

2-ACYL-2,3-DIHYDRO-1,3-OXAZIN-6-ONES AND PYRROLO[1,2-a]PYRIMIDINES

FROM 5(2H)-ISOXAZOLONES

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(Received in UK 29 June 1988)

**Abstract** - The reaction between the sodium salts of isoxazolin-5-ones **1** and  $\alpha$ -haloketones affords 2-acyl-2,3-dihydro-1,3-oxazin-6-ones **3** and pyrrolo[1,2-a]pyrimidines **4**.

5(2H)-Isoxazolones have been found to be a very good starting material for simple and high yield-synthesis of 1,3-oxazin-6-ones, e.g. 2-dialkylamino-1,3-oxazin-6-ones<sup>1</sup> and 2,3-dihydro-1,3-oxazin-6-ones.<sup>2</sup>

In view of the recently reported<sup>3</sup> synthesis of 1,3-oxazin-6-ones from 5(2H)-isoxazolones and 1,1-dihalo-compounds, we have considered the reaction between 5(2H)-isoxazolones and  $\alpha$ -haloketones.

Now we wish to report that 2-acyl-2,3-dihydro-1,3-oxazin-6-ones **3** and pyrrolo[1,2-a]pyrimidines **4** can be obtained from the sodium salts of isoxazolin-5-ones **1'** by reaction with  $\alpha$ -haloketones in DMF solution. As haloketones we used chloroacetone **2a** and  $\alpha$ -chloroacetophenone **2b**.

1,1'	R	R'
a	Me	CH <sub>2</sub> Ph
b	Me	n-C <sub>12</sub> H <sub>25</sub>
c	n-C <sub>3</sub> H <sub>7</sub>	CH <sub>2</sub> Ph
d	Me	CH <sub>2</sub> CH <sub>2</sub> Ph
e	Me	Ph
f	CH <sub>3</sub>	CH <sub>2</sub> CO <sub>2</sub> Me
g	t-C <sub>4</sub> H <sub>9</sub>	CH <sub>2</sub> Ph

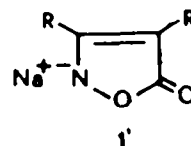
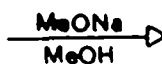
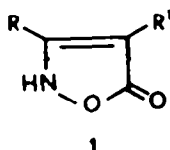


Table 1. Compounds prepared.

Starting material	Products <sup>a</sup>	R <sup>2</sup>	Ratio of eluent <sup>b</sup>	Yield (%)	mp(°C) (solvent) <sup>c</sup>
1a	3aa	Me	1:1	33	69-71 (Et <sub>2</sub> O-Hx)
	4aa			24	127 (Et <sub>2</sub> O)
1a	3ab	Ph	1:2	29	117-119 (isoPr <sub>2</sub> O)
	4ab			33	161-163 (CH <sub>2</sub> Cl <sub>2</sub> -Et <sub>2</sub> O)
	5ab			4	190-192 (Et <sub>2</sub> O)
	6ab			3	76-77 (Et <sub>2</sub> O-Hx)
1b	3ba	Me	3:1	52	53-54 (Et <sub>2</sub> O-Hx)
	4ba			36	64-65 (Hx)
1b	3bb	Ph	3:1	31	40-41 (Et <sub>2</sub> O-Hx)
	4bb			35	68-69 (Et <sub>2</sub> O)
	5bb			4	75-77 (Et <sub>2</sub> O-Hx)
	6bb			3	54-56 (Et <sub>2</sub> O-Hx)
1c	3ca	Me	1:1	59	118-120 (Et <sub>2</sub> O-Hx)
	4ca			11	85-87 (Hx)
1c	3cb	Ph	1:1	49	87-89 (Et <sub>2</sub> O-Hx)
	4cb			7	oil
	6cb			18	66-68 (Et <sub>2</sub> O-Hx)
1d	3da	Me	-- <sup>d</sup>	88	63-65 (isoPr <sub>2</sub> O)
	4da			11	177-179 (CH <sub>2</sub> Cl <sub>2</sub> -Et <sub>2</sub> O)
1d	3db	Ph	1:1	30	98-100 (Et <sub>2</sub> O-Hx)
	4db			30	180-182 (Et <sub>2</sub> O-Hx)
1e	3ea	Me	-- <sup>e</sup>	60	128-129 (CH <sub>2</sub> Cl <sub>2</sub> -Et <sub>2</sub> O)
	4ea			3	231-233 (CH <sub>2</sub> Cl <sub>2</sub> -Et <sub>2</sub> O)
1e	3eb	Ph	1:1	60	79-80 (Et <sub>2</sub> O-Hx)
	4eb			7	191-193 (CH <sub>2</sub> Cl <sub>2</sub> -Hx)
	6eb			9	121-122 (Et <sub>2</sub> O)
1f	3fa	Me	-- <sup>f</sup>	41	120-122 (Et <sub>2</sub> O-Hx)
	4fa			13	125-127 (Et <sub>2</sub> O-Hx)
1g	3ga	Me	1:1	5	142-144 (Et <sub>2</sub> O-Hx)
	6ga			74	72 (Hx)

