

Studies on Isocyanides and Related Compounds.
Investigation on the Reaction between (*Z*)-Alkyl
3-Dimethylamino-2-isocyanoacrylates and Acyl Chlorides

Ricardo Bossio, Stefano Marcaccini* and Roberto Pepino

CNR, Centro di Studio sulla Chimica e la Struttura dei Composti Eterociclici e
loro Applicazioni, Dipartimento di Chimica Organica "Ugo Schiff", Università di Firenze,
via G. Capponi 9, I-50121 Firenze, Italy

Paola Paoli

Dipartimento di Energetica, Università di Firenze,
via S. Marta 3, I-50139 Firenze, Italy

Cecilia Polo

Departamento de Química Orgánica, Facultad de
Veterinaria, Universidad de Extremadura,

E-10071 Cáceres, Spain
Received February 5, 1993

The reaction between (*Z*)-methyl 3-dimethylamino-2-isocyanoacrylate (**1a**) and acyl chlorides **2a,b** did not afford methyl 2-acyl-1-methyl-1*H*-imidazole-4-carboxylates **3a,b**, as previously reported, but 2-acyl-4-dimethylaminomethyleneoxazol-5(4*H*)-ones **4a,b**.

J. Heterocyclic Chem., **30**, 575 (1993).

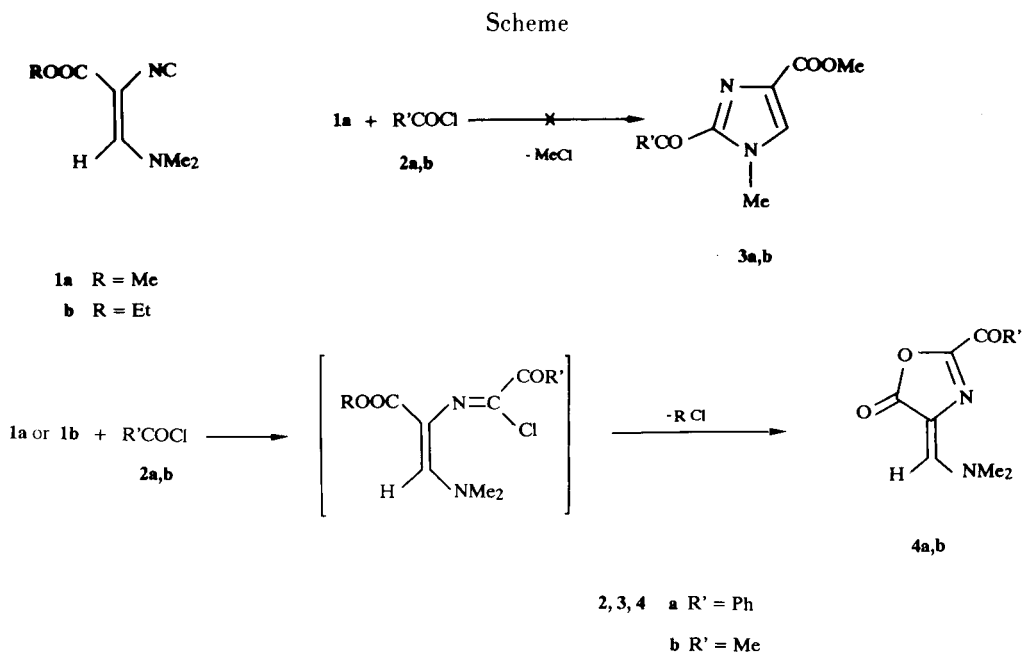
It was reported [1] that the reaction of acyl chlorides with (*Z*)-methyl 3-dimethylamino-2-isocyanoacrylates affords methyl 2-acyl-1-methyl-1*H*-imidazole-4-carboxylates.

In a previous paper [2] we reported that the reaction of arenesulfonyl chlorides with **1a,b** affords 2-arylthio-4-dimethylaminomethyleneoxazol-5(4*H*)-ones, the ester group being involved in the cyclization step.

