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Ring opening with molybdenum hexacarbonyl of functionalized isoxazoles is a valuable synthetic process. Tetrazolopyridine **4** and pyrazolopyridine **9** were obtained from isoxazolopyridines **3** and **6**, respectively, whereas the isoxazole **14** gave ketone **16** through the intermediate **17**.

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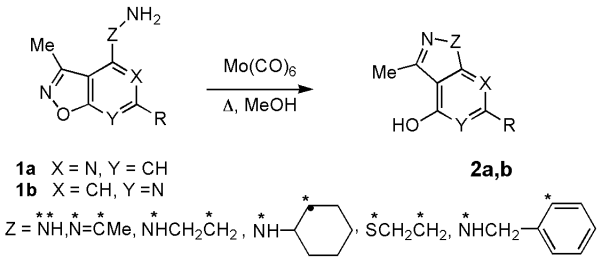
Recently we reported [1] that ring opening - ring closure of suitably substituted 3-methylisoxazolopyridines in the presence of $Mo(CO)_6$ is an efficient and versatile procedure for the preparation of functionalized pyrido-condensed heterocycles, an important class of biologically active molecules. In this way, from compounds **1** we

Scheme 1



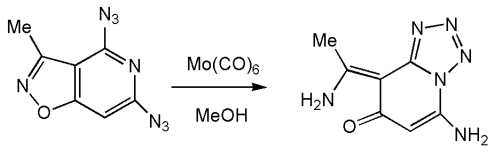
obtained the heterocycles **2**, containing from five to eight atoms in the ring condensed to the pyridine moiety. All the products are formed by NH_2 attack on keto/imino group obtained after the reductive ring opening of isoxazole by the $Mo(CO)_6$.

For a deeper insight of this reaction, we planned to consider a series of isoxazole derivatives in which the final condensation of the NH_2 group is strongly prevented. In this way other possible pathways may be opened, and the synthetic potentiality of the reaction extended.

i) When 4,6-diazido-3-methylisoxazolo[4,5-c]pyridine **3** was heated with $Mo(CO)_6$ we obtained the tetrazolopyridone **4**, whose X-ray structural determination we recently reported [2].

In this case, in addition to the expected reductive ring opening of the isoxazole, chemoselective reduction of the

Scheme 2



6-azido group and tetrazole formation by the 4-azido group was observed (Scheme 2). The extensive delocalization of the tetrazole ring electrons, as deduced from X-ray structure [2], stabilizes the enaminic form of compound **4**.

ii) Compound **6** (with a small quantity of **7**) was obtained by site-selective nucleophilic substitution of 4,6-dichloro-3-methylisoxazol[5,4-*b*]pyridine **5** with 2-aminobenzylamine (Scheme 3).

Reaction of $Mo(CO)_6$ on 4-substituted amine **6** yielded two compounds, which were separated by crystallization. One of these was the expected acetylpyridone **8**, but any attempt to cyclize this compound to obtain the pyridoazocine **10** was unsuccessful, only giving decomposition material. The second product was identified as 1-(2-aminobenzyl)-6-chloro-3-methyl-1,5-dihydro-pyrazolo[4,3-*c*]pyridin-4-one **9**, on the basis of X-ray structure determination (Figure 1 and Tables 1 and 2) of the *N*-methyl-derivative **11**, obtained with the corresponding *O*-methyl-derivative **12** by reaction of **9** with diazomethane.

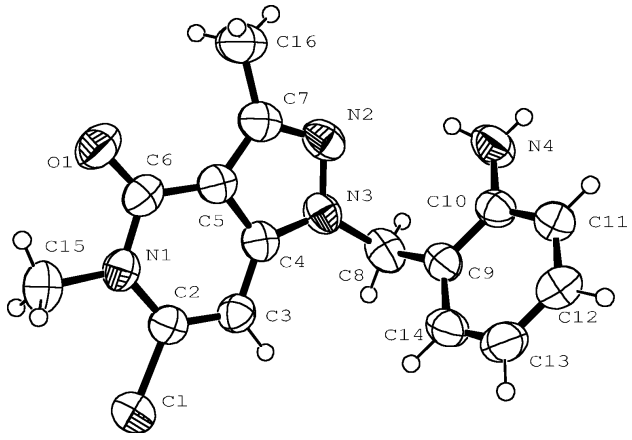


Figure 1. ORTEP plot of pyrazolopyridone **11**.