<sup>a</sup>Satisfactory elemental analysis obtained: C,H,N ± 0.2. <sup>b</sup>Eluent: petroleum ether-Et<sub>2</sub>O. <sup>c</sup>Hx=n-hexane. <sup>d</sup>Eluent: n-hexane-CH<sub>2</sub>Cl<sub>2</sub>, 1:2. <sup>e</sup>Eluent: CH<sub>2</sub>Cl<sub>2</sub>-Et<sub>2</sub>O, 20:1. <sup>f</sup>Eluent: CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN, 10:1.

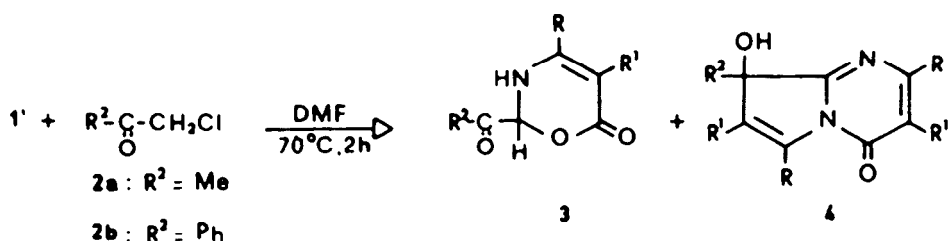
Table 2. IR and  $^1\text{H-NMR}$  data of new compounds.

