followed by 14.7 g of light yellow oil, bp 150–160 °C (0.6 mm). A 4-g portion of the oil was separated by high-performance LC on silica gel using 40% chloroform in cyclopentane into 2.3 g (50%) of the colorless 4*H*-pyran **6** [^{1}H NMR δ 1.20 (3 H, t), 2.27 (3 H, s), 3.20 (2 H, dq), 4.15 (2 H, q), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ –87.5 (t, J_{HF} = 5 Hz); exact mass, *m/e* calcd for $C_{15}H_{15}FO_3Se$ 342.0170, found 342.0169] and 0.96 g (19%) of **8** [^{1}H NMR 1.20 and 1.25 (3 H, 2 t), 1.7–2.9 (m), 2.18 and 2.25 (s) (5 H), 3.1–3.8 (1 H, m), 3.9–4.4 (3 H, m), 7.1–7.7 (5 H, m); ^{19}F NMR δ –68.99 and –69.20 (2 d, J_{HF} = 9 Hz); exact mass, *m/e* calcd for $C_{15}H_{17}F_3O_3Se$ 382.0294, found 382.0311].

Reaction of 4 with Ethyl Acetoacetate. A mixture of 4.08 g (0.02 mol) of **4**, 5.2 g (0.04 mol) of ethyl acetoacetate, 3.04 g (0.02 mol) of DBU, and 30 mL of toluene was refluxed overnight under N_2. After being cooled to room temperature, the solution was washed with 50 mL of 5% HCl and 50 mL of H_2O, dried ($MgSO_4$), and concentrated on a rotary evaporator to 6.7 g of dark liquid. Kugelrohr distillation of the liquid at 0.11 mm gave 5.0 g of faintly yellow liquid which distilled at a pot temperature of 140–150 °C. The oil was chromatographed on 100 g of silica gel packed in petroleum ether and eluted in 50-mL fractions with 5% ether in petroleum ether. Fractions 8–10 contained 4.07 g (69%) of the colorless 4*H*-pyran **7**: ^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, t), 2.30 (3 H, s), 3.13 (2 H, dq), 4.15 (2 H, q), 7.1–7.5 (5 H, m); ^{19}F NMR δ –91.2 (t, J_{HF} = 5 Hz); exact mass, *m/e* calcd for $C_{15}H_{15}FO_3S$ 294.0723, found 294.0721.

Reaction of 3 with Diethyl Malonate. A solution of 10 g (0.04 mol) of **3**, 16 g (0.1 mol) of diethyl malonate, 7.5 g (0.05 mol) of 1,5-diazabicyclo[5.4.0]undec-5-ene, and 100 mL of toluene was refluxed for 1.5 h. The dark solution was concentrated on a rotary evaporator to 21.7 g of oil. Distillation of the oil through a short-path still gave 8.1 g of recovered diethyl malonate, bp 43–45 °C (0.6 mm), followed by 9.94 g of golden liquid, bp 147–159 °C (0.5 mm). A 4-g portion of this liquid was separated by high-performance LC on silica gel using 30% methylene chloride in cyclopentane into 2.6 g (41%) of **9** [^{1}H NMR ($CDCl_3$) δ 1.20 (3 H, t), 1.25 (3 H, t), 2.33 (2 H, m), 3.45 (1 H, m), 4.15 (2 H, q), 4.20 (2 H, q), 3.8–4.4 (1 H, m), 7.1–7.7 (5 H, m); ^{19}F NMR ($CDCl_3$) δ –69.3 (d, J_{HF} = 9 Hz); exact mass, *m/e* calcd for $C_{16}H_{19}F_3O_4Se$ 412.0400, found 412.0384] and 0.84 g (13%) of **10** [^{1}H NMR ($CDCl_3$) δ 1.20 (6 H, t), 2.81 (2 H, dt), 3.77 (1 H, t), 4.13 (4 H, q), 7.1–7.5 (5 H, m); ^{19}F NMR ($CDCl_3$) δ –76.10 (1 F, dt, J_{FF} = 24 Hz), –80.06 (dt); exact mass, *m/e* calcd for $C_{16}H_{18}F_2O_4Se$ 392.0337, found 392.0327].

Reaction of 3 with *n*-Butyllithium. A solution of 5.02 g (0.02 mol) of **3** in 100 mL of ether was cooled under N_2 to –70 °C. A solution of *n*-butyllithium in hexane (1.6 M, 16 mL, 0.025 mol) was added over 10 min. After being stirred for 1 h at –72 °C, the solution was quenched by pouring it into 300 mL of ice water containing 10 mL of concentrated HCl. The ether layer was dried ($MgSO_4$) and concentrated on a rotary evaporator to give 4.15 g of oil. Short-path distillation gave 3.4 g (80%) of phenyl butyl selenide, bp 67–71 °C (0.5 mm).

