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The Reactions of 4-Substituted-7-aminothieno-[3,4-d]pyridazines and 2-Methyl-6-aminothienopyridine-5-thione with Electron-Poor Olefins and Acetylenes

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ABSTRACT

Cycloadditions of thienopyridazines and a thienopyridine with electron-poor olefins and acetylenes as dienophiles are described. The nonisolable adducts undergo subsequent loss of hydrogen sulfide to give substituted phthalazines and substituted isoquinolines, respectively. © 1997 John Wiley & Sons, Inc.

DISCUSSION

Benzoazines are very interesting as potential agrochemicals [1–3] and as pharmaceuticals [4–8]. Some of our studies have been aimed at developing simple and efficient syntheses of polyfunctional heteroaromatics from readily obtainable starting materials [9–11]. The established syntheses of benzoazines utilizing suitably substituted benzene derivatives cannot be employed industrially, as they require very expensive substituted benzene derivatives as starting materials. Recently, however, we have reported [12] that thienoazines **1** and **16** react readily with acrylonitrile, ethyl acrylate, and maleic anhydride to yield benzoazines via 4 + 2 cycloadditions and subsequent hydrogen sulfide elimination. We then became interested to investigate whether this synthetic approach can be extended as a new general route to benzoazines. In the present article, we report results of our investigations in this area. Thus, it has been found that **1a–c** react with phenyl vinyl ketone, generated in situ by heating of the hydrochloride **2** in DMF, to yield the product of a cycloaddition with subsequent hydrogen sulfide elimination. These were characterized as **4a–c** rather than **3** based on ^{1}H NMR spectroscopy, which revealed H-7 and H-8 as two doublets with J = 9 Hz. The reaction of **4** is assumed to proceed via cycloadduct **5**, which cannot be isolated. Compounds **I** were prepared by reactions of compound **6** with elemental sulfur in dioxane solution in the presence of piperidine.

Dedicated to Professor Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

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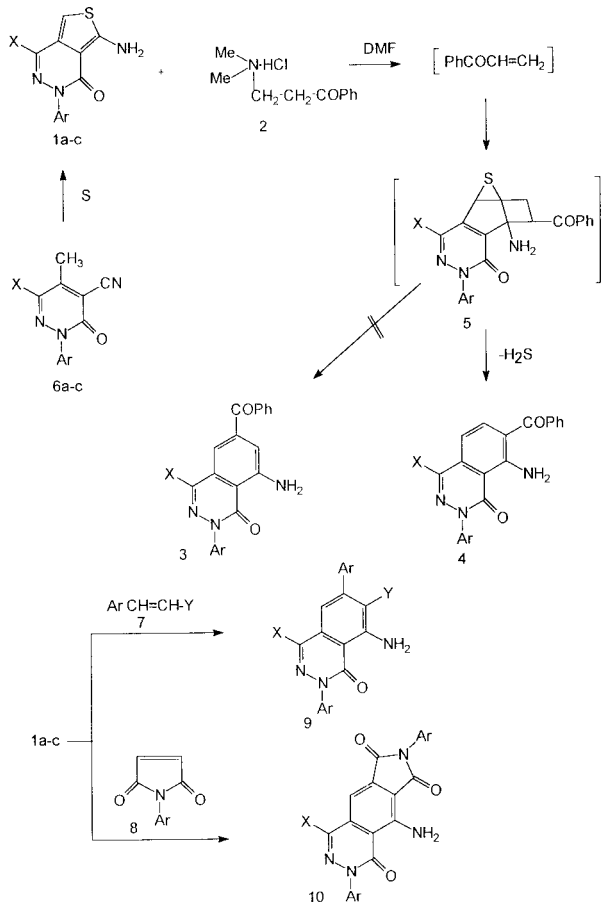
Similar to the behavior of **1a–c** toward phenyl vinyl ketone, compounds **1a–c** reacted with chalcones **7a–c** and *β*-nitrostyrenes **7d–h** to yield the corresponding phthalazines **9a–h**. Compounds **1a–c** also reacted with *p*-anisylmaleimide **8** to yield the pyrrolophthalazines **10a–c**. Attempts to prepare **9a–h** by reactions of **6a–c** with **7a–h** failed (Scheme 1).