Compd.	IR (nujol) $\nu(\text{cm}^{-1})$	$^1\text{H-NMR}$ ( $\text{CDCl}_3/\text{TMS}$ ) $\delta$ , J(Hz)
3aa	3296, 1721, 1655	7.25(5H, s), 5.73(1H, bs) <sup>a</sup> , 5.3(1H, d, J=3) <sup>b</sup> , 3.72(1H, d, J=15), 3.66(1H, d, J=15), 2.49(3H, s), 2.08(3H, s).
3ab	3383, 1688, 1590	8.15(2H, m), 7.55(3H, m), 7.28(5H, m), 6.1(2H, m; 1H, s after $\text{D}_2\text{O}$ ), 3.78(1H, d, J=12), 3.72(1H, d, J=12), 2.1(3H, s).
3ba	3260, 1726, 1650	5.53(1H, bs) <sup>a</sup> , 5.23(1H, d, J=3) <sup>b</sup> , 2.48(3H, s), 2.2(2H, m), 2.09(3H, s), 1.32(20H, m), 0.9(3H, m).
3bb	3345, 1690, 1670	8.18(2H, m), 7.53(3H, m), 6.05(1H, d, J=3) <sup>b</sup> , 5.97(1H, bs) <sup>a</sup> , 2.3(2H, m), 2.1(3H, s), 1.32(20H, m), 0.9(3H, m).
3ca	3240, 1731, 1650	7.22(5H, s), 5.78(1H, bs) <sup>a</sup> , 5.3(1H, d, J=3) <sup>b</sup> , 3.72(1H, d, J=18), 3.68(1H, d, J=18), 2.46(3H, s), 2.27(2H, m), 1.52(2H, m), 0.92(3H, m).
3cb	3350, 1695, 1670	8.15(2H, m), 7.6(3H, m), 6.08(2H, d, J=4) <sup>b</sup> , 5.91(1H, bs) <sup>a</sup> , 3.8(1H, d, J=15), 3.73(1H, d, J=15), 2.40(2H, m), 1.57(2H, m), 0.98(3H, m).
3da	3310, 1730, 1667	7.21(5H, s), 5.6(1H, bs) <sup>a</sup> , 5.24(1H, d, J=3.5) <sup>b</sup> , 2.77(2H, m), 2.62(2H, m), 2.45(3H, s), 1.78(3H, s).
3db	3300, 1692, 1668	8.12(2H, m), 7.56(3H, m), 7.21(5H, s), 6.02(1H, d, J=4) <sup>b</sup> , 5.9(1H, bs) <sup>a</sup> , 2.78(2H, m), 2.62(2H, m), 1.71(3H, s).
3ea	3270, 1733, 1675	7.32(5H, m), 6(1H, bs) <sup>a</sup> , 5.45(1H, d, J=3) <sup>b</sup> , 2.52(3H, s), 1.97(3H, s).
3eb	3375, 1693, 1685	8.13(2H, m), 7.5(3H, m), 7.27(5H, m), 6.47(1H, bs) <sup>a</sup> , 6.25(1H, d, J=3) <sup>b</sup> , 1.95(3H, s).
3fa	3180, 1732, 1662	6.1(1H, bs) <sup>a</sup> , 5.35(1H, d, J=3) <sup>b</sup> , 3.73(3H, s), 3.37(2H, s), 2.48(3H, s), 2.1(3H, s).
3ga	3300, 1731, 1650	7.18(5H, s), 5.82(1H, bs) <sup>a</sup> , 5.18(1H, d, J=4.5) <sup>b</sup> , 3.89(2H, s), 2.41(3H, s), 1.35(9H, s).
4aa	3200, 1680, 1660	7.27(10H, s), 4(1H, s) <sup>a</sup> , 3.95(2H, s), 3.7(2H, s), 2.56(3H, s), 2.4(3H, s), 1.43(3H, s).
4ab	3320, 1668, 1640	7.25(15H, m), 3.9(2H, s), 3.55(1H, d, J=15), 3.3(1H, d, J=15), 3.42(1H, s) <sup>a</sup> , 2.6(3H, s), 2.28(3H, s).
4ba	3160, 1682, 1665	3.8(1H, bs) <sup>a</sup> , 2.48(2H, m), 2.47(3H, s), 2.36(3H, s), 2.3(2H, m), 1.6(3H, s), 1.32(40H, m), 0.9(6H, m).
4bb	3320, 1670, 1640	7.3(5H, s), 3.86(1H, s) <sup>a</sup> , 2.56(3H, s), 2.5(2H, m), 2.25(3H, s), 2.1(2H, m), 1.3(40H, m), 0.9(6H, m).
4ca	3200, 1682, 1665	7.44(10H, m), 4.2(1H, bs) <sup>a</sup> , 4.01(2H, bs), 3.72(2H, bs), 2.96(2H, m), 2.66(2H, m), 1.64(4H, m), 1.46(3H, s), 0.94(6H, m).

