21] (1.1 g, 0.005 mol) was used in place of 2-benzylidene-1,3-indandione. The crude product was dissolved in chloroform, and the solution was mixed with activated alumina and evaporated to dryness. Chromatography of the residue over an alumina packed column (elution with benzene) gave 0.19 g (23%) of **8a** as colorless needles: mp 187–189° (ethanol); ir 1600–1540 (C=C and C=N absorptions) and 750–690 cm^{-1} (aromatic bending); nmr showed a singlet at 3.93 (2, CH_2) and an aromatic multiplet at 7.36–8.94 (14 protons). The position of the methylene protons was the same as that found in 2-benzylidene-1-indandone (δ 3.90).

Anal. Calcd for $C_{23}H_{16}N_2$: C, 86.25; H, 5.00; N, 8.75. Found: C, 86.39; H, 5.27; N, 8.39.

2,4-Diphenyl-5*H*-indeno[1,2-*d*]pyrimidine (8a). B. From Compound 4a.—A mixture of **4a** (0.96 g, 0.003 mol), 95% hydrazine (0.48 ml, 0.015 mol), potassium hydroxide (1.0 g, 0.018 mol), and diethylene glycol (15 ml) was heated (oil bath) to 120° and maintained for 1 hr. The condenser was removed and the mixture was heated to 200° and maintained at this temperature for 3 hr. The cooled solution was added to ice-cold water (150 ml). The precipitate was collected, dried, and chromatographed on alumina (elution with benzene) to give 0.61 g (64%) of **8a** as cream-colored crystals, mp 185–187° (ethanol), identical (mixture melting point and spectra) with compound **8a** prepared as described under A.

This compound was also obtained by heating at reflux for 1 hr a mixture of **4a** (0.34 g, 0.001 mol), 1-propanol (30 ml), and 95% hydrazine (0.2 ml), adding acetic acid (0.05 ml), refluxing for 3 days, and cooling overnight. The precipitate was collected, washed with methanol and then with water, and dried to give 0.21 g (63%) of **8a**. Mixture melting point with a sample of **8a**, prepared as described above, showed no depression.

2-Phenyl-4-(*p*-tolyl)-5*H*-indeno[1,2-*d*]pyrimidine (8b).—It was prepared following the procedure B described above for **8a**, except that compound **4b** (1.05 g, 0.003 mol) was used in place of **4a**. Chromatography gave 0.65 g (65%) of **8b** as cream-colored crystals, mp 185–187°.

Anal. Calcd for $C_{24}H_{18}N_2$: C, 86.23; H, 5.39; N, 8.38. Found: C, 86.24; H, 5.44; N, 8.28.

6-(Para-substituted benzylidene)-5*H*-1-pyrindine-5,7-(6*H*)-diones (9a–e).—These compounds were prepared from 6-(methoxycarbonyl)-5*H*-1-pyrindine-5,7(6*H*)-dione and the appropriate aldehyde by following the procedure described by Neiland and Vanags for the preparation of compound **9a**.[12] The melting points, yields, and analytical data of compounds **9b–e** together with those of **9a** are listed in Table II. The ir spectra showed two bands at 1750–1720 and at 1700–1690 cm^{-1} (C=O), bands at 1610–1540 cm^{-1} (C=C and C=N), and aromatic bendings at 768–755 cm^{-1}. Compound **9d** showed bands also at 1266 and 1195 cm^{-1} and compound **9e** at 1380 cm^{-1}.

Mixed 2,4-Diaryl-5*H*-pyrido[2′,3′:4,5]cyclopenta[1,2-*d*]-pyrimidin-5-ones [10a–e] and 2,4-Diaryl-5*H*-pyrido[2′,3′:5,4]-cyclopenta[1,2-*d*]pyrimidin-5-ones (11a–e).—These mixtures were obtained by reacting compounds **9** with benzamidine according to the procedure above described for preparing compounds **4**. The crystallized products (benzene–ethanol mixtures) had broad melting points. Tlc showed the presence of two components, which could not be separated by fractional crystallization from benzene or ethanol or by column chromatography. The melting points, yields, and analytical data of these mixtures are listed in Table III. The ir spectra showed a single C=O band in the 1730–1710-cm^{-1} region, C=C and C=N absorptions at 1600–1500 cm^{-1}, consisting of several strong bands, and aromatic absorptions at 776–760 and 690–685 cm^{-1}; uv λ_{max} 242–249 mμ (ε 22,000–31,000) and 295–308 (26,000–32,000); nmr showed a singlet at 2.45 and an aromatic multiplet at 7.3–9.05 (integration 3:12) for mixture **10b** and **11b** and a singlet at 3.94 and an aromatic multiplet at 7.02–9.08 (integration 3:12) for mixtures **10d** and **11d**.

Registry No.—**1d**, 31316-87-7; **3**, 31570-93-1; **4a**, 31570-63-5; **4a** 2,4-DNPH, 31570-64-6; **4b**, 31570-65-7; **4c**, 31570-66-8; **4d**, 31570-67-9; **4e**, 31570-68-0; **4e** 2,4-DNPH, 31570-69-1; **4f**, 31570-70-4; **5a**, 31570-71-5; **5b**, 31570-72-6; **6**, 31570-73-7; **7**, 31570-74-8; **8a**, 31570-75-9; **8b**, 31570-76-0; **9a**, 31570-77-1; **9b**, 31570-78-2; **9c**, 31570-79-3; **9d**, 31570-80-6; **9e**, 31570-81-7; **10a**, 31570-82-8; **10b**, 31570-83-9; **10c**, 31570-84-0; **10d**, 31570-85-1; **10e**, 31570-86-2; **11a**, 31570-87-3; **11b**, 31570-88-4; **11c**, 31570-89-5; **11d**, 31570-90-8; **11e**, 31570-91-9; 2-benzylidene-1,3-indandione–acetamidine 1:1 adduct, 31570-92-0.

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[21] A. Hassner and N. H. Cromwell, *J. Amer. Chem. Soc.*, **80**, 893 (1958).