Reaction of 4 with *n*-Butyllithium. A solution of 120 mL of ether and 40 mL of 1.6 M *n*-butyllithium in hexane (0.064 mol) was cooled to –70 °C. A solution of 8.2 g (0.04 mol) of **4** in 40 mL of ether was added dropwise over 15 min. The resulting colorless solution was stirred for 1 h at –70 °C. The solution was quenched by pouring it into 200 mL of ice water containing 10 mL of concentrated HCl. The ether layer was dried ($MgSO_4$) and concentrated on a rotary evaporator to 10 g of yellow oil. Short-path distillation gave 9.6 g (79%) of **12**: bp 82–85 °C (0.4 mm); ^{1}H NMR ($CDCl_3$) δ 0.70–2.30 (11 H, m), 7.1–7.5 (5 H, m); ^{19}F NMR δ –83.07, –82.15 (AB q, J_{FF} = 27 Hz); exact mass, *m/e* calcd for $C_{13}H_{16}F_2S$ 242.0941, found 242.0928.

Reaction of 12 with *n*-Butyllithium. A solution of 200 mL of ether and 70 mL of 1.6 M *n*-butyllithium in hexane (0.112 mol) was cooled to –70 °C. A solution of 8.4 g (0.035 mol) of **12** in 40 mL of ether was added over 10 min. The resulting colorless solution was stirred for 0.5 h at –70 °C and for 1 h at –40 °C. The solution was quenched by pouring it into 400 mL of ice water containing 20 mL of concentrated HCl. The ether solution was dried ($MgSO_4$) and concentrated on a rotary evaporator to 9.8 g of faintly yellow liquid. Short-path distillation gave 9.44 g (97%) of colorless liquid: bp 127–134 °C (0.6 mm); exact mass, *m/e* calcd for $C_{17}H_{25}FS$ 280.1659, found 280.1661. GLPC analysis of the liquid on a 10 ft × 0.25 in. 10% SE-30 column at 200 °C showed two peaks, A (57%, retention time 15.2 min) and B (43%, retention time 27.2 min). Samples of A and B were obtained by preparative GLPC and identified as (*Z*)-**13** [^{1}H NMR ($CDCl_3$) δ 0.70–2.6 (20 H, m), 7.23 (5 H, s); ^{19}F NMR ($CDCl_3$) δ –92.78 (t, t, J_{HF} = 23 Hz, 3.5 Hz)] and (*E*)-**13** [^{1}H NMR ($CDCl_3$) δ 0.70–2.70 (20 H, m), 7.27 (5 H, s); ^{19}F NMR ($CDCl_3$) δ –90.75 (t, J_{HF} = 23 Hz)].

Registry No. 1, 73194-30-6; **2**, 73194-31-7; **3**, 73194-32-8; **4**, 73194-33-9; **5**, 73194-34-0; **6**, 73194-35-1; **7**, 73194-36-2; **8**, 73194-37-3; **9**, 73194-38-4; **10**, 73194-39-5; 11, 28622-61-9; **12**, 73194-40-8; (*E*)-**13**, 73194-41-9; (*Z*)-**13**, 73194-42-0; phenylselenenyl chloride, 5707-04-0; 3,3,3-trifluoropropene, 677-21-4; phenylsulfenyl chloride, 931-59-9; ethyl acetoacetate, 141-97-9; diethyl malonate, 105-53-3; butyllithium, 109-72-8.

Heterocyclic Systems. 8.[1] Condensation Reactions of 4-Oxo-4*H*-[1]benzopyran-3-carbonitrile

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Condensation reactions of 4-oxo-4*H*-[1]benzopyran-3-carbonitriles (1; X = H, CH_3, Cl, and Br) with 1,2-diamines, acetylglycine, and themselves have been investigated. The compounds **1** on being refluxed with ethylenediamine in ethanol give initially 1,4-addition products that undergo further transformation to 2-amino-3-formylchromones **2** (45–75%) and 1,3,4,5-tetrahydro-2-[(2-hydroxybenzoyl)methylene]imidazoles **3** (7–15%). On the contrary, *o*-phenylenediamine undergoes 1,2-addition to the nitrile functions of compounds **1** to form intermediate amidines, which on further cyclization and subsequent air oxidation afford 6-amino-7-oxo-7*H*-[1]benzopyrano[2,3-*b*]-[1,5]benzodiazepines **12** (22–36%). The nitriles **1** condense with acetylglycine to afford 2-methyl[1]benzopyrano[2,3-*b*]pyridino[3,2-*d*]oxazol-5(5*H*)-ones **15** (47–54%). When refluxed with ammonium acetate in acetic acid, compounds **1** undergo self-condensation, giving 2-(4-oxo-4*H*-[1]benzopyran-3-yl)[1]benzopyrano[3,2-*e*]pyrimidin-5(5*H*)-ones **17** in 13–27% yield. **15** and **17** are also obtained by condensation of **2** with acetylglycine and **1**, respectively.