It is to be noted that the formation of the pyrazole **9** requires the attack of the nitrogen in position 4 onto the isoxazole nitrogen, probably by way of a nitrene-like intermediate [3]. This process was not found for the [4,5-*c*] condensed system [1] and it was previously observed only

Scheme 3

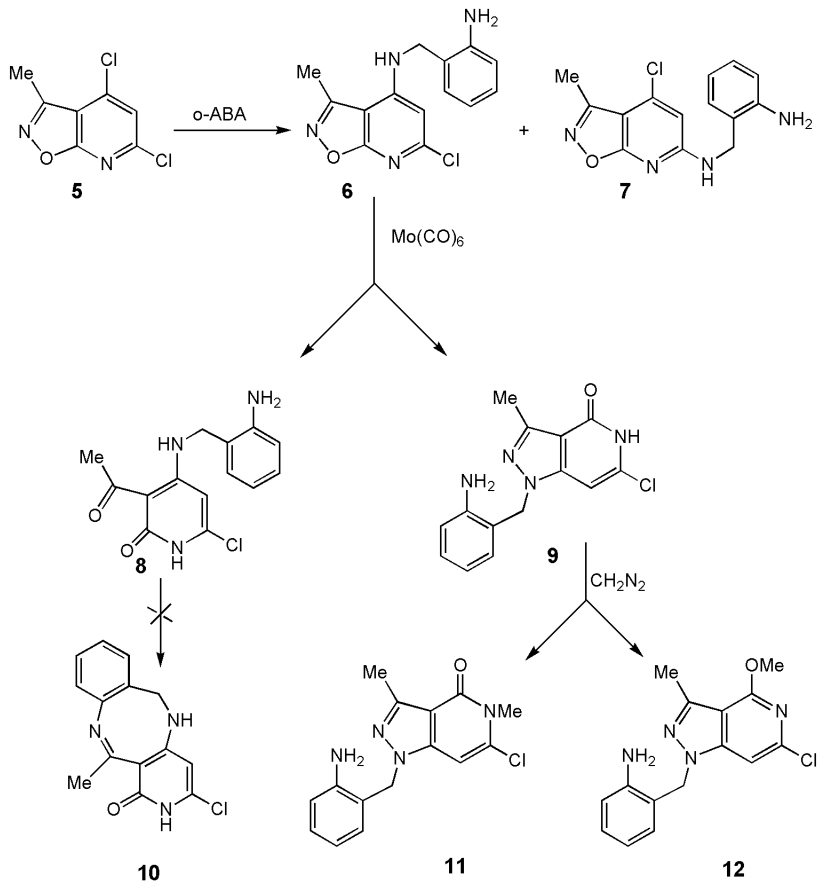


Table 1

Single Crystal X-Ray Crystallographic Analysis of **11**

Empirical formula	$C_{15}H_{15}ClN_4O$
Formula weight	302.76
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 7.366(1)Å alpha = 90°
	b = 10.695(1)Å beta = 98.09(1)°
	c = 18.500(2)Å gamma = 90°
Volume	1442.9(3) A^3
Z	4
Calculated density	1.394 Mg/m^3
Absorption coefficient	0.269 mm^{-1}
F(000)	632
Crystal size	0.4 x 0.2 x 0.15 mm
Theta range for data collection	2.21 to 25.00 °
Limiting indices	-1<=h<=8,-1<=k<=12,-21<=l<=21
Reflections collected	3542
Indipendent reflections	2543 [R(int) = 0.0216]
Observed reflections [I>2σ(I)]	1987
Completeness to theta = 25.00	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2543/0/250
Goodness-of-fit on F^2	1.047
Final R indices [I>2σ(I)]	R1 = 0.0399, wR2 = 0.0941
R indices (all data)	R1 = 0.0548, wR2 = 0.1026
Largest diff. peak and hole	0.137 and -0.263 $e.A^{-3}$

in the course of photochemical rearrangement of isoxazolopyridine derivatives [4] or when isothiazolopyridines were formed by reaction of $Mo(CO)_6$ with isoxazolopyridine-4-thiols [5].

