SOME HETEROCYCLES FROM DEHYDRO-L-ASCORBIC ACID

Sohila H. Mancy, Kamal F. Atta, and Mohamed A. El Sekily*

Chemistry Department, Faculty of Science
El Horria Street, Alexandria University
Alexandria, Egypt.

الخلاصة :

عند معالجة ٣ - فورميل - ١ - فينيل - ٤، ٥ - بيرازوليدين ٤ - فينيل هيدرازون (٢) بالهيدروكسيل أمين ، نتج الـ ٣ - فورميل أوكسيم (٣) ، والذي عند أستلته بأندريد حمض الخليك أنتج مشتق الأسيتوكسيم (٤) ، وإضافة إلى البنزويل أوكسيم (٥) . ومن جهه أخرى ، فإنَّ معالجة مركب (٢) بكلوريد البنزويل والبيريدين لمدة طويلة أنتج مشتق ثنائي الحلقة (٦) . أما مركب ٣ - فورميل ثيوسمي كاربازون (٥) فقد أنتج مشتق البيرازول ثياديازولين (٧) و (٨) عند معالجته بأندريد حمض الخليك أو بكلوريد البنزويل في البيريدين .

تحلل مركب (٧) بالهيدرازين نتج مشتق الأمين الذي بدورة أنتج مشتق البيرازول ثياديازول (١٠) عند الأكسدة .

ABSTRACT

Treatment of 3-formyl-1-phenyl-4,5-pyrazolinedione 4-phenylhydrazone (**2**) with hydroxylamine, gave the 3-formyloxime (**3**), which upon acetylation with acetic anhydride, gave the acetoxime derivative (**4**). Also it gave the benzoyloxime (**5**). On the other hand, treatment of (**2**) with benzoylchloride and pyridine for long time gave the bicyclic (**6**). The 3-formylthiosemicarbazone (**5**) afforded the pyrazole thiadiazoline derivative (**7**) and (**8**) upon treatment with acetic anhydride or with benzoylchloride in pyridine. Hydrolysis of (**7**) with hydrazine hydrate afforded the amine derivative that gave the pyrazole thiadiazole derivative (**10**) upon oxidation.

* To whom correspondence should be addressed.

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INTRODUCTION

Dehydro-L-ascorbic acid (L-*threo*-2,3-hexodiulosono-1,4- lactone) obtained by mild oxidation of L-ascorbic acid is considered an excellent precursor for the synthesis of many nitrogen heterocycles [1–6] through its reaction with hydrazines or diamines. It is known that some of the 4,5-pyrazolinediones and their derivatives were evaluated [7–10] as potential drugs for central nervous system, and also as antidiabetic, antidiuretic, antiviral, and anticancer agents. In this respect, we have tried to prepare some pyrazolinediones connected to heterocycles containing sulfur, in the quest for new chemotherapeutic compounds, especially as potential carcinostatic or antiviral agents.

Thus, treatment of 1-phenyl-3-(L-*threo*-glycerol-1-yl)-4,5- pyrazolinedione 4-(phenylhydrazone) [11] (**1**) with sodium metaperiodate, afforded 3-formyl-1-phenyl-4,5-pyrazolinedione 4- (phenylhydrazone) [11] (**2**), that gave the 3-oxime derivative (**3**) upon treatment with hydroxylamine. Its IR spectrum showed a hydroxyl band at 3450 cm^{-1}, in addition to an amide band at 1660 cm^{-1}. Acetylation of compound (**3**) with boiling acetic anhydride or with acetic anhydride and pyridine, gave 3-formyl-1-phenyl- 4,5-pyrazolinedione 4-(phenylhydrazone) 3-acetoxime (**4**) whose IR spectrum showed an ester band at 1783 cm^{-1} in addition to an amide band at 1700 cm^{-1}. ^1H NMR showed one acetyl group signal at δ 2.27 and the phenyl protons at δ 7.22–8.07. Also a signal for one proton C_3-CH at δ 8.27 in addition to an NH proton signal at δ 13.27.

