Tetrahedron Vol 45, No 6, pp 1823 to 1832, 1989
Printed in Great Britain

0040-4020/89 $3.00+.00

IMINOPHOSPHORANE-MEDIATED ANNELATION OF AN IMIDAZOLE RING INTO A BENZIMIDAZOLE RING: SYNTHESIS OF IMIDAZO[1,5-a]BENZIMIDAZOLE DERIVATIVES. CRYSTAL STRUCTURE OF 1-(4-METHOXYPHENYLIMINO)-2-(4-METHOXYPHENYLCARBAMOYL)-2,3-DIHYDRO-1H-IMIDAZO[1,5-a]BENZIMIDAZOLE

P. Molina*, M. Alajarín, C. López-Leonardo and I. Madrid.

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Murcia, 30001 Murcia, Spain.

C. Foces-Foces and F.H. Cano.

U.E.I. de Cristalografía, Instituto de Química Física "Rocasolano", Serrano 117. 28006 Madrid, Spain.

(*Received in UK 22 December* 1988)

Abstract - *1-Aroyl-2-azidomethylbenzimidazoles 2 react with tertiary phosphines to give the corresponding 1-aroyl-4H-imidazo[1,5-a]benzimidazoles 4. On the other hand, iminophosphorane 5 derived from 2-azidomethylbenzimidazole and triphenylphosphine, reacts with aromatic isocyanates to give 1-aryl-imino-2-arylcarbamoyl-2,3-dihydro-1H-imidazo[1,5-a]benzimidazoles 9. The molecular structure of 9 has been established by means of 2D-NMR analysis and X-ray crystallography.*

The aza-Wittig reaction of iminophosphoranes with heterocumulenes is a very useful reaction in synthetic heterocyclic chemistry[1]. Consequently, improvements which increase the efficiency or enlarge its applicability are always desirable and the discovery of novel functionalised iminophosphoranes bearing a moiety able to react with the aza-Wittig product is important in this respect.

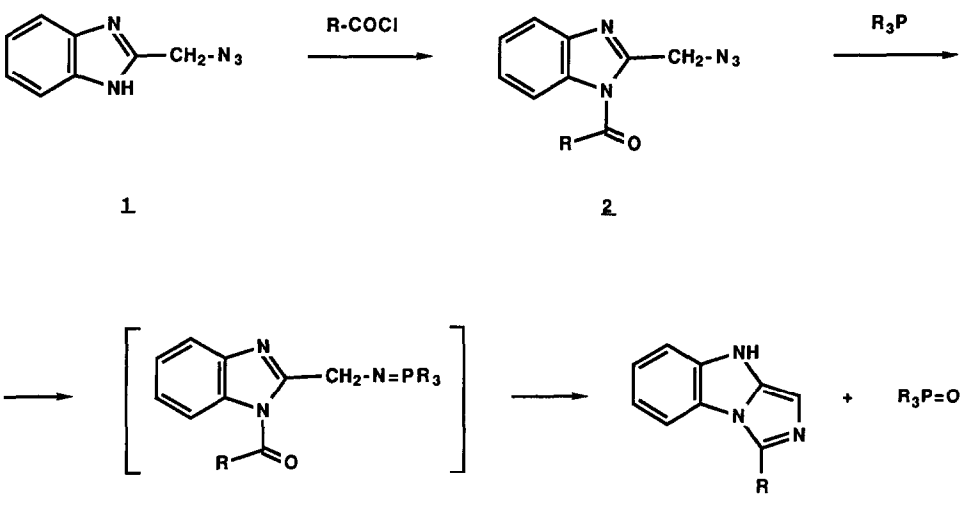
In the course of our studies directed toward the iminophosphorane-mediated synthesis of heterocycles we had occasion to explore heterocyclization reactions based on a tamden aza-Wittig reaction/heterocumulene-mediated anulation[2], intramolecular aza-Wittig reaction[3] and tamden aza-Wittig reaction/electrocyclic ring closure[4].

We now describe two general methods for the preparation of some derivatives of the otherwise not readily available imidazo[1,5-a]benzimidazole ring system. The first method involves reaction of 1-acyl-2-azidomethylbenzimidazoles with tributylphosphine. The second one is based on the reaction of the iminophosphorane derived from 2-azidomethylbenzimidazole with isocyanates. The imidazo[1,5-a]benzimidazole ring system is rare and its synthesis has been achieved in only a limited number of ways, mostly involving the use of 2-aminomethylbenzimidazoles as starting materials. These 2-aminomethylbenzimidazoles are either converted directly to imidazo[1,5-a]benzimidazoles by the action of aldehydes[5] or indirectly by processes involving acylation

