Substituted Benzopyranopyridopyrimidine Ring Syntheses by the Ternary Condensation of Malononitrile, Salicylaldehyde, and Aromatic Ketones in the Presence of Ammonium Acetate

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Various 2,5-diarylbenzopyranopyridopyrimidines (1) and substituted 4-amino-5-iminobenzopyranopyridine (2 and 3) were prepared directly by condensation of malononitrile, salicylaldehyde, and aromatic ketones in the presence of ammonium acetate. Moreover, reaction of the resulting 2 and 3 with acetic anhydride in boiling pyridine led to such benzopyranopyridopyrimidines as 2-aryl-5-methyl derivatives 5 and 2-acetamino-1-cyano-5-methyl derivatives 6, respectively.

Previous papers have shown that ethyl cyanoacetate condensed with salicylaldehyde and ketones or aldehydes in the presence of ammonium acetate afford substituted benzopyranopyridines[2,3] (from ketone or aliphatic aldehyde) and benzopyranopyrimidines[3] (from aromatic aldehyde).

The present paper deals with syntheses of 2,5-diaryl, 2-aryl-5-methyl, and 2-acetamino-1-cyano-5-methyl derivatives of [2,3,4-*de*]benzopyrano[2,3-*d*]pyridopyrimidine, 4-amino-5-imino[1]benzopyrano[3,4-*c*]pyridine derivatives by condensation of malononitrile, salicylaldehyde, or 3-methoxysalicylaldehyde, and aromatic ketones, *e.g.*, acetophenone, *o*- and *p*-hydroxy-, *p*-methyl-, *p*-methoxy-, and *m*-nitroacetophenone, in the presence of ammonium acetate.

The reaction of malononitrile, salicylaldehyde, and aromatic ketones (molar ratio of 1:1:1) in the presence of ammonium acetate (slight excess) gave a mixture of ~10–17% 2-aryl-5-(*o*-hydroxyphenyl)[2,3,4-*de*]-benzopyrano[2,3-*d*]pyridopyrimidines (1) and ~4–10% 1-cyano-2,4-diamino-5-imino[1]benzopyrano[3,4-*c*]pyridine (3a) except for the reactions when *m*-nitroacetophenone or *p*-methylacetophenone were used as the ketone reactant.

The use of 3-methoxysalicylaldehyde instead of salicylaldehyde gave a mixture of ~9–11% type 1 (R = OCH_3), ~8–10% 3b, and ~6–10% 4-amino-2-aryl-5-imino-7-methoxy[1]benzopyrano[3,4-*c*]pyridines (2). In addition, on treatment with acetic anhydride in refluxing pyridine, both 2 and 3 gave good yields of cyclization products such as 2-aryl-5-methyl- (5) or its 8-methoxy derivative (57–95%) and 2-acetamino-1-cyano-5-methyl[2,3,4-*de*]benzopyrano[2,3-*d*]pyridopyrimidine (6) or its 8-methoxy derivative (79–94%), respectively, as indicated in Scheme I (yields based on 2 or 3). When heated with hydrochloric acid in ethanol, 2c was converted to 5-oxo derivative 7b (Scheme I), which was proved to be the same type as those obtained by the condensation of ethyl cyanoacetate, salicylaldehyde, and ketones[2] or aliphatic aldehydes[3] previously reported, on the basis of their ir spectral studies.

It seems reasonable to assume that the formation of 1, 2, and 3 may be achieved by the following process. Malononitrile first condensed with salicylaldehyde to give 3-cyanocoumarinimide (8), which is in turn converted to 3-amidinocoumarinimide (9). Then, 9 condenses with ketones to afford 2, which further reacts with salicylaldehyde, finally yielding 1. Also, when intermediate 9 was treated with malononitrile, 3 was formed as indicated in Scheme II. Indeed, when heated with acetophenone and ammonium acetate in ethanol, crude 8a gave 2a. Furthermore, in the same reaction with salicylaldehyde, 2a gave 1a. Reaction of malononitrile, salicylaldehyde, or 3-methoxysalicylaldehyde with *m*-nitroacetophenone afforded mainly 2 (18–24%) accompanied by a small amount of 1 (5%) and 3 (6–8%).

