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Heterocyclic Synthesis Using Nitrilimines-Part 1 Synthesis of Substituted Dihydro- and Tetrahydro-1,2,4,5-Tetrazines

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The reaction of C-phenylaminocarbonyl-N-arylnitrilimines (**2a, b**) with 1-substituted-1-methylhydrazines (**3–7**) afford the formation of the respective amidrazones (**8a, b**) when R = CH_3, Ph, and to the acyclic adducts (**9–11a, b**) when R = —CHO, —$COCH_3$ and —COOEt. The acyclic adducts underwent thermal oxidative cyclization at —CH_3 to give the unexpected 1,2,4,5-tetrazines (**12–14a, b**) rather than the expected tetrazinones (**16a, b**) when R = —COOEt. Dihydro-1,2,4,5-tetrazines (**15a, b**) were also separated when R = —CHO.

Key Words: Nitrilimines, Methylhydrazines, Amidrazones, Dihydrotetrazines, Tetrahydrotetrazines.

INTRODUCTION

Nitrilimines are known to undergo cyclocondensation reactions with nucleophilic substrates incorporating suitably located electrophilic centres to give various heterocyclic products[1–3]. The reaction of nitrilimines with different 1-substituted-1-methylhydrazines was recently reported to give acyclic adducts which upon thermal oxidative cyclization produced the tetrahydro-1,2,4,5-tetrazines[3–5].

1,2,4,5-Tetrazines represent an important class of heterocyclic compounds that find many practical and synthetic applications[6]. This study aims to investigate the reaction of C-phenylaminocarbonyl nitrilimines (**2a, b**) with 1-substituted-1-methylhydrazines (**3–7**; H_2N—NCH_3R; R = CH_3, Ph, CHO, $COCH_3$, COOEt) in an attempt to synthesize a new class of substituted tetrahydro-1,2,4,5-tetrazines.

EXPERIMENTAL

Melting points were determined on Electrothermal Mel. Temp. apparatus and are uncorrected. IR spectra were obtained by using Perkin-Elmer 237 infrared spectrometer (KBr discs). NMR spectra were recorded on a Bruker instrument at 400 MHz for ^1H NMR and at 100 MHz for ^{13}C NMR using TMS as internal

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reference. Electron impact mass spectra were run on Finnigan Mat 8200 spectrometer at 70 eV. Elemental analysis was performed at Cairo University, Egypt. Hydrazonoyl halides (**1a, b**)[7], 1-formyl-1-methylhydrazine (**5**)[8], 1-acetyl-1-methylhydrazine (**6**)[9], and 1-ethoxycarbonyl-1-methylhydrazine (**7**)[10] were prepared according to known literature procedures. 1,1-Dimethylhydrazine and 1-methyl-1-phenylhydrazine were purchased from Acros Organics Company and used as such without further purification.

Reaction of Nitrilimines (1) with 1-Substituted-1-methylhydrazines (3–7)

To a stirred cold (0°C) solution of hydrazonoyl halides (**1a, b**) (0.01 mol) and 1-substituted-1-methylhydrazines (**3–7**) (0.02 mol) in tetrahydrofuran (100 mL) was dropwise added triethylamine (0.05 mol) in tetrahydrofuran (20 mL). Stirring was continued overnight, the precipitated triethylamine salt was filtered off, and the solvent was removed in *vacuo*. The residue was washed with water (100 mL) and the resulting crude solid product was collected and recrystallized from ethanol. The following compounds were prepared by this procedure:

2-Amino-4-phenyl-1-phenylamino-3,4-diaza-2-buten-1-one (8a)

^{1}H NMR: 9.95 (s, 1H, NH—Ar′), 9.0 (s, 1H, PhNHCO), 7.6–7.2 (m, 10H, aromatic), 5.7 (s, 2H, NH_2); ^{13}C NMR: 159.9 (Ar—C=O), 139.9 (C=N), 144.8, 136.8, 131.7, 130.8, 129.3, 127.5, 123.9, 114.3 (8 aromatic carbons); IR (cm^{-1}): 3480–3200 ν(NH, broad), 1650 ν(Ar—C=O).