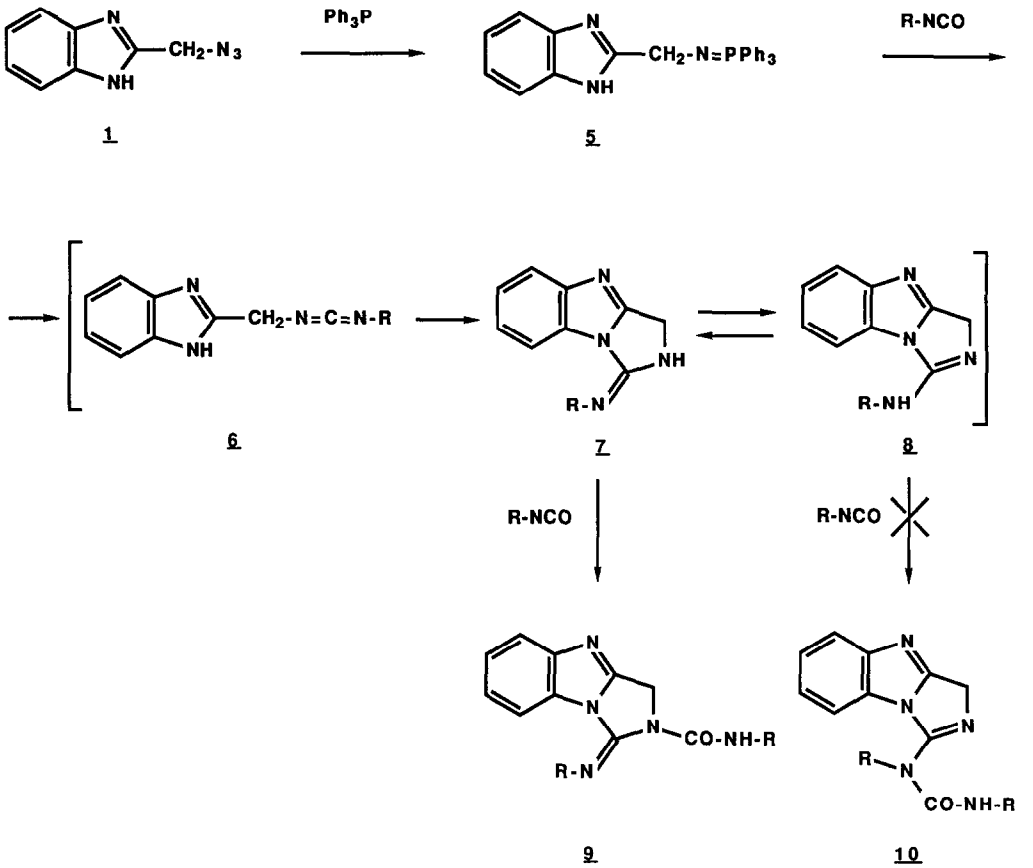
followed by cyclodehydration[6].

The 2-azidomethylbenzimidazole 1, readily available from 2-chloromethylbenzimidazol and sodium azide[7], is acylated to products 2 with carboxylic acid chlorides in a pyridine solution. The reaction of compounds 2 with tertiary phosphines in dry chloroform at room temperature leads directly to 1-susbtituted-4H-imidazo[1,5-a]benzimidazole 4 in good yields. Best results are obtained when tributylphosphine is used as cyclocondensation agent. We believe that the 2→4 conversion involves initial Staudinger reaction[8] to give an iminophosphorane derivative 3 as intermediate which easily undergoes intramolecular aza-Wittig reaction to give 4. Despite its apparent simplicity, intramolecular aza-Wittig reaction involving an amide carbonyl group is rare. To our knowledge it has been briefly mentioned[9] that iminophosphorane derived from N-acetyl ethylenediamine undergoes intramolecular aza-Wittig reaction at 180°C to give 2-methylimidazoline, but it remains as sole example.

The ^{1}H-NMR spectra of compounds 4 show among others a singlet at δ 6.75-7.10 ppm due to the H-3 proton; this chemical shift is in good agreement with the previously reported[10]; the NH proton appears at δ 11.30-11.70 ppm as a broad singlet. Mass spectra show the expected molecular ion peaks, being the peak at m/z 130 due to the fragment [M^+ - ArCN] the base peak.



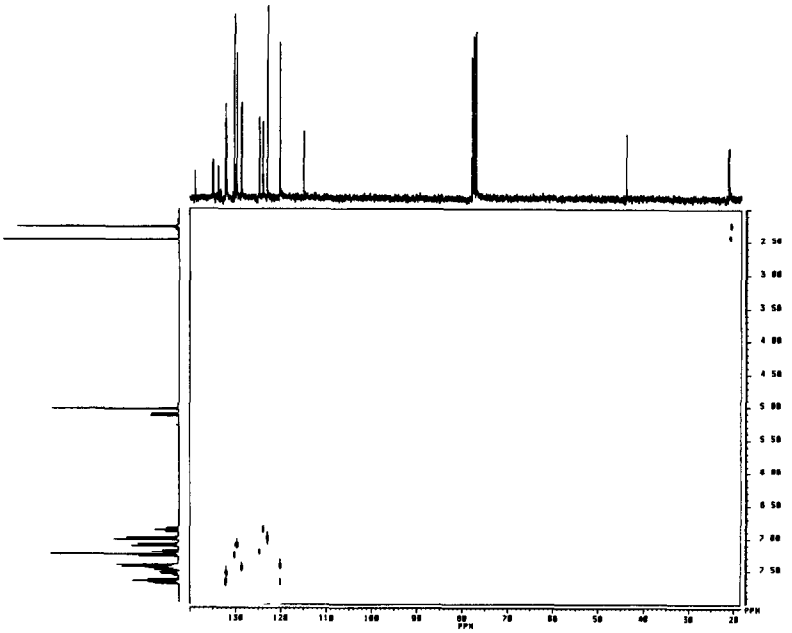
On the other hand iminophosphorane 5, readily available from 2-azidomethylbenzimidazole 1 and triphenylphosphine, reacts with aromatic isocyanates in dry benzene at room temperature to yield the corresponding imidazo[1,5-a]benzimidazole derivatives 9 in fair yields. The first indication of a structure type 9 or 10 is obtained from ^{1}H and ^{13}C-NMR spectra which clearly show that there are two groups of signals for the aryl residue; in addition, in the ^{1}H-NMR the methylene protons at position 3 appear at δ 5.03 ppm as a singlet, and the aromatic proton at position 10 is unusually shielded to δ 5.12 ppm as a doublet. In the ^{13}C-NMR spectra the carbon atoms at C-3 and C-10 positions appear at δ 43.47 ppm and 114.82 ppm respectively. The assignments have been done by 2D-NMR HCCOR and DEPT experiments.