Analogous to the foregoing findings, compounds **1a–c** reacted with di-*t*-butyl acetylenedicarboxylate **11** to yield the 1:1 adducts **14**. Compound **14** was confirmed by IR and ^{1}H NMR spectral data and by mass spectra. Compound **14** is assumed to have been formed via intermediate **13** by loss of H_2S. Compounds **1a–c** also reacted with tetracyanoethylene to yield 1:1 adducts **15a–c** (Scheme 2).

Similar to the previously mentioned reactions between **1a–c** and dienophiles, the thienopyridinethione **16** reacted with *β*-nitrostyrene, di-*t*-butyl acetylenedicarboxylate and with tetracyanoethylene to give the compounds **17**, **18**, and **19**, respectively (Scheme 3).



SCHEME 1

EXPERIMENTAL

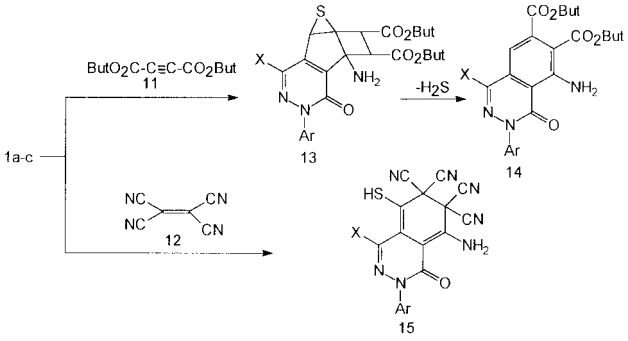
All melting points are uncorrected. The IR spectra were obtained as KBr pellets on a PERKIN ELMER 1430 spectrophotometer. ^{1}H NMR spectra were measured in dimethyl sulfoxide (DMSO) using tetramethylsilane (TMS) as an internal standard on a Varian EM 360 spectrophotometer. Microanalyses were performed by the Microanalytical Unit at Cairo University.

1-Acetyl-5-amino-3,4-dihydro-4-oxo-3-phenylthieno[3,4-d]pyridazine (**1c**).

Equimolar amounts of **6c** (2.5 g, 0.01 mole) and elemental sulfur (0.32 g, 0.01 mole) in dioxane (50 mL) were treated with a few drops of piperidine. The reaction mixture was refluxed for 2 hours. A solid product was collected by filtration and recrystallized from dioxane to afford green crystals; yield 1.5 g (71%); mp 260°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1700 cm^{-1} (CO); 1650 cm^{-1} (CO); ^{1}H NMR (DMSO-d_6): δ = 3.2 (s, 3H, CH_3); 7.0–7.8 (m, 8H, aromatic protons, thiophene H, and NH_2). Found: C, 59.2; H, 4.1; N, 15.0; S, 11.4; calcd for $C_{14}H_{11}N_3O_2S$: C, 58.94; H, 3.89; N, 14.73; S, 11.2%.

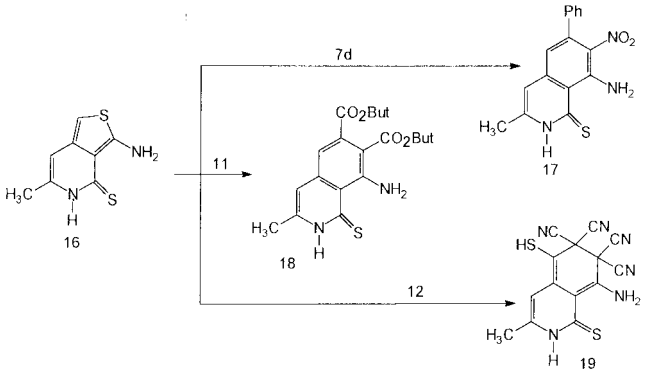
Reactions of (**1a–c**) *with Mannich Compound* **2***: General Procedure*

Compounds **Ia–c** (0.01 mole) and the Mannich compound **2** (0.01 mole) in 20 mL of dimethylformamide (DMF) containing a few drops of acetic acid as cat-



1-15	X	Y	Ar	Ar^1
a	CO_2Et	COPh	p-Tolyl	p-Anisyl
b	$CSNH_2$	COPh	Ph	p-Anisyl
c	$COCH_3$	COPh	Ph	p-Anisyl
d	CO_2Et	NO_2	p-Tolyl	Ph
e	CO_2Et	NO_2	p-Tolyl	p-Anisyl
f	$CSNH_2$	NO_2	Ph	p-Anisyl
g	$COCH_3$	NO_2	Ph	Ph
h	$COCH_3$	NO_2	Ph	P-Anisyl

SCHEME 2



SCHEME 3

alyst were refluxed for 2 hours and poured into ice water. The solid product formed in each case was collected by filtration and recrystallized from the proper solvent.