The use of *p*-methylacetophenone as the ketone reactant afforded 1b, 3a, and 7a, respectively. In this case, when the reaction was carried out in ethanol, 1b was formed as the main product, while the reaction in ethanol–pyridine (2:1) gave 7a as the main product. Reaction of malononitrile, 3-methoxysalicylaldehyde, and acetophenone afforded 1f, 2c, and 3b under reflux, while in the same reaction at room temperature 1f was not obtained. These facts are taken to indicate that in many cases in the present study the course of the reaction was markedly influenced by choice of solvent and/or reaction temperature. However, type 3 compounds (4–10%) were formed under all conditions.

The ir spectra of type 1 compounds showed absorption bands in the 1630–1500-cm^{-1} region attributed to a hetero ring, but they did not show any band in the amino, imino, or cyano region. However, 4 (acetyl derivatives of 1) exhibited new absorption bands at 1770–1750 cm^{-1}. This indicates the presence of a hydroxy group in type 1, since their bands can be attributed to the carbonyl band of acetoxy group. This acetoxy group showed doublet carbonyl absorption except for 4e (Table I). It is probably attributable to the rotational isomerism around the C—C bond or the Fermi resonance. On the other hand, compounds 2 showed absorption bands at 3450–3150 cm^{-1} (three to four bands) (Table II) due to a primary amino and imino groups and at 1650 cm^{-1} due to a C=N bond, whereas compounds 5 (obtained when 2 was refluxed with acetic anhydride in pyridine) gave no absorption bands for a amino or imino groups, and their spectra were very similar to those of compounds 1. The nmr spectrum (CF_3CO_2H) of compound 5b indicated a methyl singlet corresponding to three protons at 3.2 ppm, while the ir spectrum gave no absorption band for an acetyl carbonyl group. This suggests that the 4 position of amino group and the 5 position of imino group of type 2 were involved in this cyclization;

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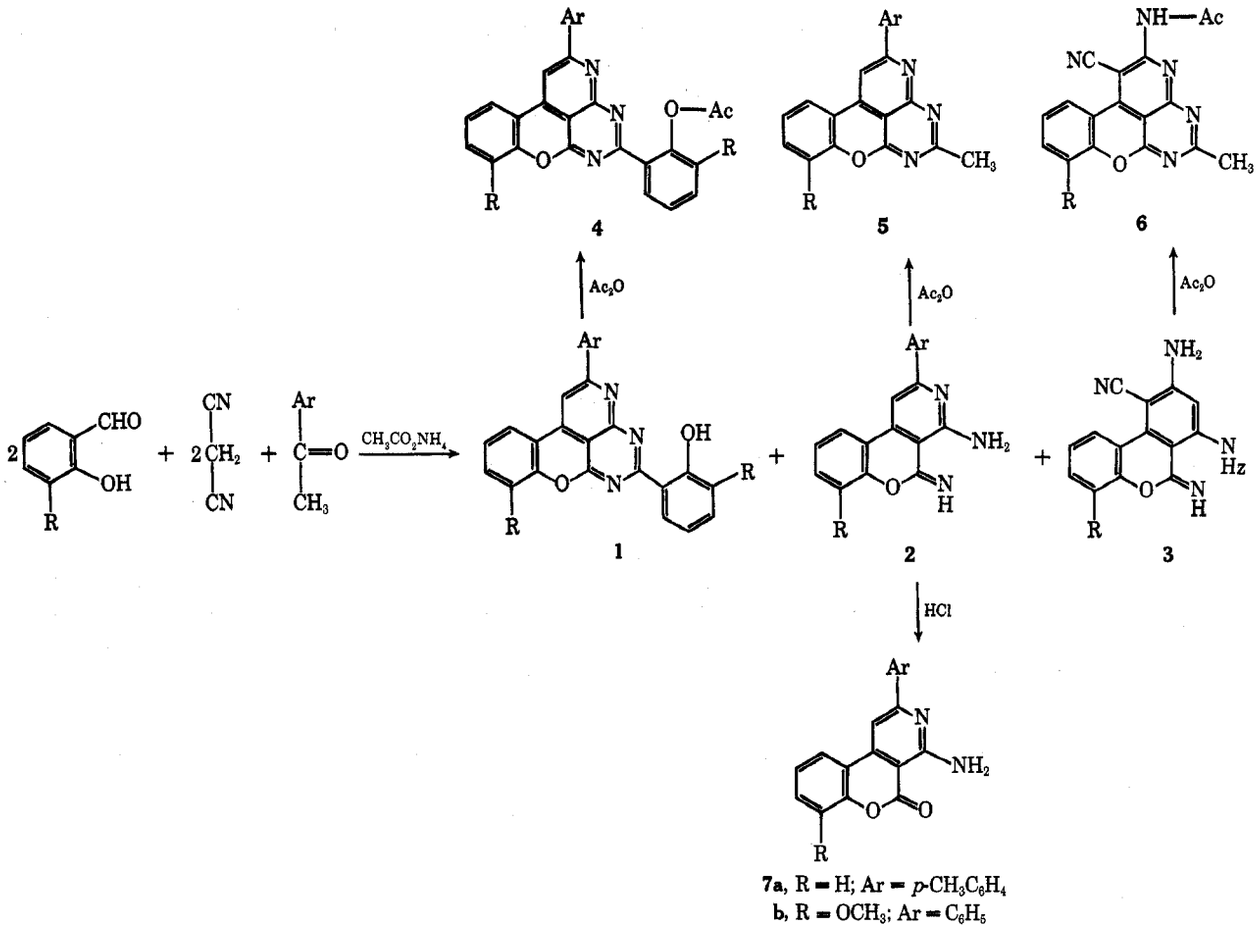
SCHEME I



