New Heterocyclic Syntheses from Hydrazidoyl Halides. Convenient Syntheses of Fused Pyrimidines, Pyridazines, and Quinazolines [1]

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Aminocyanopyrazole derivatives and pyrazolo[2,3-*a*]quinazolones were obtained in good yields from hydrazidoyl halides and malononitrile. Pyrazolo[3,4-*d*]pyridazine and pyridazo[4',5': 1,2]pyrazolo[1,5-*a*]quinazoline derivatives were synthesized in quantitative yields by reaction of hydrazine hydrate with **2** and **16**, respectively. A novel ring system, a 3-substituted tetrahydro derivative of 7-oxo-6*H*,8*H*-pyridazo[3',4',5'-*c'd'*]-pyrazolo[3,4-*d*]pyrimidine was prepared by reaction of **6** with dimethyl carbonate. Pyrazolo[3,4-*d*]pyrimidine-4,6-dithiones were obtained in good yields by reaction of **2** with carbon disulfide. The structures of the products were assigned and confirmed on the basis of their elemental analyses, spectral data, and alternate synthesis wherever possible. The structures of the parent fused heterocyclic systems discussed in this work are summarized in Scheme 1.

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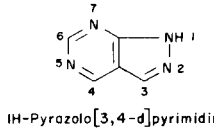
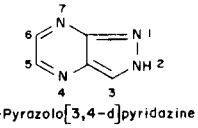
Introduction.

Over the past ten years we have published a number of reports dealing with the utilization of hydrazidoyl halides in heterocyclic syntheses [4-26]. As a continuation of our work, we have investigated the use of these intermediates in the synthesis of 4,6(5*H*,7*H*)-pyrazolo[3,4-*d*]pyrimidinedithiones, pyrazolo[2,3-*a*]quinazolines, pyrazolo[3,4-*d*]pyridazines, pyridazo[4',5':1,2]pyridazo[1,5-*a*]quinazolines, and pyridazo[3',4',5'-*c'd'*]pyridazo[3,4-*d*]pyrimidines. These compounds are expected to be of pharmacological and commercial interest. For example, the related fused pyrimidinethiones have found use as pharmacologically interesting purine analogs [27] and pyrazoloquinazolines are used as sensitizers [28]. The parent fused heterocyclic systems are summarized in Scheme 1 [*cf* ref 29]. The melting points and the analytical data on the new compounds are summarized in Tables I and II.

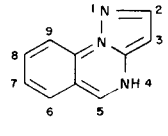
Scheme 1



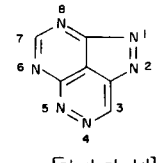
1H-Pyrazolo[3,4-d]pyrimidine



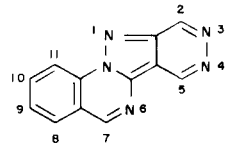
2H-Pyrazolo[3,4-d]pyridazine



4H-Pyrazolo[2,3-a]quinazoline



Pyridazo[3',4',5'-c'd']-pyrazolo[3,4-d]pyrimidine



Pyridazo[4',5':1,2]pyrazolo-[1,5-a]quinazoline

Table I

Synthesized Substituted Pyrazoles

Compound No.	Mp, °C	Molecular Formula	Analysis Calcd. (Found) C,%	H,%	N,%
2a	157	$C_{13}H_{12}N_4O_2$	60.93 (60.6)	4.72 (4.6)	21.86 (21.6)
2b	209	$C_{17}H_{13}N_5O$	67.32 (67.2)	4.32 (4.2)	23.09 (23.2)
2d	185	$C_{17}H_{12}N_4O$	70.82 (70.4)	4.20 (4.1)	19.43 (19.3)
2e	175	$C_{18}H_{14}N_4O$	71.51 (71.1)	4.67 (4.7)	18.53 (18.7)
3c	178	$C_{12}H_{10}N_4O$	63.73 (63.3)	4.45 (4.3)	24.76 (24.8)
3d	135	$C_{17}H_{12}N_4O$	70.82 (70.2)	4.20 (4.4)	19.43 (19.3)
3e	163	$C_{18}H_{14}N_4O$	71.51 (71.7)	4.67 (4.8)	18.53 (18.3)

Results and Discussion.