The condensation reactions of 4-oxo-4*H*-[1]benzopyran-3-carbonitrile (henceforth called chromone-3-nitrile) are little known.[2] In its reaction with sodium azide, it behaves as a simple arylnitrile to form 3-(1*H*-tetrazol-5-

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Table I. 2-Amino-4-oxo-4*H*-[1]benzopyran-3-carboxaldehydes 2

	yield, %	mp, °C	formula[a]	NMR solvent	^{1}H NMR, δ CHO (s)	NH$_2$ (br s, exch)	ArH	ArCH$_3$
2a	45	250	$C_{10}H_7NO_3$	Me_2SO-d_6	10.23	9.66	8.15-7.36	
2b	47	220	$C_{11}H_9NO_3$	Me_2SO-d_6	10.07	9.53	7.80-7.29	2.40
2c	80	290 dec	$C_{10}H_6NO_3Cl$	CF_3COOD	9.73	10.70	7.70-6.90	
2d	72	287 dec	$C_{10}H_6NO_3Br$	CF_3COOD	9.76	10.63	7.73-6.91	

[a] All the compounds gave satisfactory elemental analysis: C, ±0.32; H, ±0.36; N, ±0.28.

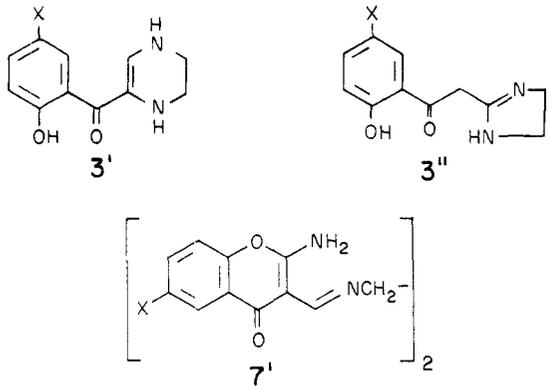
Table II. 2-[(2-Hydroxybenzoyl)methylene]-1,3,4,5-tetrahydroimidazoles 3

	yield, %	mp, °C	formula[a]	^{1}H NMR (Me_2SO-d_6), δ OH (s, exch)	2 NH (br s, exch)	ArH (m)	=CHCO (s, exch)	CH_2CH_2 (br s)
3a	15	176	$C_{11}H_{12}N_2O_2$	15.25	8.30	7.67-6.63	5.34	3.58
3b[b]	7	188	$C_{12}H_{14}N_2O_2$	14.77	8.21	7.21-6.61	5.33	3.56
3c	13	220	$C_{11}H_{11}N_2O_2Cl$	15.56	8.30	7.53-6.80	5.40	3.66
3d	10	230	$C_{11}H_{11}N_2O_2Br$	15.54	8.39	7.58-6.75	5.37	3.60

[a] All the compounds gave satisfactory analysis for C, H, and N. [b] CH_3 protons appeared as singlet at δ 2.20.

yl)chromone.[3] It condenses with reactive methylene compounds such as acetylacetone, ethyl acetoacetate, diethyl malonate, and ethyl cyanoacetate to give [1]benzopyrano[2,3-*b*]pyridine derivatives.[4,5] Condensation of this nitrile with hydrazine and phenylhydrazine has also been reported from our laboratory.[5] Some new condensation reactions of chromone-3-nitrile are reported in this paper.

The reaction of chromone-3-nitriles 1 with 1,2-diamines, aliphatic as well as aromatic, was studied first. On being refluxed with ethylenediamine in ethanol, the nitriles 1[3] gave 2-amino-3-formylchromones **2** together with minor products (7–15%). The structure of the former **2** was established from the spectral data (Table I) and by comparison with an authentic sample.[6] The minor products give a deep violet coloration with ferric chloride, showing the presence of a phenolic hydroxy group. The IR spectra shows further that this hydroxy group is chelated with a carbonyl group. On the basis of IR and analytical data, three structures (**3**, **3′**, and **3″**) may be proposed for these



compounds. The structure **3″** is not compatible with the NMR spectrum (Table II) that shows an exchangeable two-proton broad singlet at about δ 8.34 attributable to two NH groups as in **3** or **3′**. Again, of these two structures

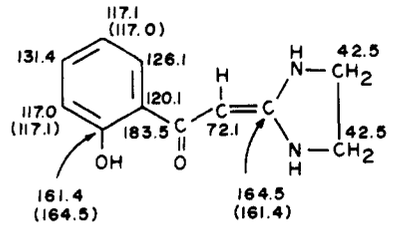


Figure 1. ^{13}C NMR peak assignments for **3a**.

3 and **3′**, the former is preferred as the compound gives another exchangeable one-proton singlet at δ 5.35 characteristic of H-α of an enamino ketone.[7] Moreover, the tetrahydropyrazine **3′** should disproportionate to the corresponding pyrazine and piperazine.[8] The structure **3** is further corroborated by ^{13}C NMR spectra (peak assignment[9] for **3a** is shown in Figure 1). The most significant peak is an upfield doublet at δ 72.1, quite expected for C-α of an enamino ketone[10] having an electron-donating group at the β-position as in **3**.

