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Synthetic Studies on Fused Nitrogen-heterocycles from *N*-Amino-*N,N'*-dihydrodiazinediones (I). Condensation of *N*-Amino-*N,N'*-dihydrodiazinediones with 1,3-Dicarbonyl Compounds

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The condensation of 1-amino-1,2-dihydro-3,6-pyridazinedione (**1**) and 2-amino-2,3-dihydro-1,4-phthalazinedione (**2**) with 1,3-diketones or 1,3-dialdehydes in polyphosphoric acid gave 6,9-dihydro-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazines (**3**—**6**) and 6,11-dihydro-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazines (**7**—**10**), respectively. The condensation of **2** with 2,4-pentanedione in acetic acid gave *N*-alkylidene intermediate (**11**), which was cyclized to **9** by treatment with polyphosphoric acid.

Introduction

Of the three possible triazine systems the 1,2,3-triazines are by far the least studied class. Recently, interest in the 1,2,3-triazines has increased as a result of the wide range of biological activity associated with many derivatives of 1,2,3-benzotriazin-4(2*H*)-one[1]. There have been known a variety of fused 1,2,3-triazines. However, only a limited number of fused 1,2,3-triazines in which two nitrogen atoms are common to two adjacent ring have been reported[2].

We prepared 1-amino-1,2-dihydro-3,6-pyridazinedione (**1**) and 2-amino-2,3-dihydro-1,4-phthalazinedione (**2**) from 1,2-dihydro-3,6-pyridazinedione and 2,3-dihydro-1,4-phthalazinedione, respectively, by *N*-amination with hydroxylamine-*O*-sulfonic acid[3]. It was hoped that **1** and **2** as a 1,3-dinitrogencyclophile would condense with 1,3-dicarbonyl or α,β-unsaturated carbonyl compounds to afford N-N fused 1,2,3-triazines.

We have recently reported[4] that the condensation of **1** and **2** with 2,4-pentanedione, 4-methyl-3-penten-2-one or diethyl 2-butynoate yields the novel heterocyclic ring systems, pyridazino[1,2-*a*][1,2,3]triazines and 1,2,3-triazino-[1,2-*b*]phthalazines, respectively. We describe here the full details of the condensation of **1** and **2** with various 1,3-dicarbonyl compounds to synthesize these heterocycles.

Results and Discussion

The syntheses of fused nitrogen-heterocycles from condensation of 1,3-dinitrogencyclophiles with 1,3-dicarbonyl compounds can be achieved with acidic cyclizing agents, such as sulfuric acid, polyphosphoric acid (PPA), acetic acid etc. Recently it was reported[5] that phosphoryl chloride containing a small amount of PPA was a good cyclizing agent in these condensations.

We have found that PPA was a good cyclizing agent for the condensation of *N*-amino-*N,N'*-dihydrodiazinediones with 1,3-dicarbonyl compounds. Thus 1-amino-1,2-dihydro-3,6-pyridazinedione (**1**) and 2-amino-2,3-dihydro-1,4-phthalazinedione (**2**) was mixed well with PPA preheated to 60-90 °C and reacted with 1,3-propanedial, 3-oxobutanal, 2,4-pentanedione or 1,3-diphenyl-1,3-propanedione for 40-60 min

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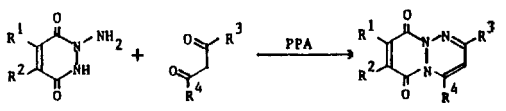
at 75-95 °C to give pyridazino[1,2-*a*]triazine and 1,2,3-triazino[1,2-*b*]phthalazine derivatives (**3-10**), respectively, in good yields. The condensation of **1** and **2** with 3-oxobutanal, an unsymmetrical dicarbonyl compound, gave single product, 2-methyl derivative in preference to the 4-methyl isomer.