On treatment with equimolar amounts of malononitrile in ethanol in the presence of sodium ethoxide, the hydrazidoyl halides **1a-1b** were converted into the pyrazole de-

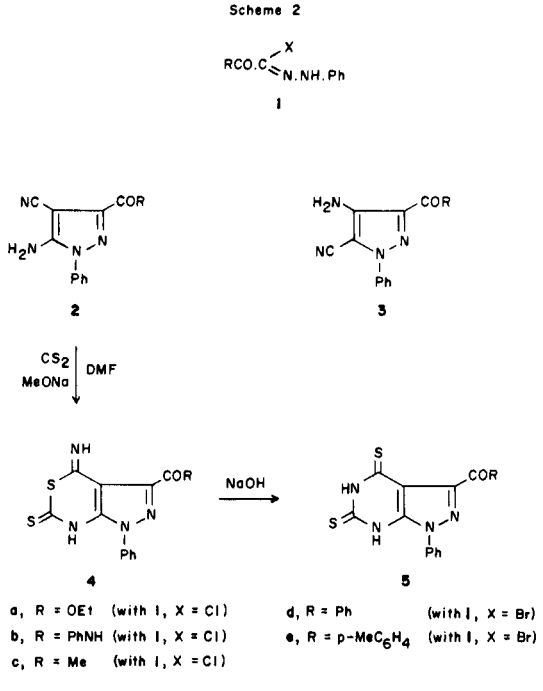
Table II

Synthesized Pyrazolo[3,4-*d*]pyrimidines and Pyrazolo[3,4-*a*]quinazolines

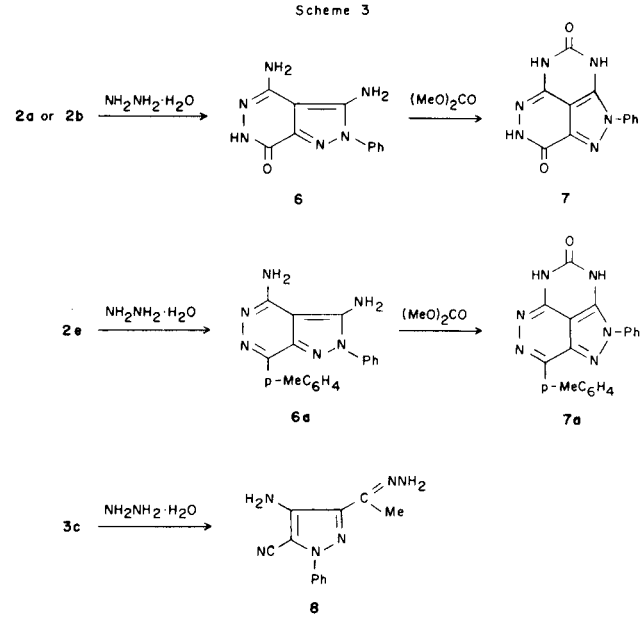
Compound No.	Mp, °C	Molecular Formula	Analysis Calcd. (Found) C,%	H,%	N,%
5a	189	$C_{14}H_{12}N_4O_2S_2$	50.59 (50.7)	3.64 (3.5)	16.85 (16.6)
5b	213	$C_{18}H_{13}N_5OS_2$	56.97 (56.9)	3.45 (3.6)	18.46 (18.4)
5c	191	$C_{13}H_{10}N_4OS_2$	51.64 (51.8)	3.33 (3.4)	18.53 (18.4)
5d	231	$C_{18}H_{12}N_4OS_2$	59.32 (59.4)	3.32 (3.2)	15.37 (15.7)
16j	290	$C_{14}H_{10}N_4O_3$	59.57 (59.4)	3.57 (3.5)	19.85 (19.6)
16k	328	$C_{18}H_{11}N_5O_2$	65.65 (65.7)	3.36 (3.7)	21.27 (21.3)
16ℓ	282	$C_{13}H_8N_4O_2$	61.90 (61.4)	3.19 (3.4)	22.21 (22.1)
16m	252	$C_{18}H_{10}N_4O_2$	68.78 (68.9)	3.20 (3.4)	17.82 (17.5)

rivatives **2a-2b**, respectively. On the other hand, under similar conditions, the chloride **1c** reacted with malononitrile with the formation of a product identified as **3c**. Also, the bromides **1d-1e** yielded, in each case, a mixture of the corresponding **2d-2e** and **3d-3e**, respectively, when treated with malononitrile in ethanolic sodium ethoxide. The assignment of the structure **2** follows from the presence of a sharp nitrile absorption band near 2230 cm^{-1} and two or three bands in the 3100-3400 cm^{-1} region due to the presence of an amino group in the ir spectra of **2a-2e** (Table III). The pmr spectra of **2a-2e** revealed the presence of a two-proton singlet which disappears when the solution is shaken with deuterium oxide. Additional supporting evidence for the structures **2a-2e** was obtained from their chemical behavior summarized in Schemes 2 and 3.