4cb	3390, 1668, 1660	7.23(10H, m), 3.97(1H, d, J=14), 3.9(1H, d, J=14), 3.5(1H, d, J=15), 3.33(1H, d, J=15), 3.3(1H, bs) <sup>a</sup> , 2.9(2H, m), 2.5(2H, m), 1.5(4H, m), 0.9(6H, m).
4da	3150, 1690, 1668	7.25(10H, s), 4.27(1H, bs) <sup>a</sup> , 2.9(2H, m), 2.83(4H, bs), 2.6(2H, m), 2.38(3H, s), 2.24(3H, s), 1.62(3H, s).
4db	3360, 1680, 1650	7.25(15H, m), 3.8(1H, bs) <sup>a</sup> , 2.82(4H, s), 2.45(4H, m), 2.38(3H, s), 2.1(3H, s).
4ea	3180, 1680, 1663	7.4(10H, m), 4.4(1H, bs) <sup>a</sup> , 2.57(3H, s), 2.28(3H, s), 1.66(3H, s).
4eb	3320, 1660, 1640	7.3(15H, m), 3.8(1H, bs) <sup>a</sup> , 2.63(3H, s), 2.18(3H, s).
4fa	3340, 1735, 1685	4.38(1H, s) <sup>a</sup> , 3.77(6H, s), 3.6(2H, s), 3.38(1H, d, J=18), 3.32(1H, d, J=18), 2.51(3H, s), 2.38(3H, s), 1.57(3H, s).
5ab	1771, 1678	7.95(2H, m), 7.53(3H, m), 7.2(5H, m), 3.76(2H, s), 3.1(2H, s), 2(3H, s).
5bb	1779, 1674	7.95(2H, m), 7.5(3H, m), 3.6(1H, d, J=18), 3.5(1H, d, J=18), 2(3H, s), 1.75(2H, m), 1.3(20H, m), 0.9(3H, m).
6ab	1690, 1652	7.93(2H, m), 7.6(3H, m), 7.28(5H, s), 5.61(2H, s), 3.75(2H, s), 2.1(3H, s).
6bb	1690, 1648	7.95(2H, m), 7.6(3H, m), 5.58(2H, s), 2.32(2H, m), 2.22(3H, s), 1.35(20H, m), 0.9(3H, m).
6cb	1710, 1650	7.83(2H, m), 7.47(3H, m), 7.18(5H, s), 5.5(2H, s), 3.67(2H, s), 2.37(2H, t, J=8), 1.52(2H, m), 0.88(3H, t, J=8).
6eb	1695, 1640	7.9(2H, m), 7.45(8H, m), 5.64(2H, s), 2.38(3H, s).
6ga	1752, 1650	7.23(5H, bs), 4.8(2H, s), 3.87(2H, s), 2.18(3H, s), 1.28(9H, s).

<sup>a</sup>Exchange with D<sub>2</sub>O. <sup>b</sup>Singlet after D<sub>2</sub>O.

The expected 2-acyl-2,3-dihydro-1,3-oxazin-6-ones **3** were, in all cases, formed in satisfactory yields (Table 1) and easily obtained in the pure state by column chromatography on Florisil.



It is our opinion that the dihydrooxazinones **3** are formed by the initial attack of the haloketone **2** at position 2 of the isoxazolyl anion, followed by ring opening of the intermediate N-substituted isoxazolin-5-one (never isolated in the cases we studied) and cyclisation as shown:

Table 3. Final positional parameters for non-H atoms of 4ab with standard deviations in parentheses.

Atom	x	y	z
O(18)	0.7504(1)	0.12118(9)	-0.07843(8)
O(27)	0.3744(1)	0.0430(1)	0.26018(9)
N(1)	0.3997(2)	0.2082(1)	0.0841(1)
N(5)	0.6385(1)	0.13017(9)	0.07775(9)
C(2)	0.4087(2)	0.2399(1)	-0.0207(1)
C(3)	0.5267(2)	0.2168(1)	-0.0781(1)
C(4)	0.6477(2)	0.1534(1)	-0.0302(1)
C(6)	0.7452(2)	0.0742(1)	0.1537(1)
C(7)	0.6872(2)	0.0665(1)	0.2477(1)
C(8)	0.5347(2)	0.1203(1)	0.2434(1)
C(9)	0.5140(2)	0.1572(1)	0.1276(1)
C(10)	0.2758(3)	0.3021(2)	-0.0643(2)
C(11)	0.5390(2)	0.2531(1)	-0.1923(1)
C(12)	0.6590(2)	0.3732(1)	-0.1904(1)
C(13)	0.5905(3)	0.4593(2)	-0.2305(2)
C(14)	0.6998(3)	0.5689(2)	-0.2288(2)
C(15)	0.8799(3)	0.5941(2)	-0.1869(2)
C(16)	0.9513(3)	0.5095(2)	-0.1475(2)
C(17)	0.8419(3)	0.4001(2)	-0.1489(2)
C(19)	0.8966(3)	0.0399(2)	0.1226(2)
C(20)	0.7544(3)	0.0131(1)	0.3486(1)
C(21)	0.8662(2)	0.0983(1)	0.4450(1)
C(22)	1.0167(3)	0.1817(2)	0.4347(2)
C(23)	1.1121(3)	0.2631(2)	0.5220(2)
C(24)	1.0595(3)	0.2599(2)	0.6203(2)
C(25)	0.9148(3)	0.1757(2)	0.6332(2)
C(26)	0.8181(3)	0.0957(2)	0.5458(1)
C(28)	0.5864(2)	0.2241(1)	0.3277(1)
C(29)	0.7189(2)	0.3203(2)	0.3166(2)
C(30)	0.7767(3)	0.4131(2)	0.3960(2)
C(31)	0.7018(3)	0.4099(2)	0.4865(2)
C(32)	0.5700(3)	0.3158(2)	0.4975(2)
C(33)	0.5096(3)	0.2226(2)	0.4182(1)