Considering that the analogous [4,5-*c*] derivative gave the azocine in good yields with no trace of the corresponding pyrido-pyrazole, this case shows that the ring junction plays an important, but not easy explicable, role. Further work is planned to rationalize this factor.

iii) Finally, we considered non condensed isoxazoles. Compound **14** was chosen also as a part of our interest for hindered phenols with potential antioxidant properties [6] and it can be prepared from 4-bromomethylisoxazole **13** (Scheme 4) by electrophilic attack on the corresponding phenol. In this case, reaction of $Mo(CO)_6$ on **13** afforded, as reported in the Scheme 4, the aromatic ketone **16**. The

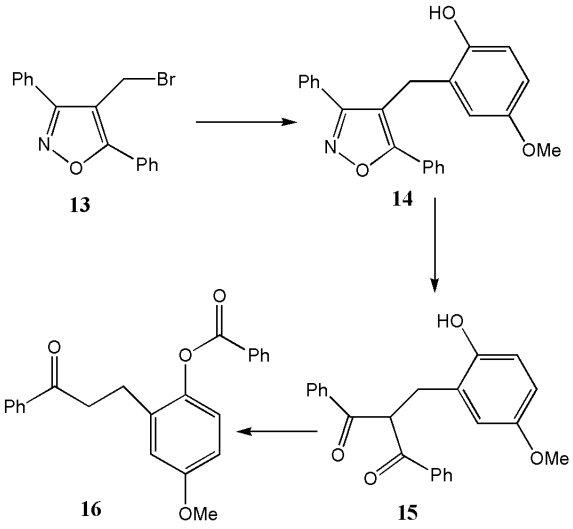
Table 2

Bond Lengths (A) and Angles (deg) for **11**

Cl-C(2)	1.722(2)
N(1)-C(2)	1.380(2)
N(1)-C(6)	1.408(3)
N(1)-C(15)	1.475(3)
N(2)-C(7)	1.328(3)
N(2)-N(3)	1.381(2)
N(3)-C(4)	1.347(2)
N(3)-C(8)	1.464(3)
N(4)-C(10)	1.391(3)
O(1)-C(6)	1.230(2)
C(2)-C(3)	1.346(3)
C(3)-C(4)	1.411(3)
C(4)-C(5)	1.386(3)
C(5)-C(7)	1.414(3)
C(5)-C(6)	1.432(3)
C(7)-C(16)	1.489(3)
C(8)-C(9)	1.498(3)
C(9)-C(14)	1.394(3)
C(9)-C(10)	1.400(3)
C(10)-C(11)	1.395(3)
C(11)-C(12)	1.369(3)
C(12)-C(13)	1.372(3)
C(13)-C(14)	1.375(3)
C(2)-N(1)-C(6)	121.8(2)
C(2)-N(1)-C(15)	121.2(2)
C(6)-N(1)-C(15)	117.1(2)
C(7)-N(2)-N(3)	106.0(2)
C(4)-N(3)-N(2)	111.0(2)
C(4)-N(3)-C(8)	128.3(2)
N(2)-N(3)-C(8)	120.3(2)
C(3)-C(2)-N(1)	124.5(2)
C(3)-C(2)-Cl	119.1(2)
N(1)-C(2)-Cl	116.4(1)
C(2)-C(3)-C(4)	115.4(2)
N(3)-C(4)-C(5)	107.1(2)
N(3)-C(4)-C(3)	130.3(2)
C(5)-C(4)-C(3)	122.6(2)
C(4)-C(5)-C(7)	105.6(2)
C(4)-C(5)-C(6)	121.2(2)
C(7)-C(5)-C(6)	133.3(2)
O(1)-C(6)-N(1)	119.7(2)
O(1)-C(6)-C(5)	125.7(2)
N(1)-C(6)-C(5)	114.6(2)
N(2)-C(7)-C(5)	110.3(2)
N(2)-C(7)-C(16)	120.8(2)
C(5)-C(7)-C(16)	128.8(2)
N(3)-C(8)-C(9)	113.5(2)
C(14)-C(9)-C(10)	118.7(2)
C(14)-C(9)-C(8)	120.9(2)
C(10)-C(9)-C(8)	120.4(2)
N(4)-C(10)-C(11)	121.0(2)
N(4)-C(10)-C(9)	120.4(2)
C(11)-C(10)-C(9)	118.5(2)
C(12)-C(11)-C(10)	121.3(2)
C(11)-C(12)-C(13)	120.7(2)
C(12)-C(13)-C(14)	118.9(2)
C(13)-C(14)-C(9)	121.9(2)