Scheme 2



Scheme 3



The reaction of **2a-2d** with carbon disulfide and sodium methoxide in dimethylformamide (reflux for 45 hours and the subsequent work-up) yielded the corresponding 3-substituted 1-phenyl-4,6(5*H*,7*H*)-pyrazolo[3,4-*d*]pyrimidinedithiones **5a-5d** as yellow crystalline materials in 80-90% yields. In principle, this reaction is analogous to the conversion of aromatic *o*-aminonitriles with carbon disulfide in pyridine to the corresponding quinazolinedithiones [30], and thus it is expected to follow the same sequence which involves the 1,3-thiazine **4** as intermediate (Scheme 1). The rearrangement of the latter to the corresponding pyrimidinedithiones **5** is similar to the rearrangement of 5-amino-4-substituted 2(3*H*)thiazolethiones in the presence of a strong base to imidazole-2,4(1*H*,3*H*)dithiones [31]. The new products **5a-5d** showed no nitrile band in their ir spectra but exhibited a weak NH band near 3200 cm^{-1} (Table III).

When **2a** was refluxed with hydrazine hydrate in ethanol, 2*H*-pyrazolo[3,4-*d*]pyridazinone **6** was obtained in 80% yield. The latter product was also formed by hydrazinolysis of **2b**. The structure of **6** was elucidated on the basis of its formation, elemental analysis , and its spectral data. For example, its pmr spectrum showed the absence of the characteristic signals of the ethoxy protons,

Table III

The Infrared Spectral Data of Compounds under Study [a]

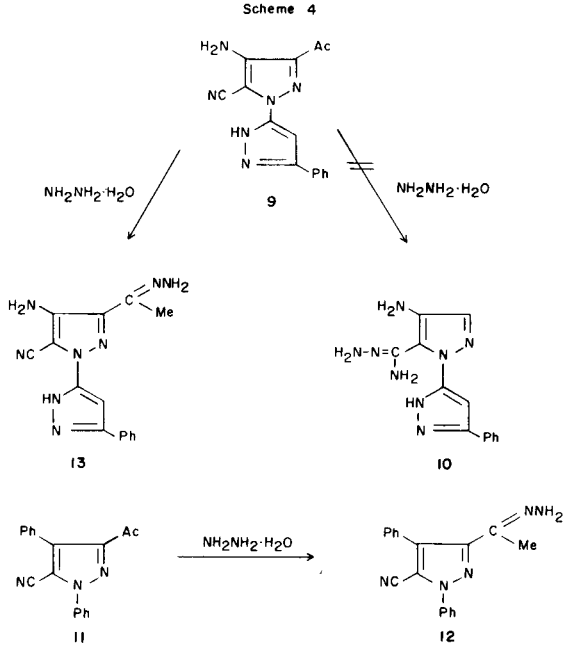
Compound No.	νCO (cm^{-1})	νCN (cm^{-1})	νNH (cm^{-1}) [b]
2a	1710	2230	3320, 3300, 3600
2b	1680	2220	3350, 3380, 3460
2d	1675	2220	3350, 3440
2e	1640	2225	3380
3c	1690	2220	3180, 3270, 3360, 3410
3d	1650	-	3180, 3300
3e	1630	2220	2350
5a	1710	-	3200 (w)
5b	1650	-	3200 (w)
5c	1660	-	3200 (w)
5d	1660	-	3200 (w)
6	1680	-	3300, 3350, 3420
6a	-	-	3150, 3280, 3360
7	1640, 1670	-	3180 (w)
7a	1660	-	3300 (w)
8	-	2220	3340, 3360, 3420
9	1660	2220	3180, 3270, 3360
11	1680	2225	-
12	-	2230	3300
13	-	2220	3200, 3300
14f	1720, 1700, 1690	2250	-
15f	1720, 1690	2220	3250
16j	1715, 1680	2250	3300 (w)
16k	1690, 1680	2250	3300 (w)
16ℓ	1710 sh, 1680	2250	3300 (w)
16m	1680, 1660	2250	3300 (w)
18	1675, 1690	-	3300 (w)
19a	1680	-	3180, 3400
19b	1680	-	3180, 3360
20	1635, 1680	-	3180, 3400