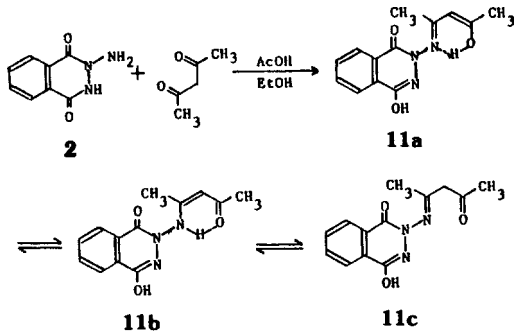
1 or **2** **3-10**

1 R^1-R^2-H
2 R^1+R^2-(CH-CH)$_2$
3 R^1-R^2-R^3-R^4-H
4 R^1-R^2-R^4-H, R^3-CH_3
5 R^1-R^2-H, R^3-R^4-CH_3
6 R^1-R^2-H, R^3-R^4-Ph
7 R^1+R^2-(CH=CH)$_2$, R^3-R^4-H
8 R^1+R^2-(CH=CH)$_2$, R^3-CH_3, R^4-H
9 R^1+R^2-(CH=CH)$_2$, R^3-R^4-CH_3
10 R^1+R^2-(CH=CH)$_2$, R^3-R^4-Ph

Scheme 1

The IR spectra of the products (**3-10**) showed the disappearance of amino and enolic hydroxy absorption. Their ^{1}H NMR spectra displayed C-2, C-3, and C-4 proton signals at 7.45-7.49, 5.56-6.62, and 8.06-8.10 ppm, respectively. The coupling constants $J_{2,3}$, $J_{3,4}$, $J_{2,4}$, and $J_{3,4\text{-Me}}$ were in close agreement with those reported for the related compounds, pyrimido[1,2-*b*]pyridazines[6]. Their mass spectra showed, besides the expected molecular ion (M^+), very similar fragmentation pathways.

When **2** was refluxed for 10 min with 2,4-pentanedione in acetic acid-ethanol (1:1), 2-(1-methyl-3-oxobutylidene)amino-2,3-dihydro-1,4-phthalazinedione (**11**) was obtained in 70% yield, which was cyclized to **9** by treatment with PPA at 95 °C for 1 hr. The ^{1}H NMR spectrum of **11** in DMSO-d_6 shows that it is a mixture of three tautomers **11a**, **11b**, and **11c** in the approximate molar ratio 1:7:2 (Scheme 2). The compound **11** is similar to the intermediate in Combes quinoline synthesis by the condensation of 1,3-diketones or 1,3-dialdehydes with anilines[7]. This result suggests that the condensation of **1** and **2** with 1,3-diketones or 1,3-dialdehydes in PPA may proceed though *N*-alkylidene derivatives, such as **11**, as an intermediate.



2 **11a**

11b **11c**

Scheme 2

Experimental

Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by the Lucky Central Research Institute. ^{1}H NMR spectra were recorded on Varian EM-360 and XL-100 spectrometer, and the data were give in δ units downfield from TMS. IR spectra were obtained with Perkin-Elmer 283 infrared spectrometer. Mass spectra were measured with a Shimadzu LKB 900 GC mass spectrometer.

Analytical tlc was done on silica gel 60G (E. Merck). Column chromatography was done on silica gel 60 (70-230 mesh ASTM, E. Merck). Hydroxylamine-*O*-sulfonic acid[8], 1,2-dihydro-3,6-pyridazinedione[9], 2,3-dihydro-1,4-phthalazinedione[10], 1-amino-1,2-dihydro-3,6-phthalazinedione[3], and 2-amino-2,3-dihydro-1,4-phthalazinedione[3] were prepared by the method described in the literature. Other chemicals and solvents were used without further purification.

2-Amino-2,3-dihydro-1,4-phthalazinedione (2). The compound **2** was prepared by previously reported procedure[3] with slight modification. To 100 m*l* of 6 *M* potassium hydroxide solution heated to 80 °C was added 2,3-dihydro-1,4-phthalazinedione (15.0 g, 93 mmol) with stirring. A solution of 25 g (220 mmol) of hydroxylamine-*O*-sulfonic acid in 40 m*l* of water was added slowly, and the mixture was refluxed for 2 hr. It was cooled to room temperature and adjusted to pH 5 with acetic acid. The precipitated solid was filtered, washed with water, and dried. It was recrystallized from methanol to give 7.4 g (45%) of pure **2**.