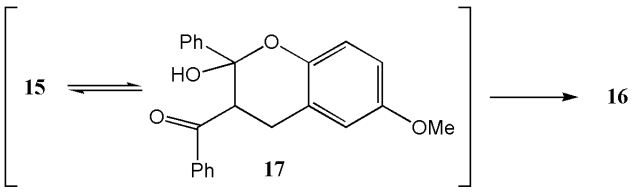
structure of this compound was assigned on the basis of analytical and spectral properties. In particular, a useful datum was the presence, in the ^{1}H-nmr spectrum of the two triplets at 2.70 and 3.02 attributable to the -CH_2-CH_2- moiety. The ^{13}C signals (experimental) confirmed the structural assignment.

Scheme 4



The unexpected formation of compound **16** can be explained according to the mechanism reported in Scheme 5. Isoxazole ring opening produces an intermediate dioxo-compound **15**, which undergoes intramolecular cyclization by reversible attack of the phenolic hydroxyl on a carbonyl group to give the intermediate emiketal **17**. Finally, ring opening of **17** forms the more stable compound **16** by a retro-Claisen like mechanism.

Scheme 5



Conclusions.

Reaction of molybdenum hexacarbonyl with isoxazole derivatives is a valuable synthetic procedure, allowing the easy access to several heterocyclic systems. The opening of the N-O bond bringing to a methyliminic intermediate, is usually followed by hydrolysis to a keto group, which may perform a ring closure if a NH_2 group is located in a suitable position. However, depending on the structure of the starting materials, trapping of the nitrene intermediate, or further rearrangement of the products can also be involved. The trapping of nitrene-like intermediate

appears particularly promising for the synthesis of new heterocycles, and therefore factors affecting this pathway are actually under investigation.

EXPERIMENTAL

Melting points were determined on a Kofler hot stage and are uncorrected. Infrared spectra were obtained for KBr discs with a Perkin Elmer 782 spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC 200 spectrometer at 200.13 MHz and 50.33 MHz, respectively. Chemical shifts are reported in ppm from internal TMS. All reagents were of reagent grade and were used without purification. EI ms spectra were recorded on a VG 70 250S instrument; electrospray ms spectra were recorded with an LCQ-DECA Thermo Finnigan instrument. TLC was performed on precoated 5x20 silica gel 60 F_{254} plates (Macherey-Nagel) with detection by UV light. Column chromatography was carried out on Silica gel (E. Merck, 0.063-0.2 mm). Elemental analyses were performed at the Department of Organic Chemistry, University of Florence, Italy.

5-Amino-8-(1-amino-ethylidene)-8*H*-tetrazolo[1,5-*a*]pyridin-7-one (**4**).