1 5 6 7 8 9 10

However, the NMR data are consistent with both structures 9 and 10. In order to identify unambiguously the structure of the reaction product X-ray structure determination has been performed and its study confirms that the compound has the structure 9. Table 1 gives the main geometrical characteristics of the molecule (see Fig. 1). As far as the constitution is concerned it seems worth to note the localization of the double bonds at N5-C4 and at C1-N13. Angular asymmetry is present (see Table 1) around C1, C17, C22 and C28. The central five-membered ring is planar but the other one, fused to it, is not, adopting a quasi-twist conformation. The conformation of the molecule, as described by the torsion angles, leaves the -OMe substituents quite coplanar with the phenyl rings, with one oxygen , O31, involved in two intermolecular interactions, along the c axis, with phenyl hydrogen atoms. The C14,..,C19 ring is almost perpendicular to the C6,..,C11 fused ring, presenting contacts with it through H10 (see Fig. 1 and Table 1). The C25,..,C30 ring is separated from the mean plane of the fused system by small torsions, leaving O23 just in between H30 and H3A,B, the distance O23....H30 being shorter than the others. An intramolecular interaction is present at N24-H24...N13, but the angle at H24, the acceptor angles at N13 and the pseudo-torsion angles at N13...H24 and at N24-H24 (see Table 1) make it doubious hydrogen bond.

In summary, the NMR and X-ray studies confirm that compound 9 has the same structure in the solid state and in solution: 1-Arylimino-2-arylcarbamoyl-2,3-dihydro-1H-imidazo[1,5-a]benzimidazole.



2D-NMR HCCOR spectrum of compound 9b.

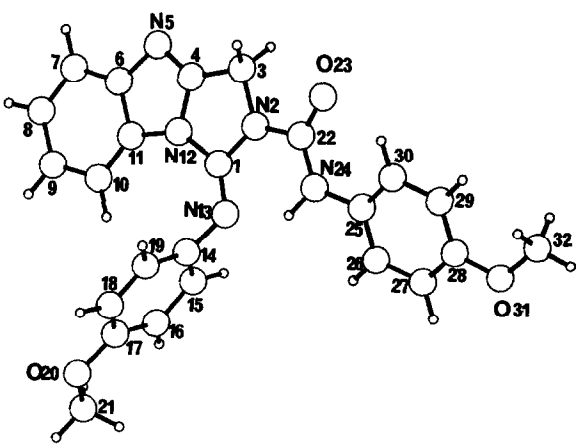


Fig.1. Molecular structure[11] of 9c with the numbering system used in the crystallographic work.

Table 1 . Selected geometrical parameters (A, °)

C1-N2	1.399(3)	C1-N12	1.406(3)
C1-N13	1.259(3)	N2-C3	1.465(4)
N2-C22	1.403(4)	C3-C4	1.482(5)
C4-N5	1.290(4)	C4-N12	1.382(3)
N5-C6	1.405(4)	C6-C11	1.405(4)
C11-N12	1.407(3)	N13-C14	1.417(3)
C17-O20	1.378(3)	O20-C21	1.400(5)
C22-O23	1.210(4)	C22-N24	1.339(4)
N24-C25	1.416(4)	C28-O31	1.380(4)
O31-C32	1.415(4)		
N12-C1-N13	132.4(2)	N2-C1-N13	123.0(2)
N2-C1-N12	104.6(2)	C1-N2-C22	128.6(2)
C1-N2-C3	113.6(2)	C22-N2-C3	117.6(2)
N2-C3-C4	100.6(2)	C3-C4-N12	109.6(3)
C3-C4-N5	135.1(3)	C3-C4-N12	115.3(3)
C4-N5-C6	103.3(3)	N5-C6-C11	112.0(2)
C6-C11-N12	103.4(2)	C4-N12-C11	106.1(2)
C1-N12-C11	142.2(2)	C4-N12-C1	111.4(2)
C1-N13-C14	125.1(2)	N13-C14-C19	119.6(2)
N13-C14-C15	121.8(2)	C16-C17-O20	124.7(3)
C18-C17-O20	115.0(3)	N2-C22-N24	115.3(2)
N2-C22-O23	118.2(3)	O23-C22-N24	126.5(3)
C22-N24-C25	126.9(2)	C27-C28-O31	116.0(2)
C29-C28-O31	124.7(2)	C28-O31-C32	117.7(2)
H24...N13-C1	97(1)	H24...N13-C14	137(1)
N2-C1-N12-C4	3.7(3)	N12-C1-N2-C3	-1.6(3)
C1-N2-C3-C4	-0.9(3)	N2-C3-C4-N12	3.2(3)
C3-C4-N12-C1	-4.5(3)	N12-C1-N13-C14	-9.2(5)
C1-N13-C14-C19	-82.0(4)	C16-C17-O20-C21	6.8(5)
C3-N2-C22-O23	4.2(4)	C1-N2-C22-N24	10.4(4)
N2-C22-N24-C25	171.5(2)	C22-N24-C25-C30	19.5(4)
C29-C28-O31-C32	-7.8(4)		
C1-N13...H24-N24	15(4)	N13...H24-N24-C22	-14(4)
N13....N24	2.691(3)	N13....H24	1.97(4)
N13....H24-N24	136(3)	N24-H24	0.91(3)
O23....H3A	2.75(4)	O23....H3B	2.62(4)
O23....H30	2.37(3)	C14....H10	2.57(3)
O31....H9i	2.65(4)	O31....H18ii	2.67(4)
i= -1/2+x, 1/2-y, 3/2+z		ii= -1/2+x, 1/2-y, 1/2+z	

