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Synthesis of Imidazo[1,5-c][1,3]benzodiazepines *via* an Aza-Wittig/Carbodiimide-Mediated Annulation Process.

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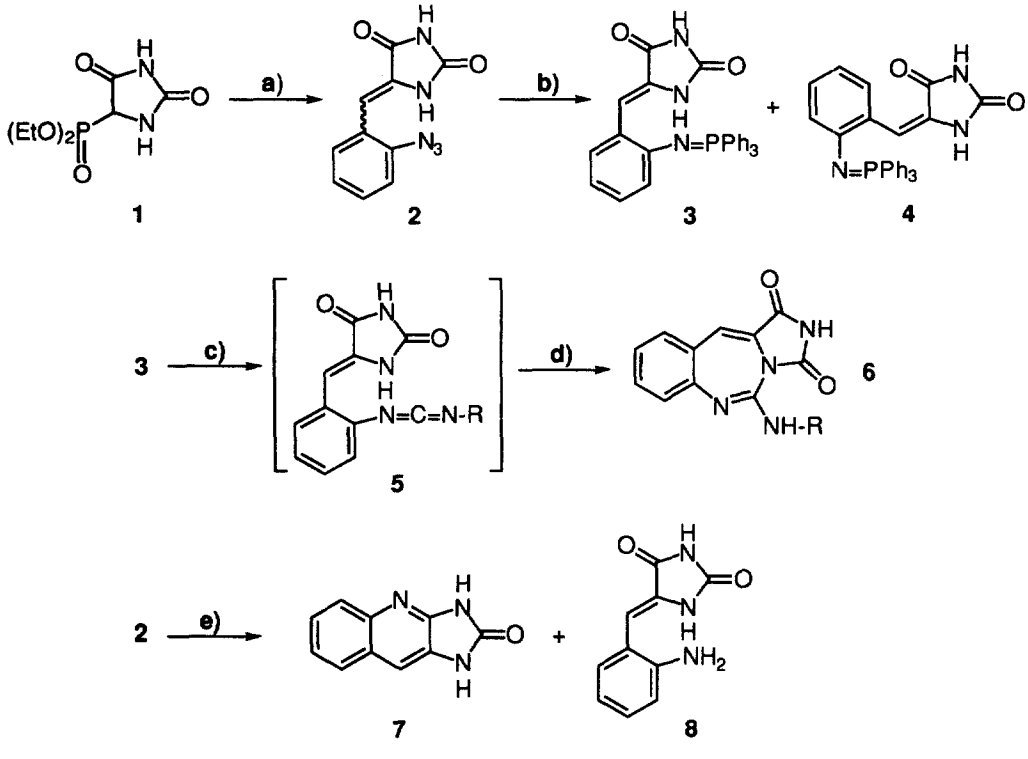
Abstract: The first synthesis of the imidazo[1,5-c][1,3]benzodiazepine ring system has been carried out by reaction of the iminophosphorane derived from the *(Z)*-5-(*o*-azidoarylidene)hydantoin with isocyanates. The isomeric *(E)*-tributyliminophosphorane undergoes intramolecular aza Wittig reaction to give the imidazo[4,5-b]quinolin-2-one ring. © 1997 Elsevier Science Ltd.

Classical methods for the preparation of fully unsaturated 1,3-diheteroseven-membered rings involve ring transformation of six-membered rings. In this sense, [1,3]benzodiazepines are synthesized by the photochemical ring expansion of quinoline-N-imides[1]. Recently two methods, based on the iminophosphorane chemistry, which allow the preparation of fully unsaturated fused [1,3]diazepines have appeared. The first one which involves intramolecular aza-Wittig reaction of iminophosphoranes derived from *o*-acylamino azidocinnamates, leads to [1,3]benzodiazepines[2] whereas in the second one, the reaction of bis(iminophosphoranes) derived from the pyrazole ring with isocyanates or acyl chlorides affords [1,3]pyrazolodiazepines[3].