2-Amino-4-(4-chlorophenyl)-1-phenylamino-3,4-diaza-2-buten-1-one (8b)

^{1}H NMR: 9.94 (s, 1H, NH—Ar′), 9.0 (s, 1H, PhNHCO), 7.6–7.16 (m, 9H, aromatic), 5.6 (s, 2H, NH_2); ^{13}C NMR: 159.8 (Ar—C=O), 139.9 (C=N), 144.0, 136.9, 131.7, 130.5, 129.0, 127.6, 123.2, 114.2 (8 aromatic carbons); IR (cm^{-1}): 3400–3100 ν(NH, broad), 1655 ν(Ar—C=O).

2-Methyl-6-phenyl-4-phenylaminocarbonyl-2,3,5,6-tetraaza-4-hexenal (9a)

^{1}H NMR: 10.10 (s, 1H, NH—Ar′), 9.08 (s, 1H, PhNHCO), 8.85 (s, 1H, CHO), 7.68–7.23 (m, 10H, aromatic), 6.70 (s, 1H, NH), 3.11 (s, 3H, NCH_3); ^{13}C NMR: 162.3 (H—C=O), 159.9 (Ar—C=O), 137.6 (C=N), 141.3, 135.3, 134.7, 132.4, 129.4, 127.9, 127.5, 115.5 (8 aromatic carbons), 42.4 (N—CH_3); IR (cm^{-1}): 3500, 3360, 3260 ν(NH), 1670 ν(H—C=O), 1650 ν(PhNH—C=O), 1595 ν(C=N).

6-(4-Chlorophenyl)-2-methyl-4-phenylaminocarbonyl-2,3,5,6-tetraaza-4-hexenal (9b)

^{1}H NMR: 10.10 (s, 1H, NH—Ar′), 9.08 (s, 1H, PhNHCO), 8.85 (s, 1H, CHO), 7.68–7.21 (m, 9H, aromatic), 6.72 (s, 1H, NH), 3.10 (s, 3H, NCH_3); ^{13}C NMR: 162.3 (H—C=O), 159.8 (Ar—C=O), 137.4 (C=N), 141.3, 135.3, 134.8, 132.4, 129.1, 127.9, 127.5, 115.7 (8 aromatic carbons), 42.4 (N—CH_3); IR (cm^{-1}): 3350, 3320, 3280 ν(NH), 1680 ν(H—C=O), 1640 ν(PhNH—C=O), 1593 ν(C=N).

3-Methyl-7-phenyl-5-phenylaminocarbonyl-3,4,6,7-tetraaza-5-hepten-2-one (10a)

^{1}H NMR: 10.50 (s, 1H, NH—Ar′), 8.50 (s, 1H, PhNHCO), 8.10 (s, 1H, NH), 7.62–7.16 (m, 10H, aromatic), 3.02 (s, 3H, NCH_3), 2.0 (s, 3H, $COCH_3$); ^{13}C NMR: 170.2 (CH_3—C=O), 159.9 (Ar—C=O), 137.2 (C=N), 141.2, 134.8, 129.3, 129.1, 126.8, 124.5, 119.8, 115.1 (8 aromatic carbons), 42.3 (N—CH_3); 21.1 (CH_3—CO); IR (cm^{-1}): 3380, 3330, 3300 ν(NH), 1670 ν(CH_3—C=O), 1650 ν(Ar—C=O), 1594 ν(C=N).

7-(4-Chlorophenyl)-3-methyl-5-phenylaminocarbonyl-3,4,6,7-tetraaza-5-hepten-2-one (10b)

^{1}H NMR: 10.51 (s, 1H, NH—Ar′), 8.45 (s, 1H, PhNHCO), 8.10 (s, 1H, NH), 7.65–7.18 (m, 9H, aromatic), 3.04 (s, 3H, NCH_3), 2.1 (s, 3H, $COCH_3$); ^{13}C NMR: 170.1 (CH_3—C=O), 159.9 (Ar—C=O), 137.2 (C=N), 141.3, 134.6, 129.4, 129.0, 126.9, 124.3, 119.6, 115.3 (8 aromatic carbons), 42.5 (N—CH_3); 21.1 (CH_3—CO); IR (cm^{-1}): 3370, 3360, 3280 ν(NH), 1670 ν(CH_3—C=O), 1660 ν(Ar—C=O), 1596 ν(C=N).