[a] In nujol. [b] Sh indicates a shoulder, w a weak band.

whereas its ir spectrum exhibited a carbonyl band at 1680 cm^{-1} and several NH bands in the 3200-3400 cm^{-1} region (Table III). These data also indicate that **6** exists in the oxo form as shown in the formula.

A similar treatment of **2e** with hydrazine hydrate yielded the corresponding substituted derivative or 2*H*-pyrazolo[3,4-*d*]pyridazine (**6a**). Hydrazinolysis of **3c** gave the hydrazone **8**. The structures of both **6a** and **8** can be deduced from their spectra and elemental analyses. For example, the ir spectrum of **6a** showed neither the carbonyl nor the nitrile bands; it contained the amino bands near 3150 and 3400 cm^{-1} (Table III). The pmr spectrum of **8** exhibited a three-proton singlet signal due to a methyl group. It is worth mentioning here that hydrazinolysis of **3c** did not result in the cleavage of the 3-acetyl group contrary to the behavior of **9** which was reported [32] to give **10** upon treatment with hydrazine hydrate. To shed more light on this problem, hydrazinolysis of 1,4-diphenyl-3-acetyl-5-cyanopyrazole **11**, prepared from **1c** and the sodium salt of phenacyl cyanide in ethanol, was examined. The reaction was found to give a product identified as **12**. The structure of the latter product follows from its pmr spectrum which showed signals at δ 2.5 (3H, s, Me), 6.00 (2H, broad, NH_2) and 7.3-7.8 (10H, m, ArH) ppm. The signal at 6.00 ppm disappears when the solution of **12** in deuterated chloroform is shaken with deuterium oxide. The ir spectrum of **12** revealed the presence of a nitrile band near 2230 cm^{-1} and the absence of a carbonyl band (Table III). These findings have prompted us to reinvestigate the hydrazinolysis of **9**. In our experiment, this reaction yielded a product whose elemental analysis and spectra indicate that its structure is **13** and not **10**, as evidenced by the presence of a nitrile band near 2220 cm^{-1} in its ir spectrum and a methyl proton singlet near 2.8 ppm in its pmr spectrum.

Scheme 4



Reaction of **6** and **6a** with dimethyl carbonate in dimethylformamide yielded the novel compounds **7** and **7a**, respectively. Both the results of elemental analyses and the spectral data are compatible with the assigned structures. Thus, the ir spectrum of **7a** revealed the presence of one carbonyl band near 1660 cm^{-1} and a weak NH band near 3300 cm^{-1}. Compound **7** exhibits two carbonyl bands at 1640 and 1670 cm^{-1} and an amide NH band near 3180 cm^{-1} (Table III). The formation of **7** through the sequence **1** → **2** → **6** → **7** represents a convenient route to this condensed fused tricyclic ring system.

The reaction of malononitrile with the hydrazidoyl chlorides **1f-1i** and **1j-1m** was examined as the next one in this synthetic study. The reaction products formed were found to depend on the order of addition of the reactants and the reaction conditions. Thus, addition of sodium ethoxide to a mixture of malononitrile and **1f** in ethanol followed by refluxing the reaction mixture yielded a colored product with an empirical formula $C_{27}H_{26}N_6O_8$. Bas-