The mechanism for the formation of these two products **2** and **3** by the reaction of ethylenediamine with the nitriles **1** is depicted in Scheme I. Here the nucleophile is undergoing 1,4-addition; the intermediate adduct may have three structures (**4**–**6**). The intermediate **5** cyclizes to the aldimino derivative **7** which undergoes facile hydrolysis (partial in ethanolic medium and complete during crystallization from acetic acid) to afford the aminochromone **2**. The intermediate **6** loses a molecule of hydrogen cyanide, and the resultant intermediate **8** undergoes intramolecular 1,4-addition with concomitant opening of the pyrone ring to form the tetrahydroimidazole **3**. 3-Bromochromanones are known to undergo base-catalyzed

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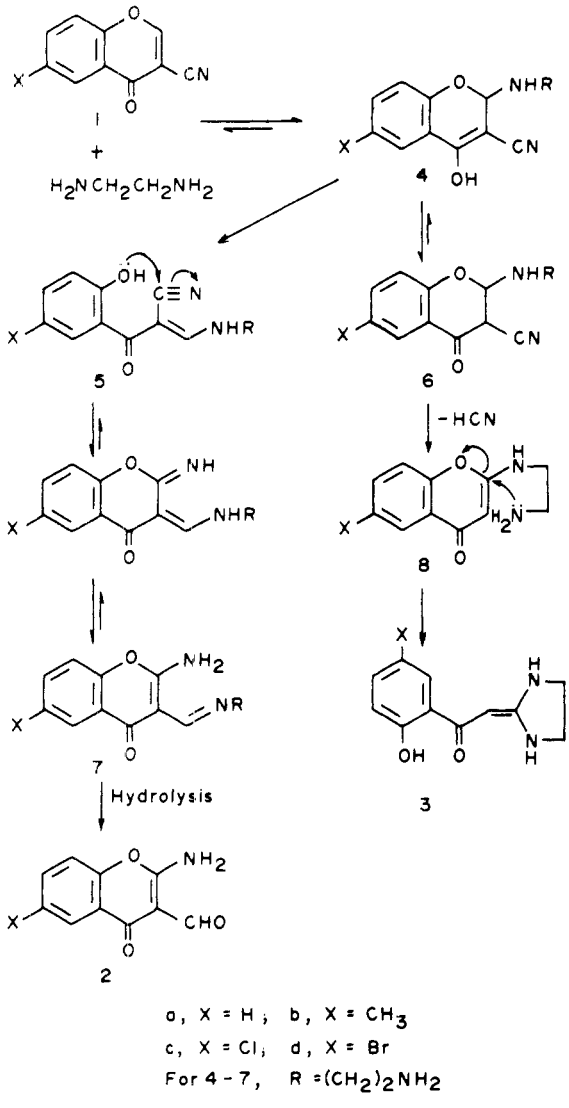
(2) G. P. Ellis, *Heterocycl. Compd.*, **35**, 903 (1972).
(3) A. Nohara, *Tetrahedron Lett.*, 1187 (1974); A. Nohara, H. Kuriki, T. Saijo, H. Sugihara, M. Kanno, and T. Sanno, *J. Med. Chem.*, **20**, 141 (1977).
(4) C. K. Ghosh, *Synth. Commun.*, **8**, 487 (1978).
(5) C. K. Ghosh, D. K. Sinha Roy, and K. K. Mukhopadhyay, *J. Chem. Soc., Perkin Trans. 1*, 1964 (1979).
(6) U. Peterson and H. Heitzer, *Justus Liebigs Ann. Chem.*, 1659 (1976).
(7) E. J. Cone, R. H. Garner, and W. Hayes, *J. Org. Chem.*, **37**, 4436 (1972).
(8) G. R. Ramage and J. K. Landquist, "Chemistry of Carbon Compounds", Vol. 4B, E. H. Rodd, Ed., Elsevier, Amsterdam, 1959, p 1336. 1,2,3,4-Tetrahydro-1,4-bis(arenesulfonyl)pyridazines are, however, known to be stable: J. E. Franz, M. W. Dieterich, A. Henshall, and C. Osuch, *J. Org. Chem.*, **31**, 2847 (1966); U. Eisner and A. J. Williams, *J. Chem. Soc., Chem. Commun.*, 606 (1979).
(9) Peak assignments to the phenyl carbons are based on the shielding parameters of hydroxy and carbonyl ortho to each other (J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, 1972, p 192). The triplet at δ 42.5 is possibly due to one carbon of the CH_2CH_2 group, that due to the other carbon merging with the peaks of Me_2SO appearing at a little bit upfield beyond δ 42.5.
(10) D. Tourwe, G. Van Binst, S. A. G. De Graft, and U. K. Pandit, *Org. Magn. Reson.*, **7**, 433 (1975).