Fig. 1. ORTEP of 4ab

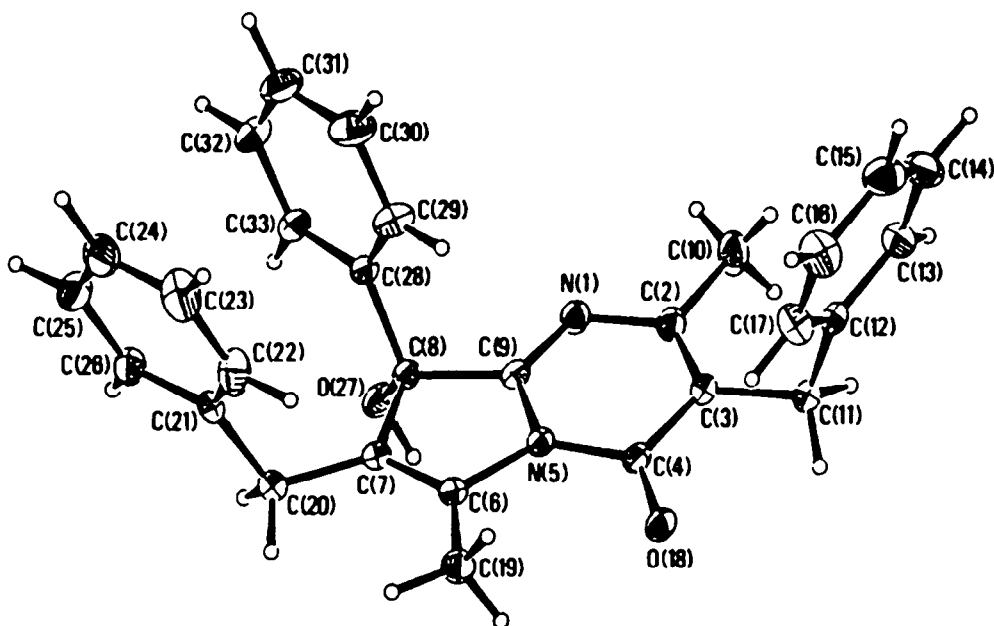


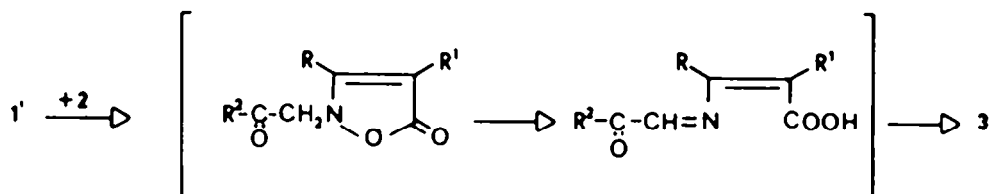
Table 4. Selected portion of the molecular geometry of 4ab with standard deviations in parentheses.

## a) Bond lengths (Å)

O(18)-C(4)	1.237(2)	O(27)-C(8)	1.418(2)
N(1)-C(2)	1.381(2)	N(1)-C(9)	1.287(2)
N(5)-C(4)	1.392(2)	N(5)-C(6)	1.462(2)
N(5)-C(9)	1.369(2)	C(2)-C(3)	1.363(2)
C(2)-C(10)	1.497(3)	C(3)-C(4)	1.451(2)
C(3)-C(11)	1.514(2)	C(6)-C(7)	1.332(2)
C(6)-C(19)	1.490(3)	C(7)-C(8)	1.525(2)
C(7)-C(20)	1.509(2)	C(8)-C(9)	1.516(2)
C(8)-C(28)	1.524(2)	C(11)-C(12)	1.513(2)
C(20)-C(21)	1.513(2)		