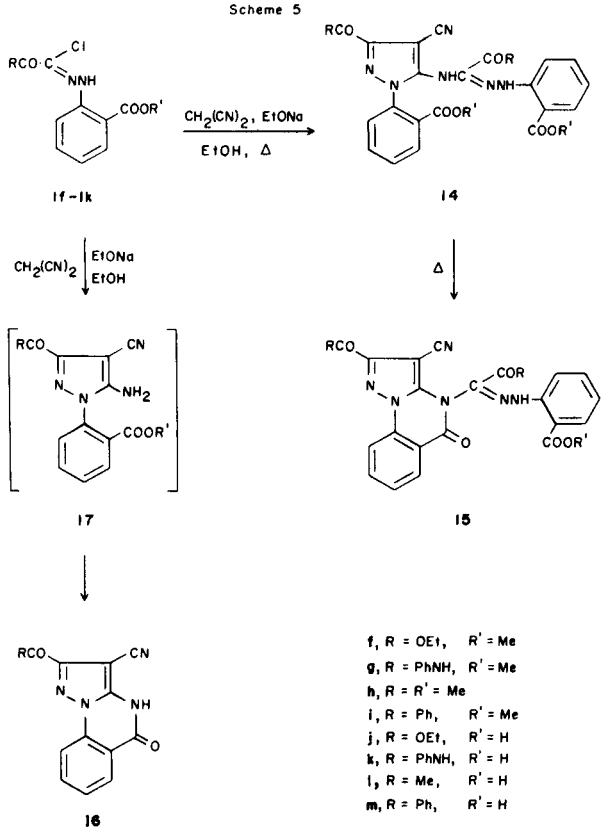
ed on its elemental analysis and the spectral data (see Experimental), it was assigned the pyrazole structure **14f**. When **14f** is heated in xylene, the pyrazolo[2,3-*a*]quinazolone derivative **15f** is obtained. The pmr spectrum of the latter showed two overlapping triplets (6H, 2 OMe), two overlapping quartets (4H, 2 OEt), a singlet at 4.2 (3H, OMe), and a multiplet at 7.0-9.0 (9H, ArH) ppm. Its ir spectrum exhibited a nitrile absorption near 2220 cm^{-1}, several overlapping carbonyl bands in the 1650-1700 cm^{-1} region, and weak NH band near 3250 cm^{-1} (Table III).

However, addition of the hydrazidoyl chloride **1f** to the sodium salt of malononitrile in ethanol and stirring of the mixture at room temperature yielded product identified as the pyrazolo[2,3-*a*]quinazolone derivative **16j**. The hydrazidoyl chlorides **1g-1i** reacted similarly and gave **16k-16m**, respectively. The products **16j-16m** were also obtained from **1j-1m** and malononitrile in the presence of sodium ethoxide. The structures assigned to **16k-16m** were compatible with their spectra. For example, the ir spectra of these products revealed the absence of bands due to amino and hydroxyl groups. The exhibited two characteristic carbonyl bands near 1680 and 1700 cm^{-1}, a weak amide NH band near 3300 cm^{-1}, and a nitrile band at 2250 cm^{-1} (Table III). The pmr spectra of all compounds **16j-16m** showed the absence of COOMe, NH_2 and COOH proton signals. The formation of **16j-16m** from either **1f-1i** or **1j-1m** and malononitrile further substantiates the formation of the 4-cyano-5-aminopyrazole derivative **17** as the intermediate. The latter undergoes spontaneous cyclization through the loss of water (in the case of **17**, R′ = H) or methanol (in the case of **17**, R′ = Me) to yield the final product **16**.

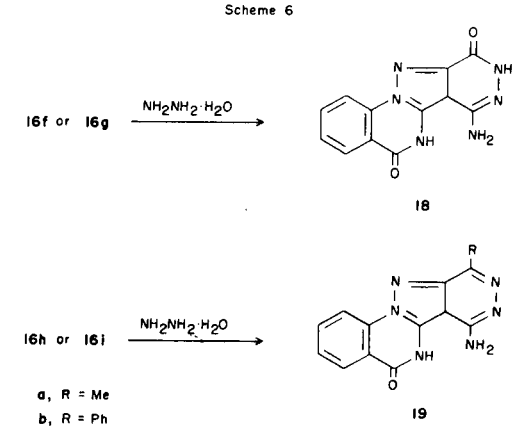
When **16j** was refluxed with hydrazine hydrate in ethanol, the 2*H*-pyrazolo[3,4-*d*]pyridazino[1,5-*a*]quinazolone **18** was obtained in 80% yield (Scheme 6). The latter product was also formed by hydrazinolysis of **16k**. The structure of **18** was elucidated on the basis of its formation, elemental analysis, and its spectral data. Thus, *e.g.*, its pmr spectrum showed the absence of the characteristic signals of the ethoxy protons while its ir spectrum possessed two carbonyl bands near 1675 and 1690 cm^{-1}, and a weak amide NH band near 3300 cm^{-1} (Table III). Also, these data provide supporting evidence for the oxo structure of **18** as shown in the formula.