Ethyl 2-methyl-6-phenyl-4-phenylaminocarbonyl-2,3,5,6-tetraaza-4-hexenoate (11a)

^{1}H NMR: 10.35 (s, 1H, NH—Ar′), 9.20 (s, 1H, PhNHCO), 7.7–7.2 (m, 10H, aromatic), 6.50 (s, 1H, NH), 4.27 (q, 2H, CH_3, J = 7 Hz), 3.10 (s, 3H, NCH_3), 1.3 (t, 3H, CH_3, J = 7 Hz); ^{13}C NMR: 159.9 (Ar—C=O), 158.2 (O—C=O), 137.8 (C=N), 141.9, 135.2, 134.7, 129.4, 126.9, 124.9, 122.1, 115.3 (8 aromatic carbons), 63.0 (O—CH_2), 37.2 (N—CH_3), 14.6 (CH_3); IR (cm^{-1}): 3500, 3340, 3320 ν(NH), 1710 ν(O—C=O), 1650 ν(Ar—C=O), 1597 ν(C=N).

Ethyl 6-(4-chlorophenyl)-2-methyl-4-phenylaminocarbonyl-2,3,5,6-tetraaza-4-hexenoate (11b)

^{1}H NMR: 10.40 (s, 1H, NH—Ar′), 9.10 (s, 1H, PhNHCO), 7.7–7.2 (m, 9H, aromatic), 6.60 (s, 1H, NH), 4.25 (q, 2H, CH_2, J = 7 Hz), 3.20 (s, 3H, NCH_3), 1.3 (t, 3H, CH_3, J = 7 Hz); ^{13}C NMR: 159.8 (Ar—C=O), 158.2 (O—C=O), 137.6 (C=N), 141.8, 135.1, 134.3, 129.5, 126.6, 124.7, 119.4, 115.1 (8 aromatic carbons), 63.1 (O—CH_2), 37.1 (N—CH_3), 14.6 (CH_3); IR (cm^{-1}): 3450, 3390, 3300 ν(NH), 1720 ν(O—C=O), 1655 ν(Ar—C=O), 1598 ν(C=N).

Thermal Cyclization of Compounds (9–11)

Compounds **(9–11)** (0.005 mol) and charcoal (0.5–1.0 g) in benzene (50 mL) were refluxed for 4–6 h. The reaction mixture was then filtered and the solvent was minimized. Petroleum ether (bp. 40–60°C) was then added to effect complete crystallization of the desired cyclic compounds **(12–14).** In case of compounds **(12)**, the oxidation products **(15)** were also obtained as side reaction products which were separated on TLC plates, using silica gel as the adsorbent, and CH_2Cl_2/pet. ether (5 : 1 v/v) as developing solvent. The following compounds were synthesized using this method:

2-Formyl-4-phenyl-6-phenylaminocarbonyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (12a)

^{1}H NMR: 9.10 (s, 1H, PhNHCO), 8.40 (s, 1H, CHO), 7.60–7.21 (m, 10H, aromatic), 6.50 (s, 1H, NH), 5.70 (s, 2H, CH_2); ^{13}C NMR: 162.2 (H—C=O), 158.9 (Ar—C=O), 136.4 (C=N), 143.5, 128.6, 128.1, 126.0, 123.7, 121.5, 119.2, 116.0 (8 aromatic carbons), 44.3 (N—CH_2—N); IR (cm^{-1}): 3350, 3255, ν(NH), 1670 ν(H—C=O), 1655 ν(Ar—C=O), 1596 ν(C=N).

4-(4-Chlorophenyl)-2-formyl-6-phenylaminocarbonyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (12b)

^{1}H NMR: 9.15 (s, 1H, PhNHCO), 8.50 (s, 1H, CHO), 7.65–7.20 (m, 9H, aromatic), 6.50 (s, 1H, NH), 5.71 (s, 2H, CH_2); ^{13}C NMR: 162.1 (H—C=O), 158.8 (Ar—C=O), 136.2 (C=N), 143.3, 128.8, 128.2, 125.9, 123.7, 121.7, 119.4, 116.1 (8 aromatic carbons), 44.2 (N—CH_2—N); IR (cm^{-1}): 3315, 3260, ν(NH), 1675 ν(H—C=O), 1650 ν(Ar—C=O), 1597 ν(C=N).