Presumably the conversion 5 → 9 involves initial aza-Wittig reaction between the iminophosphorane 5 and the isocyanate to give a carbodiimide 6 as highly reactive intermediate which undergoes cyclization by nucleophilic attack of the NH group of the benzimidazole ring on the more reactive "aliphatic" substituted C=N double bond of the carbodiimide moiety[12] to give 1-arylimino-2,3-dihydro-1H-imidazo[1,5-a]benzimidazole 7 which by reaction with the isocyanate leads to 9. Although reaction of carbodiimides with several amino compounds have been reported[13], to our knowledge this is the first example reported of heterocyclization based on the reaction of carbodiimides with the NH group of the imidazole ring.

In conclusion, the results presented here confirm that the not readily available imidazo[1,5-a]benzimidazole ring system may be prepared under mild conditions from readily available starting materials.

EXPERIMENTAL

All melting points were determined using a Kofler hot-stage microscope and are uncorrected; I.R. spectra were recorded with a Nicolet FT 5DX spectrometer. ^{1}H and ^{13}C-NMR spectra were recorded on one of the following spectrometers: Varian FT-80 (80 MHz) and Varian XL-300 (300 MHz). Two-dimensional spectra were recorded using standard conditions[14]. Mass spectra (70 eV) were obtained using a Hewlett-Packard 5993C instrument. Combustion analyses were performed with a Perkin-Elmer 240C instrument.

The crystallographic analysis is summarized in Table 2 and the final atomic coordinates are presented in Table 3. Lists of the structure factors, thermal components and hydrogen parameters have been deposited[15].

TABLE 2. Crystal analysis parameters at room temperature

Crystal data	
Formula	$C_{24}H_{21}N_5O_3$
Crystal habit	Transparent prism
Crystal size (mm)	0.50 x 0.27 x 0.17
Symmetry	Monoclinic, $P2_1/c$
Unit cell determination:	Least-squares fit from 92 reflections ($\theta < 45°$)
Unit cell dimensions	17.2890(8), 22.3531(11), 5.4243(1)Å, β=97.216(3)°
Packing: $V(A^3)$, Z	2079.7(2), 4
$Dc(g.cm^{-3})$, M, F(000)	1.365, 427.46, 896
$\mu(cm^{-1})$	7.20
Experimental data	
Technique	Four circle diffractometer Bisecting geometry Graphite oriented monochromator: CuK_α $\omega/2\theta$ scans, scan width: 1.6° Detector apertures 1.0x1.0°
Total measurements	Up to 65° in θ
Speed	1 min./reflec.
Number of reflections:	
Independent	3544
Observed	2528 [$3\sigma(I)$ criterion]
Standard reflections:	2 reflections every 90 minutes Variation: no
Solution and refinement	
Solution	Direct methods
Refinement	L.S. on F_{obs}, full matrix
Parameters:	
Number of variables	373
Degrees of freedom	2155
Ratio of freedom	6.8
H atoms	Difference synthesis
Final shift/error	0.04
Weigthing scheme	Empirical as to give no trends in $<w\Delta^2F>$ vs.$<\|Fobs\|>$ or $<\sin\theta/\lambda>$
Max. thermal value	$U_{33}[023]=0.132(2)Å^2$
Final ΔF peaks	0.26 $e.Å^{-3}$
Final R and R_w	0.048, 0.054
Computer and programs	VAX 11/750 XRAY76 System[15], Multan80[16]
Scattering factors	Int.Tables for X-Ray Crystallography[17]

TABLE 3.FINAL ATOMIC COORDINATES AND THERMAL PARAMETERS AS IN :

$$U_{eq} = (1/3).\ \Sigma\ (U_{ij}.a^*_i.a^*_j.a_i.a_j.\mathrm{Cos}(a_i,a_j))$$

ATOM	x/a	y/b	z/c	$U_{eq}.10^4$
C1	0.5556(1)	0.1627(1)	0.8006(5)	488(7)
N2	0.5610(1)	0.1096(1)	0.9381(4)	575(7)
C3	0.6298(2)	0.0736(1)	0.9047(7)	704(11)
C4	0.6656(2)	0.1113(1)	0.7245(6)	642(10)
N5	0.7252(2)	0.1062(1)	0.6045(6)	776(10)
C6	0.7233(2)	0.1593(1)	0.4653(5)	629(10)
C7	0.7746(2)	0.1775(2)	0.3004(6)	764(12)
C8	0.7618(2)	0.2322(2)	0.1881(6)	741(12)
C9	0.7003(2)	0.2690(2)	0.2366(6)	668(10)
C10	0.6483(2)	0.2512(1)	0.3964(5)	557(8)
C11	0.6602(1)	0.1960(1)	0.5068(4)	503(8)
N12	0.6228(1)	0.1632(1)	0.6789(4)	504(7)
N13	0.4992(1)	0.1984(1)	0.7978(5)	634(8)
C14	0.4952(1)	0.2558(1)	0.6858(5)	486(8)
C15	0.4491(2)	0.2668(1)	0.4639(5)	545(9)
C16	0.4415(2)	0.3255(1)	0.3708(5)	609(9)
C17	0.4794(2)	0.3716(1)	0.5029(6)	607(9)
C18	0.5250(2)	0.3606(1)	0.7214(6)	670(10)
C19	0.5313(2)	0.3037(1)	0.8130(6)	647(10)
O20	0.4762(2)	0.4307(1)	0.4296(5)	921(10)
C21	0.4251(3)	0.4470(2)	0.2195(9)	923(16)
C22	0.5133(2)	0.0896(1)	1.1122(5)	598(9)
O23	0.5338(1)	0.0459(1)	1.2351(5)	991(10)
N24	0.4481(1)	0.1213(1)	1.1220(4)	579(7)
C25	0.3856(2)	0.1067(1)	1.2565(5)	497(8)
C26	0.3153(2)	0.1346(1)	1.1822(5)	557(8)
C27	0.2506(2)	0.1221(1)	1.2974(5)	588(9)
C28	0.2553(2)	0.0811(1)	1.4895(5)	538(8)
C29	0.3259(2)	0.0543(1)	1.5690(5)	579(9)
C30	0.3911(2)	0.0672(1)	1.4530(5)	573(9)
O31	0.1872(1)	0.0710(1)	1.5913(4)	717(7)
C32	0.1874(2)	0.0248(2)	1.7698(7)	758(13)