A similar treatment of **16***l* and **16m** with hydrazine hydrate afforded the corresponding substituted derivatives **19a** and **19b**, respectively. Their structures have been assigned on the basis of their elemental analyses and the spectral data. The ir spectrum of **19a** contained a carbonyl band at about 1680 cm^{-1} and amino bands in the 3180-3400 cm^{-1} region (Table III).

Scheme 5



Scheme 6



EXPERIMENTAL

All melting points are uncorrected. The infrared (ir) spectra in nujol were recorded on a Perkin-Elmer model 710B spectrometer (Table III). The electronic absorption spectra were taken in ethanol on Perkin-Elmer model 552 and Cary 118 spectrophotometers. The pmr spectra were obtained with a Varian T60-A instrument in chloroform-*d* and trifluoroacetic acid using tetramethylsilane as the internal standard. Elemental analyses were performed by the microanalytical laboratory, Department of Chemistry, University of Cairo, Giza, Egypt, and MicAnal, Tucson, Arizona. The hydrazidoyl halides **1a-1m** were prepared as previously described [7, 25, 33-38].

Reaction of Hydrazidoyl Halides **1a-1e** with Malononitrile.

Malononitrile (0.33 g, 0.005 mole) was added with stirring to an ethanolic solution of sodium ethoxide obtained by dissolving sodium metal (0.11 g, 0.005 g-atom) in ethanol (20 ml). The appropriate hydrazidoyl halide (0.005 mole) was added to the resulting solution and

the stirring was continued for 3 hours at room temperature. The solid which precipitated was collected and crystallized from ethanol. The pyrazole derivatives **2a, 2b, 2d, 2e** and **3c, 3d,** and **3e** obtained and their physical constants are summarized in Table I.

Reaction of Hydrazidoyl Chlorides **1f-1m** with Malononitrile. Method A.

A mixture of **1f** (1.1 g, 0.005 mole) and malononitrile (0.33 g, 0.005 mole) in ethanol (30 ml) was heated. Ethanolic sodium ethoxide solution prepared from sodium metal (0.11 g, 0.005 g-atom) and ethanol (10 ml) was added dropwise to the resulting hot solution over a period of 10 minutes. The mixture was refluxed for one hour, filtered, and the filtrate was evaporated under reduced pressure. The oily residue solidified upon trituration with a small amount of methanol. The solid was collected. Crystallization from ethanol gave **14f** (70%), mp 164°; ir (nujol): 2250 (CN), 1720, 1700, 1690 cm^{-1} (ester CO), pmr: 1.3-1.7 (6H, two triplets), 3.8 (3H, s), 4.3-4.8 (4H, two quartets), 7.7-8.0 (9H, ArH), 9.3-10 ppm (2H, broad).

Anal. Calcd. for $C_{27}H_{26}N_6O_6$: C, 57.65; H, 4.66; N, 14.94. Found: C, 58.2; H, 4.1; N, 15.1.

Method B.

This is, in principle, similar to that described for the synthesis of **2a-2e**, except that the reaction mixture was stirred at room temperature for 24 hours. The solid that precipitated was collected and crystallized from dimethylformamide. The pyrazoloquinazoline derivatives **16j-16m** were obtained in 60-70% yields. The compounds prepared and their physical constants are listed in Table II.

When the reaction was repeated using **1j-1m** instead of **1f-1i**, the products obtained were identical in all respects (mp, mixed mp, and the spectra) with those obtained from **1f-1i**.