2-Acetyl-4-phenyl-6-phenylaminocarbonyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (13a)

^{1}H NMR: 8.9 (s, 1H, PhNHCO), 7.70–7.18 (m, 10H, aromatic), 6.40 (s, 1H, NH), 5.30 (s, 2H, CH_2); ^{13}C NMR: 170.0 (CH_3—C=O), 159.2 (Ar—C=O), 137.2 (C=N), 144.3, 128.6, 128.3, 125.6, 125.0, 123.3, 119.4, 115.8 (8 aromatic carbons), 43.2 (N—CH_2—N), 26.0 (CH_3); IR (cm^{-1}): 3350, 3280, ν(NH), 1660 ν(CH_3—C=O), 1650 ν(Ar—C=O), 1595 ν(C=N).

2-Acetyl-4-(4-Chlorophenyl)-6-phenylaminocarbonyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (13b)

^{1}H NMR: 9.0 (s, 1H, PhNHCO), 7.60–7.21 (m, 9H, aromatic), 6.42 (s, 1H, NH), 5.25 (s, 2H, CH_2); ^{13}C NMR: 169.7 (CH_3—C=O), 158.9 (Ar—C=O), 137.4 (C=N), 144.5, 128.5, 128.1, 125.3, 124.9, 123.6, 119.2, 116.2 (8 aromatic carbons), 43.10 (N—CH_2—N), 26.1 (CH_3); IR (cm^{-1}): 3330, 3260, ν(NH), 1680 ν(CH_3—C=O), 1660 ν(Ar—C=O), 1593 ν(C=N).

2-Ethoxycarbonyl-4-phenyl-6-phenylaminocarbonyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (14a)

^{1}H NMR: 9.7/9.4 (s, 1H, NH), 9.2/8.8 (s, 1H, PhNHCO), 7.6–7.16 (m, 10H, aromatic), 5.1/4.9 (s, 2H, NCH_2N), 4.25/4.20 (q, 2H, O—CH_2), 1.2/1.1 (t, 3H, CH_3); ^{13}C NMR: 159.8/159.2 (Ar—C=O), 156.8/153.2 (O—C=O), 143.3/140.8 (C=N), 148.6/144.3, 140.1/136.3, 135.4/133.9, 132.9/131.7, 130.7/129.5, 128.9/127.4, 126.8/125.1, 119.7/116.5 (8 aromatic carbons), 60.5/56.3 (NCH_2N), 63.5/62.2 (O—CH_2), 14.7 (CH_3); IR (cm^{-1}): 3330, 3240, ν(NH), 1700 ν(O—C=O), 1670 ν(Ar—C=O), 1595 ν(C=N).

4-(4-Chlorophenyl)-2-ethoxycarbonyl-6-phenylaminocarbonyl-1,2,3,4-tetrahydro-1,2,4,5-tetrazine (14b)

^{1}H NMR: 9.6/9.3 (s, 1H, NH), 9.1/8.7 (s, 1H, PhNH—CO), 7.7–7.2 (m, 9H, aromatic), 5.1/4.95 (s, 2H, NCH_2N), 4.30/4.25 (q, 2H, O—CH_2), 1.20/1.15 (t, 3H,

CH_3); ^{13}C NMR: 159.6/159.1 (Ar—C=O), 156.8/153.5 (O—C=O), 143.2/140.1 (C=N), 148.2/144.3, 139.8/135.9, 135.1/134.5, 133.1/131.2, 129.7/129.0, 128.6/127.5, 126.4/125.7, 119.2/116.1 (8 aromatic carbons), 60.6/56.3 (N—CH_2—N), 63.5/62.3 (O—CH_2), 14.7 (CH_3); IR (cm^{-1}): 3320, 3250 ν(NH), 1705 ν(O—C=O), 1665 ν(Ar—C=O), 1594 ν(C=N).