Following our work on the preparation of azo-fused diazepines[4], we report now an efficient and general method for the preparation of the previously unreported tricyclic imidazo[1,3]benzodiazepine ring system. Our approach is based on the construction of the central seven-membered ring by nucleophilic attack of a NH group on the central carbon atom of a carbodiimide generated by aza-Wittig reaction. This methodology also allows the formation of the imidazo[4,5-b]quinolin-2-one ring, which has recently attracted attention as a synthetic target[5] because it forms the chromophoric element of the iron-chelating siderophore azotobactin[6]. In addition, some derivatives of this ring system are potent inhibitors of blood platelet low Km CAMP phosphodiesterase and induced aggregation and exhibit antithrombotic activity[7].

Reaction of *o*-azidobenzaldehyde[8] with a slight excess of phosphonate[5b] **1** in ethanol, in the presence of sodium ethoxide at room temperature provided the 5-arylidene hydantoin derivative **2** as a 1:1 mixture of *Z* and *E* isomers in 91% yield. All attempts to separate the isomers by column chromatography failed and only decomposition products were detected. For this reason, compound **2** was used without purification for the next step. Staudinger reaction of compound **2** with triphenylphosphine in dry acetonitrile afforded a 1:1 mixture of iminophosphoranes **3** and **4** which were separated by crystallization from ethanol in 33% and 22% yield, respectively. The ^{13}C n.m.r. spectrum of compound **3** shows a signal at 113.5 ppm due to the olefinic carbon atom, whereas in compound **4** this carbon atom appears at 108.7 ppm. An X-Ray structure determination confirmed unambiguously the *Z*-configuration of **3** (Fig. 1).



Reagents and conditions: a) *o*-azidobenzaldehyde, NaEtO, EtOH, r.t.; b) Ph_3P, CH_3CN, r.t.; c) R-NCO, CH_2Cl_2, r.t.; d) CH_2Cl_2, reflux; e) Bu_3P, CH_2Cl_2, r.t., then reflux.

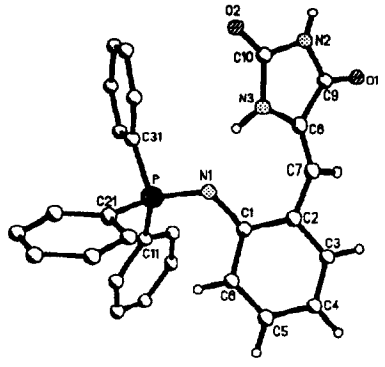


Figure 1. Labelling scheme of **3**.

Reaction of iminophosphorane **3** with a variety of aromatic isocyanates led directly to the previously unreported imidazo[1,5-c][1,3]benzodiazepines **6** in yields ranging from 65% to 85%. The experimental procedure is characterized by operational simplicity and isolation of **6** entails simply filtration of the crystalline products. This experimentally convenient sequence provides direct access to fused [1,3]diazepines in one-flask process. In general, this annulation reaction proceeded without complications for a range of substrates.

The i.r. of compounds **6** show two strong absorptions bands in the region 1771-1752 cm^{-1} and 1729-1714 cm^{-1} due to the two carbonyl groups. In the ^{13}C n.m.r. spectra the C-11 and C-5 carbon atoms appear at δ 116.7-116.9 ppm and 145.2-146.2 ppm, respectively, whereas the ^{1}H n.m.r. spectra shows the H-11 at δ 6.4-6.5 ppm.

The formation of fused diazepines **6** can be explained by an initial aza Wittig-type reaction between the iminophosphorane **3** and the isocyanate to give the carbodiimide **5** (as evidenced by i.r.), which undergoes cyclization by nucleophilic attack of the NH group of hydantoin ring on the central carbon atom of the carbodiimide moiety, to afford **6**.