Ethyl 5-Amino-6-benzoyl-3,4-dihydro-4-oxo-3-p-tolylphthalazine-1-carboxylate (**4a**)

Gray crystals from ethanol; yield 1.4 g (61%); mp 142°C; IR (KBr) 3441–3385 cm^{-1} (NH_2); 1727 cm^{-1} (ester CO); 1662 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 1.23 (t, 3H, CH_3, J = 7 Hz); 2.21 (s, 3H, CH_3); 4.22 (q, 2H, CH_2, J = 7 Hz); 7.0–7.5 (m, 11H, aromatic protons, and NH_2); 8.0 (d, 1H, H-7, J = 9 Hz); 8.2 (d, 1H, H-8, J = 9 Hz); MS: m/z = 427. Found: C, 70.1; H, 4.8; N, 9.6; calcd for $C_{25}H_{21}N_3O_4$: C, 70.25; H, 4.95; N, 9.83%.

5-Amino-6-benzoyl-3,4-dihydro-4-oxo-3-phenylphthalazine-1-thiocarboxamide (**4b**)

Brown crystals from ethanol/dioxane; yield 1.1 g (71%); mp 173°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1660 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 3.5 (br, 2H, NH_2); 7.0–7.7 (m, 12H, aromatic protons, and NH_2); 7.9 (d, 1H, H-7, J = 9 Hz); 8.1 (d, 1H, H-8, J = 9 Hz); MS: m/z = 400. Found: C, 65.9; H, 3.9; N, 13.8; S, 8.2; calcd for $C_{22}H_{16}N_4O_2S$: C, 65.99; H, 4.03; N, 13.99; S, 8.01%.

1-Acetyl-5-amino-6-benzoyl-3,4-dihydro-4-oxo-3-phenylphthalazine (**4c**)

Brown crystals from ethanol/DMF; yield 1.8 g (85%); mp > 300°C; IR (KBr) 3425–3305 cm^{-1} (NH_2); 1725 cm^{-1} (CO); 1662 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 3.2 (s, 3H, CH_3); 6.8–7.4 (m, 12H, aromatic protons, and NH_2); 7.8 (d, 1H, H-7, J = 9 Hz); 8.1 (d, 1H, H-8, J = 9 Hz); MS: m/z = 383. Found: C, 72.3; H, 4.8; N, 11.0; calcd for $C_{23}H_{17}N_3O_3$: C, 72.05; H, 4.47; N, 10.96%.

Reactions of (**Ia–c**) *with Olefins: General Procedure*

Equimolecular amounts of **Ia–c** (0.01 mole), **7a–h**, and **8** (0.01 mole) in 20 mL of dioxane and containing a few drops of acetic acid were heated under reflux for 2 hours, then poured into ice water. The solid product formed in each case was collected by filtration and recrystallized from the proper solvent.

Ethyl 5-Amino-7-p-anisyl-6-benzoyl-3,4-dihydro-4-oxo-3-p-tolylphthalazine-1-carboxylate (**9a**)

Green crystals from ethanol; yield 0.9 g (70%); mp 180°C; IR (KBr) 3456–3330 cm^{-1} (NH_2); 1731 cm^{-1} (ester CO); 1650 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 1.34 (t, 3H, CH_3, J = 7 Hz); 3.1 (s, 3H, CH_3); 3.5 (s, 3H, OCH_3); 4.22 (q, 2H, CH_2, J = 7 Hz); 7.0–7.7 (m, 15H, aromatic protons, and NH_2); MS: m/z = 533. Found: C, 72.0; H, 5.0; N, 7.7; calcd for $C_{32}H_{27}N_3O_5$: C, 72.03; H, 5.10; N, 7.88%.