1-Phenyl-3-phenylaminocarbonyl-1,6-dihydro-1,2,4,5-tetrazine (15a)

^1H NMR: 9.6 (s, 1H, PhNHCO), 7.6–7.25 (m, 10H, aromatic), 5.3 (s, 2H, CH_2); ^{13}C NMR: 160.2 (Ar—C=O), 139.8 (C=N), 153.7, 136.8, 134.0, 133.4, 130.9, 129.9, 127.8, 121.8 (8 aromatic carbons), 67.3 (CH_2); IR: (cm^{-1}): 3260 ν(NH), 1660 ν(Ar—C=O), 1597 ν(C=N).

1-(4-Chlorophenyl)-3-phenylaminocarbonyl-1,6-dihydro-1,2,4,5-tetrazine (15b)

^1H NMR: 9.6 (s, 1H, PhNHCO), 7.6–7.2 (m, 9H, aromatic), 5.3 (s, 2H, CH_2); ^{13}C NMR: 160.1 (Ar—C=O), 139.7 (C=N), 153.5, 136.9, 133.9, 133.0, 130.3, 129.6, 128.2, 121.3 (8 aromatic carbons), 67.3 (CH_2); IR: (cm^{-1}): 3270 ν(NH), 1650 ν(Ar—C=O), 1598 ν(C=N).

RESULTS AND DISCUSSION

In the present work, we found that substituted methylhydrazines **(3–7)** react readily with nitrilimines **(2a, b)**, generated in *situ* from the action of triethylamine onto the hydrazonoyl chlorides **(1a, b)**, yielding the corresponding amidrazones **(8)** when R = CH_3 and Ph, and the acyclic adducts **(9–11)** when R = CHO, $COCH_3$ and $COOC_2H_5$. Thermal cyclization of latter acyclic adducts gave tetrahydro-1,2,4,5-tetrazines **(12–14)**. Dihydro-1,2,4,5-tetrazines **(15)** were also obtained upon elimination of formaldehyde from compounds **(12)** (**Scheme 1**, Table 1).

A plausible reaction mechanism for this cyclization starts by the oxidation of the acyclic adducts **(9–11)** to formazanes, which cyclize as reported by Neugebauer, *et al.*[11] to corresponding tetrahydro-1,2,4,5-tetrazines. It is worth mentioning that this kind of cyclization of alkyl formazanes is the most frequently used method for the preparation of tetrahydro-1,2,4,5-tetrazines[12].

The assignment of structures **(8–15)** is based on analytical and spectral data. The electron impact spectra (Table 1) display the correct molecular ions in accordance with the suggested structures. The IR spectra of each of the amidrazones **(8)** exhibits characteristic NH_2 and N—H bands in the 3400–3100 cm^{-1} region, in addition to C=O bonds at about 1650 cm^{-1}. The IR of the acyclic adducts **(9–11)** reveal three N—H bands in the region 3500–3200 cm^{-1}, and two C=O bands at about 1660 and 1720 cm^{-1} assignable to Ar—C=O and lactam C=O, respectively.

One of the N—H bands is absent in the spectra of cyclic compounds **(12–14)**. The N—H band and C=O band of the formyl group disappear in IR spectra of compounds **(15)**. ^1H and ^{13}C NMR spectra of compounds **(9–15)** show all the

signals of the proposed structures. The N—CH_3 signal ($\delta = 3.2–3.0$ ppm) of compounds **(9–11)** is replaced by a highly deshielded CH_2 signal ($\delta = 5.7–5.1$ ppm) in compounds **(12–15)**. All the NMR signals of compounds **(14)** are doubled, apparently, because of their presence in two tautomeric forms in solution. Similar tautomerism was reported for s-tetrazines by Ryabokon *et al.*[12]

TABLE-1
PHYSICAL DATA AND ELEMENTAL ANALYSIS FOR COMPOUNDS (8–15)