Similarly, benzoylation of compound (**3**) with benzoyl chloride and pyridine, gave 3-formyl-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) 3-benzoyloxime (**5**). On the other hand, treatment of compound (**3**) with benzoyl chloride and pyridine for long time, afforded the bicyclic triazine derivative (**6**), namely 6,7-dihydro-7-oxo-2,6-diphenyl-2*H*-pyrazolo[4,3-*d*]-1,2,3-triazine, on the basis of elemental analysis, IR and NMR data. Its elemental analysis agreed with the molecular formula $C_{16}H_{11}N_5O$ and its IR spectrum showed an amide band at 1655 cm^{-1} and there was no NH absorption. The ^1H NMR spectrum of (**6**) showed one proton signal at δ 7.23 C_4-CH, in addition to the aromatic protons at δ 7.33–8.0, and there were no signals for NH. Treatment of compound (**6**) with bromine in water, substitution occurred in the *p*-position of the two phenyl groups to give (**7**).

Similarly, treatment of 1-*p*-bromophenyl-3-formyl-4,5- pyrazolinedione 4-(*p*-bromophenylhydrazone) (**8**) [11] with hydroxylamine, afforded the corresponding oxime (**9**) which, upon treatment with benzoyl chloride and pyridine for a long time, gave compound (**7**).

Treatment of the formyl pyrazole derivative (**2**) with thiosemicarbazide, afforded 3-formyl-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) 3-thiosemicarbazone (**10**), which on treatment with acetic anhydride and boiling or with acetic anhydride and pyridine, gave 3-[2-(acetamido)-4-acetyl-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl-4,5-pyrazolinedione-4-(phenylhydrazone) (**11**). This reaction is similar to that conducted on thiosemicarbazones of simple aldehydes [13]. The IR spectrum of (**11**) showed two acetyl bands at 1695 and 1639 cm^{-1} in addition to an amide band at 1660 cm^{-1}, where its ^1H NMR spectrum revealed two acetyl group signals at δ 2.10 and 2.20; the first at δ 2.10 was assigned to the 2-acetamido group, and the second at δ 2.20 was due to the N(4) acetyl group. The C_5-CH appeared at δ 6.90 and the phenyl protons appeared at δ 7.27–8.80. Similarly, treatment of the thiosemicarbazone (**10**) with benzoyl chloride and pyridine, gave 3-[2-benzoylamido-4-benzoyl-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) (**12**) whose IR spectrum showed two benzoyl bands at 1724 and 1683 cm^{-1} in addition to an amide band at 1643 cm^{-1}. Furthermore, treatment of the diacetyl derivative (**11**) with hydrazine hydrate, furnished the corresponding amino derivative (**14**) whose ^1H NMR spectrum showed only one acetyl group signal at δ 2.30 corresponding to the acetyl group at N(4). In the same time the monoacetyl derivative (**14**) readily reverts to compound (**11**) upon treatment with acetic anhydride and boiling, and to compound (**13**) upon treatment with benzoyl chloride and pyridine.

Oxidation of 3-[4-acetyl-2-amino-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl-4,5-pyrazolinedione-4-(phenylhydrazone) (**14**) with ferric chloride, resulted in the formation of 3-[2-amino-1,3,4-thiadiazol-5-yl]-1-phenyl-4,5-pyrazolinedione-4-(phenylhydrazone) (**15**) which on acetylation with acetic anhydride and boiling,

furnished the acetyl derivative (**16**), whose ^{1}H NMR spectrum showed one acetyl group signal at δ 2.37 in addition to the expected proton signals.

EXPERIMENTAL

General Methods

Melting points were determined with a Tottoli (Büchi) apparatus and are uncorrected. Infrared spectra were determined with a Perkin–Elmer 1430 spectrometer, and ^{1}H NMR spectra were determined with a Varian EM-390 spectrometer, with tetramethylsilane as internal standard. Chemical shifts are given on the δ scale. Microanalyses were carried out in the Department of Chemistry, Cairo University, Cairo, Egypt.

3-Formyl-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone)-oxime (3)

A solution of compound (**2**) [11] (1.5 g; 5 mmol) in ethanol (30 ml) was treated with hydroxylamine hydrochloride (0.69 g, 10 mmol) and sodium acetate (0.82 g; 10 mmol) and acetic acid (5 ml). The mixture was heated under reflux for 2 h, and concentrated to small volume. Hot water (10 ml) was added, and the solid that separated was filtered off, washed with water and ethanol, and dried (yield 1.5 g; 98%). It was recrystallized from chloroform–ethanol to give orange needles, m.p. 248–249°C; ν_{max}^{KBr} 3141 (OH), 3045 (NH), 1658 (OCN), and 1601 cm^{-1} (C=N); ^{1}H NMR data (DMSO): δ 7.0–8.0 (m, 10 H, aromatic protons), 8.15 (s, 1 H, formyl proton), 11.86 (s, OH) and 13.73 (s, 1 H, NH).