## b) Bond angles (°)

C(2)-N(1)-C(9)	116.1(1)	C(6)-N(5)-C(9)	109.4(1)
C(4)-N(5)-C(9)	121.4(1)	C(4)-N(5)-C(6)	129.2(1)
N(1)-C(2)-C(10)	113.0(1)	N(1)-C(2)-C(3)	123.2(1)
C(3)-C(2)-C(10)	123.7(1)	C(2)-C(3)-C(11)	123.4(1)
C(2)-C(3)-C(4)	119.9(1)	C(4)-C(3)-C(11)	116.7(1)
N(5)-C(4)-C(3)	113.7(1)	O(18)-C(4)-C(3)	124.8(1)
O(18)-C(4)-N(5)	121.5(1)	N(5)-C(6)-C(19)	120.9(1)
N(5)-C(6)-C(7)	109.0(1)	C(7)-C(6)-C(19)	130.0(1)
C(6)-C(7)-C(20)	127.8(2)	C(6)-C(7)-C(8)	111.0(1)
C(8)-C(7)-C(20)	121.2(1)	O(27)-C(8)-C(7)	113.1(1)
C(7)-C(8)-C(28)	111.9(1)	C(7)-C(8)-C(9)	101.3(1)
O(27)-C(8)-C(28)	108.5(1)	O(27)-C(8)-C(9)	112.0(1)
C(9)-C(8)-C(28)	110.0(1)	N(5)-C(9)-C(8)	109.4(1)
N(1)-C(9)-C(8)	125.2(1)	N(1)-C(9)-N(5)	125.5(1)
C(3)-C(11)-C(12)	113.1(1)	C(7)-C(20)-C(21)	114.2(1)



Results are reported in Table 1. The structure of new compounds was assigned from analytical and spectroscopic data. In the  $^1\text{H-NMR}$  spectra of dihydrooxazinones 3 a signal in the range 5.6-6.47  $\delta$  corresponds to the NH group and the signal associated with the proton at C-2 position appears as a doublet ( $J=3-4.5$  Hz) in the range 5.18-6.25  $\delta$ . This signal became a singlet after deuteration (Table 2).

Besides dihydrooxazinones 3, the pyrrolo[1,2-a]pyrimidines 4 are formed in variable yields which, in some cases, are of the same order of magnitude as those of the dihydrocompounds 3. Compounds 4, very well detected from compounds 3 by t.l.c., are also visible at 366 nm, and can be isolated in pure condition by column chromatography on Florisil, also when present in low yields (Table 1).

The structure of compounds 4 was assigned from analytical and spectroscopic data as well as by single-crystal X-ray diffraction analysis of compound 4ab.

Figure 1 shows the molecular shape and numbering scheme, while the final position parameters are reported in Table 3 and some details of the geometry are given in Table 4.

The C-C distances in phenyl rings vary between 1.356 and 1.390 Å and the C-H bond lengths are in the range 0.93-1.02 Å. C-C-C bond angles in phenyl groups and angles involving H atoms are in the usual range.

The least-squares plane A through the pyrrolopyrimidine ring is not strictly planar: the maximum torsion angle on the perimeter is  $5.0(2)^\circ$  for C(2)-C(3)-C(4)-N(5). The phenyl group bonded to C(11) (plane B) is quite planar, being the maximum deviation 0.005(3) Å for C(15); those bonded to C(20) (plane C) and to C(8) (plane D) are more distorted, being the greatest deviations 0.017(3) and 0.010(2) Å for C(22) and C(33) respectively. The last two groups are strongly coupled; in fact, the dihedral angle between C and D is  $15.32(7)^\circ$  and their mass centers are separated by only 3.588 Å; such an interaction explains the distortion of C and D systems.

To minimizing intramolecular hindrance, the phenyl groups are nearly perpendicular to pyrrolopyrimidine plane: the dihedral angles AAB, AAC and AAD are in fact  $72.71(5)$ ,  $81.69(5)$  and  $84.97(5)^\circ$  respectively.