Table III. 6-Amino-7-oxo-7*H*,13*H*-[1]benzopyrano[2,3-*b*][1,5]benzodiazepines 12[a] and Their Precursors 9[a]

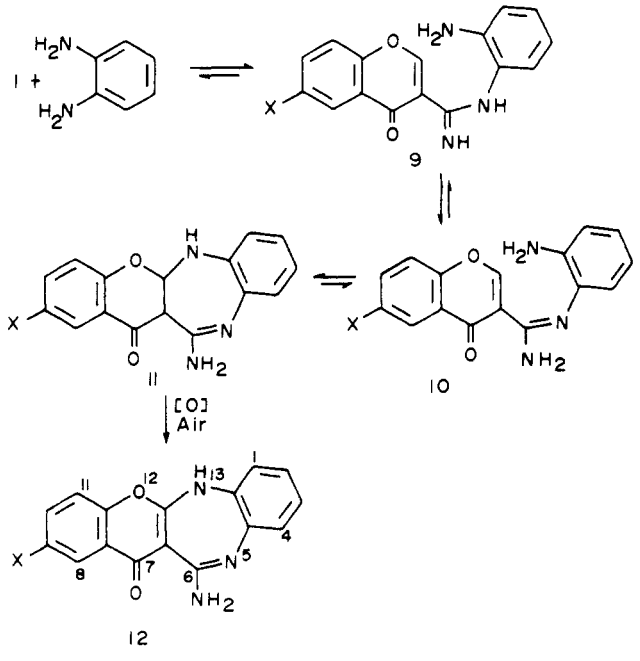
	compds 9		compds 12							
							^{1}H NMR, δ			
	yield, %	mp, °C	yield,[b] %	mp, °C	formula	NMR solvent	NH (s, exch)	ArH (m)	NH_2 (br s, exch)	$ArCH_3$
a	62	210	24	270	$C_{16}H_{11}N_3O_2$	Me_2SO-d_6	9.38	7.98-7.48	7.20	
b	64	255	30	265	$C_{17}H_{13}N_3O_2$	$CDCl_3$	9.33	8.13-7.20[c]		2.50
c	60	225	22	260	$C_{16}H_{10}N_3O_2Cl$	Me_2SO-d_6	9.36	8.16-7.08[c]		
d	57	210	36	275	$C_{16}H_{10}N_3O_2Br$	Me_2SO-d_6	9.38	8.30-7.48	7.18	

[a] All the compounds gave satisfactory elemental analysis for C, H, and N. [b] Based on chromone-3-nitriles 1. [c] NH_2 protons merge with aromatic protons.

Scheme I



Scheme II



dehydrobromination to give chromones,[11] providing an anology for the elimination of HCN from **6**. Furthermore, treatment of **1** with 0.5 molar equiv of ethylenediamine produced the same two products, **2** and **3**, nearly 35% of **1** being recovered unchanged. Thus it is unlikely that the dimeric species **7′** is involved in the ethylenediamine-mediated conversion of **1** to **2**. When the nitrile **1** was refluxed with 0.5 molar equiv of *n*-propylamine in 85% ethanol, the product **2** was formed exclusively. This experiment points to the fact that the aliphatic primary amino group in **7** has no role for the conversion of **7** to **2**. The (iminomethyl)-chromone **7** (R = alkyl or aryl) is extremely susceptible to hydrolysis.[12] So the traces of water present in the reaction medium are sufficient to hydrolyze the initially formed imine **7**, and the amine thus released brings about the transformation of the remaining nitrile **1**.

In order to study the behavior of an aromatic 1,2-diamine toward chromone-3-nitriles **1**, the latter were refluxed with *o*-phenylenediamine in ethanol. The resultant amidine derivatives **9**, which might also exist in the other tautomeric form **10**, on further refluxing in glacial acetic acid gave 6-amino-7-oxo-7*H*,13*H*-[1]benzopyrano[2,3-*b*]-[1,5]benzodiazepines **12** (Table III). The behavior of an aromatic 1,2-diamine toward the nitriles **1** is evidently different from that of an aliphatic 1,2-diamine. Here the nucleophile undergoes 1,2-addition to the nitrile function of the substrate **1** to form the amidine **9** which on further cyclization and subsequent air oxidation produces the fused diazepine **12** (Scheme II). Air oxidation or spontaneous dehydrogenation of some dihydro[1]benzopyrano[2,3-*b*][1,5]benzothiazepinones and -diazepinones has also been recently reported by Fitton et al.[13] The reactions of **1** with *o*-phenylenediamine are analogous to the formation of 7-oxo-7*H*,13*H*-[1]benzopyrano[2,3-*b*]-[1,5]benzodiazepines (**12**, H in place of NH_2) by reaction of chromone-3-carboxaldehyde with *o*-phenylenediamine.[14] The UV spectra of compounds **12** are similar to those of

(11) G. Zemplen and L. Mester, *Ber. Dtsch. Chem. Ges.*, **76**, 776 (1943).

(12) A. O. Fitton, J. R. Frost, P. G. Houghton, and H. Suschitzky, *J. Chem. Soc., Perkin Trans. 1*, 1691 (1979).

(13) A. O. Fitton, P. G. Houghton, and H. Suschitzky, *Synthesis*, 337 (1979).

(14) C. K. Ghosh and S. Khan, *Synthesis*, in press.