On the other hand, attempts to promote the intramolecular aza-Wittig reaction in compound **4** failed even at temperatures higher than 200 °C for long periods of time. However, when the E/Z azide **2** was treated with tributylphosphine at room temperature and the resulting iminophosphoranes were heated at reflux temperature in dichloromethane, the 1,2-dihydroimidazo[4,5-b]quinolin-2-one[9] **7** (23%) and the 5-benzylidene hydantoin derivative **8** (35%) were isolated.

Formation of compound **7** probably occurs by intramolecular aza Wittig reaction of the initially formed *E* - iminophosphorane, which could not be isolated, whereas the *Z*-iminophosphorane was hydrolysed during the work-up to give **8**. This compound can be converted into **7** by a photo-assisted annulation reaction[10].

In conclusion, we have developed a simple and highly reliable iminophosphorane-mediated synthesis of the previously unreported imidazo[1,5-c][1,3]benzodiazepine ring system with varied substituents at the [1,3]diazepine ring. This relatively complex structures are assembled in a simple one-flask procedure in good yield, under mild conditions and from readily available starting material. It should be noted that this methodology also allows the preparation of the imidazo[4,5-b]quinolin-2-one ring. Although iminophosphorane-mediated synthesis of nitrogen heterocycles have been mainly utilized for five- and six-membered rings[11], this work significantly expands the scope of the method for the synthesis of seven-membered rings.

Experimental.

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained as Nujol emulsions on a Nicolet 5DX spectrophotometer. NMR spectra were re-corded on a Bruker AC 200 (200 MHz) or a Varian Unity 300 (300 MHz). Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer and on a VG AutoSpec Fisons instrument. Microanalyses were performed on a Perkin-Elmer 240C instrument.

X-Ray Crystallography

Crystal Data. $C_{28}H_{22}N_3O_2P$; Fwt. 463.46; monoclinic; $P2_1/c$; a = 8.2124(10) Å, b = 17.263(2) Å, c = 16.372(2) Å, b = 95.044(8)°; V = 2312.1(4) $Å^3$; Z = 4, D_{calc} 1.331 g/cm^{-3}; crystal size 0.62 x 0.40 x 0.38 mm; F_{000} 968; m(MoKa) 0.150 mm^{-1}.

Data Collection. A fluorescent yellow prism of **3** was mounted in inert oil on a glass fibre and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). Unit cell parameters were determined from a least-squares fit of 65 accurately centered reflections (10.3 < 2q < 25.1). A total of 9569 intensity data were collected at 173(2) K with graphite monochromated Mo-Ka radiation (l = 0.71073 Å) to $2q_{max}$ = 55°. Merging equivalents gave 5302 unique data (R_{int}= 0.022), which were used for calculations.

Structure Solution and Refinement. The structure was solved by the heavy-atom method and refined anisotropically on F^2 (program SHELXTL)[12]. The hydrogen atoms H02 and H03 (NH groups) were located in a difference Fourier synthesis and refined with a restrained N-H bond length. Other hydrogen atoms were included using a riding model. The final R(F) was 0.0353, for 316 parameters and 4071 obseved reflections [I > 2s(I)] and wR(F^2) was 0.0926 for all data. The weighting scheme was $w^{-1} = s^2(F^2) + (aP)^2 + bP$, where 3P = $(2F_c^2 + F_o^2)$ and a and b are constants adjusted by the program. Maximum D/s = 0.001, maximum Dr = 0.28 $eÅ^3$.