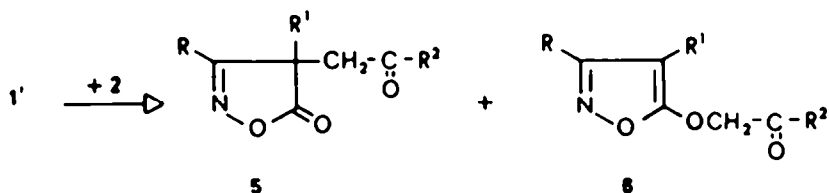
As shown by Table 4, there is no strained bond in the molecule. The double bond C(6)=C(7) is well localized (bond length 1.332(2) Å), while the C(2)=C(3) [1.363(2) Å] and N(1)=C(9) [1.287(2) Å] bonds are longer than expected<sup>4</sup> for insulated systems, but shorter than expected<sup>4</sup> for the pyrimidine nucleus; this fact

and the shortness of C(4)-C(3), N(1)-C(2) and N(5)-C(9) single bonds indicate a non-aromatic conjugation through the system N(5)-C(9)-N(1)-C(2)-C(3)-C(4)-O(18).

There is no unusually short intermolecular distance and the molecular packing appears to be due only to dispersions forces.

The pyrrolo[1,2-a]pyrimidines **4** arise from the reaction between one equivalent of the haloketone **2** and two equivalents of the isoxazolin-5-one sodium salt **1'**. It is clear that both the electrophilic centers of the haloketone molecule are involved, and that the two molecules of the isoxazolyl anion react at position 4 and 2 respectively. Further studies are planned to fully clarify the reaction mechanism.

By products are always present, and in the reaction with  $\alpha$ -chloroacetophenone **2b** we were able to isolate compounds **5**, derived from the attack of the haloketone at position 4, and compounds **6**, derived from the attack at the oxygen atom of the isoxazolyl anion.



With chloroacetone **2a**, only in the reaction with **1'g** was the O-alkylated compound **6ga** isolated. Only in this case was this compound the main product, pointing out the dramatic effect, on the course of the alkylation reaction, of the steric hindrance due to the group in position 3. For C- and O-substituted isoxazolin-5-ones **5** and **6**, not only analytical and  $^1\text{H-NMR}$  data, but also IR spectra are decisive in structure assignment, as is known from literature data.<sup>5</sup>

#### EXPERIMENTAL

**General methods.** Melting points were determined on a Buchi apparatus and are uncorrected. IR spectra were determined with a Perkin-Elmer 298 instrument, in Nujol mull for solids and liquid film or oils.  $^1\text{H-NMR}$  spectra were recorded on a Varian EM-390 or on a Bruker WP80 SY spectrometer, in deuteriochloroform ( $\text{CDCl}_3$ ) solution unless otherwise stated, with tetramethylsilane as internal standard. Column chromatography was performed on Florisil, 0.150-0.250 mm. Thin layer chromatography (TLC) was performed using Merck silica gel (Kieselgel 60 F<sub>254</sub>) analytical plates. Magnesium sulfate was used as drying agent. Evaporation was carried out under vacuum in a rotary evaporator. The starting materials were prepared according to literature procedures: **1a**<sup>6</sup>; **1b**<sup>7</sup>; **1c,d,f,g**<sup>2</sup>; **1e**<sup>8</sup>. The isoxazolones sodium salts have been prepared as previously reported.<sup>3</sup>



Reaction of Isoxazolones sodium salts 1' with chloroacetone 2a or  $\alpha$ -chloroacetophenone 2b; General Procedure

The sodium salt of the appropriate isoxazolin-5-one (1' a-g, 5 mmol) is dissolved in DMF (30 mL) and then the appropriate haloketone (2a or 2b, 6 mmol) is added. The mixture is heated at 70°C for 2h.

After evaporation of the solvent, water (50 mL) is added and the mixture extracted with  $\text{CH}_2\text{Cl}_2$  (2x40mL). The organic layer is dried, filtered and evaporated. The residue is purified by column chromatography on Florisil to give pure compounds (see Table 1 and 2).

X-ray analysis of 4ab and crystal data.

Crystals suitable for single crystal X-ray diffraction were obtained by slow evaporation of  $\text{CH}_2\text{Cl}_2$  solution.

For  $\text{C}_{29}\text{H}_{26}\text{N}_2\text{O}_2$ : Mol. wt. 434.5; triclinic, space group P1,  $a=7.940(1)$ ,  $b=12.259(2)$ ,  $c=12.412(2)\text{\AA}$ ,  $\alpha=92.15$ ,  $\beta=101.20(1)$ ,  $\gamma=106.09(1)$ ,  $V=1133.4(3)\text{\AA}^3$ ,  $Z=2$ ,  $\rho_{\text{calc}}=1.273\text{g}\cdot\text{cm}^{-3}$ ,  $P(000)=460$ ; MoK $\alpha$  radiation (graphite monochromator)  $\lambda=0.71073\text{\AA}$ ,  $\mu(\text{MoK}\alpha)=0.75\text{ cm}^{-1}$ , room temperature.