A solution of the diazide **3** [7] (1.08 g, 5 mmoles) in MeOH (30 ml) was treated with molybdenum hexacarbonyl (1.32 g, 5 mmol) and refluxed for two hours. The insoluble material was removed by filtration, washed with MeOH and the combined solutions were evaporated *in vacuo*. The residue was chromatographed with $CHCl_3$ - MeOH (95:5 v/v) on a short column of silica gel to yield 0.57 g (50%) of **4** as white plates ($CHCl_3$), mp: after a partial modification around 90 °C, it decomposes at 295 °C without melting; ir: 3650-2540 br, 1620 cm^{-1}; ^{1}H nmr ($CDCl_3$ + DMSO-d_6): δ 2.48 (s, 3H, Me), 5.37 (s, 1H, 6-H) 6.31 (brs, 2H, NH_2, D_2O-exchangeable), 8.73, 12.54 (2 brs, 2H, NH_2, D_2O-exchangeable); ^{13}C nmr ($CDCl_3$ + DMSO-d_6): δ 21.8 (Me), 88.7 (C-6), 90.2, 142.6, 149.9, 169.8, 178.8; ms: (70 ev, electron impact) m/z 192 (M+).

Anal. Calcd. for $C_7H_8N_6O\bullet 2H_2O$: C, 36.84; H, 5.38; N, 36.83. Found: C, 36.57; H, 5.41; N, 36.64.

(2-Amino-benzyl)-(6-chloro-3-methyl-isoxazolo[5,4-*b*]pyridin-4-yl)-amine (**6**) and (2-Amino-benzyl)-(4-chloro-3-methyl-isoxazolo[5,4-*b*]pyridin-6-yl)-amine (**7**).

To a solution of dichloroderivative **5** (1.4 g, 6.9 mmol) in THF (6 ml) 2-aminobenzylamine (2 g, 16.4 mmol) was added with stirring. After 24 hours at room temperature the solvent was removed *in vacuo* and the residue treated with water (10 ml) to give a solid that was collected by filtration, dried and treated with hot $CHCl_3$ (10 ml). The insoluble material was collected by filtration to give compound **6**. Evaporation of the $CHCl_3$ solution gave a residue that was column chromatographed with $CHCl_3$ - MeOH (95:5 v/v) to give (in order of elution) compound **7** and a second crop of compound **6**.

(2-Amino-benzyl)-(6-chloro-3-methyl-isoxazolo[5,4-*b*]pyridin-4-yl)-amine (**6**).

This compound was obtained as a white solid, yield 1.35 g, 68%, m.p. 186-188 °C (ethanol/water); ir: 3440, 3360, 3220, 1605 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.53 (s, 3H, Me), 3.86 (brs, 2H, NH_2, D_2O-exchangeable), 4.36 (d, 2H, J = 4.7 Hz, CH_2), 5.13 (brt, 1H, NH, D_2O-exchangeable), 6.44 (s, 1H, H-5), 6.79-7.22 (m, 4H, C_6H_4); ^{13}C nmr ($CDCl_3$ + DMSO-d_6): δ 12.3 (3-Me), 43.7 (CH_2), 98.6 (C-3a), 99.1 (C-5), 115.5, 116.9, 119.7, 128.0, 145.6 (C_6H_4), 151.3, 152.7, 153.9, 170.1 (C-7a); ms: (70 ev, electron impact) m/z 288/290 (M+).

Anal. Calcd. for $C_{14}H_{13}ClN_4O$: C, 58.24; H, 4.54; N, 19.40. Found: C, 57.89; H, 4.36; N, 19.72.

(2-Amino-benzyl)-(4-chloro-3-methyl-isoxazolo[5,4-*b*]pyridin-6-yl)-amine (**7**).