Preparation of 5-[(2-Azidophenyl)methylene]imidazolidin-2,4-dione **2**

To a cooled at 0°C solution of Na (0.07 g, 3 mmol) in dry ethanol (30 ml), diethyl 2,4-dioxoimidazolidine-5-phosphonate **1** (0.708 g, 3 mmol) was added in one portion, and the reaction mixture was stirred under nitrogen for 15 min. Then, a solution of o-azidobenzaldehyde (0.441 g, 3 mmol) in ethanol (20 ml) was added dropwise, and the mixture stirred under nitrogen for 18 h. The solvent was removed under reduced pressure and after addition of water (40 ml) a white solid precipitated which was separated by filtration, washed with water (20 ml) and dried to give **2**, in 91% yield, as a mixture of *Z/E* (1:1) isomers which was used without further purification.; m.p. 189-192°C. i.r. (Nujol): 3278, 3234, 2135, 2091, 1804, 1784, 1741, 1666, 1460, 1373, 1298, 1093, 999, 763, 732 cm^{-1}; ^1H n.m.r. δ (DMSO d_6): 6.37 (s, 1H), 6.47 (s, 1H), 7.02-7.37 (m, 6H), 7.59 (d, 1H, J=8.0 Hz), 8.04 (d, 1H, J=8.0 Hz), 10.50 (bs, 4H). ^{13}C n.m.r. δ (DMSO d_6): 102.2, 109.0, 117.9, 118.5, 124.0, 124.4, 124.5, 124.8, 129.1, 129.4, 129.5, 129.7, 130.5, 130.9, 137.6, 137.9, 153.9 (C=O), 155.6 (C=O), 163.4 (C=O), 165.3 (C=O); m/z (%): 229 (M^+, 6), 201 (6), 186 (3), 158 (35), 130(65), 103 (100), 76 (36), 71 (5).

Table 1 Selected bond lengths (Å) and angles (°) for **3**.

lengths (Å)			
P-N(1)	1.5920(11)	P-C(11)	1.8047(14)
P-C(31)	1.8074(14)	P-C(21)	1.8102(14)
O(1)-C(9)	1.225(2)	O(2)-C(10)	1.216(2)
N(1)-C(1)	1.395(2)	N(2)-C(9)	1.366(2)
N(2)-C(10)	1.400(2)	N(3)-C(10)	1.362(2)
N(3)-C(8)	1.395(2)	C(1)-C(6)	1.416(2)
C(1)-C(2)	1.422(2)	C(2)-C(3)	1.408(2)
C(2)-C(7)	1.468(2)	C(3)-C(4)	1.376(2)
C(4)-C(5)	1.386(2)	C(5)-C(6)	1.376(2)
C(7)-C(8)	1.335(2)	C(8)-C(9)	1.482(2)
angles (°)			
N(1)-P-C(11)	111.80(6)	N(1)-P-C(31)	105.86(6)
C(11)-P-C(31)	110.45(6)	N(1)-P-C(21)	114.98(6)
C(11)-P-C(21)	107.09(6)	C(31)-P-C(21)	106.54(7)
C(1)-N(1)-P	124.71(9)	C(9)-N(2)-C(10)	111.66(12)
C(10)-N(3)-C(8)	111.37(11)	N(1)-C(1)-C(6)	122.53(12)
N(1)-C(1)-C(2)	120.52(12)	C(6)-C(1)-C(2)	116.92(12)
C(3)-C(2)-C(1)	119.16(12)	C(3)-C(2)-C(7)	115.30(12)
C(1)-C(2)-C(7)	125.50(13)	C(4)-C(3)-C(2)	122.21(13)
C(3)-C(4)-C(5)	118.94(14)	C(6)-C(5)-C(4)	120.45(13)
C(5)-C(6)-C(1)	122.30(13)	C(8)-C(7)-C(2)	131.40(13)
C(7)-C(8)-N(3)	129.92(12)	C(7)-C(8)-C(9)	124.48(12)
N(3)-C(8)-C(9)	105.30(12)	O(1)-C(9)-N(2)	126.40(12)
O(1)-C(9)-C(8)	128.34(13)	N(2)-C(9)-C(8)	105.25(11)
O(2)-C(10)-N(3)	128.65(13)	O(2)-C(10)-N(2)	125.09(13)
N(3)-C(10)-N(2)	106.26(12)		