SCHEME II

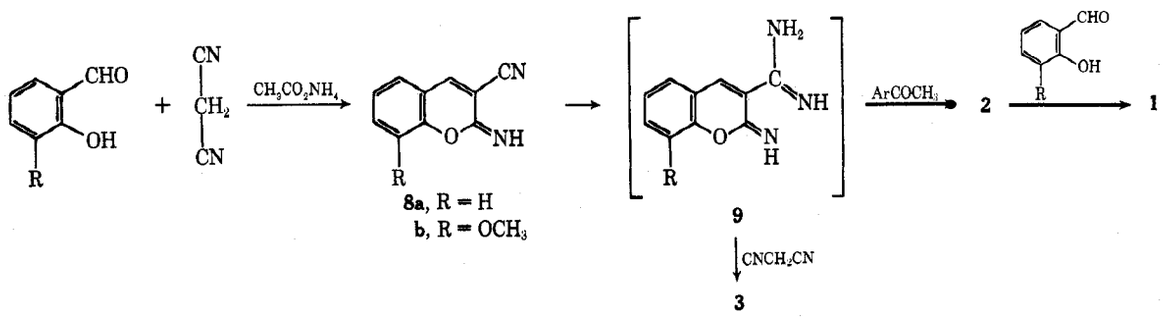


TABLE I

2-ARYL-5-(*o*-HYDROXYPHENYL)[2,3,4-*de*]BENZOPYRANO[2,3-*d*]PYRIDOPYRIMIDINE (1) and ITS ACETYL DERIVATIVES 4[a]

Compd	R	Ar	Mp, °C	Yield, %	Ir (KBr), $\nu_{C=O}$, cm^{-1}	Nmr (CH_3), ppm[b]
1a	H	C_6H_5	303–304	12		
1b	H	*p*-$CH_3C_6H_4$	299–300	12		
1c	H	*p*-OHC_6H_4	>340	11		
1d	H	*o*-OHC_6H_4	>340	10		
1e	H	*p*-$CH_3OC_6H_4$	278–279	17		
1f	OCH_3	C_6H_5	291–294	11		
1g	OCH_3	*p*-$CH_3OC_6H_4$	273–275	10		
4a	H	C_6H_5	248–251	91	1765, 1750	2.25 (s, 3 H)
4b	H	*p*-$CH_3OC_6H_4$	224–226	91	1770, 1750	2.25 (s, 3 H)
4c	H	*p*-$AcOC_6H_4$	262–264	67	1765, 1755	2.3 (s, 3 H), 2.6 (s, 3 H)
4d	H	*m*-$O_2NC_6H_4$	>335	82	1770, 1760	
4e	OCH_3	C_6H_5	270–271	73	1770	

[a] Satisfactory analytical values (±0.4% for C, H, N) for all compounds were reported: Ed. [b] Parts per million downfield from tetramethylsilane in CF_3CO_2H; s, singlet.