1-Aroyl-2-azidomethylbenzimidazoles 2.

To a well-stirred solution of 2-azidomethylbenzimidazole 1 (3.98 g, 23 mmol) in pyridine (25 ml), the appropriate aroyl chloride (23 mmol) was added. The reaction mixture was stirred at room temperature for 2 h and the solution was poured on to ice/water. The precipitated solid was separated by filtration, washed with water (3x20 ml), ethanol (2x10 ml) and finally recrystallized from acetone/n-hexane (1:1 v/v) to give 2. The following derivatives 2 were obtained:

2a 1-Phenyl (83%), m.p.67-69°C (colourless needles). (Found: C 65.15; H 3.92; N 25.17. $C_{15}H_{11}N_5O$ requires: C 64.97; H 4.00; N 25.26); i.r. (Nujol): 2095 (s), 1715 (vs), 1308 (s), 1257 (s), 1211 (s), 1177 (m), 1098 (m), 752 (m) and 701 (m) cm^{-1}; δ ($CDCl_3$): 4.95 (s, 2H), 6.80 (dd, 1H), 7.0-8.1 (m, 8H); m/z (%): 277 (M^+, 10), 235 (9), 220 (15), 105 (100), 90 (15), 77 (64), 63 (12), 51 (21).

2b 1-(p-Tolyl) (72%), m.p. 78-80°C (colourless prisms). (Found: C 65.82; H 4.69; N 23.92. $C_{16}H_{13}N_5O$ requires: C 65.97; H 4.50; N 24.04); i.r. (Nujol): 2101 (s), 1698 (vs), 1608 (m), 1347 (m), 1302 (s), 1262 (s), 1217 (s), 1177 (s), 922 (m), 906 (m), 832 (m), 768 (m) and 752 (s) cm^{-1}; δ ($CDCl_3$) 2.60 (s, 3H), 4.95 (s, 2H), 7.10 (dd, 1H), 7.3-8.1 (m, 7H); m/z (%): 291 (M^+, 10), 249 (6), 236 (8), 234 (18), 120 (15), 119 (100), 91 (36), 90 (13), 65 (20).

2c 1-(p-Methoxyphenyl) (60%), m.p. 87-88°C (colourless needles). (Found: C 62.43; H 4.34; N 22.57. $C_{16}H_{13}N_5O_2$ requires: C 62.53; H 4.26; N 22.79); i.r. 2095 (s), 1687 (vs), 1602 (s), 1574 (m), 1511 (m), 1313 (m), 1296 (m), 1262 (s), 1177 (s), 1030 (m), 922 (m), 849 (m) and 735 (s)

cm^{-1}; δ ($CDCl_3$): 4.00 (s, 3H), 4.95 (s, 2H), 7.0-7.5 (m, 5H), 7.7-8.2 (m, 3H); m/z (%): 307 (M^+, 10), 265 (5), 145 (5), 136 (15), 135 (100), 107 (11), 92 (18), 77 (19).

2d 1-(p-Chlorophenyl) (68%), m.p. 74-76°C (colourless needles). (Found: C 57.93; H 3.33; N 24.31. $C_{15}H_{10}ClN_5O$ requires: C 57.80; H 3.23; N 22.47); i.r. (Nujol): 2101 (s), 1698 (vs), 1591 (m), 1381 (m), 1347 (m), 1313 (s), 1296 (s), 1262 (s), 1217 (s), 1087 (m), 922 (m), 769 (m) and 735 (s) cm^{-1}; δ ($CDCl_3$): 4.95 (s, 2H), 6.85 (dd, 1H), 7.2-8.1 (m, 7H); m/z (%): 313 (M^++2, 3), 311 (M^+, 9), 271 (2), 269 (6), 256 (6), 254 (15), 141 (35), 139 (100), 113 (15), 111 (39), 90 (11).

