Dibromotriphenylphosphorane Promoted Synthesis of Condensed Heterocyclic Systems from Aromatic Diamines

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A new and rather widely applicable method for the synthesis of a number of tri, tetra-, and pentacyclic compounds from *ortho*-aminodiacylarylimides and dibromotriphenylphosphorane *via* an intramolecular cyclization is reported. A mechanism for this cyclization is proposed.

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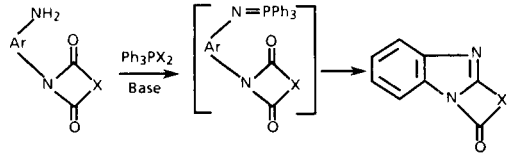
The synthesis of pyrido[1,2-*a*]indoles and pyrrolo[1,2-*a*]-indoles *via* an intramolecular Wittig reaction involving an imide was recently reported by us [1] and others [2].

We now wish to communicate on a similar ring closure starting with dibromotriphenylphosphorane and *ortho*-aminodiacylarylimides. It proceeds presumably by an aza-Wittig reaction according to Scheme I.

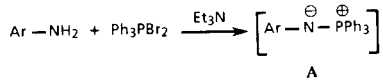
Scheme I



Ar = various aromatic species
X = various groups

Although intramolecular aza-Wittig reactions have been previously reported [3], to our knowledge a cyclization reaction between an imide carbonyl group and a phosphinimine has never been observed before. Thus, for the cyclization according to Scheme I to occur, a phosphinimine of type A, would be required. Generally the most widely applicable method for the synthesis of phosphinimines is the reaction of primary amines with dibromotriphenylphosphorane in the presence of at least two equivalents of triethylamine [4-6].

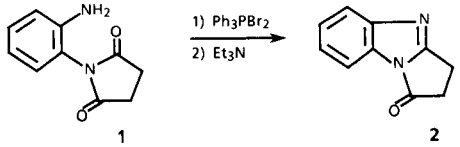
Scheme II



A

However, when *N*-[2-aminophenyl]-2,5-pyrrolidinedione **1** was treated with dibromodiphenylphosphorane and triethylamine 2,3-dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazol-1-one **2** was obtained directly (Scheme III).

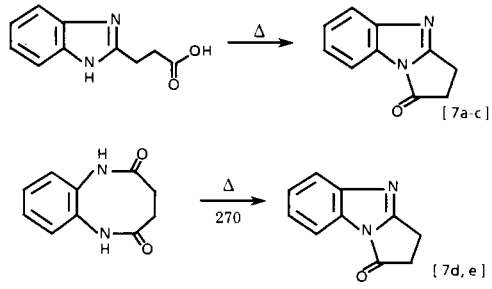
Scheme III



1 2

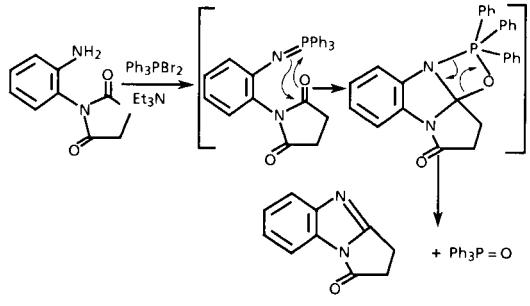
Compound **2** has previously been synthesized by two other routes both involving pyrolysis reaction at fairly high temperatures (Scheme IV). Physical constants of the product of our reaction agreed with the reported values by the previous authors.

Scheme IV



Even though we were not able to isolate the phosphinimine intermediate A according to Scheme II, we believe that the reaction pathway in the light of the cited previous results [4-6] is as shown in Scheme V.