Table IV

The Electronic Absorption Spectral Data of Compounds under Study [a]

Compound No.	λ max, nm (log ε) [b]
2a	280 (3.20), 229 (3.74)
2b	266 (3.69), 2.19 (3.94)
2d	268 (3.78), 219 (3.96)
2e	254 (3.84), 220 (4.04)
3c	290 sh (3.44), 224 (4.28)
3d	252 (3.20)
3e	266 (3.57), 220 (3.76)
5a	308 (3.92), 274 (3.98)
5b	303 (3.60), 274 (3.65)
5c	302 (3.60), 275 (3.69)
5d	302 (3.60), 275 (3.69)
6	224 (4.39)
6a	226 (5.06)
7	238 (5.13)
7a	207 (4.69)
8	274 (3.83), 232 (5.09)
9	225 (5.06)
11	236 (3.73)
12	232 (3.77)
13	232 (3.65)
14f	333 (3.59), 262 (4.34), 225 (4.14)
15f	202 (4.25)
16j	267 (4.44)
16k	263 (4.31)
16ℓ	245 (3.84), 238 (4.30)
16m	276 (4.97)
18	231 (5.08)
19a	233 (5.05)
19b	233 (5.05)
20	274 (3.83), 232 (5.09)

[a] In ethanol. [b] Sh indicates a shoulder.

Preparation of **9**.

A similar treatment of 3-phenylpyrazol-5-yl hydrazidoyl chloride with malononitrile in the presence of sodium ethoxide afforded **9**, mp 200° (lit mp 200° [32]); ir (nujol): 1660 (CO), 2220 (CN), and 3180, 3270, and 3360 cm^{-1} (NH, NH_2).

Preparation of **11**.

To an ethanolic solution prepared by dissolving sodium metal (0.11 g, 0.005 g-atom) in ethanol (25 ml), ω-cyanoacetophenone (0.75 g, 0.005 mole) was added with stirring. Hydrazidoyl chloride **1c** (0.9 g, 0.005 mole) was added to the resulting solution and stirring was continued for 24 hours. The solid was collected and crystallized from ethanol to give **11** (75%), mp 163°; ir (nujol): 1680 (CO) and 2225 cm^{-1} (CN); pmr (deuteriochloroform): 2.8 (3H, s), 7.7-8.0 ppm (10H, ArH).

Anal. Calcd. for $C_{18}H_{13}N_3O$: C, 75.25; H. 4.56; N, 14.63. Found: C, 75.0; H, 4.5; N, 14.4.

Thermolysis of **14f**.

Compound **14f** (2.0 g, 0.003 mole) in xylene was refluxed for two hours. The solid that precipitated upon cooling of the mixture was collected. Its crystallization from ethanol gave **15f** in an almost quantitative yield, mp 197°C; ir (nujol): 2220 (CN), 1720 (ester CO), 1690 cm^{-1} (amide CO); pmr (deuteriochloroform): 1.2-1.8 (6H, two triplets), 4.2 (3H, s, Me), 4.3-4.7 (4H, two quartets), 7.2-8.3 ppm (9H, m, ArH).

Anal. Calcd. for $C_{26}H_{22}N_6O_7$: C, 58.86; H, 4.18; N, 15.84. Found: C, 58.7; H, 3.9; N, 15.7.

Hydrazinolysis of **2, 3c, 9, 11,** and **16j-16m.**

A mixture of the appropriate pyrazole derivative **2, 9, 11,** or **16j-16m** (0.005 mole) and hydrazine hydrate (10 ml) was refluxed for 4 hours and cooled. Upon dilution with water, the crude pyrazolo[3,4-*d*]pyridazine derivative precipitated. The solid was collected and crystallized from dimethylformamide. Hydrazinolysis of **2a** and **2b** gave an identical product identified as **6**, mp 298°.

Anal. Calcd. for $C_{11}H_{10}N_6O$: C, 54.54; H, 4.16; N, 34.69. Found: C, 54.3; H, 4.0; N, 34.9.

Compound **6a** had a mp 302°.

Anal. Calcd for $C_{18}H_{16}N_6$: C, 68.34; H. 5.10; N, 26.56. Found: C, 68.4; H, 4.9; N, 26.6.

A similar treatment of **9** with hydrazine hydrate gave the product **13**, mp 249°; ir (nujol): 2200 cm^{-1} (CN), 3200, 3300 cm^{-1} (NH_2); pmr (trifluoroacetic acid): 2.8 (3H, s, Me), 7.7-8.0 ppm (5H, ArH).

Anal. Calcd. for $C_{15}H_{14}N_8$: C, 58.81; H. 4.61; N, 36.58. Found: C, 58.5; H, 4.4; N, 36.8.