Table IV. 2-Methyl[1]benzopyrano[2,3-*b*]pyridino[3,2-*d*]oxazol-5(5*H*)-ones 15

	yield, %	mp, °C	formula[a]	^{1}H NMR (CF_3COOD), δ H-4	other ArH	CH_3-2	CH_3-7
15a	53	300	$C_{14}H_8N_2O_3$	8.70	7.85-6.90	2.00	
15b	54	305	$C_{15}H_{10}N_2O_3$	8.88	7.72-7.18	2.07	2.48
15c	51	275	$C_{14}H_7N_2O_3Cl$	8.83	7.82-6.96	2.03	
15d	47	300 dec	$C_{14}H_7N_2O_3Br$	8.81	7.78-7.01	2.05	

[a] Elemental analysis (C, H, and N) is in good agreement with the molecular formula.

Table V. 2-(4-Oxo-4*H*-[1]benzopyran-3-yl)[1]benzopyrano[3,2-*e*]pyrimidin-5(5*H*)-ones 17

	yield, %	mp, °C	formula[a]	^{1}H NMR ($CDCl_3$), δ H_a (s)	H_b (s)	H_c (dd)	other ArH (m)	$ArCH_3$
17a	18	240	$C_{20}H_{10}N_2O_4$	9.66	9.06	8.33	7.90-7.23	
17b	13	297	$C_{22}H_{14}N_2O_4$	9.73	9.03	8.16	7.76-7.30	2.50
17c	27	290 dec	$C_{20}H_8N_2O_4Cl_2$	9.70	9.04	8.25	7.81-7.31	
17d	24	295 dec	$C_{20}H_8N_2O_4Br_2$	9.71	9.03	8.22	7.79-7.28	

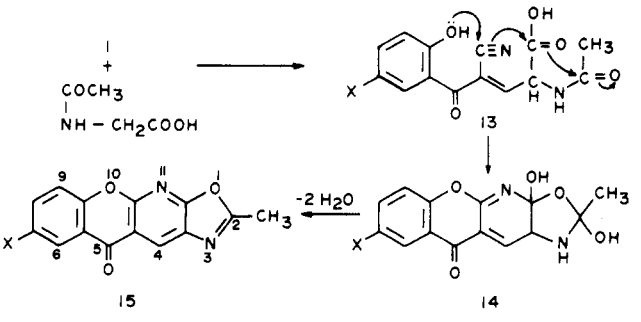
[a] All the compounds gave satisfactory elemental analysis (C, H, and N).

the corresponding deaminated products; for example, **12b** has a UV spectrum with maxima at 207 nm (log ε 4.40), 247 (4.23), 289 (4.30), 309 (4.22), comparable to that [λ_{max} 207 nm (log ε 4.46), 247 (4.28), 289 (4.35), 309 (4.27)] exhibited by the corresponding deaminated compound[14] prepared from 6-methyl-3-formylchromone and *o*-phenylenediamine.

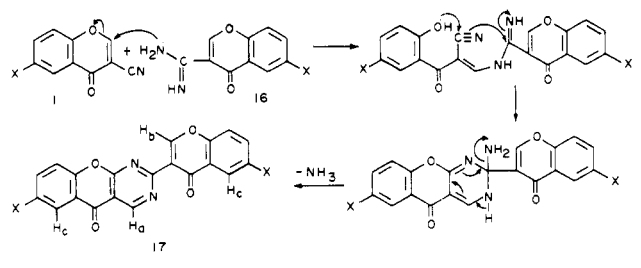
Chromone-3-carboxaldehyde has been converted to the pyrrole derivative by treating its azalactone with a base.[15] In order to find out if it was possible to form a new heterocyclic system by reacting 1 with acylglycine, we refluxed **1a** with acetylglycine in acetic anhydride containing fused sodium acetate. A compound analyzing for $C_{14}H_8N_2O_3$ (*m/e* 252, M^+) resulted. On the basis of its spectral data, this compound was assigned as 2-methyl[1]benzopyrano-[2,3-*b*]pyridino[3,2-*d*]oxazol-5(5*H*)-one (**15a**). The physical data of the various oxazolones **15** similarly prepared are listed in Table IV. The carbanion formed by the action of fused sodium acetate on acetylglycine attacks at C-2 of the chromone 1 with concomitant opening of the pyrone ring to give the intermediate hydroxy nitrile **13** which undergoes triple cyclization to yield the oxazolone **15** via the dihydroxy compound 14 (Scheme III). No intermediate product could be isolated in the conversion 1 → **15**. The oxazolone **15** was also formed when the aldehyde **2** was subjected to reaction with acetylglycine under the conditions of azalactone synthesis. Thus the reaction of 1 with acetylglycine to give **15** appears to have some resemblance to a typical azalactone synthesis, but it does not involve the intermediacy of the aldehyde **2** as the latter could not be formed even on prolonged refluxing of 1 with acetic anhydride and fused sodium acetate.