2e 1-(p-Bromophenyl) (70%), m.p. 93-95°C (colourless needles). (Found: C 50.63; H 2.72; N 19.74. $C_{15}H_{10}BrN_5O$ requires: C 50.58; H 2.83; N 19.66); i.r. (Nujol): 2101 (s), 1704 (vs), 1693 (s), 1585 (s), 1545 (m), 1313 (m), 1262 (s), 1212 (s), 1183 (m), 1064 (m), 1013 (m), 922 (s), 905 (s), 764 (s) and 736 (s) cm^{-1}; δ ($CDCl_3$): 5.00 (s, 2H), 6.85 (dd, 1H), 7.1-7.5 (m, 4H), 7.9-8.2 (m, 3H); m/z (%): 357 (M^++2, 5), 355 (M^+, 5), 315 (5), 313 (5), 300 (7), 298 (7), 185 (99), 183 (100), 157 (36), 155 (37), 104 (10), 90 (15), 76 (23).

General Procedure for the Preparation of 1-Aryl-4H-imidazo[1,5-a]benzimidazoles 4.

To a solution of the appropriate 1-aroyl-2-azidomethylbenzimidazole 2 (1 mmol) in dry chloroform (5 ml), a solution of tributylphosphine (0.20 g, 1 mmol) in dry ether was added. After the reaction mixture had been stirred at room temperature for 2 h a precipitated solid was deposited. The crude material was separated by filtration and recrystallized from dimethylsulfoxide to give 4. Elimination of the solvent from the filtrate leads to a crude product which was found to be tributylphosphine oxide. The following derivatives 4 were obtained:

4a 1-Phenyl (57%), m.p. 217-219°C (colourless needles). (Found: C 77.18; H 4.87, N 17.92. $C_{15}H_{11}N_3$ requires: C 77.23; H 4.75; N 18.01); i.r. (Nujol): 1653 (m), 1619 (s), 1591 (vs), 1517 (s), 1336 (m), 1313 (m), 1245 (m), 968 (m), 741 (s), 724 (s) and 701 (s) cm^{-1}; δ (DMSO-d_6): 6.80 (s, 1H), 7.2-8.2 (m, 9H), 11.30 (s broad, 1H); m/z (%): 233 (M^+, 15), 131 (10), 130 (100), 129 (10), 105 (11), 103 (58), 102 (10), 77 (25).

4b 1-(p-Tolyl) (58%), m.p. 163-165°C (colourless needles). (Found: C 77.63; H 5.25; N 17.19. $C_{16}H_{13}N_3$ requires: C 77.71; H 5.30; N 16.99); i.r. (Nujol): 1622 (vs), 1610 (s), 1532 (m), 1469 (s), 1245 (m), 1090 (m), 976 (m), 818 (m), 737 (s) and 710 (s) cm^{-1}; δ (DMSO-d_6): 2.40 (s, 3H), 6.75 (s, 1H), 7.2-8.1 (m, 8H), 11.40 (s broad, 1H); m/z (%): 247 (M^+, 100), 131 (10), 130 (80), 118 (10), 117 (15), 103 (41), 91 (10), 90 (30), 76 (10).

4c 1-(p-Methoxyphenyl) (60%), m.p. 166-168°C (colourless needles). (Found: C 73.15; H 4.79; N 16.09. $C_{16}H_{13}N_3O$ requires: C 72.99; H 4.98; N 15.96); i.r. (Nujol): 1619 (vs), 1531 (s), 1291 (m), 1244 (s), 1027 (m), 975 (m), 840 (m), 740 (s), 723 (s) and 705 (m) cm^{-1}; δ (DMSO-d_6): 3.90 (s 3H), 6.80 (s, 1H), 7.1-8.1 (m, 8H), 11.30 (s broad, 1H); m/z (%): 263 (M^+, 89), 248 (15), 161 (15), 133 (87), 130 (100), 107 (10), 103 (72), 76 (19).

4d 1-(p-Chlorophenyl) (57%), m.p. 220-222°C (colourless needles). (Found: C 67.21; H 3.85; N 15.62. $C_{15}H_{10}ClN_3$ requires: C 67.30; H 3.77; N, 15.70); i.r. (Nujol): 1619 (vs), 1591 (s), 1336 (m), 1279 (m), 1245 (m), 1149 (m), 1092 (s), 1019 (m), 973 (s), 832 (s), 741 (s), 713 (s) and 696 (s) cm^{-1}, δ (DMSO-d_6): 7.10 (s, 1H), 7.3-8.4 (m, 8H), 11.70 (s broad, 1H); m/z (%): 269 (M^++2, 19), 267 (M^+, 57), 137 (10), 135 (6), 130 (100), 113 (4), 111 (12), 103 (60), 90 (30), 76 (21).

4e 1-(p-Bromophenyl) (65%), m.p. 227-229°C (colourless needles). (Found: C 57.85; H 3.16; N 13.62. $C_{15}H_{10}BrN_3$ requires: C 57.71; H 3.23; N 13.46); i.r. (Nujol): 1619 (vs), 1591 (s), 1506 (s), 1336 (m), 1246 (m), 1092 (m), 1070 (m), 973 (m), 826 (m), 741 (s) and 713 (s) cm^{-1}; δ (DMSO-d_6): 6.90 (s, 1H), 7.2-8.2 (m, 8H), 11.50 (s, broad, 1H); m/z (%): 313 (M^++2, 18), 311 (M^+, 18), 183 (10), 181 (10), 157 (5), 155 (5), 130 (100), 103 (47), 90 (19), 76 (14).

2-Triphenylphosphoranylideneaminomethylbenzimidazole 5.