The same procedure in the case of the reaction of **11** with hydrazine hydrate afforded compound **12** in a 60% yield, mp 155°; ir (nujol): 2230 (CN), 3300 cm^{-1} (NH), no CO bands; pmr (deteuriochloroform): 2.5 (3H, s, Me), 6.0 (2H, broad, NH_2), 7.3-7.5 ppm (10H, m, ArH).

Anal. Calcd. for $C_{18}H_{15}N_5$: C, 71.74; H, 5.02; N, 23.24. Found: C, 71.9; H, 5.1; H, 22.8.

A similar treatment of **16j** with hydrazine hydrate gave the product **18**. Hydrazinolysis of both **16j** and **16k** yielded an identical product identified as **18**, mp > 360°.

Anal. Calcd. for $C_{12}H_8N_6O_2$: C, 53.73; H, 3.00; N, 31.33. Found: C, 53.7; H, 2.9; N, 31.6.

Compound **19a** had mp > 360°.

Anal. Calcd. for $C_{13}H_{10}N_6O$: C, 58.64; H, 3.78; N, 31.56. Found: C, 58.4; H, 3.8; N, 31.2.

Compound **19b** had a mp 295°.

Anal. Calcd. for $C_{18}H_{12}N_6O$: C, 65.84; H, 3.68; N, 25.59. Found: C, 65.4; H, 3.8; N, 25.9.

When **3c** was treated with hydrazine hydrate, it afforded **8** in quantitative yield, mp 254°; ir (nujol): 1630 (conjugated C=C), 2220 (CN), and 3340, 3360, and 3420 cm^{-1} (NH, NH_2).

Anal. Calcd. for $C_{12}H_{12}N_6$: C, 59.99; H, 5.03; N, 34.98. Found: C, 60.1; H, 5.3; N, 34.8.

Reaction of **6** with Dimethyl Carbonate.

A mixture of **6** (0.2 g, 0.0008 mole) and dimethyl carbonate (5 ml, 0.05 mole) in dimethylformamide (30 ml) was refluxed for 24 hours. The reaction mixture was then distilled off under reduced pressure and the residue was triturated with water. The solid formed was collected. Its crystallization from dimethylformamide gave **7**, mp 322°.

Anal. Calcd. for $C_{12}H_8N_6O_2$: C, 53.73; H, 3.01; N, 31.11. Found: C, 53.6; H, 2.7; N, 31.3.

Compound **7a** was prepared similarly from **6a** and hydrazine hydrate and had a mp of 325°.

Anal. Calcd. for $C_{19}H_{14}N_6O$: C, 66.66; H, 4.12; N, 24.55. Found: C, 66.9; H, 4.4; N, 23.9.

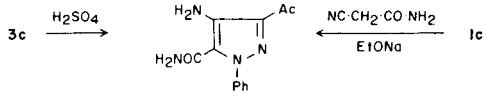
Preparation of Fused Pyrimidinedithiones **5**.

To a solution of **2** (0.005 mole) in dimethylformamide (30 ml), carbon disulfide (10 ml) and sodium methoxide (0.5 g, 0.009 mole) were added and the mixture was refluxed for 45 hours. The mixture was then evaporated under reduced pressure and a solution of sodium hydroxide (1 *M*, 30 ml) was added to the residue. The resulting solution was filtered. Acidification of the filtrate with diluted hydrochloric acid gave the corresponding pyrimidinedithione derivative as a yellow solid. It was collected and crystallized from ethanol. Table II lists the compounds **5a-5d** prepared together with their physical constants.

Hydrolysis of **3c**.

A solution of **3c** (0.3 g, 0.013 mole) in concentrated sulfuric acid (4 ml) was stirred at room temperature for 2 days. The reaction mixture was poured onto ice with water and the precipitated yellowish crystals were collected and recrystallized from ethanol to give the amide **20** (75% yield), mp 212°, ir (nujol): 1635, 1680 (CO), 3180-3400 (NH_2) cm^{-1} (Scheme 7).

Scheme 7



20

Anal. Calcd. for $C_{12}H_{12}N_4O_2$: C, 59.01; H, 4.95; N, 22.94. Found: C, 58.7; H, 4.9; N, 22.9.

The latter product was also formed by the reaction of **1c** and cyanoacetamide in the presence of sodium ethoxide at room temperature (Scheme 7).

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