From the previous reports[4,5] and from results presented here so far, it is evident that the nucleophiles hydrazine and aniline undergo 1,2-addition to the nitrile functions of chromone-3-nitriles 1. On the other hand, hydroxide ion[6] or an aliphatic amine attacks the chromones 1 at the 2-position with rearrangement to 2-amino-3-formylchromones **2**. It was of interest to see how ammonia would react with the nitriles 1. 1,2-Addition of ammonia to the nitrile function[16] would give the amidines **16**, good synthons for preparing the imidazole[17] and pyrimidine[18] systems bearing a chromone moiety at their 2-position.

Scheme III



Scheme IV



Chromone-3-nitriles 1 underwent extensive degradation when an alcoholic solution of the compound was warmed with ammonia.[19] However, when the nitriles 1 were refluxed with a potential ammonia source such as ammonium acetate in acetic acid, 2-(4-oxo-4*H*-[1]benzopyran-3-yl)-[1]benzopyrano[3,2-*e*]pyrimidin-5(5*H*)-ones **17** (Table V), the self-condensation products of 1, were obtained. So it is likely that ammonia converts the nitriles 1 to the amidines **16** which further react with the unchanged nitriles 1 to yield compounds **17** (Scheme IV). The poor yields (13–27%) of the products **17** again point to the decomposition of the substrate or the product itself by excess ammonia generated in the reaction medium.[19]

Finally, we anticipated that **17** could also be prepared by condensation of 1 with **2**, both bearing the identical group at their 6-position, provided the amino function of the latter underwent 1,2-addition to the nitrile function of the former and the amino or imino group of the resultant amidine intermediate underwent intramolecular addition to the aldehyde function followed by water elimination. Our anticipation was proved to be correct as compounds **17** were prepared in more than 70% yields by

(15) A. O. Fitton, J. R. Frost, H. Suschitzky, and P. G. Houghton, *Synthesis*, 133 (1977).
(16) F. C. Shaefer and A. P. Krapcho, *J. Org. Chem.*, **27**, 1255 (1962).
(17) K. T. Pots, *Chem. Rev.*, **61**, 89 (1961), and references therein.
(18) G. W. Kenner and A. Todd, *Heterocycl. Compd.*, **6**, 243 (1957).
(19) K. Kostka, *Rocz. Chem.*, **40**, 1683 (1966).

refluxing an equimolar mixture of the appropriate 1 and 2 in acetic acid.

Experimental Section

UV spectra were taken in ethanol solution with a Beckman DB-G; IR spectra were recorded for samples in Nujol mulls with a Beckman IR-20A, NMR with a Varian EM-390 spectrometer operating at 90 MHz, and mass spectra with a Hitachi RMU-6L instrument at 70 eV. Melting points were determined in open capillaries and are uncorrected.

Reaction of Chromone-3-nitriles 1 with Ethylenediamine (1:1). Typical Procedure. A mixture of **1a** (0.85 g, 5 mmol) and ethylenediamine (0.30 g, 5 mmol) was refluxed in ethanol (30 mL) for 3 h, and the precipitated solid was filtered, washed with ethanol, and crystallized from acetic acid to afford 2-amino-3-formylchromone **2a** (0.42 g) identical (melting point, mixture melting point, and superimposable IR spectra) with an authentic sample prepared by treating the nitrile **1a** with alkali.[6] It had the following: λ_{max} 260 nm (log ϵ 4.16), 231 (4.28), 264 (4.15), 292 (4.04); ν_{max} 3440, 3365 (NH_2), 1675 (CHO), 1645 (CO) cm^{-1}; mass spectrum, *m/e* (relative intensity) 189 (28, M^+), 161 (100, M − CO), 133 (M − 2 CO), 120 (64, $C_7H_4O_2$).

The filtrate from the foregoing experiment on concentration gave 2-[(2-hydroxybenzoyl)methylene]-1,3,4,5-tetrahydroimidazole (**3a**, 0.15 g): mp 176 °C (chloroform–methanol); λ_{max} 209 nm (log ϵ 4.14), 244 (3.90), 272 (3.62), 333 (4.11); ν_{max} 3340 (NH), 3220 (OH chelated with carbonyl), 1610 (CO) cm^{-1}; mass spectrum, *m/e* (relative intensity) 204 (100, M^+), 187 (29), 175 (18, M − CH_2CH_3), 84 (75, M − $C_7H_4O_2$).

Reaction of 1 with Ethylenediamine (1:0.5). **1a** (0.85 g, 5 mmol) was reacted with ethylenediamine (0.15 g, 2.5 mmol) as described above. After **2a** (0.22 g, 25% based on **1a**) was filtered out, the filtrate was concentrated after first crystallizing out nitrile **1a** (0.29 g, 35%); the imidazole **3a** (0.06 g, 6% based on **1a**) was collected from the mother liquor.

Reaction of 1a with *n*-Propylamine. The nitrile **1a** (1.71 g, 10 mmol) was refluxed with *n*-propylamine (0.30 g, 5 mmol) in ethanol (85%, 100 mL) for 4 h. The precipitated solid was filtered and washed with ethanol to afford **2a** (0.61 g, 75%).