TABLE II

4-AMINO-5-IMINO[1]BENZOPYRANO[3,4-*c*]PYRIDINE DERIVATIVES 2 AND 3[a]

Compd	R	Ar	Mp, °C	Yield, %	Ir (KBr) ν_{NH_2}, NH, cm^{-1}
2a	H	C_6H_5	193–196	29[b]	3330, 3300, 3160
2b	H	*m*-$O_2NC_6H_4$	261–263	24	
2c	OCH_3	C_6H_5	214–215	10	3450, 3310, 3240
2d	OCH_3	*m*-$O_2NC_6H_4$	228–229	18	
2e	OCH_3	*p*-$CH_3OC_6H_4$	216–217	6	
3a	H		293–295 dec	4–10	3420, 3330, 3310, 3140[c]
3b	OCH_3		>320	8–10	

[a] Satisfactory analytical values (±0.4% for C, H, N) for all compounds were reported: Ed. [b] Yield based on **8a**. [c] ν_{CN} 2200.

TABLE III

5-METHYL[2,3,4-*de*]BENZOPYRANO[2,3-*d*]PYRIDOPYRIMIDINE DERIVATIVES 5 AND 6[a]

Compd	R	Ar	Mp, °C	Yield, %	Ir (KBr), cm^{-1} ν_{NH}	Ir (KBr), cm^{-1} $\nu_{C=N}$	Nmr δ_{CH_3}[b]
5a	H	C_6H_5	219–220	95			
5b	H	*m*-$O_2NC_6H_4$	330–333	57			3.2 (s, 3 H)
5c	OCH_3	C_6H_5	255–257	95			
5d	OCH_3	*m*-$O_2NC_6H_4$	313–314	67			
6a	H		296–298 dec	79	3240	2230	
6b	OCH_3		>320	94	3230	2220	3.15 (s, 3 H) 2.75 (s, 3 H)

[a] Satisfactory analytical values (±0.4% for C, H, N) for all compounds were reported: Ed. [b] Parts per million downfield from tetramethylsilane in CF_3CO_2H; s, singlet; br, broad. In **6b** spectrum, δ_{NH} 8.7–9.1 ppm (br, 1 H).

therefore, the above spectral characteristics are taken as evidence for assignment of the structure **5**. The ir spectrum of compound **3b** showed absorption bands in the 3470–3140-cm^{-1} region (four to five bands) for a primary amino and imino groups and at 2200 cm^{-1} for a conjugated cyano group. On the other hand, compound **6b** (obtained when **3b** was heated with acetic anhydride in pyridine) revealed absorptions at 3230, 2220, and at 1685 cm^{-1} (Table III). These observations show that the same cyclization occurred as in the case of the compounds **2**, since the bands at 3230 and 1685 cm^{-1} were assigned to a imino and carbonyl bands of the acetamino group (2 position), respectively. Thus, the structure of **6b** was deduced from the above ir data, the elemental analysis, and the nmr spectrum which has two methyl singlets at 3.15 and 2.75 ppm corresponding to three protons, respectively. The former signal (3.15 ppm) was assigned to a methyl group of the 5 position, by a comparison of nmr chemical shift observed for the methyl proton in **5b** (3.2 ppm). Therefore, the latter signal (2.75 ppm) was assigned to a methyl proton due to the acetamino group of the 2 position (Table III).

Experimental Section

All melting points are uncorrected. The ir spectra were determined by means of potassium bromide pellets. Nmr spectra were determined in trifluoroacetic acid at 60 Mc, using tetramethylsilane as the internal standard. Chemical shifts are reported as parts per million downfield from TMS.

Reaction of Malononitrile, Salicylaldehyde, and Aromatic Ketones.—A mixture of malononitrile (0.03 mol), aldehyde (0.03 mol), ketone (0.03 mol), and ammonium acetate (0.03–0.04 mol) in ethanol (20–30 ml) was refluxed for 0.5–2 hr. Yellow-orange crystals which precipitated during the reaction were collected and washed with hot ethanol. Compounds **1a–e** and **3a** were isolated by means of fractional crystallizations from pyridine, dimethyl sulfoxide, or ethanol.