Preparation of (Z)- and (E)-5-[(2-Triphenylfosforanylideneaminophenyl)methylene]imidazolidin-2,4-dione **3** *and* **4.**

To a suspension of ***(Z/E)*-2** (0.916 g, 4 mmol) in dry acetonitrile (80 ml) a solution of triphenylphosphine (0.948 g, 4 mmol) in the same solvent (10 ml) was added dropwise under nitrogen and the mixture was stirred at room temperature for 18 h. The crude yellow solid precipitated was separated by filtration and after crystallization from ethanol (80 ml) the *Z*-isomer (0.61g, 33%) was isolated as yellow prisms. The filtrate was concentrated under reduce pressure and the residual product was chromatographed on a silica gel column with ethyl acetate/n-hexane (3:1) as eluent, to give the *E*-isomer (R_f=0.56) (0.40g, 22%), which was crystallized from ethanol (10 ml).

3: m.p. 189-190°C. (Found: C, 72.41; H, 4.63; N, 9.20. $C_{28}H_{22}N_3O_2P$ requires: C, 72.56; H, 4.78; N, 9.07). i.r. (Nujol): 3141, 1757, 1716, 1658, 1593, 1552, 1487, 1435, 1370, 1294, 1112, 1013, 901, 848, 778, 749, 725, 690 cm^{-1}; ^1H n.m.r. δ ($CDCl_3$): 6.49 (d, 1H, J=8.1 Hz), 6.68 (t, 1H, J=7.5 Hz), 6.80 (s, 1H), 6.82 (t, 1H, J=7.2Hz), 7.23 (d, 1H, J=7.8 Hz), 7.45-7.70 (m, 15H), 8.73 (s, 1H, NH), 10.67 (s, 1H, NH). ^{13}C n.m.r. δ ($CDCl_3$): 113.5, 118.3, 123.6 (d, J^{P-C}=12 Hz), 127.0, 128.4 (d, J^{P-C}=22 Hz), 128.9 (d, J^{P-C}=12 Hz), 129.0 (d, J^{P-C}=99 Hz), 129.4, 132.4 (d, J^{P-C}=3 Hz), 132.6 (d, J^{P-C}=10 Hz), 133.7 (d, J^{P-C}=3.5 Hz), 149.1 (d, J^{P-C}=3.5 Hz), 153.0 (C=O), 165.3 (C=O); m/z (%): 463 (M^+, 100), 277 (28), 276 (29), 262 (83), 207(20), 185(29), 183(99), 108(35), 77(17).

4: m.p. 196-197°C. (Found: C, 72.38; H, 4.70; N, 8.90. $C_{28}H_{22}N_3O_2P$ requires: C, 72.56; H, 4.78; N, 9.07). i.r. (Nujol): 3140, 1744, 1719, 1656, 1466, 1437, 1366, 1290, 1114, 752, 724, 684 cm^{-1}; ^1H n.m.r. δ (DMSO d_6):

6.30 (d, 1H, J=8.1 Hz), 6.48 (t, 1H, J=7.5 Hz), 6.74 (t, 1H, J=7.0 Hz), 7.51-7.80 (m, 16H), 8.25 (d, 1H, J=8.3 Hz), 10.33 (s, 1H, NH), 10.93 (s, 1H, NH). ^{13}C n.m.r. δ (DMSO d_6): 106.7, 117.2, 121.1 (d, J^{P-C}=11 Hz), 125.9, 127.0 (d, J^{P-C}=22 Hz), 129.2 (d, J^{P-C}=12 Hz), 129.6, 129.9(d, J^{P-C}=99 Hz), 132,1 (d, J^{P-C}=3 Hz), 132.2 (d, J^{P-C}=10 Hz), 133.4, 150.7, 155.6 (C=O), 166.0 (C=O)); m/z (%): 463 (M^+, 12), 277 (24), 276 (8), 262 (12), 207 (8), 185 (28), 183 (100), 108 (34), 77 (63);

General Procedure for the Preparation of 5-Aminosubstituted-1,3-dioxoimidazo[1,5-c][1,3]benzodiazepines **6**.