6,9-Dihydro-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazine(3). 1-Amino-1,2-dihydro-3,6-pyridazinedione (**1**, 1.0 g, 7.8 mmol) was added to polyphosphoric acid (PPA, 6 g) preheated to 60 °C and mixed well with stirring. After elevating the temperature to 95 °C, 1,1,3,3-tetramethoxypropane (1.3 g, 7.9 mmol) was added in small portions. The mixture was stirred for 1 hr and allowed to cool to room temperature. Water (50 m*l*) was added and the resulting solution was extracted with chloroform (3 × 100 m*l*). The chloroform layer was washed with 10% aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated, yielding the crude product, which was recrystallized from ethyl acetate to give 0.40 g (31%) of pure **3**: mp 197 °C; ^{1}H NMR($CDCl_3$) δ 5.57(dd, 1H, J = 8, 4 Hz, NC = CH), 7.13(d, 1H, J = 11 Hz, COCH =), 7.34(d, 1H, J = 11 Hz, COCH =), 7.49(dd, 1H, J = 4, 2 Hz, N = CH), 8.10(dd, 1H, J = 8, 2 Hz, NCH =); IR(KBr) 3090, 1630 cm^{-1}; MS m/e 163(M^+, 20), 107(4), 82(40), 79(26), 54(17), 27(9.6), 26(100). *Anal.* Calcd for $C_7H_5N_3O_2$: C, 51.54; H, 3.08; N, 25.75. Found: C, 51.42; H, 3.06; N, 26.10.

6,9-Dihydro-2-methyl-6,9-dioxopyridazino[1,2-*a*][1,2,3]triazine(4). Compound **4** was prepared from **1** (1.0 g, 7.8 mmol) and 4,4-dimethoxy-2-butanone (0.70 g, 7.8 mmol) by a similar method. Purification of the crude product by column chromatography on silica gel using ethyl acetate as eluting solvent and by recrystallization from ethyl acetate gave 1.0 g(70%) of pure **4**: mp 214 °C; ^{1}H NMR($CDCl_3$) δ 2.30(s, 3H, N=CCH_3), 5.71(d, 1H, J = 8 Hz, NC = CH), 7.06(d, 1H, J = 11 Hz, COCH =), 7.33(d, 1H, J = 11 Hz, COCH =), 8.10(d, 1H, J = 8 Hz, NCH =); IR(KBr) 3050, 1630, 1380, 680 cm^{-1}; MS m/e 177(M^+, 25.2), 121(10), 93 (20.1), 82(52.6), 54(100), 41(18.3). *Anal.* Calcd for $C_8H_7N_3O_2$: C, 54.24; H, 3.98; N, 23.71. Found: C, 54.00; H, 3.81; N, 24.46.

6,9-Dihydro-2,4-dimethyl-6,9-dioxopyridazino[1,2-*a*]-[1,2,3]triazine(5). Compound **5** was prepared from **1** (1.0 g, 7.8 mmol) and 2,4-pentanedione (0.78 g, 7.8 mmol) by a similar method. Recrystallization from ethyl acetate gave 1.2 g (79%) of pure **5**: mp 151-152 °C; ^{1}H NMR($CDCl_3$) δ 2.17(s, 3H, N-CCH_3), 2.46(d, 3H, J = 2 Hz, N = CCH_3), 5.56(d, 1H,

J = 2 Hz, NC = CH), 6.94(d, 1H, J = 11 Hz, COCH =), 7.20(d, 1H, J = 11 Hz, COCH =); IR(KBr) 3050, 1650, 1380, 680 cm^{-1}; MS m/e 191(M^+, 28.3), 163(0.9), 135(10.8), 107(12.3), 82(80.5), 81(2.6), 54(100), 41(8.7). *Anal.* Calcd for $C_9H_9N_3O_2$: C, 56.55; H, 4.74; N, 21.97. Found: C, 56.23; H, 4.65; N, 22.21.