Analysis: *Calc.* for $C_{16}H_{13}N_5O_2$: C, 62.54; H, 4.23; N, 22.79. *Found:* C, 62.36; H, 4.15; N, 22.70.

3-Formyl-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone)-acetoxime (4)

Method (a)

A suspension of compound (**3**) (0.3 g; 1 mmol) in acetic anhydride (10 ml) was heated under reflux for 1 h. The mixture was cooled and poured onto crushed ice. The product that separated was filtered off, successively washed with water and ethanol, and dried (yield 0.3 g; 85%). It was recrystallized from chloroform–ethanol in orange needles, m.p. 158–159°C; ν_{max}^{KBr} 3043 (NH), 1783 ($OCOCH_3$), 1702 (OCN), and 1593 cm^{-1} (C=N). ^{1}H NMR data ($CDCl_3$): δ 2.27 (s, 3 H, $OCOCH_3$), 7.27–8.07 (m, 10 H, aromatic protons), 8.27 (s, 1 H, formyl), and 13.27 (s, 1 H, NH).

Analysis: *Calc.* for $C_{18}H_{15}N_5O_3$: C, 61.88; H, 4.30; N, 20.05. *Found:* C, 61.60; H, 4.20; N, 19.90.

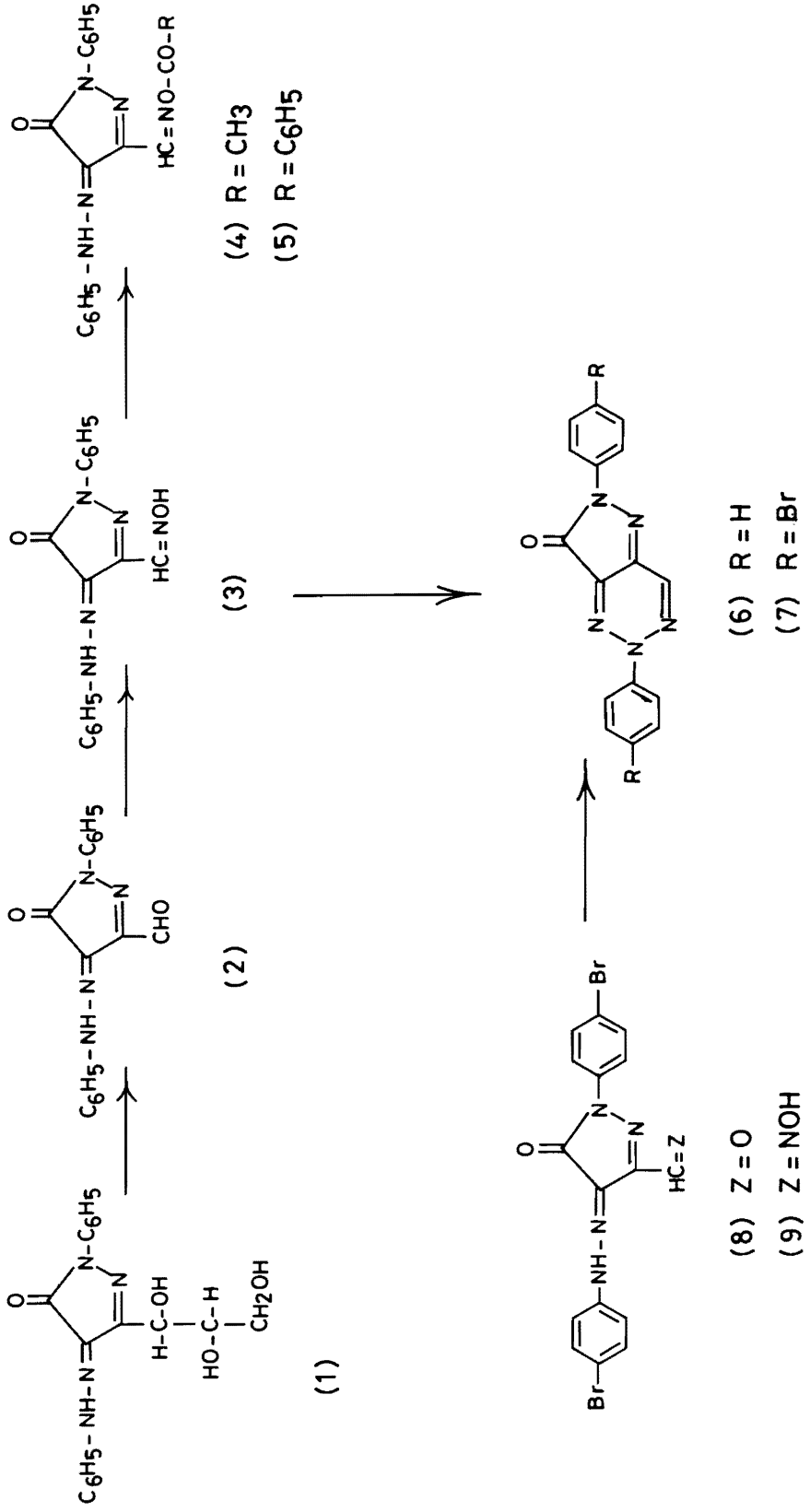
Method (b)