To a suspension of *(Z)*- **2** (0.463 g, 1 mmol) in dry dichloromethane (25 ml) an equimolecular amount of the appropriate isocyanate was added and the resulting mixture was stirred at room temperature under nitrogen until total formation of the corresponding carbodiimide which was then refluxed, under nitrogen, for 18 h. On cooling, the resulting solid was separated by filtration and recrystallized from ethanol to give **6**.

6a: (R=C_6H_5) red prisms, m.p. 240-241°C; (85%) (Found: C, 66.95; H, 3.80; N, 18.49. C_{17} $H_{12}N_4O_2$ requires: C, 67.10; H, 3.97; N, 18.41). i.r. (Nujol); 3150, 1761, 1716, 1634, 1563, 1462, 1369, 1284, 1244, 1102, 1009, 900, 775, 755, 666 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 6.43 (s, 1H), 6.78-6.91 (m, 2H), 7.07-7.19 (m, 4H), 7.33 (t, 2H, J=7.5 Hz), 7.61 (d, 2H, J=7.7 Hz), 9.73 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 116.8, 120.7, 123.4, 124.4, 126.2, 128.6, 128.8, 129.6, 132.1, 133.2, 136.9, 138.6, 145.3, 153.8 (C=O), 161.3 (C=O); m/z (%): 304 (M^+, 100), 275 (14), 260 (48), 233 (87), 205 (32), 187 (20), 156 (33), 129 (18), 116 (30), 103 (46), 77 (39).

6b: (R=*p* -CH_3-C_6H_4) red prisms, m.p. 280-282°C; (80%) (Found: C, 67.87; H, 4.52; N, 17.48. C_{18} $H_{14}N_4O_2$ requires: C, 67.92; H, 4.43; N, 17.60). i.r. (Nujol): 3199, 1771, 1715, 1662, 1610, 1386, 1297, 1247, 1108, 1007, 806, 762, 672 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 2.26 (s, 3H), 6.37 (s, 1H), 6.73-6.83 (m, 2H), 7.09-7.11 (m, 4H), 7.47 (d, 2H, J=7.0 Hz), 9.69 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 21.2, 116.9, 120.9, 124.1, 125.9, 128.5, 129.1, 131.9, 132.4, 133.0, 136.0, 136.7, 145.4, 153.6 (C=O), 161.0 (C=O); m/z (%): 318 (M^+, 100), 289 (14), 274 (52), 247 (75), 246 (60), 231 (31), 156 (21), 129 (12), 123 (30), 106 (8), 103 (24), 91 (31).

6c: (R=*o* -CH_3-C_6H_4) red needles, m.p. 229-231°C; (82%) (Found: C, 67.78; H, 4.38 ; N, 17.72. C_{18} $H_{14}N_4O_2$ requires: C, 67.92; H, 4.43; N, 17.60). i.r. (Nujol): 3164, 1752, 1719, 1636, 1615, 1572, 1289, 1107, 758, 725, 686 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 2.29 (s, 3H), 6.41 (s, 1H), 6.78 (d, 1H, J=7.7 Hz), 6.88 (d, 2H, J=7.4 Hz), 7.12-7.24 (m, 3H), 7.39 (s, 1H), 7.46 (d, 1H, J=8.1 Hz), 7.55-7.60 (m, 1H), 9.70 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 21.2, 116.8, 117.8, 121.1, 124.1, 124.3, 126.1, 128.5, 128.6, 129.4, 132.1, 133.1, 136.7, 138.0, 138.5, 145.3, 153.6 (C=O), 161.1 (C=O); m/z (%): 318 (M^+, 100), 289 (9), 275 (26), 247 (68), 246 (37), 231 (18), 156 (10), 123 (10), 103 (9), 91 (13).