6-Amino-7-oxo-7*H*,13*H*-[1]benzopyrano[2,3-*b*][1,5]benzodiazepines 12. Typical Procedure. A solution of **1a** (0.85 g, 5 mmol) and *o*-phenylenediamine (0.54 g, 5 mmol) in ethanol (60 mL) was heated under reflux for 3 h. The precipitated solid **9a** (0.86 g) was filtered out and further refluxed in acetic acid for 3 h. The reaction mixture was filtered hot to remove the undissolved solid, if any, and the filtrate was concentrated, cooled, and diluted with water. The deposited solid was filtered, dried, and crystallized from chloroform to afford the yellow diazepine **12a**: ν_{max} 3450, 3360 (NH_2), 1640 (CO) cm^{-1}; mass spectrum, *m/e* (relative intensity) 277 (2, M^+), 262 (100, M + 1 − NH_2), 234 (9, 262 − CO), 206 (24), 194 (28), 180 (6), 142 (21), 130 (15).

2-Methyl[1]benzopyrano[2,3-*b*]pyridino[3,2-*d*]oxazol-5-(5*H*)-ones 15. Typical Procedure. A mixture of **1b** (1.28 g, 7.5 mmol), acetylglycine (0.88 g, 7.5 mmol), and fused sodium acetate (0.72 g, 7.5 mmol) was refluxed in acetic anhydride (20 mL) for 3 h. The solid that precipitated out on cooling of the reaction mixture was filtered and crystallized from acetic acid to afford the oxazolone **15b**: 1.08 g; λ_{max} 205 nm (log ϵ 4.32), 238 (4.70), 298 (4.34), 348 (4.15); ν_{max} 1660 (CO), 1635 (C=N or C=C) cm^{-1}; mass spectrum, *m/e* (relative intensity) 266 (100, M^+), 251 (8, M − CH_3), 237 (7), 225 (12, M − CH_3CN), 197 (17, M − CH_3CN − CO), 169 (16, M − CH_3CN − 2 CO), 140 (13), 118 (12), 114 (7), 105 (8).

Preparation of the Oxazolones 15 from 2-Amino-3-formylchromone. General Procedure. A mixture of **2** (1 mmol), acetylglycine (1 mmol), and fused sodium acetate (2 mmol) was refluxed in acetic anhydride (10 mL) for 2 h. The precipitated solid was filtered and crystallized from acetic acid to afford **15** (60–73% yield), identical with that obtained from the appropriate nitrile **1** as described before.

2-(4-Oxo-4*H*-[1]benzopyran-3-yl)[1]benzopyrano[3,2-*e*]-pyrimidin-5(5*H*)-ones 17. Typical Procedure. The nitrile **1a** (0.85 g, 5 mmol) together with ammonium acetate (1.54 g, 20 mmol) was refluxed in glacial acetic acid (20 mL) for 4 h. A portion of the solvent was then distilled out, the reaction mixture was cooled and diluted with water, and the deposited solid was filtered and crystallized from acetic acid to afford the pyrimidinone **17a**: 0.16 g; λ_{max} 209 nm (log ϵ 4.50), 244 (4.43), 312 (4.21); ν_{max} 1650 (CO) cm^{-1}; mass spectrum, *m/e* (relative intensity) 342 (100, M^+), 313 (14, M − CO), 286 (10, M − CO − HCN), 172 (41), 92 (25, C_6H_4O).

Preparation of the Pyrimidinones 17 from the Aldehydes 2. General Procedure. A mixture of **2a** (0.47 g, 2.5 mmol) and **1a** (0.43 g, 2.5 mmol) in acetic acid (30 mL) was heated under reflux for 3 h. A portion (nearly 15 mL) of acetic acid was distilled out, and the reaction mixture was cooled and diluted with water. Filtration and subsequent crystallization (acetic acid) of the deposited solid gave **17a** (0.64 g, 75%), identical (melting point, mixture melting point, and superimposable IR) with the product obtained by treatment of **1a** with ammonium acetate as described earlier. The other substituted pyrimidinones **17b,c,d** were similarly prepared in 71, 73, and 78% yields, respectively.

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Registry No. **1a**, 50743-17-4; **1b**, 50743-18-5; **1c**, 50743-20-9; **1d**, 52817-13-7; **2a**, 61424-76-8; **2b**, 68301-75-7; **2c**, 68301-77-9; **2d**, 73262-04-1; **3a**, 73262-05-2; **3b**, 73262-06-3; **3c**, 73262-07-4; **3d**, 73262-08-5; **9a**, 73262-09-6; **9b**, 73262-10-9; **9c**, 73262-11-0; **9d**, 73262-12-1; **12a**, 73262-13-2; **12b**, 73262-14-3; **12c**, 73262-15-4; **12d**, 73262-16-5; **15a**, 73262-17-6; **15b**, 73262-18-7; **15c**, 73262-19-8; **15d**, 73262-20-1; **17a**, 73262-21-2; **17b**, 73262-22-3; **17c**, 73262-23-4; **17d**, 73262-24-5; ethylenediamine, 107-15-3; propylamine, 107-10-8; *o*-phenylenediamine, 95-54-5; acetylglycine, 543-24-8; ammonium acetate, 631-61-8.