5-Amino-7-p-anisyl-6-benzoyl-3,4-dihydro-4-oxo-3-phenylphthalazine-1-thiocarboxamide (**9b**)

Brown crystals from ethanol/dioxane; yield 2 g (74%); mp > 300°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1650 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 3.5 (s, 3H, OCH_3); 4.22 (br, 2H, NH_2); 6.9–7.8 (m, 17H, aromatic protons, and NH_2); MS: m/z) = 506. Found: C, 68.6; H, 4.2; N, 11.0; S, 6.2; calcd for $C_{29}H_{22}N_4O_3S$: C, 68.76; H, 4.38; N, 11.06; S, 6.33%.

1-Acetyl-5-amino-7-p-anisyl-6-benzoyl-3,4-dihydro-4-oxo-3-phenylphthalazine (**9c**)

Brown crystals from ethanol; yield 1.5 g (67%); mp 170°C; IR (KBr) 3400–3300 cm^{-1} (NH2); 1710 cm^{-1} (CO); 1650 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 3.0 (s, 3H, CH_3); 6.9–7.5 (m, 17H, aromatic protons and NH_2); MS: m/z = 489. Found: C, 73.8; H, 4.9; N, 8.4; calcd for $C_{30}H_{23}N_3O_4$: C, 73.61; H, 4.74; N, 8.58%.

Ethyl 5-amino-3,4-dihydro-6-nitro-4-oxo-7-phenyl-3-p-tolylphthalazine-1-carboxylate (**9d**)

Gray crystals from ethanol; yield 1.9 g (81%); mp 200°C; IR (KBr) 3420–3350 cm^{-1} (NH_2); 1710 cm^{-1} (CO); 1650 cm^{-1} (ring CO); ^1H NMR (DMSO-d_6): δ = 1.23 (t, 3H, CH_3, J = 7 Hz); 2.21 (s, 3H, CH_3); 4.22 (q, 2H, CH_2, J = 7 Hz); 7.0–7.8 (m, 12H, aromatic

protons, and NH_2); MS: m/z = 444. Found: C, 64.6; H, 4.4; N, 12.5; calcd for $C_{24}H_{20}N_4O_5$: C, 64.86; H, 4.54; N, 12.61%.

Ethyl 5-Amino-7-p-anisyl-3,4-dihydro-6-nitro-4-oxo-3-p-tolylphthalazine-1-carboxylate (**9e**)

Yellow crystals from ethanol; yield 1.8 g (80%); mp 70°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1720 cm^{-1} (ester CO); 1655 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ = 1.4 (t, 3H, CH_3, J = 7 Hz); 3.1 (s, 3H, CH_3); 3.5 (s, 3H, OCH_3); 4.3 (q, 2H, CH_2, J = 7 Hz); 7.2–7.7 (m, 11H, aromatic protons, and NH_2). Found: C, 63.1; H, 4.4; N, 11.6; calcd for $C_{25}H_{22}N_4O_6$: C, 63.29; H, 4.67; N, 11.81%.

5-Amino-7-p-anisyl-3,4-dihydro-6-nitro-4-oxo-3-phenylphthalazine-1-thiocarboxamide (**9f**)

Brown crystals from ethanol/dioxane; yield 1.1 g (64%); mp > 300°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1650 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 2.9 (s, 2H, NH_2); 3.1 (s, 3H, OCH_3); 7.0–7.7 (m, 11H, aromatic protons, and NH_2); 7.9 (s, 1H, H-8). Found: C, 59.0; H, 3.6; N, 15.6; S, 7.0; calcd for $C_{22}H_{17}N_5O_4S$: C, 59.05; H, 3.82; N, 15.65; S, 7.16%.

1-Acetyl-5-amino-3,4-dihydro-3,7-diphenyl-6-nitro-4-oxophthalazine (**9g**)

Gray crystals from ethanol/DMF; yield 1.6 g (74%); mp 210°C; IR (KBr) 3410–3300 cm^{-1} (NH_2); 1690 cm^{-1} (CO); 1660 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 3.1 (s, 3H, CH_3); 6.9–7.4 (m, 12H, aromatic protons, and NH_2); 8.0 (s, 1H, H-8); MS: m/z = 400. Found: C, 65.8; H, 4.0; N, 1.3; calcd for $C_{22}H_{16}N_4O_4$: C, 66.00; H, 4.03; N, 13.99%.