This compound was obtained as a white solid, yield 0.2 g, 10%. An analytical sample of compound **7** was obtained by crystallization from ethanol; m.p. 186-187 °C; ir: 3435, 3360, 3325, 1605 cm^{-1}; ^{1}H nmr ($CDCl_3$): δ 2.58 (s, 3H, Me), 4.16 (brs, 2H, NH_2, D_2O-exchangeable), 4.59 (d, J = 5.6 Hz, 2H, CH_2), 5.16 (brt, 1H, NH, D_2O-exchangeable), 6.32 (s, 1H, H-5), 6.68-7.20 (m, 4H, C_6H_4); ^{13}C nmr ($CDCl_3$): δ 12.1 (3-Me), 43.1 (CH_2), 102.5 (C-3a), 106.1 (C-5), 115.5, 116.1, 118.5, 121.8, 129.3, 130.4, 145.4 (C_6H_4), 139.3, 155.0, 159.7, 171.3 (C-7a); ms: (70 ev, electron impact) m/z 288/290 (M+).

Anal. Calcd for $C_{14}H_{13}ClN_4O$: C, 58.24; H, 4.54; N, 19.40. Found: C, 58.02; H, 4.68; N, 19.22.

3-Acetyl-4-(2-amino-benzylamino)-6-chloro-1*H*-pyridin-2-one (**8**) and 1-(2-Amino-benzyl)-6-chloro-3-methyl-1,5-dihydro-pyrazolo[4,3-*c*]pyridin-4-one (**9**).

To a solution of the amine **6** (0.6 g, 2.1 mmol) in MeOH molybdenum hexacarbonyl (0.55 g, 2.1 mmol) was added and the mixture was refluxed for 1 hour. Solvent was removed in *vacuo*, the residue was treated with 2 *N* sodium hydroxide, filtered and the solution acidified to pH 5-6 with concentrated hydrochloric acid. On cooling a green solid was collected by filtration and crystallised from MeOH to give compound **8** (yield 0.22 g, 36%). The mother liquid was evaporated and the residue crystallised from ethyl acetate to give compound **9** (yield 0.24 g, 39.5%).

3-Acetyl-4-(2-amino-benzylamino)-6-chloro-1*H*-pyridin-2-one (**8**).

White needles (MeOH), mp 229-230 °C; ir: 3460, 3375, 3300-2280, 1650, 1625 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 2.49 (s, 3H, Me), 4.36 (d, J = 5.2 Hz, 2H, CH_2), 5.07 (brs, 2H, NH_2, D_2O-exchangeable), 6.16 (s, 1H, 5-H), 6.51-6.71 and 6.97-7.05 (m, 4H, C_6H_4), 10.99 (brt, 1H, NH, D_2O-exchangeable), 11.88 (brs, 1H, NH, D_2O-exchangeable); ^{13}C nmr (DMSO-d_6): δ 32.7 (Me), 42.8 (CH_2), 94.1 (C-5), 115.1, 116.1, 128.1, 128.2 (Aryl CH), 100.4, 119.9, 140.8, 146.1, 159.9, 163.4, 199.3; ms: (electrospray) m/z (M+ +1)*:* 292/294.

Anal. Calcd. for $C_{14}H_{14}ClN_3O_2$: C, 57.64; H, 4.84; N, 14.40. Found: C, 57.89; H, 4.62; N, 14.68.

1-(2-Amino-benzyl)-6-chloro-3-methyl-1,5-dihydro-pyrazolo[4,3-*c*]pyridin-4-one (**9**).

This compound was obtained as white powder, m.p. 266-268 °C (decomp.), ir: 3425, 3350, 3240, 3130-2300 (broad), 1660 cm^{-1}; ^{1}H nmr (DMSO-d_6): δ 2.42 (s, 3H, Me), 5.10 (brs, 2H, NH_2, D_2O-exchangeable), 5.24 (s, 2H, CH_2), 6.48-6.59, 6.65-6.70 and 6.85-7.04 (m, 4H, C_6H_4), 6.84 (s, 1H, 7-H); 11.91 (brs, 1H, NH, D_2O-exchangeable); ^{13}C nmr (DMSO-d_6): δ 12.6 (Me), 49.0 (CH_2), 92.0 (C-7), 115.4, 116.3, 128.6, 129.1 (Aryl CH), 109.3, 119.9, 132.3, 144.4, 145.7, 146.4, 158.6; ms: (electrospray) m/z 289/291 (M+ +1).