Scheme V

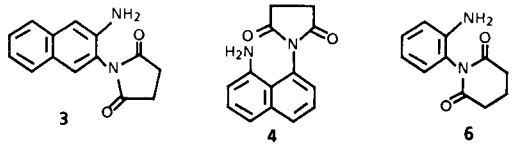


The *N*-substituted amines **1** and **3-9** were obtained by refluxing the appropriate diamines and acid anhydrides in tetrahydrofurane. They are reported in Table 1. The synthesis of **1** was previously reported by a multiple step reaction starting with 2-nitroaniline [8]. As expected, compounds **1** and **3-9** show a noticeable hydrogen bonding. Their ^{1}H-nmr spectra exhibit the absorption of the amino group protons as broad ill-defined signals at a rather low field generally in the area between δ 9-12. Further evi-

dence for hydrogen bonding was obtained from the ir spectra. Thus, *e.g.* compound **5** exhibited the peak for the amino group as a broad band between 3500-3100 cm^{-1}. The carbonyl groups caused medium strong bands at 1660 and 1600 cm^{-1}. The low frequencies positions for the imide carbonyl bonds can be explained by the effect of the hydrogen on the carbonyl stretching mode in this compound.

Table 1

N-[2-aminoaryl]2,5-pyrrolidiones and -piperidiones



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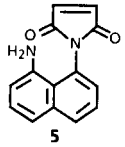

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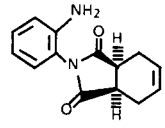

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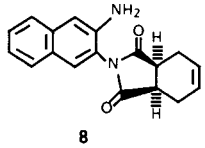

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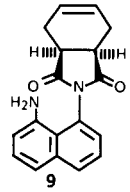

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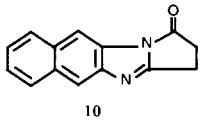
Compounds **1, 3-9** could then be used without purification or identification for the synthesis of the following heterocyclic compounds (Table 2) according to Scheme II.

Table 2
Novel Condensed Heterocyclic Systems



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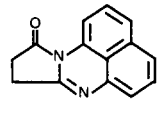

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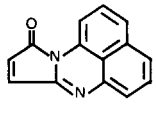

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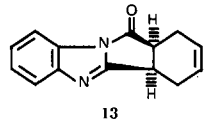

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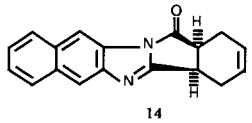

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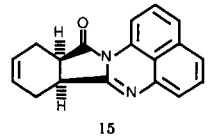

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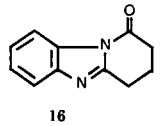

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EXPERIMENTAL

All melting points are uncorrected. Elemental analyses were obtained from MHW Laboratories, Phoenix, AZ. Proton magnetic resonance spectra were measured with an IBM FTQNMR 80 MHz using tetramethylsilane as an internal standard.

N-[2-Aminophenyl]-2,5-pyrrolidinedione (**1**).

This compound was obtained by refluxing 5 g of 1,2-phenylenediamine **17** (0.046 moles) and 5.1 g (1.1 equivalents) of succinic anhydride **18** in 15 ml of tetrahydrofuran for 10 hours. The resulting solid was collected and recrystallized from ethanol, 56% yield, mp 235-237°, (mp 230-232° [8c], 236-238° [8b], 244-245° [8a]).

N-[2-(3-Aminonaphthyl)]-2,5-pyrrolidinedione (**3**).

This compound was obtained analogously from 2,3-diaminonaphthalene **19** and **18**, 56% yield, mp 204-205° (pyridine/ethanol, 1:3); ^{1}H-nmr (deuteriodimethylsulfoxide): δ 2.4 (m, 4H), 7.4 (m, 2H), 7.8 (m, 2H), 8.1 (s, 1H), 9.3 (s, 1H), 12.1 (b, 2H).

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03. Found: C, 69.79; H, 5.14.

N-[1-(8-Aminonaphthyl)]-2,5-pyrrolidinedione (**4**).

This compound was obtained analogously from 1,8-diaminonaphthalene **20** and **18**, 64% yield, mp 280-281° (pyridine); ^{1}H-nmr (deuteriodimethylsulfoxide): δ 2.5 (m, 4H), 3.2 (b, 2H), 6.3 (m, 2H), 7.0 (m, 4H).

Anal. Calcd. for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03. Found: C, 69.86; H, 5.01.

N-[1-(8-Aminonaphthyl)]-2,5-pyrrolinedione (**5**).