1-Acetyl-5-amino-7-p-anisyl-3,4-dihydro-6-nitro-4-oxo-3-phenylphthalazine (**9h**)

Brown crystals from ethanol; yield 1.7 g (69%); mp > 300°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1725 cm^{-1} (CO); 1662 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 2.9 (s, 3H, CH_3); 3.5 (s, 3H, OCH_3); 7.0–7.4 (m, 11H, aromatic protons, and NH_2); 8.2 (s, 1H, H-8); MS: m/z = 430. Found: C, 63.9; H, 4.3; N, 12.8; calcd for $C_{23}H_{18}N_4O_5$: C, 64.18; H, 4.22; N, 13.02%.

Ethyl 5-amino -7-p-anisyl-3,4-dihydro-4,6,8-trioxo-3-p-tolylpyrrolo [3,4-f]phthalazine-1-carboxylate (**10a**)

Red crystals from dioxane; yield 0.8 g (48%); mp > 300°C; IR (KBr) 3465–3451 cm^{-1} (NH_2); 1728 cm^{-1} (ester CO); 1680 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 1.34 (t, 3H, CH_3, J = 7 Hz); 3.1 (s, 3H, CH_3); 3.5 (s, 3H, OCH_3); 4.3 (q, 2H, CH_2, J = 7 Hz); 7.0–7.6 (m, 11H, aromatic protons, and NH_2); MS: m/z = 498. Found: C, 65.0; H, 4.3; N, 11.1; calcd for $C_{27}H_{22}N_4O_6$: C, 65.06; H, 4.45; N, 11.24%.

5-Amino-7-p-anisyl-3,4-dihydro-4,6,8-trioxo-3-phenylpyrrolo[3,4-f]phthalazine-1-thiocarboxamide (**10b**)

Brown crystals from dioxane; yield 1.0 g (61%); mp 240°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1650 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 2.8 (s, 2H, NH_2); 3.5 (s, 3H, OCH_3); 6.9–7.5 (m, 12H, aromatic protons, and NH_2); MS: m/z = 471. Found: C, 61.3; H, 3.6; N, 15.1; S, 6.0; calcd for $C_{24}H_{17}N_5O_4S$: C, 61.14; H, 3.63; N, 14.85; S, 6.80.

1-Acetyl-5-amino-7-p-anisyl-3,4-dihydro-4,6,8-trioxo-3-phenylpyrrolo[3,4-f]phthalazine (**10c**)

Brown crystals from dioxane; yield 0.9 g (58%); mp 270°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1730 cm^{-1} (CO); 1655 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 1.7 (br, 2H, NH_2); 2.8 (s, 3H, CH_3); 3.9 (s, 3H, OCH_3); 7.2–7.8 (m, 10H, aromatic protons). Found: C, 66.3; H, 4.1; N, 12.6; calcd for $C_{25}H_{18}N_4O_5$: C, 66.08; H, 3.99; N, 12.33%.

Reactions of **1a,b** *with di-t-butyl Acetylenedicarboxylate: General Procedure*

Equimolecular amounts of **1a,b** (0.01 mole) and di-*t*-butyl acetylenedicarboxylate (0.01 mole) in 20 mL of dioxane containing several drops of acetic acid were refluxed for 20 minutes and poured into ice water. The solid product formed in each case was recrystallized from the proper solvent.

Ethyl 5-amino-3,4-dihydro-6,7-di-t-butyl-4-oxo-3-p-tolylphthalazine-1,6,7-tricarboxylate (**14a**)

Orange crystals from ethanol; yield 1.2 g (60%); mp 135°C; IR (KBr) 3400–3300 cm^{-1} (NH**2**); cm^{-1} (CO); 1655 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ = 1.2 (t, 3H, CH_3, J = 7 Hz); 2.2 (s, 3H, CH_3); 3.3 (m, 18H, $6CH_3$); 4.3 (q, 2H, CH_2, J = 7 Hz); 7.0–7.6 (m, 7H, aromatic protons, and NH_2); MS: m/z = 523. Found: C, 64.2; H, 6.3; N, 8.0; calcd for $C_{28}H_{33}N_3O_7$: C, 64.23; H, 6.35; N, 8.03%.