To a solution of compound (**3**) (0.3 g; 1 mmol) in dry pyridine (10 ml) was added acetic anhydride (5 ml) and kept overnight at room temperature. The mixture was poured onto crushed ice, and the solid that separated was filtered off, successively washed with water and ethanol, and dried (yield 0.3 g; 85%). It was recrystallized from chloroform–ethanol in orange needles, m.p. 158–159°C alone or mixed with the product from method (*a*). Both products had identical spectral data.

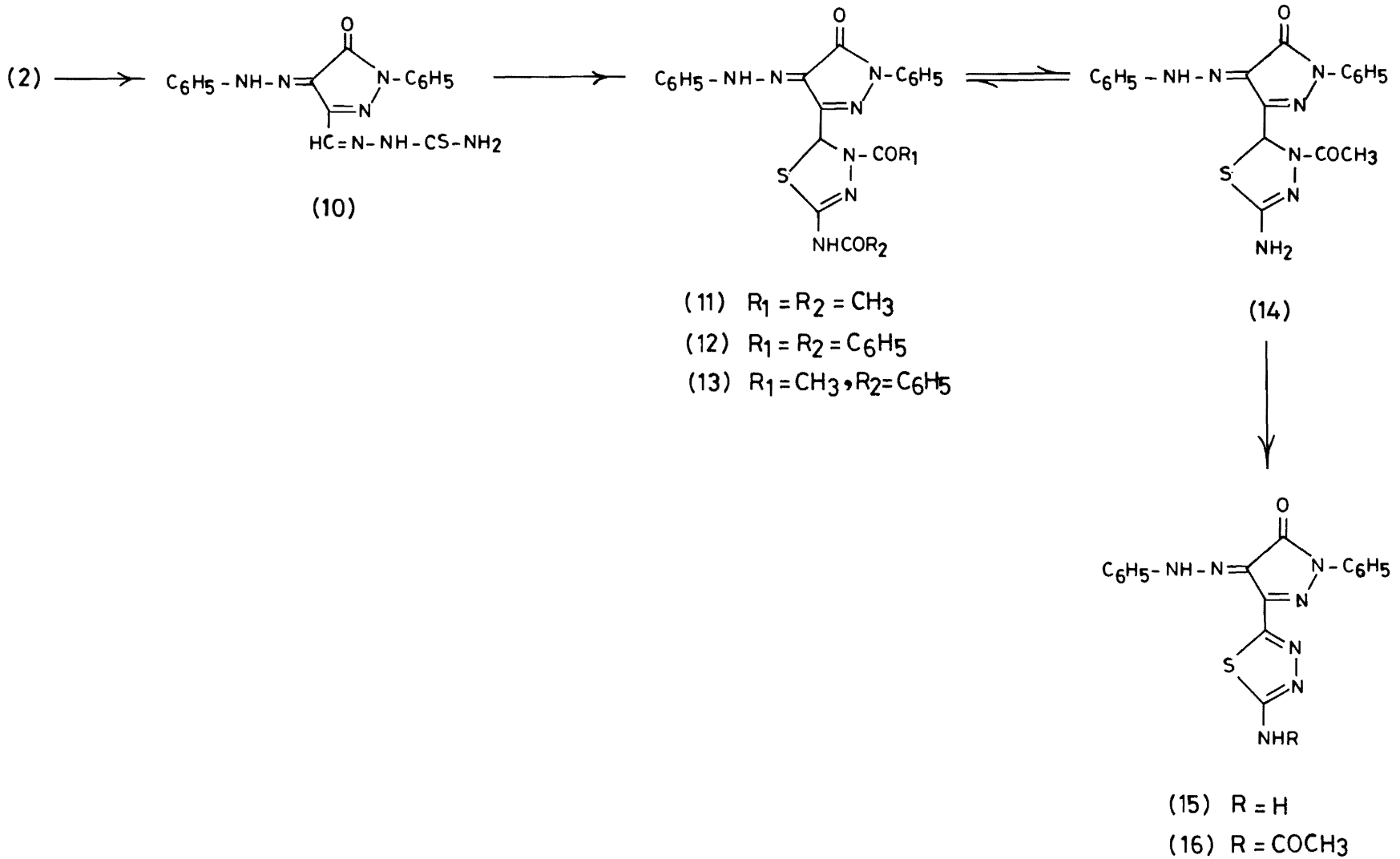
3-Formyl-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone)-benzoyloxime (5)