To a well stirred solution of 2-azidomethylbenzimidazole 1 (2 g, 11.5 mmol) in dry chloroform (20 ml), a solution of triphenylphosphine (3.16 g, 12 mmol) in dry benzene was added dropwise and the reaction mixture was stirred at room temperature for 1 h . The separated solid was collected by

filtration, air-dried and recrystallized from chloroform to give title iminophosphorane 5 (4.2 g, 82 %) as white prisms, m.p. 167-169°C. (Found: C 76.64; H 5.44; N 10.31, $C_{26}H_{22}N_3P$ requires: C 76.49; H 5.40; N 10.16); i.r. (Nujol): 1528 (m), 1445 (s), 1438 (vs), 1421 (s), 1319 (m), 1257 (m), 1211 (s), 1121 (m), 1100 (m), 741 (vs), 718 (s) and 696 (s) cm^{-1}; δ ($CDCl_3$): 4.75 (d, 2H, J_{H-P} = 18 Hz), 7.2-8.0 (m, 20H); m/z (%): 407 (M^+, 5), 277 (36), 276 (77), 201 (37), 199 (34), 183 (41), 152 (34), 148 (32), 119 (59), 118 (35), 77 (100).

General Procedure for the Preparation of 1-Arylimino-2-arylcarbamoyl-2,3-dihydro-1H-imidazo[1,5-a]benzimidazoles 9.

To a solution of the iminophosphorane 5 (0.407 g, 1 mmol) in dry benzene (15 ml), the appropriate aryl isocyanate (2 mmol) was added. The resultant solution was stirred at room temperature for 5 h and the precipitated solid was collected by filtration, dried and recrystallized from n-hexane/chloroform (1·1 v:v) to give 9. Elimination of the solvent from the filtrate leads to a crude product which recrystallized from diethyl ether gave triphenylphosphine oxide. The following derivatives 9 were obtained.

9a 1-Phenylimino-2-phenylcarbamoyl (83%), m.p. 214°C (colourless needles). (Found: C 72.18; H 4.53; N 18.91. $C_{22}H_{17}N_5O$ requires: C 71.92; H 4.66; N 19.06); i.r. (Nujol): 1721 (vs), 1602 (m), 1557 (s), 1353 (s), 1313 (m), 1223 (m), 1183 (m), 752 (m), 718 (m) and 684 (m) cm^{-1}; δ ($CDCl_3$): 5.10 (s, 2H), 5.12 (d, 1H), 6.6-7.9 (m, 13H), 11.76 (s broad, 1H); m/z (%): 367 (M^+, 10), 248 (20), 131 (100), 119 (32), 104 (15), 91 (17), 90 (10), 73 (13).

9b 1-(p-Tolylimino)-2-(p-tolylcarbamoyl) (64%), m.p. 186°C (colourless needles). (Found: C 72.94; H 5.21, N 17.53. $C_{24}H_{21}N_5O$ requires: C 72.89; H 5.35; N 17.71); i.r. (Nujol): 1710 (vs), 1636 (m), 1602 (m), 1557 (m), 1506 (m), 1347 (m), 1313 (m), 1285 (m), 1223 (m), 1183 (m), 1126 (m), 1081 (m), 815 (m), 735 (m), 718 (m) and 696 (m) cm^{-1}; δ ($CDCl_3$): 2.30 (s, 3H), 2.57 (s, 3H), 5.22 (s, 2H), 5.41 (d, 1H), 7.1-8.1 (m, 11H), 8.68 (s, 1H); m/z (%): 395 (M^+, 5), 262 (18), 134 (7), 133 (67), 131 (100), 105 (10), 104 (37), 91 (20), 77 (22).

9c 1-(p-Methoxyphenylimino)-2-(p-methoxyphenylcarbamoyl) (48%), m.p. 212°C (colourless prisms). (Found: C 67.32; H 5.13; N 16.53. $C_{24}H_{21}N_5O_3$ requires: C 67.44; H 4.95; N 16.38); i.r. (Nujol): 1710 (vs), 1625 (s), 1562 (s), 1511 (s), 1347 (s), 1319 (s), 1285 (s), 1245 (s), 1217 (s), 1036 (s), 769 (m), 747 (m), 724 (m) and 696 (m) cm^{-1}; δ ($CDCl_3$): 4.88 (s, 3H), 5.00 (s, 3H), 6.12 (s, 2H), 6.37 (d, 1H), 6.9-7.9 (m, 11H), 11.73 (s, 1H); m/z (%): 427 (M^+, 6), 278 (16), 150 (10), 149 (100), 131 (78), 121 (15), 107 (10), 106 (61).

9d 1-(p-Chlorophenylimino)-2-(p-chlorophenylcarbamoyl) (40%), m.p. 195°C (colourless needles). (Found: C 60.36; H 3.56; N 15.91. $C_{22}H_{15}Cl_2N_5O$ requires: C 60.56; H 3.46; N 16.05); i.r. (Nujol): 1698 (vs), 1625 (s), 1612 (m), 1557 (s), 1489 (s), 1325 (s), 1310 (m), 1240 (m), 1189 (m), 1092 (m), 837 (m), 809 (m), 792 (m), 760 (m) and 747 (m) cm^{-1}; δ ($CDCl_3$): 5.21 (s, 2H), 5.42 (d, 1H), 7.1-8.1 (m, 11H), 11.70 (s, 1H); m/z (%): 437 (M^++2, 2), 435 (M^+, 6), 282 (10), 155 (20), 154 (6), 153 (55), 131 (100), 127 (10), 125 (31), 113 (5), 111 (13), 90 (23).