A crystal of approximate dimensions 0.30x0.24x0.16mm was used to collect data.

Cell parameters were obtained from a least-squares treatment of the automatically determined setting angles of 25 reflections with  $2\theta$  values in the range 30-44°.

The intensity of all accessible reflections with  $2\theta < 55^\circ$  were measured by variable-rate  $\theta/2\theta$  technique. The periodic measurement of three standard reflections showed no appreciable trend. Out of 5191 independent reflections measured, 1372, having  $I < \sigma(I)$  were assigned zero weight; all other reflections were assigned variances  $\sigma^2(I)$  based on counting statistics plus the additional term  $(0.02S)^2$ , where S is the scan count. Diffraction data were corrected for Lorentz and polarization factors but not for absorption.

The structure was solved by direct methods using the program MULTAN<sup>9</sup> and refined by least-squares technique. All H atoms, with the exclusion of those bonded to C(10), were located in difference map during the course of the refinement. It was impossible to clearly recognize H atoms of C(10); coordinates for these atoms with two different torsion angles around C(2)-C(10) bond were calculated; the corresponding 6 H atoms were assigned a multiplicity factor of 0.5; they were used for structural factors calculation, but not refined.

The quality minimized was  $\sum w(\Delta F)^2$ , with weights  $w=4I/\sigma^2(I_0)$ . In the final cycles 391 parameters were simultaneously adjusted: coordinates and anisotropic thermal parameters for 33 heavy atoms, coordinates and isotropic temperature coefficients for 23 hydrogen atoms, a scale factor, and a secondary extinction parameter g. The

final results are  $R=0.045$  and  $R_w=0.043$  for the 3819 reflection classified as observed ( $R=0.077$  for all 5191 reflection). The goodness-of-fit, defined as  $[\Sigma w(\Delta F)^2/(m-s)]^{1/2}$ , where  $m$  is the number of reflections and  $s$  is the number of parameters, is 1.97. Atomic scattering factors were from ref. 10. Final atomic coordinates for heavy atoms are given in Table 3\*; the final value of the extinction coefficient  $g$  is  $13(2) \times 10^{-7}$ . No residue greater than  $0.20 \text{e}\text{\AA}^{-3}$  was found on the final difference map.

#### REFERENCES

- <sup>1</sup>E.M.Beccalli, A.Marchesini, J. Org. Chem., 52, 3426 (1987).
- <sup>2</sup>E.M.Beccalli, M.L.Gelmi, A.Marchesini, T.Pilati, J. Org. Chem., 52, 1666 (1987).
- <sup>3</sup>E.M.Beccalli, T.Benincori, A.Marchesini, Synthesis, in press.
- <sup>4</sup>F.H.Allen, O.Kennard, D.G.Watson, L.Brammer, A.G.Orpen, R.Taylor, J. Chem. Soc. Perkin II S1-S19 (1987).
- <sup>5</sup>R.Jacquier, C.Petrus, F.Petrus, I.Verducci, Bull. Soc. Chim. Fr. 2690 (1970).
- <sup>6</sup>A.Silveira Jr, S.K.Satra, J. Org. Chem., 44, 873 (1978).
- <sup>7</sup>J.Schreiber, Bull. Soc. Chim. Fr. 1361 (1956).
- <sup>8</sup>R.Jacquier, C.Petrus, F.Petrus, I.Verducci, Bull. Soc. Chim. Fr. 2685 (1970)
- <sup>9</sup>G.Germain, P.Main, M.M.Wolfson, Acta Cryst., A27, 368 (1971).
- <sup>10</sup>O.Kennard, International Table for X-ray Crystallography, Vol. III, Table 4.2.2. Kynoch Press, Birmingham (1962).

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\*Lists of anisotropic thermal parameters for heavy atoms, coordinates and isotropic thermal parameters for H atoms and Table of structure factors have been deposited with Cambridge Crystallographic Data Centre, Lensfield, Cambridge CB2 1EW, England.