6,9-Dihydro-2,4-diphenyl-6,9-dioxopyridazino[1,2-*a*]-[1,2,3]triazine(6). Compound **6** was prepared from **1** (1.0 g, 7.8 mmol) and 1,3-diphenyl-1,3-propanedione (1.8 g, 8.0 mmol) by a similar method. Recrystallization from ethyl acetate gave 1.8 g (73%) of pure **6**: mp 178 °C; ^{1}H NMR($CDCl_3$) δ 6.47(s, 1H, NC = CH), 7.02(d, 1H, J = 11 Hz, COCH =), 7.30(d, 1H, J = 11 Hz, COCH =), 7.40-8.15(m, 10H, 2 Ph); IR(KBr) 3080, 1670, 690 cm^{-1}; MS m/e 315(M^+, 51.1), 287 (9.3), 259(29.2), 231(8.2), 205(10), 103(22.3), 102(54.1), 82 (100), 54(71). *Anal.* Calcd for $C_{19}H_{13}N_3O_2$: C, 72.38; H, 4.13; N, 13.33. Found: C, 71.95; H, 4.21; N, 13.10.

6,11-Dihydro-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazine(7). Compound **7** was prepared from 2-amino-2,3-dihydro-1,4-phthalazinedione (**2**, 1.0 g, 5.6 mmol) and 1,1,3-3-tetramethoxypropane (0.92 g, 5.6 mmol) using PPA preheated to 75 °C by a similar method (reaction time and temperature, 40 min at 75 °C). Purification of the crude product by column chromatography on silica gel using chloroform as eluting solvent and by recrystallization from ethanol gave 0.3 g (25%) of pure **7**: mp 226-228 °C; ^{1}H NMR($CDCl_3$) δ 5.64 (dd, 1H, J = 8, 4 Hz, NC = CH). 7.45(dd, 1H, J = 4, 2 Hz, N = CH), 8.06(dd, 1H, J = 8, 2 Hz, NCH =), 7.90-8.72(m, 4H, C_6H_4); IR(KBr) 3090, 1650, 680 cm^{-1}; MS m/e 213(M^+, 30), 157(26), 129(21), 104(100), 103(44), 76(99), 66(16), 50(70), 28(49), 26(26). *Anal.* Calcd for $C_{11}H_7N_3O_2$: C, 62.00; H, 3.28; N, 19.70. Found: C, 60.33; H, 3.15; N, 19.17.

6,11-Dihydro-2-methyl-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazine(8). Compound **8** was prepared from **2** (1.0 g, 5.6 mmol) and 4,4-dimethoxy-2-butanone (0.65 g, 5.6 mmol) using PPA preheated to 85 °C by a similar method (reaction time and temperature, 40 min at 85 °C). Recrystallization from ethyl acetate gave 0.68 g (67%) of pure **8**: mp 195-196 °C; ^{1}H NMR($CDCl_3$) δ 2.24(s, 3H, N = CCH_3), 5.72 (d, 1H, J = 8 Hz, NC = CH), 7.90-8.65(m, 5H, C_6H_4 + NCH =); IR(KBr) 3100, 1630, 1370, 680 cm^{-1}; MS m/e 227(M^+, 53), 199(5), 171(34), 143(19), 132(3), 115(8), 104(100), 77(9), 76 (67), 41(2), 40(3). *Anal.* Calcd for $C_{12}H_9N_3O_2$: C, 63.46; H, 3.96; N, 18.49. Found: C, 62.75; H, 3.75; N, 18.20.