9e 1-(m-Tolylimino)-2-(m-Tolylcarbamoyl) (50%), m.p. 178°C (colourless needles). (Found: C 73.10, H 5.25; N 17.63. $C_{24}H_{21}N_5O$ requires: C 72.89; H 5.35; N 17.71); i.r. (Nujol): 1710 (vs), 1630 (s), 1596 (s), 1568 (s), 1319 (s), 1240 (m), 1206 (m), 1126 (m), 775 (m), 741 (m) and 718 (m) cm^{-1}; δ ($CDCl_3$): 3.90 (s, 6H), 5.10 (s, 2H), 5.35 (d, 1H), 6.8-7.9 (m, 11H), 11.70 (s, 1H); m/z (%): 395 (M^+, 5), 262 (20), 134 (10), 131 (100), 104 (35), 91 (20).

9f 1-(m-Methoxyphenylimino)-2-(m-methoxyphenylcarbamoyl) (58%), m.p. 189-190°C (colourless needles). (Found: C 67.31; H 5.16; N 16.22. $C_{24}H_{21}N_5O_3$ requires: C 67.44; H 4.95; N 16.38); i.r. (Nujol): 1710 (vs), 1636 (m), 1596 (s), 1562 (s), 1355 (s), 1325 (s), 1279 (m), 1257 (m), 1211 (m), 1160 (m), 1121 (m), 1053 (m), 1036 (m), 951 (m), 803 (m), 769 (m), 741 (m) and 724 (m) cm^{-1}; δ ($CDCl_3$): 3.86 (s, 6H), 5.10 (s, 2H), 5.40 (d, 1H), 6.6-7.8 (m, 11H), 11.36 (s, 1H); m/z (%): 427 (M^+, 6), 278 (20), 149 (70), 131 (100), 120 (15), 107 (8), 106 (27).

9g 1-(m-Chlorophenylimino)-2-(m-chlorophenylcarbamoyl) (52%), m.p. 190°C (colourless needles).

(Found: C 60.34; H 3.66; N 15.89. $C_{22}H_{15}Cl_2N_5O$ requires: C 60.56; H 3.46, N 16.05); i.r. (Nujol): 1715 (vs), 1630 (m), 1591 (s), 1551 (m), 1353 (m), 1319 (m), 1217 (m), 798 (m), 775 (m), 736 (m), 722 (m) and 697 (m) cm^{-1}; δ ($CDCl_3$): 5.10 (s, 2H), 5.30 (d, 1H), 6.8-7.9 (m, 11H), 11.56 (s, 1H); m/z (%): 437 (M^++2, 3), 435 (M^+, 9), 282 (15), 155 (29), 154 (8), 153 (100), 131 (72), 125 (51), 111 (5), 90 (62).

Acknowledgements.

The authors wish to thank to Dirección General de Investigación Científica y Técnica for financial support, Project number PB86-0039.

References

1.- Molina, P.; Bull. Soc. Chim. Belg., 1986, 95, 973 and references cited therein.

2.- Molina, P.; Alajarín, M.; Vidal, A; Tetrahedron Lett., 1988, 3849.

3.- Molina, P.; Alajarín, M.; Vidal, A; Elguero, J.; Claramunt, R. M.; Tetrahedron, 1988, 44, 2249.

4.- Molina, P.; Arques, A.; Vinader, M. V.; Becher, J.; Brondum, K.; Tetrahedron Lett., 1987, 4451; ibid, J. Org. Chem., 1988, 53, 4654; Molina, P.; Fresneda, P. M.; Vinader, M. V.; Foces-Foces, M. C.; Cano, F.H.; Chem. Ber., in the press.; Molina, P.; Fresneda, P. M.; J. Chem. Soc. Perkin Trans. I, 1988, 1819.

5.- Schubert, H.; Lettau, M.; Fischer, J.; Tetrahedron, 1974, 30, 1231; Saczewski, F.; Foks, H.; Sawlewicz, J.; Acta Pol. Pharm., 1984, 41, 31.

6.- Aryuzina, V. M.; Shchukina, M. N.; Khim. Geterotsikl. Soedin., 1966, 605; 1968, 509; 1970, 525; 1973, 395.

7.- Hideg, K.; Hankovszky, H. O.; Synthesis, 1978, 313.

8.- Staudinger, H.; Meyer, J.; Helv. Chim. Acta, 1919, 2, 635.

9.- Gololobov, Y. G.; Gusar, N. I.; Chaus, M. P.; Tetrahedron, 1985, 41, 793.

10.- Takeuchi, T.; Yeh, H. J. C.; Kirk, K. L.; Cohen, L. A.; J. Org. Chem., 1978, 43, 3565.

11.- Motherwell, W. D. S. (1978) PLUTO. A program for plotting crystal and molecular structures: Cambridge University. England.

12.- Ulrich, H.; Richter, R.; Tucker, B., Chem. Ber., 1987, 120, 849; J. Heterocyclic Chem., 1987, 24, 1121.

13.- Mikolajczyk, M.; Kielbasinsky, P.; Tetrahedron, 1981, 37, 233.

14.- Croasman, W. R.; Carlson, R. M. K.; Two-Dimensional NMR Spectroscopy. Application for Chemist and Biochemist, VCH, New York, 1987.

15.- Structure factors, thermal components and hydrogen parameters are available on request from the Director of the Cambridge Cristallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompained by the full literature citation for this paper.

16.- Stewart, J. M., Machin, P. A.; Dickinson. C. W.; Ammon. H. L.; Heck, H.; Flack, H.; The X-Ray System (1976). Technical report TR-446. Computer Science Center. University of Maryland. USA.

17.- Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declerq, J. P.; Woolfson, M. M.; Multan 80 System (1980). University of York. England.

18.- International Tables for X-ray Crystallography (1974) vol. 4. Birmingham. Kynoch Press. England.