Anal. Calcd for $C_{25}H_{15}N_3O_2$ (**1a**): C, 77.11; H, 3.88; N, 10.79. Found: C, 76.93; H, 3.95; N, 10.99. Calcd for $C_{26}H_{17}N_3O_2$ (**1b**): C, 77.40; H, 4.25; N, 10.42. Found: C, 77.46; H, 4.27; N, 10.75. Calcd for $C_{25}H_{15}N_3O_3$ (**1c**): C, 74.06; H, 3.73; N, 10.37. Found: C, 73.67; H, 3.88; N, 10.42. Calcd for $C_{25}H_{15}N_3O_3$ (**1d**): C, 74.06; H, 3.73; N, 10.37. Found: C, 73.88; H, 3.79; N, 10.65. Calcd for $C_{26}H_{17}N_3O_3$ (**1e**): C, 74.45; H, 4.09; N, 10.02. Found: C, 74.33; H, 3.87; N, 10.33. Calcd for $C_{13}H_9N_3O$ (**3a**): C, 62.14; H, 3.61; N, 27.88. Found: C, 62.03; H, 3.65; N, 28.06.

The use of *m*-nitroacetophenone as the ketone reactant afforded **2b** and **3a** along with a small amount of type **1** when treated as above. This substance **1** (R = H; Ar = *m*-$O_2NC_6H_4$) was confirmed by the acetylated compound (**4d**) owing to the insolubility in common organic solvents. Experimental results are summarized in Tables I and II.

Anal. Calcd for $C_{18}H_{12}N_4O_3$ (**2b**): C, 65.05; H, 3.64; N, 16.86. Found: C, 65.18; H, 3.77; N, 17.05.

Reaction of Malononitrile, Salicylaldehyde, and *p*-Methylacetophenone.—To a mixture of malononitrile (2.64 g, 0.04 mol), salicylaldehyde (4.88 g, 0.04 mol), and *p*-methylacetophenone (5.36 g, 0.04 mol) in ethanol (25 ml), ammonium acetate (3.08 g, 0.04 mol) was added and heated for 5 min. The reaction mixture gave 1 g (12%) of **1b**, 0.5 g (10%) of **3a**, and 0.5 g (4%) of **7a**, mp 233–235°. When this reaction was carried out in ethanol (20 ml) and pyridine (10 ml), the reaction mixture afforded 1.5 g (10%) of **7a**, 0.7 g (7%) of **1b**, and 0.4 g (6%) of **3a**. The ir spectrum of **7a** gave bands at 3430, 3330 (NH_2), and 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{14}N_2O_2$: C, 75.48; H, 4.67; N, 9.27. Found: C, 75.78; H, 4.70; N, 9.34.

Reaction of Malononitrile, 3-Methoxysalicylaldehyde, and Aromatic Ketones.—A mixture of malononitrile (0.04 mol), aldehyde (0.04 mol), ketone (0.04 mol), and ammonium acetate (0.05 mol) in ethanol (40 ml) was refluxed for 1–2 hr. The reaction mixture gave **1f–g** (10–11%), **2c–e** (6–18%), and **3b** (8–10%) when treated as in the case of salicylaldehyde mentioned above. Experimental results are summarized in Tables I and II.

Anal. Calcd for $C_{27}H_{19}N_3O_4$ (**1f**): C, 72.15; H, 4.26; N, 9.35. Found: C, 72.17; H, 4.30; N, 9.22. Calcd for $C_{28}H_{21}N_3O_5$ (**1g**): C, 70.14; H, 4.41; N, 8.76. Found: C, 69.82; H, 4.48; N, 8.81. Calcd for $C_{19}H_{15}N_3O_2$ (**2c**): C, 71.91; H, 4.76; N, 13.24. Found: C, 71.91; H, 4.83; N, 13.13. Calcd for $C_{19}H_{14}N_4O_4$ (**2d**): C, 62.98; H, 3.89; N, 15.46. Found: C, 63.20; H, 3.80; N, 15.52. Calcd for $C_{20}H_{17}N_3O_3$

(2e): C, 69.15; H, 4.93; N, 12.10. Found: C, 69.00; H, 5.03; N, 12.06. Calcd for $C_{14}H_{11}N_5O_2$ (3b): C, 59.78; H, 3.94; N, 24.90. Found: C, 59.56; H, 4.14; N, 24.57.