6d: (R=*p* -CH_3O-C_6H_4) red prisms, m.p. 214-215°C; (78%) (Found: C, 64.76; H, 4.16; N, 16.87. C_{18} $H_{14}N_4O_3$ requires: C, 64.67; H, 4.22; N, 16.76). i.r. (Nujol): 3422, 3222, 1770, 1724, 1609. 1463, 1378, 1232, 1031, 745, 721 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 3.90 (s, 3H), 6.40 (s, 1H), 7.23-7.27 (m, 3H), 7.47-7.56 (m, 4H), 7.89 (d, 1H, J=8.0 Hz), 8.10 (d, 1H, J=7.8 Hz), 9.80 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 55.6, 111.4, 116.8, 119.9, 126.2, 128.9, 129.1, 129.6, 132.1, 133.2, 136.8, 140.0, 145.3, 153.5 (C=O, 155.5, 161.1 (C=O); m/z (%): 334 (M^+, 100), 290 (76), 263 (40), 220 (25), 146 (22), 131 (18), 103 (25).

6e: (R=*m* -CH_3O-C_6H_4) red prisms, m.p. 220-222°C; (83%) (Found: C, 64.82; H, 4.20; N, 16.66. C_{18} $H_{14}N_4O_3$ requires: C, 64.67; H, 4.22; N, 16.76). i.r. (Nujol): 3433, 3194, 1770, 1724, 1636, 1461, 1385, 1298, 1093, 767, 662 cm^{-1}; ^{1}H n.m.r. δ (DMSO d_6): 3.75 (s, 3H), 6.41 (s, 1H), 6.70-7.40 (m, 8H), 9.75 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 55.1, 106.1, 109.0, 112.7, 116.9, 124.5, 126.2, 128.4, 129.4, 129.5, 132.2, 133.2, 136.7,

139.8, 145.2, 153.6 (C=O), 159.6, 161.1 (C=O); m/z (%): 334 (M^+, 100), 290 (13), 263 (31), 220 (21), 131 (10), 103 (7).

6f: (R=*p* -Cl-C_6H_4) red prisms, m.p. 279-281°C; (69%) (Found: C, 60.09; H, 3.13; N, 16.59. $C_{17}H_{11}ClN_4O_2$ requires: C, 60.28; H, 3.27; N, 16.54). i.r. (Nujol): 3126, 1763, 1724, 1629, 1610, 1563, 1484, 1376, 1288, 1244, 1104, 1004, 829, 764, 671 cm^{-1}; ^1H n.m.r. δ (DMSO d_6): 6.41 (s, 1H), 6.80 (d, 1H, J=7.5 Hz), 6.88 (t, 1H, J=6.6 Hz), 7.12-7.18 (m. 2H), 7.25 (d, 2H, J=8.1 Hz), 7.63 (d, 2H, J=8.1 Hz), 9.78 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 116.7, 122.2, 124.5, 126.1, 126.9, 128.5, 129.5, 131.5, 133.1, 136.7, 137.5, 145.0, 153.6 (C=O), 161.2 (C=O); m/z (%): 340 (M^++2, 33), 338 (M^+, 100), 297 (5), 296 (10), 295 (15), 294 (24), 269 (15), 267 (45), 232 (37), 231 (25), 205 (32), 128 (3), 126 (8), 113 (5), 111 (15).