Di-t-butyl 5-amino-3,4-dihydro-4-oxo-3-phenyl-1-thiocarboxamidophthalazine-6,7-dicarboxylate (**14b**)

Gray crystals from ethanol/DMF; yield 1.0 g (62%); mp 300°C; IR (KBr) 3410–3310 cm^{-1} (NH_2); 1730

cm^{-1} (CO); 1650 cm^{-1} (CO); 1590 cm^{-1} (CS); ^1H NMR (DMSO-d_6): δ = 3.3 (m, 18H, $6CH_3$); 4.5 (br, 2H, NH_2); 7.0–7.5 (m, 8H, aromatic protons, and NH_2); MS = 496. Found: C, 60.6; H, 5.6; N, 11.5; S, 6.2; calcd for $C_{25}H_{28}N_4O_5S$: C, 60.47; H, 6.08; N, 11.28; S, 6.46%.

Reactions of (**Ia–c**) *with Tetracyanoethylene: General Procedure*

Equimolecular amounts of **Ia–c** (0.01 mole) and tetracyanoethylene (0.01 mol) in 20 mL dioxane containing several drops of acetic acid were stirred overnight. The solid product formed in each case was recrystallized from the proper solvent.

Ethyl 5-amino-3,4-dihydro-4-oxo-6,6,7,7-tetracyano-3-p-tolyl-8-thioxophthalazine-l-carboxylate (**15a**)

Violet crystals from ethanol; yield 1.7 g (76%); mp > 300°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 2220 cm^{-1} (CN); 1720 cm^{-1} (CO); ^1H NMR: δ = 1.2 (t, 3H, CH_3, J = 7 Hz); 2.2 (br, 2H, NH_2); 3.2 (s, 3H, CH_3); 4.2 (q, 2H, CH_2, J = 7 Hz); 5.2 (s, 1H, SH); 6.8–7.5 (m, 4H, aromatic protons); MS: m/z = 457. Found: C, 57.5; H, 3.2; N, 21.4; S, 6.9; calcd for $C_{22}H_{15}N_7O_3S$: C, 57.76; H, 3.30; N, 21.43; S, 7.0%.

5-Amino-3,4-dihydro-4-oxo-3-phenyl-6,6,7,7-tetracyano-8-thioxophthalazine-1-thiocarboxamide (**15b**)

Deep violet crystals from ethanol/dioxane; yield 1.4 g (77%); mp > 330°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1720 cm^{-1} (CO); 2220 cm^{-1} (CN); ^1H NMR (DMSO-d_6): δ = 5.2 (s, 1H, SH); 7.0–7.6 (m, 9H, aromatic protons, and $2NH_2$); MS: m/z = 430. Found: C, 53.1; H, 2.1; N, 26.0; S, 14.9; calcd for $C_{19}H_{10}N_8O_2S$: C, 53.01; H, 2.34; N, 26.30; S, 14.90%.

1-Acetyl-5-amino-3,4-dihydro-4-oxo-3-phenyl-6,6,7,7-tetracyano-8-thioxophthalazine (**15c**)

Deep violet crystals from ethanol, yield 1.3 g (70%); mp > 300°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 2220 cm^{-1} (CN); 1720 cm^{-1} (CO); ^1H NMR (DMSO-d_6): δ = 3.1 (s, 3H, CH_3); 5.3 (s, 1H, SH); 7.2–7.6 (m, 7H, aromatic protons, and NH_2); MS: m/z = 413. Found: C, 58.0; H, 2.5; N, 23.2; S, 7.6; calcd for $C_{20}H_{11}N_7O_2S$: C, 58.11; H, 2.8; N, 23.72; S, 7.75%.

Reactions of **16** *with Electron Deficient Olefines: General Procedure*

Equimolecular amounts of compound **16**, di-*t*-butyl acetylenedicarboxylate or tetracyanoethylene (0.01 mole) in dioxane (30 mL) and acetic acid (5 mL) were refluxed for 3 hours and then poured into ice water. The solid product in each case was recrystallized from the proper solvent.