6,11-Dihydro-2,4-dimethyl-6,11-dioxo[1,2,3]triazino[1,2-*b*]phthalazine(9). Compound **9** was prepared from **2** (1.0 g, 5.6 mmol) and 2,4-pentanedione (0.58 g, 5.8 mmol) using PPA preheated to 95 °C by a similar method (reaction time and temperature, 40 min at 95 °C). Recrystallization from ethyl acetate gave 1.1 g (79%) of pure **9**: mp 161-162 °C; ^{1}H NMR($CDCl_3$) δ 2.20(s, 3H, N-CCH_3), 2,45(d, 3H, J = 2 Hz, N = CCH_3), 5.63(d, 1H, J = 2 Hz, NC = CH), 7.90-8.60(m, 4H, C_6H_4); IR(KBr) 3050, 1650, 1360, 690 cm^{-1}; MS m/e 241(M^+, 80), 213(2), 185(38), 157(17), 132(5), 104(100), 76(60), 41(5), 40(5). *Anal.* Calcd for $C_{13}H_{11}N_3O_2$: C, 64.75; H, 4.56; N, 17.42. Found: C, 64.71; H, 4.80; N, 17.49.

6,11-Dihydro-2,4-diphenyl-6,11-dioxo[1,2,3]triazino-[1,2-*b*]phthalazine(10). Compound **10** was prepared from **2** (1.0 g, 5.6 mmol) and 1,3-diphenyl-1,3-propanedione (1.3 g, 5.8 mmol) using PPA (8 g) preheated to 95 °C by a similar method (reaction time and temperature, 1 hr at 95 °C). Purification of the crude product by column chromatography on silica gel using chloroform as eluting solvent and by recrystallization from ethyl acetate-hexane gave 1.3 g (63%) of pure **10**: mp 188 °C; ^{1}H NMR($CDCl_3$) δ 6.62(s, 1H, NC = CH), 7.40-8.74(m, 14H, C_6H_4 + 2 Ph); IR(KBr) 3060, 1670, 690 cm^{-1}; MS m/e 365(M^+, 97.5), 337(6.6), 309(9.6), 281(8.5), 205(7.9), 132(5.0), 104(100), 103(9.4), 102(24.9). *Anal.* Calcd for $C_{23}H_{15}N_3O_2$: C, 75.62; H, 4 11; N, 11.51. Found: C, 76.02; H, 4.18; N, 11.73.

Reaction of 2 with 2,4-pentanedione in acetic acid. To a solution of 20 m*l* of acetic acid-ethanol (1:1) preheated to boiling point was suspended **2** (1.0 g, 5.6 mmol) with stirring. 2,4-Pentanedione (0.56 g, 5.6 mmol) was added and the resulting solution was refluxed for 10 min and allowed to cool to room temperature. The colorless solid formed was filtered and recrystallized from ethanol to give 1.0 g (70%) of 2-(1-methyl-3-oxobutylidene)amino-2,3-dihydro-1,4-phthalazinedione (**11**): mp 208.5 °C; ^{1}H NMR(DMSO-d_6) δ 1.76(s, 2.1 H, O = CCH_3), 1.84(s, 0.6H, O = CCH_3), 1.90(s, 0.3H, O-CCH_3), 2.02(s, 2.1H, N-CCH_3), 2.08(s, 0.3H, N = CCH_3), 2.28(s, 0.6 H, N = CCH_3), 2.35(s, 0.4 H, CH_2), 5.02(s, 0.1 H, O-C = CH), 5.28(s, 0.7 H, O = CCH =), 7.75-8.37(m, 4H, C_6H_4), 8.60(s, 0.7H, = NH), 11.30(br, 1.1 H, N = COH + C = COH); IR (KBr) 3000(br), 1670, 1570, 1270 cm^{-1}; MS m/e 259(M^+, 42), 244(6), 216(8), 202(100), 161(5), 133(7), 104(60), 43(86), 42(13). *Anal.* Calcd for $C_{13}H_{13}N_3O_3$: C, 60.41; H, 5.17; N, 15.72. Found: C, 60.25; H, 5.02; N, 16.21.

Cyclization of 11 to 9. Compound **11** (1.0 g, 3.9 mmol) was added to PPA (8 g) preheated to 95 °C and the mixture was stirred for 1 hr and allowed to cool to room temperature. Water (50 m*l*) was added and the resulting solution was extracted with chloroform (3 × 100 m*l*). The chloroform layer was washed with 10% aqueous $NaHCO_3$, dried over $MgSO_4$, and evaporated, yielding the crude product, which was recrystallized from ethyl acetate to give 0.86 g (92%) of pure **9**.