Anal. Calcd. for $C_{14}H_{13}ClN_4O$: C, 58.24; H, 4.54; N, 19.40. Found: C, 58.46; H, 4.43; N, 19.64.

1-(2-Amino-benzyl)-6-chloro-3,5-dimethyl-1,5-dihydropyrazolo[4,3-*c*]pyridin-4-one (**11**) and 2-(6-Chloro-4-methoxy-3-methyl-pyrazolo[4,3-*c*]pyridin-1-ylmethyl)-phenylamine (**12**).

To a suspension of compound **9** (0.29 g, 1 mmol) in MeOH (5 ml) ethereal diazomethane (0.13 g, 3 mmol) was added. After 2 hours solvent was removed *in vacuo* and the residue crystallised from a 1:1 mixture of ether and cyclohexane to give the N-methyl derivative **11**. Evaporation of the mother liquors gave a residue which was column chromatographed with 1:1 ether/cyclohexane. The faster running fraction was identified as the methoxy-derivative **12** (yield 0.08 g, 26%) and the slower running compound was a second crop of **11** (total yield 0.11 g, 36%).

1-(2-Amino-benzyl)-6-chloro-3,5-dimethyl-1,5-dihydropyrazolo-[4,3-c]pyridin-4-one (**11**).

This compound was obtained as white crystals, m.p. 185-186 °C (from cyclohexane-benzene); ir: 3395, 3340, 3250, 3230, 1675 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.59 (s, 3H, Me), 3.61 (s, 3H, NMe), 5.18 (s, 2H, NH_2, D_2O-exchangeable), 5.24 (s, 2H, CH_2), 6.43 (s, 1H, 7-H), 6.64-6.76 and 7.11-7.15 (m, 4H, C_6H_4); ^{13}C nmr ($CDCl_3$): δ 13.0 (Me), 32.0 (NMe), 51.2 (CH_2), 93.0 (C-7), 116.6, 118.1, 129.9, 130.2 (Aryl CH), 109.9, 119.8, 135.9, 142.6, 146.2, 147.3, 159.0; ms: (70 ev, electron impact) m/z 302/304 (M^+).

Anal. Calcd. for $C_{15}H_{15}ClN_4O$: C, 59.51; H, 4.99; N, 18.51. Found: C, 59.74; H, 4.74; N, 18.68.

2-(6-Chloro-4-methoxy-3-methyl-pyrazolo[4,3-*c*]pyridin-1-ylmethyl)-phenylamine (**12**).

This compound was obtained as white crystals, m.p. 130-132 °C (cyclohexane); ir: 3390, 3340, 3260, 1630, 1610 cm^{-1}; ^1H nmr ($CDCl_3$): δ 2.57 (s, 3H, Me), 4.03 (s, 3H, OMe), 4.40 (brs, 2H, NH_2, D_2O-exchangeable), 5.26 (s, 1H, 7-H) 6.62-6.78 and 7.05-7.19 (m, 4H, C_6H_4); ^{13}C nmr ($CDCl_3$): δ 13.6 (Me), 51.2 (CH_2), 54.0 (OMe), 98.3 (C-7), 116.6, 118.3, 129.8, 130.5 (Aryl CH), 108.4, 120.2, 143.0, 144.5, 146.1, 147.1, 158.3; ms: (70 ev, electron impact) m/z 302/304 (M^+).

Anal. Calcd. for $C_{15}H_{15}ClN_4O$: C, 59.51; H, 4.99; N, 18.51. Found: C, 59.30; H, 5.26; N, 18.29.

2-(3,5-Diphenylisoxazol-4-ylmethyl)-4-methoxyphenol (**14**).