This compound was obtained analogously from **20** and maleic anhydride, 60% yield, mp 269-271° (pyridine); ^{1}H-nmr (deuteriodimethylsulfoxide): δ 6.3 (m, 2H), 6.9 (m, 6H), 11.5 (b, 2H).

Anal. Calcd. for $C_{14}H_{10}N_2O_2$: C, 70.58; H, 4.23. Found: C, 70.44; H, 4.40.

N-[2-Aminophenyl]-2,6-piperidinedione (**6**).

This compound was obtained analogously from **17** and glutaric anhydride, 46% yield, mp 115-117° (ethanol); ^{1}H-nmr (deuteriodimethylsulfoxide): δ 2.0 (m, 2H), 2.5 (m, 2H), 3.0 (m, 2H), 7.1 (m, 2H), 7.5 (m, 2H). The peak due to the water molecule was partially obscured by a peak at δ ~ 2.8-3.0 due to a non-deuterated impurity of the deuteriodimethylsulfoxide.

Anal. Calcd. for $C_{11}H_{12}N_2O_2 \cdot H_2O$: C, 59.45; H, 6.35. Found: C, 59.39; H, 6.30.

Anal. Calcd. for $C_{11}H_{12}N_2O_2 \cdot H_2O$: C, 59.45; H, 6.35. Found: C, 59.39; H, 6.30.

cis-N-[2-Aminophenyl]-1,2,3,6-tetrahydrophthalic anhydride (**7**).

This compound was obtained analogously from **17** and *cis*-1,2,3,6-tetrahydrophthalic anhydride **21**, 53% yield, mp 262-263° (ethanol); ^{1}H-nmr (deuteriodimethylsulfoxide): δ 2.5 (m, 4H), 3.2 (m, 1H), 3.6 (m, 1H), 5.7 (s, 2H), 7.1 (m, 2H), 7.4 (m, 2H).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.40; H, 5.93. Found: C, 69.18; H, 5.80.

cis-N-[2-(3-Aminonaphthyl)]-1,2,3,6-tetrahydrophthalic anhydride (**8**).

This compound was obtained analogously from **19** and **21**, 53% yield, mp 270-272° (pyridine-ethanol); ^{1}H-nmr (deuteriodimethylsulfoxide): δ 2.6 (m, 4H), 3.3 (m, 1H), 3.7 (m, 1H), 5.8 (m, 2H), 7.2 (m, 2H), 7.8 (m, 4H), 12.0 (b, 2H).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52. Found: C, 74.04; H, 5.67.

cis-N-[1-(8-Aminonaphthyl)]-1,2,3,6-tetrahydrophthalic anhydride (**9**).

This compound was obtained analogously from **20** and **21** in 70% yield, mp 255-257° (pyridine-ethanol); ^{1}H-nmr (deuteriodimethylsulfox-

ide): δ 2.3 (m, 4H), 2.8 (m, 2H), 5.7 (m, 2H), 6.3 (m, 2H), 7.6 (m, 4H), 11.3 (b, 2H).

Anal. Calcd. for $C_{18}H_{16}N_2O_2$: C, 73.95; H, 5.52. Found: C, 73.77; H, 5.55.

2,3-Dihydro-1*H*-pyrrolo[1,2-*a*]benzimidazol-1-one (**2**).

A methylene chloride solution of 1 equivalent of dibromotriphenylphosphorane (from 1.38 g of triphenylphosphane and 0.84 g of bromine) was added dropwise to a solution of 1 g of **1** in 150 ml of methylene chloride; after adding to this mixture 2 equivalents of triethylamine (1.06 g, 10.52 mmoles) it was refluxed for 12 hours. The resulting solution was extracted with water. After drying the organic layer over anhydrous magnesium sulfate the solvent was distilled off. The remaining solid was recrystallized from ethanol, 60% yield, mp 175-176° (171-172° [7a,b], 170° [7c-d]); ^{1}H-nmr (deuteriochloroform): δ 3.18 (m, 4H), 7.3 (m, 2H), 7.65 (m, 1H), 7.85 (m, 1H).

Anal. Calcd. for $C_{10}H_8N_2O$: C, 69.75; H, 4.68; N, 16.27. Found: C, 69.99; H, 4.85; N, 16.27.