4-Amino-1-methyl-5-nitro-6-phenyl-2,3-dihydro-3-thioxoisoquinoline (**17**)

Orange crystals from dioxane; yield 0.6 g (71%); mp 210°C; IR (KBr) 3400–3300 cm^{-1} (NH_2); 1580 cm^{-1} (CS); ^1H NMR (DMSO-d_6): δ = 3.2 (s, 3H, CH_3); 6.8–7.5 (m, 9H, aromatic protons, and NH_2); 8.1 (s, 1H, NH); MS: m/z = 311. Found: C, 61.5; H, 4.0; N, 13.4; calcd for $C_{16}H_{13}N_3O_2S$: C, 61.72; H, 4.21; N, 13.50; S, 10.30%.

Di-t-butyl 4-amino-1-methyl-2,3-dihydro-3-thioxoisoquinoline-5,6-dicarboxylate (**18**)

Orange crystals from dioxane; yield 0.7 g (74%); mp > 300°C; IR (KBr) 3430–3350 cm^{-1} (NH_2); 1720 cm^{-1} (CO); 1590 cm^{-1} (CS); ^1H NMR (DMSO-d_6): δ = 3.1–3.4 (m, 21H, $7CH_3$); 6.9–7.3 (m, 4H, aromatic protons, and NH_2); 8.3 (s, 1H, NH); MS: m/z = 390. Found: C, 61.5; H, 6.6; N, 7.0; S, 8.3; calcd for $C_{20}H_{26}N_2O_4S$: C, 61.52; H, 6.71; N, 7.17; S, 8.21%.

4-Amino-1-methyl-2,3-dihydro-3,7-dithioxoisoquinoline-5,5,6,6-tetracarbonitrile (**19**)

Gray crystals from dioxane; yield 0.5 g (59%); mp > 300°C; IR (KBr) 3450–3300 cm^{-1} (NH_2); 2220 cm^{-1} (CN); 1590 cm^{-1} (CS); ^1H NMR (DMSO-d_6): δ = 1.9 (s, 3H, CH_3); 5.2 (s, 1H, SH); 7.1–7.4 (m, 3H, aromatic protons, and NH_2); 8.5 (s, 1H, NH); MS: m/z = 323. Found: C, 51.8; H, 2.0; N, 25.8; S, 19.7; calcd for $C_{14}H_7N_6O_2S$: C, 52.00; H, 2.18; N, 25.99; S, 19.83%.

REFERENCES

[1] S. C. Benson, J. L. Gross, J. K. Synder, *J. Org. Chem., 55,* 1990, 3275.

[2] A. Thomas, M. Chakraborty, H. Ila, H. Junjappa, *Tetrahedron, 46,* 1990, 577.

[3] J. Wolff, M. Taddei, *Tetrahedron, 42,* 1986, 4267.

[4] T. Yamasaki, E. Kawaminami, F. Uchimura, Y. Okamoto, M. Furukawa, *J. Heterocycl. Chem., 29,* 1992, 825.

[5] K. Kaji, H. Nagashima, S. Nagao, K. Tabashi, H. Oda, *Chem. Pharm. Bull., 30,* 1980, 1030.

[6] T. Yamasaki, Y. Yoshihara, Y. Okamoto, T. Okawara, M. Furukawa, *J. Heterocycl. Chem., 29,* 1992, 1313.

[7] S. Chen, R. P. Panzica, *J. Org. Chem., 46,* 1981, 2467.

[8] P. Singh, S. P. Gupta, *Indian J. Med. Res., 69,* 1979, 804.

[9] M. H. Elnagdi, A. M. Negm, A. W. Erian, *Liebigs Ann. Chem.,* 1989, 1255.
[10] M. H. Elnagdi, A. W. Erian, *Liebigs Ann. Chem.,* 1990, 1215.
[11] M. H. Elnagdi, F. M. Abd EL Razek, N. S. Ibrahim, A. W. Erian, *Tetrahedron,* 1989, 53597.
[12] A. H. H. Elghandour, A. M. Hussein, M. H. Elnagdi, A. A. Harb, S. A. Metwally, *J. Pract. Chem., 334,* 1992, 723.