A mixture of 4-bromomethyl-3,5-diphenylisoxazole [8] (0.63 g, 2 mmol), 4-methoxyphenol (0.38 g, 3 mmol) and aluminum chloride (0.03 g) was heated under nitrogen in a sealed tube at 60 °C for 48 hours. The solid was treated with dichloromethane, washed with water and the organic layer evaporated *in vacuo*. Column chromatography of the residue with light petroleum/ether (from 3:1 to 1:1 v/v) gave compound **14** (yield 0.22 g, 62% based on the unrecovered starting material), white powder, m.p. 152-155 °C (cyclohexane); ir: 3420-3050 br, 1510 cm^{-1}; ^1H-nmr ($CDCl_3$): δ: 3.57 (s, 3H, OMe), 4.01 (s, 2H, CH_2), 5.15 (brs, 1H, OH D_2O-exchangeable), 6.52 (d, J = 2.7 Hz, 1H, H5), 6.63 (dd, J = 8.6, 2.7 Hz, 1H, H3), 6.73 (d, J = 8.6 Hz, 1H, H2), 7.31-7.42, 7.46-7.56 and 7.63-7.68 (m, 10H, Ph); ^{13}C nmr ($CDCl_3$): δ 23.08 (CH_2), 55.43 (OMe), 110.61, 111.97, 114.34, 115.21, 126.15, 126.55, 127.65, 127.94, 128.49, 128.63, 128.78, 129.36, 129.61, 148.36, 152.93, 164.19, 167.07 (Aryl); ms: (70 ev, electron impact) m/z: 357 (M^+).

Anal. Calcd. for $C_{23}H_{19}NO_3$: C, 77.29; H, 5.36; N, 3.92. Found: C, 77.40; H, 5.18; N, 3.73.

Benzoic Acid 4-Methoxy-2-(3-oxo-3-phenyl-propyl)-phenyl Ester (**16**).

To a solution of compound **14** (0.18 g, 0.5 mmol) in MeOH molybdenum hexacarbonyl (0.13 g, 0.5 mmol) was added and the mixture was refluxed for 24 hours. The reaction mixture was filtered and solvent was removed *in vacuo*, to give a residue that was crystallised from cyclohexane to give compound **16** as white crystals, m.p. 73-76 °C (yield 0.15 g, 84%); ir: 1735, 1685 cm^{-1}; ^1H-nmr ($CDCl_3$): δ 2.70 (t, J = 8.0 Hz, 2H, CH_2), 3.02 (t, J = 8.0 Hz, 2H CH_2), 3.52 (s, 3H, OMe), 6.53 (dd, J = 8.8, 2.9 Hz, 1H, H3), 6.63 (d, J = 2.9 Hz, 1H, H5), 6.80 (d, J = 8.6 Hz, 1H, H2), 7.06-7.40, 7.59-7.63 and 7.87-7.92 (m, 10H, 2Ph); ^{13}C nmr ($CDCl_3$): δ 25.27 (CH_2), 39.08 (CH_2), 55.57 (OMe), 112.58, 115.58, 123.23, 128.05, 128.55, 128.89, 129.35, 130.14, 133.05, 133.63, 134.32, 136.76, 142.71, 157.54 (Aryl), 165.62, 199.02 (2 CO); ms: (70 ev, electron impact) m/z 360 (M^+).

Anal. Calcd. for $C_{23}H_{20}O_4$: C, 76.65; H, 5.59. Found: C, 76.89; H, 5.63.

Crystal Structure Analysis of compound **11**.

Siemens P4 four circle diffractometer. Mo-Kα radiation λ=0.71073, graphite monochromated, ω-scan. Cell constants from 25 centred reflections. Intensity of three standard reflections checked every 97 reflections. Structure solutions by direct methods using SHELXL-97 [9] implemented in Wingx [10] package program. Anisotropic temperature factors were used for non-hydrogen atoms. The positions of hydrogen atoms were found by difference Fourier map and refined isotropically. Selected data are given in Table 1. Figure was made by Ortep-III for Windows version 1.076, implemented in Wingx package program [11]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 228428. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44-1223/336-033; e-mail:deposit@ccdc.cam.ac.uk].

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