6g: (R=*p* -NO_2-C_6H_4) red prisms, m.p. 292-294°C; (65%) (Found: C, 58.28; H, 3.30; N, 20.25. $C_{17}H_{11}N_5O_4$ requires: C, 58.46; H, 3.17; N, 20.05). i.r. (Nujol): 3103, 1758, 1729, 1649, 1577, 1462, 1375, 1338, 1102, 851, 765, 664 cm^{-1}; ^1H n.m.r. δ (DMSO d_6): 6.42 (s, 1H), 6.91-6.97 (m, 2H), 7.16-7.19 (m, 2H), 7.85 (d, 2H, J=8.0 Hz), 8.19 (d, 2H, J=8.0 Hz), 10.17 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 116.7, 119.9, 124.9, 125.4, 126.5, 128.9, 130.2, 131.7, 132.1, 133.3, 141.9, 144.5, 144.9, 153.7 (C=O), 161.4 (C=O); m/z (%): 349 (M^+, 100), 320 (29), 306 (36), 278 (74), 277 (34), 261 (37), 232 (65), 231 (75), 230 (48), 205 (48), 156 (21), 138 (23).

6h: (R= C_6H_4-CH_2) red needles, m.p. 247-248°C; (79%) (Found: C, 68.10; H, 4.39; N, 17.46. $C_{18}H_{14}N_4O_2$ requires: C, 67.92; H, 4.43; N, 17.60). i.r. (Nujol): 3332, 3148, 1763, 1714, 1665, 1584, 1460, 1373, 1292, 1243, 756, 702, 670 cm^{-1}; ^1H n.m.r. δ (DMSO d_6): 4.53 (d, 2H, J=5.2 Hz), 6.36 (s, 1H), 6.68 (d, 1H, J=8.2 Hz), 6.77 (t, 1H, J=7.4 Hz), 7.06 (d, 2H, J=7.5 Hz), 7.27-7.37 (m, 5H), 8.18 (t, 1H, J=5.2 Hz), 9.30 (s, 1H). ^{13}C n.m.r. δ (DMSO d_6): 116.8, 123.3, 125.2, 126.9, 127.8, 128.4, 128.5, 128.7, 132.0, 132.9, 139.3, 140.8, 146.3, 153.5 (C=O), 161.4 (C=O); m/z (%): 318 (M^+, 88), 247 (14), 246 (20), 170 (28), 156 (17), 144 (18), 142 (16), 107 (46), 91 (100).

Preparation of 1,3-Dihydro-2H-imidazo[4,5-b]quinolin-2-one **7** *and 5-[(2-aminophenyl)methylene]imidazolidin-2,4-diones* **8.**

To a cooled at 0°C suspension of the mixture of isomers ***(E/Z)-* 2** (1:1) (0.55 g, 2.4 mmol) in dry dichloromethane (50 ml) a solution of 85% *n*-butylphosphine (2.4 mmol) was added dropwise under nitrogen. After stirring at room temperature for 14 h, the reaction mixture was heated under reflux for 24 h and on cooling the precipitated yellow solid formed, **8**, was separated by filtration and crystallized from ethanol. The filtrate was collected and evaporated under reduced pressure and the residue was chromatographed on a silica gel column with ethyl acetate/petroleum ether (40°-60°) (7:3) as eluent to give **7**, which was crystallized from acetic acid in 23% yield; m.p. 351-353°C [9].

8: yellow prisms, m.p. 323-325°C; (35%); (Found: C, 59.23; H, 4.50; N, 20.55. $C_{10}H_9N_3O_2$ requires: C, 59.11; H, 4.46; N, 20.68). i.r. (Nujol): 3393, 3318, 3248, 1755, 1718, 1679, 1468, 1386, 1245, 1199, 1111, 1011, 760, 656 cm^{-1}; ^1H n.m.r. δ (DMSO d_6): 5.38 (bs, 2H, NH_2), 6.45 (s, 1H), 6.60-7.17 (m, 5H), 8.20 (bs, 1H). ^{13}C n.m.r. δ (DMSO d_6): 105.6, 115.5, 116.4, 117.1, 127.3, 129.0, 129.5, 147.4, 155.4 (C=O), 165.5 (C=O); m/z (%): 203 (M^+, 48), 186 (53), 160 (5), 143 (17), 132 (100). 105 (19), 104 (68), 77 (37).

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