To a solution of compound (**3**) (0.3 g; 1 mmol) in dry pyridine (10 ml) was added benzoyl chloride (1 ml) and kept overnight at room temperature. The mixture was poured onto crushed ice, and the solid that separated was filtered off, washed with water and ethanol, and dried (yield 0.3 g; 75%). It was recrystallized from ethanol in yellow needles, m.p. 159–160°C; ν_{max}^{KBr} 3057 (NH), 1746 (ester), 1700 (OCN), and 1597 cm^{-1} (C=N). ^{1}H NMR data ($CDCl_3$): δ 7.03–8.03 (m, 15 H, aromatic protons), 8.30 (s, 1 H, CH), and 13.30 (s, 1 H, NH).

Analysis: *Calc.* for $C_{23}H_{17}N_5O_3$: C, 67.15; H, 4.13; N, 17.03. *Found:* C, 67.05; H, 4.00; N, 16.85.



Scheme 1.


(2)
C6H5 - NH - N
N - C6H5
HC = N - NH - CS - NH2
(10)
N - COR1
NHCOR2
(11) R1 = R2 = CH3
(12) R1 = R2 = C6H5
(13) R1 = CH3, R2 = C6H5
N - COCH3
NH2
(14)
NHR
(15) R = H
(16) R = COCH3

Scheme 2.

6,7-Dihydro-7-oxo-2,6-diphenyl-2*H*-pyrazolo[4,3-*d*]-1,2,3-triazine (6).

To a solution of compound (**3**) (0.3 g; 1 mmol) in dry pyridine (10 ml) was added benzoyl chloride (2 ml) and the mixture was kept 3 days at room temperature. The mixture was poured onto crushed ice, and the product that separated was filtered off, successively washed with water, ethanol, and ether, and dried (yield 0.2 g; 69%). It was recrystallized from chloroform–ethanol in red needles, m.p. 188–189°C; ν_{max}^{KBr} 1655 (OCN), and 1592 cm^{-1} (C=N). ^1H NMR data ($CDCl_3$): δ 7.23 (s, 1 H, C(4)H), and 7.33–8.0 (m, 10 H, aromatic protons).

Analysis: *Calc.* for $C_{16}H_{11}N_5O$: C, 66.43; H, 3.80; N, 24.21. *Found:* C, 66.20; H, 3.70; N, 24.10.

2,6-*Bis*-(4-bromophenyl)-6,7-dihydro-7-oxo-2*H*-pyrazolo[4,3-*d*]-triazine (7).