Compd.	m.p. (°C)	Yield (%)	m.f. (M^+)	Analysis %: Calcd. (Found)		
				C	H	N
8a	218–220[a]	62	$C_{14}H_{14}N_4O$ 254	66.13 (66.50)	5.55 (5.40)	22.03 (21.85)
8b	229–231[b]	66	$C_{14}H_{13}N_4OCl$ 288/290	58.24 (58.10)	4.54 (4.60)	19.40 (19.60)
9a	121–123	72	$C_{16}H_{17}N_5O_2$ 311	61.72 (61.90)	5.50 (5.40)	22.49 (22.60)
9b	132–134	74	$C_{16}H_{16}N_5O_2Cl$ 345/347	55.58 (55.40)	4.66 (4.70)	20.25 (19.90)
10a	146–148	70	$C_{17}H_{19}N_5O_2$ 325	62.76 (62.90)	5.89 (6.10)	21.52 (21.40)
10b	123–125	72	$C_{17}H_{18}N_5O_2Cl$ 359/361	56.75 (56.60)	5.04 (4.90)	19.46 (19.60)
11a	112–114	73	$C_{18}H_{21}N_5O_3$ 355	60.83 (61.00)	5.96 (6.10)	19.71 (19.50)
11b	155–157	75	$C_{18}H_{20}N_5O_3Cl$ 389/391	55.46 (55.30)	5.17 (5.10)	17.96 (18.10)
12a	178–180	69	$C_{16}H_{15}N_5O_2$ 309	62.13 (61.90)	4.89 (5.00)	22.64 (22.70)
12b	212–214	67	$C_{16}H_{14}N_5O_2Cl$ 343/345	55.90 (56.10)	4.10 (3.90)	20.37 (20.40)
13a	186–188	74	$C_{17}H_{17}N_5O_2$ 323	63.15 (62.90)	5.30 (5.40)	21.66 (21.50)
13b	211–213	76	$C_{17}H_{16}N_5O_2Cl$ 357/359	57.07 (56.80)	4.51 (4.60)	19.57 (19.50)
14a	140–142	81	$C_{18}H_{19}N_5O_3$ 353	61.18 (60.90)	5.42 (5.30)	19.82 (19.90)
14b	139–141	83	$C_{18}H_{18}N_5O_3Cl$ 387/389	55.75 (55.60)	4.68 (4.80)	18.06 (17.90)
15a	162–164	30	$C_{15}H_{13}N_5O$ 279	64.51 (64.60)	4.69 (4.60)	25.07 (25.00)
15b	168–170	32	$C_{15}H_{12}N_5OCl$ 313/315	57.42 (57.40)	3.86 (3.90)	22.32 (22.40)

a: (Lit. m.p. 216°C)[13]; b: (Lit. m.p. 230°C)[13]

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REFERENCES

1. M.M. El-Abadelah, A.Q. Hussein, M.R. Kamal and K.H. Al-Adhami, *Heterocycles*, **27**, 917 (1988).
2. M.M. El-Abadelah, M.Z. Nazer, N.S. El-Abadlah and H. Meier, *J. Prakt. Chem.*, **90**, 339 (1997).
3. M.R. El-Haddad, A.E.S. Ferwanah and A.M. Awadallah, *J. Prakt. Chem.*, **340**, 623 (1998).
4. A.E.S. Ferwanah, A.M. Awadallah, E.A. El-Sawi and H.M. Dalloul, *Synth. Commun.*, **33**, 1245 (2003).
5. A.M. Awadallah, A.E.S. Ferwanah, E.A. El-Sawi and H.M. Dalloul, *Heterocyclic Commun.*, **8**, 369 (2002)
6. H. Neunhoeffer, Tetrazines, in: A.R. Katritzky and C.W. Rees (Eds.), *Comprehensive Heterocyclic Chemistry*, Pergmon Press, London, Vol. 3, p. 531 (1984).
7. A.S. Shawali, H.M. Hassaneen, A.A. Fahmi and N.M. Abu Nada, *Phosphorus, Sulfur and Silicon*, **53**, 259 (1990).
8. C. Th. Predersen, *Acta Chem. Scand.*, **18**, 2199 (1964).
9. F.E. Condon, *J. Org. Chem.*, **37**, 3608 (1972).
10. W.S. Wadworth, *J. Org. Chem.*, **34**, 2994 (1969).
11. G. McConnachie and F.A. Neugebauer, *Tetrahedron*, **31**, 555 (1975).
12. L.G. Ryabokon, V.N. Kalinin, O.M. Polumbrik and L.N. Markovski, *Khim. Geterotsikl. Soedin*, **10**, 1425 (1985); *Chem. Abstr.*, **104**, 108922g (1986).
13. N.M. Abu Nada, M.Sc. Thesis, Faculty of Science, Cairo University (1989).

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