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O-Acylation of Heteropolyanions Containing Two Adjacent Vanadium Atoms

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Reaction of Keggin- or Dawson-type heteropolyanions containing two adjacent vanadium atoms with acetic anhydride in the presence of acid produced acylated anions. Heteropolyanions with one or no vanadium atom do not react under the same conditions, indicating that the acyl group is attached to the bridging oxygen atom between the two vanadium atoms. A characteristic infrared band at 1760 cm^{-1} was observed for the acylated anions. The 8-line EPR spectrum shows that one of the vanadium atoms is reduced to V(IV). The acylated heteropolyanions are easily hydrolyzed, and its acyl group can also be transferred to aniline.

Introduction

An interesting, new development in the chemistry of heteropolyanions is preparation of heteropolyanions attached with organic groups.[1] Since the surface of a heteropolyanion is similar to those of some metal oxides extensively used as heterogeneous catalysts for various organic reactions, organic derivatives of heteropolyanions may be useful in clarifying the mechanism of catalysis by metal oxides.

Most organic derivatives of the Keggin-structure heteropolyanions involve replacement of peripheral metal oxygen groups by other metal-ligand groups.[2-4] A rare type involves organic groups attached to the surface oxygen atoms of heteropolyanions, a good example being the O-alkylated anions.[5]

We have been trying to attach an acyl group to the surface oxygen atoms of heteropolyanions. So far we have not been able to obtain a crystalline product, the crystal structure of which may provide direct evidence for such acylation. But various experimental data indicate that such acylation occurs for heteropolyanions containing two adjacent vanadium atoms. Details are reported in this paper.

Experimental

Preparation of Compounds. α-1,2-$K_5[PV_2W_{10}O_{40}]$ (PV_2), α-1,2,3-$K_6[PV_3W_9O_{40}]$ (PV_3), α-1,2,3-$(Bu_4N)_4H_3[PV_3W_9O_{40}]$, α-1,2,3-$(Bu_4N)_4H_3[SiV_3W_9O_{40}]$ (SiV_3) and 1,2,3-$(Bu_4N)_3KH_5[P_2V_3W_{15}O_{62}]$ (P_2V_3) were prepared according to the methods in the literature.[6-8] PV_2 or PV_3 dissolved in water was reduced by one equivalent of hydrazine dihydrochloride, and the potassium salt of $[PV(IV)VW_{10}O_{40}]^{6-}$ or $[HPV(IV)V_2W_9O_{40}]^{6-}$ was precipitated by adding potassium chloride.[14,15]

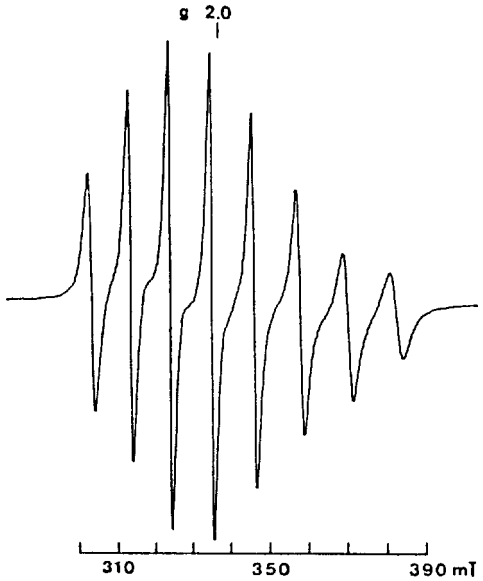

Figure 1. Solution EPR spectrum of $[(CH_3CO)PV(IV)VW_{10}O_{40}]^{5-}$.

Acylation. All of the above heteropolyanions or their one electron reduction products were acylated in the same manner. Here the procedure for PV_2 is described. 10 m*l* of acetic anhydride was added to 1g of PV_2. When a small amount (~0.3 m*l*) of boron trifluoride etherate was added to