To a suspension of compound (**6**) (0.3 g; 1 mmol) in water (25 ml), bromine (1 ml) in water (10 ml) was added in small portions with stirring. Stirring was continued for 2h at room temperature. Excess of bromine was removed by passing a stream of air through the solution, and the product that separated was filtered off, successively washed with water, ethanol, and ether, and dried (yield 0.4 g; 88%). It was recrystallized from chloroform–ethanol in red prisms, m.p. 207–208°C; ν_{max}^{KBr} 1660 (OCN), and 1588 cm^{-1} (C=N). ^1H NMR data ($CDCl_3$): δ 7.27 (s, 1 H, C(4)H), and 7.37–7.90 (m, 8 H, aromatic protons).

Analysis: *Calc.* for $C_{16}H_9Br_2N_5O$: C, 42.95; H, 2.01; N, 15.65. *Found:* C, 42.75; H, 1.90; N, 15.60.

1-*p*-Bromophenyl-3-formyl-4,5-pyrazolinedione 4-(*p*-bromophenylhydrazone)oxime (9).

A solution of compound (**8**) (0.5 g; 1 mmol) in ethanol (30 ml) was treated with hydroxylamine hydrochloride (0.7 g, 10 mmol) and sodium acetate (0.8 g; 10 mmol) and acetic acid (5 ml). The mixture was heated under reflux for 2 h, and concentrated to small volume. Hot water (10 ml) was added, and the solid was filtered off, washed with water and ethanol, and dried (yield 0.3 g; 60%). It was recrystallized from ethanol in orange needles, m.p. 226–227°C; ν_{max}^{KBr} 3200 (OH), 3100 (NH), and 1660 cm^{-1} (OCN).

Analysis: *Calc.* for $C_{16}H_{11}Br_2N_5O_2$: C, 41.29; H, 2.36; N, 15.05. *Found:* C, 41.42; H, 2.40; N, 15.37.

Reaction of Compound (9) with Benzoyl Chloride

To a solution of compound (**9**) (0.5 g; 1 mmol) in dry pyridine (10 ml) was added benzoyl chloride (2 ml) and the mixture was kept 7 days at room temperature. The mixture was poured onto crushed ice and the product was filtered off, washed with water and ethanol, and dried (yield 0.3 g; 67%). It was recrystallized from chloroform–ethanol in orange red needles, m.p. 207–208°C alone or admixed with compound (**7**). Both products had identical elemental analysis, IR and NMR data.

3-Formyl-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone)thiosemicarbazone (10)

A solution of compound (**2**) (1.5 g; 5 mmol) in ethanol (20 ml) was treated with thiosemicarbazide (0.55 g; 6 mmol) and acetic acid (5 ml), and the mixture was heated under reflux for 1 h, and then cooled. It was poured onto crushed ice and the product that separated was filtered off, successively washed with water and ethanol, and dried (yield 1.6 g; 88%). It was recrystallized from chloroform–ethanol in red needles, m.p. 228–229°C; ν_{max}^{KBr} 3150 (NH), 1650 (OCN), and 1595 cm^{-1} (C=N).

Analysis: *Calc.* for $C_{17}H_{15}N_7SO$: C, 55.88; H, 4.11; N, 26.85. *Found:* C, 55.75; H, 3.90; N, 26.80.

3-[2-Acetamido-4-acetyl-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) (11)

Method (a)

A suspension of compound (**10**) (0.7 g; 2 mmol) in acetic anhydride (10 ml) was heated under reflux for 1 h, cooled and poured onto crushed ice. The solid that separated was filtered off, washed with water and ethanol, and dried (yield 0.8 g; 90%). It was recrystallized from chloroform–ethanol in orange needles, m.p. 268–269°C; ν_{max}^{KBr}

3160 (NH), 1695 ($NHCOCH_3$), 1660 (OCN), 1640 ($NCOCH_3$), and 1597 cm^{-1} (C=N). ^1H NMR data (DMSO-d_6): δ 2.10 (s, 3 H, $NHCOCH_3$), 2.20 (s, 3 H, $NCOCH_3$), 6.90 (s, 1 H, C(5)H), 7.27–7.80 (m, 10 H, aromatic protons), 7.93 (s, 1 H, NH), and 11.80 (s, 1 H, NH, hydrazone).

Analysis: *Calc.* for $C_{21}H_{19}N_7SO_3$: C, 56.11; H, 4.23; N, 21.81. *Found:* C, 55.90; H, 4.20; N, 21.80.