3-Cyanocoumarinimide (8a) and Its 8-Methoxy Derivative 8b.—To a solution of malononitrile (3.3 g, 0.05 mol) and salicylaldehyde (6.1 g, 0.05 mol) in ethanol (30 ml), ammonium acetate (2.31 g, 0.03 mol) was added and stirred for few minutes. This mixture afforded 5.5 g (65%) of **8a**, mp 162–164° dec (lit.[4] mp 163–165° dec). When 3-methoxysalicylaldehyde was used instead of salicylaldehyde, the condensation afforded 89% **8b**: mp 172–174° dec; ν_{max}^{KBr} 3290 (NH), 2220 (C≡N), 1650 cm^{-1} (C=NH).

Anal. Calcd for $C_{11}H_8N_2O_2$: C, 65.99; H, 4.03; N, 13.99. Found: C, 65.93; H, 3.97; N, 14.20.

Formation of 4-Amino-5-imino-2-phenyl[1]benzopyrano[3,4-*c*]pyridine (2a) by the Reaction of 8a and Acetophenone.—To a mixture of **8a** (0.8 g) and acetophenone (0.72 g) in ethanol (5 ml), ammonium acetate (1 g) was added and heated for 0.5 hr. After cooling, deposited crystals were collected and recrystallized from ethanol–pyridine to give 0.4 g of pale yellow needles (Table II).

Anal. Calcd for $C_{18}H_{13}N_3O$: C, 75.24; H, 4.56; N, 14.63. Found: C, 74.92; H, 4.52; N, 14.87.

Reaction of 2a and Salicylaldehyde.—To a mixture of **2a** (0.2 g) and salicylaldehyde (0.2 g) in ethanol (5 ml), ammonium acetate (0.5 g) was added and heated for 0.5 hr. Yellow-orange crystals precipitated out during the reaction. Recrystallization from pyridine gave 0.2 g of yellow crystals, mp 301–302°. This compound was proved to be identical with **1a** by a study of their ir spectra.

Reaction of 4-Amino-5-imino-7-methoxy-2-phenyl[1]benzopyrano[3,4-*c*]pyridine (2c) and Hydrochloric Acid.—To a mixture of **2c** (0.3 g) and ethanol (7 ml), hydrochloric acid (3 ml) was added and heated for 1 hr. After the mixture cooled, the resulting precipitate was collected and recrystallized from pyridine–ethanol to afford 0.2 g of 4-amino-7-methoxy-5-oxo-2-phenyl[1]benzopyrano[3,4-*c*]pyridine (**7b**): mp 219–220°; ν_{max}^{KBr} 3400, 3280, 3170 (NH_2), 1700 cm^{-1} (C=O).

Anal. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80. Found: C, 71.44; H, 4.61; N, 9.08.

Formation of 2-Aryl-5-methyl[2,3,4-*de*]benzopyrano[2,3-*d*]-pyridopyrimidine (5) by the Reaction of 2 and Acetic Anhydride.—A mixture of **2** (0.7 mmol) and acetic anhydride (4–6 ml) in pyridine (2–4 ml) was heated for 1–2 hr. After the mixture cooled, the resulting precipitate was collected and washed with dilute methanol. Experimental results are summarized in Table III.

Anal. Calcd for $C_{20}H_{13}N_3O$ (**5a**): C, 77.15; H, 4.21; N, 13.50. Found: C, 76.87; H, 4.21; N, 13.48. Calcd for $C_{20}H_{12}N_4O_3$ (**5b**): C, 67.41; H, 3.39; N, 15.72. Found: C, 67.53; H, 3.26; N, 15.75. Calcd for $C_{21}H_{15}N_3O_2$ (**5c**): C, 73.89; H, 4.43; N, 12.31. Found: C, 73.62; H, 4.44; N, 12.40. Calcd for $C_{21}H_{14}N_4O_4$ (**5d**): C, 65.28; H, 3.65; N, 14.50. Found: C, 64.93; H, 3.51; N, 14.28.

Formation of 2-Acetamino-1-cyano-5-methyl[2,3,4-*de*]benzopyrano[2,3-*d*]pyridopyrimidine (6) by the Reaction of 3 and Acetic Anhydride.—To a solution of **3** (0.4 mmol) suspended in pyridine (2 ml), acetic anhydride (2 ml) was added and heated for 1 hr. A pale yellow crystals began to separate from the solution. Experimental results are also listed in Table III.