2,3-Dihydro-1*H*-naphtho[2,3-*d*]pyrrolo[1,2-*a*]imidazol-1-one (**10**).

This compound was obtained analogously from **3**, 36% yield, mp 262-264°; ^{1}H-nmr (deuteriochloroform): δ 3.3 (m, 4H), 7.5 (m, 2H), 7.9 (m, 2H), 8.1 (s, 1H), 8.4 (s, 1H).

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61. Found: C, 75.74; H, 4.50; N, 12.67.

8,9-Dihydro-10*H*-pyrrolo[1,2-*a*]perimidin-10-one (**11**) [9].

This compound was obtained analogously from **4**, 45% yield, mp 172-173°; ^{1}H-nmr (deuteriochloroform): δ 2.8 (m, 4H), 7.3 (m, 5H), 8.2 (dd, J_1 = 6.94, J_2 = 1.74 Hz, 1H).

Anal. Calcd. for $C_{14}H_{10}N_2O$: C, 75.66; H, 4.54; N, 12.61. Found: C, 75.55; H, 4.63; N, 12.84.

10*H*-Pyrrolo[1,2-*a*]perimidin-10-one (**12**) [10].

This compound was obtained analogously from **5**, 45% yield, mp 161-163°; ^{1}H-nmr (deuteriochloroform): δ 6.7 (d, J = 5.99 Hz, 1H), 7.3 (d, J = 5.99 Hz, 1H), 7.3 (m, 5H), 8.3 (dd, J_1 = 6.0, J_2 = 3 Hz, 1H).

Anal. Calcd. for $C_{14}H_8N_2O$: C, 76.35; H, 3.66; N, 12.72. Found: C, 76.52; H, 3.74; N, 12.86.

1,4,4a,11a-Tetrahydro-1*H*-isoindolo[2,1-*a*]benzimidazol-11-one (**13**).

This compound was obtained analogously from **7**, 48% yield, mp 141-142°; ^{1}H-nmr (deuteriochloroform): δ 2.5 (m, 4H), 3.7 (m, 2H), 5.8 (m, 2H), 7.3 (m, 2H), 7.8 (m, 2H).

Anal. Calcd. for $C_{14}H_{12}N_2O$: C, 74.98; H, 5.39; N, 12.49. Found: C, 75.09; H, 5.19; N, 12.46.

1,4,4a,13-Tetrahydro-13*H*-naphth[2′,3′:4,5]imidazo[2,1-*a*]isoindol-13-one (**14**).

This compound was obtained analogously from **8**, 51% yield, mp 206-208°; ^{1}H-nmr (deuteriochloroform): δ 2.6 (m, 4H), 3.7 (m, 2H), 5.9 (m, 2H), 7.5 (m, 2H), 7.9 (m, 2H), 8.1 (s, 1H), 8.3 (s, 1H).

Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.68; H, 5.22; N, 10.23.

7b,8,11,11a-Tetrahydro-12*H*-phthaloperin-12-one (**15**).

This compound was obtained analogously from **9**, 36% yield, mp 151-153; ^{1}H-nmr (deuteriochloroform): δ 2.6 (m, 4H), 3.2 (m, 2H), 5.9 (m, 2H), 7.2 (m, 5H), 8.1 (dd, J_1 = 6.5, J_2 = 1.9 Hz, 1H).

Anal. Calcd. for $C_{18}H_{14}N_2O$: C, 78.81; H, 5.14; N, 10.21. Found: C, 78.64; H, 5.04; N, 10.22.

Piperidino[1,2-*a*]benzimidazol-1-one (**16**).

This compound was obtained analogously from **6**, 39% yield, mp 124-126°; ^{1}H-nmr (deuteriochloroform): δ 2.0 (m, 2H), 2.8 (m, 2H), 3.1 (m, 2H), 7.3 (m, 2H), 7.6 (m, 1H), 8.15 (m, 1H).

Anal. Calcd. for $C_{11}H_{10}N_2O$: C, 70.95; H, 5.41; N, 15.05. Found: C, 70.99; H, 5.44; N, 14.89.

Acknowledgment.

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