Method (b)

To a solution of compound (**10**) (0.37 g; 1 mmol) in dry pyridine (10 ml) was added acetic anhydride (5 ml) and left overnight at room temperature. The mixture was poured onto crushed ice, and the solid that separated was filtered off, washed with water and ethanol, and dried (yield 0.35 g; 78%). It was recrystallized from chloroform–ethanol in orange needles, m.p. 268–269°C; alone or mixed with the product obtained from method (*a*). Both products had identical data.

3-[2-Benzamido-4-benzoyl-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl- 4,5-pyrazolinedione 4-(phenylhydrazone) (12).

To a solution of compound (**10**) (0.4 g; 1 mmol) in dry pyridine (10 ml) was added benzoyl chloride (2 ml) and left overnight at room temperature. The mixture was poured onto crushed ice, and the product that separated was filtered off, washed with water and ethanol, and dried (yield 0.3 g; 53%). It was recrystallized from chloroform–ethanol in orange needles, m.p. 205–206°C; ν_{max}^{KBr} 3054 (NH), 1724 (NHCOPh), 1683 (NCOPh), 1643 (OCN), and 1593 cm^{-1} (C=N). ^1H NMR data (DMSO-d_6): δ 6.90 (s, 1 H, C(5)H), 7.03– 7.77 (m, 20 H, aromatic protons), 8.06 (s, 1 H, NH), and 12.20 (s, 1 H, NH, hydrazone).

Analysis: *Calc.* for $C_{31}H_{23}N_7SO_3$: C, 64.91; H, 4.01; N, 17.09. *Found:* C, 64.70; H, 3.90; N, 16.90.

3-[4-Acetyl-2-amino-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl-4,5- pyrazolinedione 4-(phenylhydrazone) (14)

A mixture of compound (**11**) (0.9 g; 2 mmol) and hydrazine hydrate (50 ml) was left for 3 h at room temperature with stirring. The solution was acidified with acetic acid, and the solid was filtered off, washed with water and ethanol, and dried (yield 0.7 g; 85%). It was recrystallized from chloroform–ethanol to give yellow needles, m.p. 195–197°C; ν_{max}^{KBr} 3183 (NH), 1657 (OCN), 1628 ($NCOCH_3$), and 1594 cm^{-1} (C=N). ^1H NMR data (DMSO-d_6): δ 2.30 (s, 3 H, $COCH_3$), 6.80 (s, 2 H, NH_2), 7.07 (s, 1 H, C-5), 7.20–7.93 (m, 10 H, aromatic protons), 12.33 (s, 1 H, NH, hydrazone).

Analysis: *Calc.* for $C_{19}H_{17}N_7SO_2$: C, 56.01; H, 4.18; N, 24.07. *Found:* C, 55.85; H, 4.12; N, 23.90.

3-[4-Acetyl-2-benzamido-Δ^2-1,3,4-thiadiazolin-5-yl]-1-phenyl- 4,5-pyrazolinedione 4-(phenylhydrazone) (13)

To a solution of compound (**14**) (0.4 g; 1 mmol) in dry pyridine (10 ml) was treated with benzoyl chloride (1 ml) and kept overnight at room temperature. The mixture was poured onto crushed ice, and the product that separated was filtered off, washed with water and ethanol, and dried (yield 0.4 g; 78%). It was recrystallized from chloroform–ethanol giving orange needles, m.p. 183–184°C; ν_{max}^{KBr} 3057 (NH), 1681 (NHCOPh), 1661 (OCN), 1641 ($NCOCH_3$), and 1595 cm^{-1} (C=N). ^1H NMR data (DMSO-d_6): δ 2.23 (s, 3 H, $COCH_3$), 6.83 (s, 1 H, C-5), 7.0–7.76 (m, 15 H, aromatic protons), 7.90 (s, 1 H, NH), and 12.33 (s, 1 H, NH, hydrazone).

Analysis: *Calc.* for $C_{26}H_{21}N_7SO_3$: C, 61.04; H, 4.11; N, 19.17. *Found:* C, 60.90; H, 3.90; N, 19.00.