Anal. Calcd for $C_{17}H_{11}N_5O_2$ (**6a**): C, 64.35; H, 3.49; N, 22.07. Found: C, 64.21; H, 3.57; N, 22.24. Calcd for $C_{18}H_{13}N_5O_3$ (**6b**): C, 62.24; H, 3.78; N, 2 0.17. Found: C, 61.88; H, 3.60; N, 19.89.

Acetylation of 1.—Acetic anhydride (3–6 ml) was added to a solution of **1** (0.2 g) suspended in pyridine (2–3 ml) and refluxed for 2 hr. After the mixture cooled, deposited crystals were collected and recrystallized from pyridine or dimethyl sulfoxide to afford **4** as pale yellow crystals. Experimental results and spectral data (ir and nmr) are summarized in Table I.

Anal. Calcd for $C_{27}H_{17}N_3O_3$ (**4a**): C, 75.17; H, 3.94; N, 9.74. Found: C, 74.89; H, 3.72; N, 9.88. Calcd for $C_{28}H_{19}N_3O_4$ (**4b**): C, 72.87; H, 4.15; N, 9.11. Found: C, 72.63; H, 4.23; N, 8.86. Calcd for $C_{29}H_{19}N_3O_5$ (**4c**): C, 71.16; H, 3.91; N, 8.59. Found: C, 71.13; H, 3.98; N, 8.81. Calcd for $C_{27}H_{16}N_4O_5$ (**4d**): C, 68.06; H, 3.36; N, 11.76. Found: C, 67.87; H, 3.42; N, 11.66. Calcd for $C_{29}H_{21}N_3O_5$ (**4e**): C, 70.87; H, 4.31; N, 8.55. Found: C, 70.92; H, 4.28; N, 8.70.

Registry No.—**1a**, 34035-64-8; **1b**, 34035-65-9; **1c**, 34035-66-0; **1d**, 34035-67-1; **1e**, 34035-68-2; **1f**, 34035-69-3; **1g**, 34035-70-6; **2a**, 30144-15-1; **2b**, 34035-72-8; **2c**, 34035-73-9; **2d**, 34035-74-0; **2e**, 34035-75-1; **3a**, 34035-76-2; **3b**, 34035-77-3; **4a**, 34035-78-4; **4b**, 34035-79-5; **4c**, 34035-80-8; **4d**, 34035-81-9; **4e**, 34087-68-8; **5a**, 34035-82-0; **5b**, 34035-83-1; **5c**, 34035-84-2; **5d**, 34035-85-3; **6a**, 34033-67-5; **6b**, 34033-68-6; **7a**, 34033-69-7; **7b**, 34033-70-0; **8b**, 34033-71-1; malononitrile, 109-77-3; salicylaldehyde, 90-02-8; ammonium acetate, 631-61-8.

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Chemistry of α,α-Dichlorosulfenyl Chlorides

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A convenient two-step general synthesis of α(carbamoyl)-α,α-dichloromethyl sulfenyl chlorides is described. These sulfenyl chlorides have been shown to undergo normal displacement of chloride from sulfur upon reaction with primary and secondary amines, alcohols and phenols, sulfinates, *O,O*-diethyldithiophosphoric acid, and phosphites. With liquid ammonia the sulfenyl chlorides yield 1-cyanoformamides. Other characteristic sulfenyl chloride reactions of these compounds include synthesis of (1) 1,2,4-thiadiazoles from amidines, (2) carbonylsulfenyl chlorides upon treatment with sulfuric acid–water, and (3) 2-chloro-2-thioxoacetamides with triphenylphosphine. Ring closure of these sulfenyl chlorides catalyzed by aluminum chloride produces 2-indolinones.

In a recent paper[1] we reported a general synthesis of functionalized α,α-dichlorosulfenyl chlorides (*e.g.*, **1**) *via* chlorination of the appropriate benzyl sulfide.

Presently we wish to report a new route for the synthesis of related compounds (**2**) and our studies of the chemical reactivity of dichlorosulfenyl chlorides (**1**).

Chlorination of α-Mercaptoacetanilides.—Chlorination of α-mercaptoacetanilides has been found to produce α-carbamoyl-α,α-dichlorosulfenyl chlorides (**2**) in good yield. The sequence initially involves simply

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