Treatment of 3-[4-Acetyl-2-amino-Δ^2-1,3,4-thiadiazolin-5-yl]-1- phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) (14) with Acetic Anhydride

To a solution of compound (**14**) (0.4 g; 1 mmol) in pyridine (10 ml) was treated with acetic anhydride (5 ml) and kept overnight at room temperature. It was poured onto crushed ice, and the product that separated was filtered off, washed with water and ethanol, and dried (yield 0.4 g; 88%). It was recrystallized from chloroform–ethanol in orange needles, m.p. 268–269°C; alone or mixed with compound (**9**). Both products had identical elemental and spectral data.

3-[2-Amino-1,3,4-thiadiazol-5-yl]-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) (15)

A suspension of compound (**14**) (0.8 g; 2 mmol) in a solution of ferric chloride (0.81 g, 3 mmol) in 50% dioxan–water (10 ml) was heated under reflux for 3 h, and then cooled to room temperature. The solid that separated was filtered off, washed with water and ethanol, and dried (yield 0.4 g; 55%). It was recrystallized from dioxan in orange needles, m.p. 261–262°C; ν_{max}^{KBr} 3170 (NH), 1660 (OCN), and 1590 cm^{-1} (C=N). ^1H NMR data ($CDCl_3$): δ 7.13–7.63 (m, 10 H, aromatic protons), 7.80 (s, 1 H, NH), 7.87 (s, 1 H, NH), and 14.60 (s, 1 H, NH, hydrazone).

Analysis: *Calc.* for $C_{17}H_{13}N_7SO$: C, 56.19; H, 3.58; N, 26.98. *Found:* C, 56.10; H, 3.50; N, 26.90.

3-[2-Acetamido-1,3,4-thiadiazol-5-yl]-1-phenyl-4,5-pyrazolinedione 4-(phenylhydrazone) (16)

A suspension of compound (**15**) (0.4 g; 1 mmol) in acetic anhydride (3 ml) was heated under reflux for 2 h, cooled and poured onto crushed ice. The product that separated was filtered off, washed with water and ethanol, and dried (yield 0.3 g; 73%). It was recrystallized from ethanol in brown needles, m.p. > 300°C; ν_{max}^{KBr} 3150 (NH), 1695 ($NHCOCH_3$), 1657 (OCN), and 1592 cm^{-1} (C=N). ^1H NMR data (DMSO-d_6): δ 2.37 (s, 3 H, $NCOCH_3$), 7.30–7.94 (m, 10 H, aromatic protons), 8.03 (s, 1 H, NH), and 14.37 (s, 1 H, NH, hydrazone).

Analysis: *Calc.* for $C_{19}H_{15}N_7SO_2$: C, 56.29; H, 3.70; N, 24.18. *Found:* C, 56.10; H, 3.60; N, 24.10.

REFERENCES

[1] M. A. El Sekily, S. Mancy, I. El Kholy, E. S. H. El Ashry, H. S. El Khadem, and D. L. Swartz, *Carbohydr. Res.*, **59** (1977), p. 141.
[2] M. A. El Sekily and S. Mancy, *Carbohydr. Res.*, **68** (1979), p. 87.
[3] M. A. El Sekily, *Pharmazie*, 34 (1979), p. 531.
[4] M. A. El Sekily, S. Mancy, and B. Gross, *Carbohydr. Res.*, **110** (1982), p. 229.
[5] M. A. El Sekily, S. Mancy, and B. Gross, *Carbohydr. Res.*, **112** (1983), p. 151.
[6] M. A. El Sekily and S. Mancy, *Pakistan J. Sci. Ind. Res.*, **31** (1988), p. 616.
[7] H. G. Garg and C. Prakash, *J. Med. Chem.*, **14** (1971), p. 649.
[8] H. G. Garg and P. P. Singh, *J. Pharm. Sci.*, **59** (1970), p. 876.
[9] R. M. Shafik and F. S. G. Soliman, *Pharmazie*, **29** (1974), p. 290.
[10] F. S. G. Soliman and R. M. Shafik, *Pharmazie*, **30** (1975), p. 436.
[11] H. S. El Khadem and E. S. H. El Ashry, *J. Chem. Soc.* (C), (1968), p. 2248.
[12] S. Kubata, Y. Ueda, K. Fujikane, K. Toyooka, and M. Shibaya, *J. Org. Chem.*, **45** (1980), p. 1473.

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