Since the behaviour of acyl halides toward isocyanides is substantially analogous to that of arenesulfonyl chlorides [3], we have carried out a re-investigation of the reaction between acyl chlorides **2a,b** and isocyanides **1a,b**. The reaction between benzoyl chloride (**2a**) and **1a**, under

the conditions reported in the original paper [1], afforded a product whose physical and spectral data are identical to those reported for methyl 2-benzoyl-1-methyl-1*H*-imidazole-4-carboxylate (**3a**). The same product was obtained by reacting **2a** with **1b**. Analogously, the reaction of (*Z*)-alkyl 3-dimethylamino-2-isocyanoacrylates **1a,b** with acetyl chloride (**2b**) afforded a product whose physical and spectral data are identical to those reported for the product claimed to be methyl 2-acetyl-1-methyl-1*H*-imidazole-4-carboxylate (**3b**).

The above results suggested that the ring-closure step did not involve the dimethylamino group, but instead the



ester group to give 2-acyl-4-dimethylaminomethyleneoxazol-5(4*H*)-ones **4a,b**.

The X-ray analysis of the product obtained by reacting **1a** with **2a** confirmed its structure **4a**. Figure 1 shows an ORTEP view of the molecule of **4a**. An examination of the geometrical features shows the existence of an extended conjugation involving the moiety between the nitrogen atom N2 and the oxygen O2, allowing the contribution of a zwitterionic form to the description of the real structure. This conjugation is also evidenced by the almost perfect planarity of the oxazole ring with the dimethylamino residue (maximum deviation 0.114(5) Å for the C6 atom from the least-square plane passing through C7, C3, O1, C1, O2, N1, C2, C4, N2, C5, and C6). The least-square plane described by the carbon atoms of the phenyl ring and the C7 atom forms an angle of 42.2(1)° with the above plane.

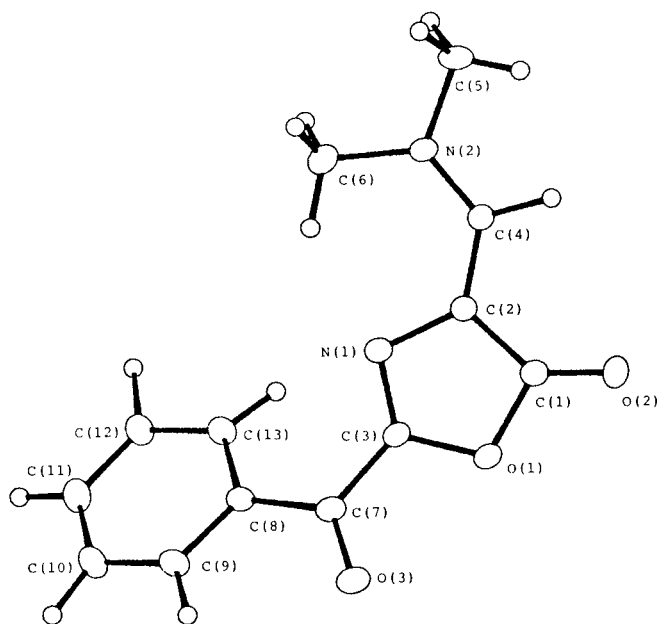


Figure 1

In the paper of Lau and Schöllkopf [1] the singlet signals at δ 3.37 and 3.40 in the proton nmr spectra of the reaction products were assigned to the NCH_3 groups of **3a** and **3b**, respectively and the singlet signals at δ 3.60 and 3.65 were assigned to the OCH_3 groups of **3a** and **3b**, respectively. The non-equivalence of the two methyl groups in the proton nmr spectra of the reaction products **4a** and **4b** is probably due to the restricted rotation about the N2-C4 bond.

EXPERIMENTAL

The molecular structure was determined by the X-ray diffraction using an Enraf-Nonius CAD4 automatic diffractometer.

X-ray Crystallographic Data of **4a**.

Crystals of $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_3$ were obtained from chloroform. A

Table 1

Bond Distances (Å) and Angles (°)

O1-C1	1.415(4)	N2-C6	1.473(5)
O1-C3	1.376(4)	C7-O3	1.232(4)
C1-C2	1.422(4)	C7-C8	1.482(6)
C1-O2	1.211(5)	C8-C9	1.384(5)
C2-N1	1.393(3)	C8-C13	1.406(5)
C2-C4	1.385(5)	C9-C10	1.375(6)
N1-C3	1.280(4)	C10-C11	1.382(6)
C3-C7	1.466(5)	C11-C12	1.372(6)
C4-N2	1.317(4)	C12-C13	1.390(6)
N2-C5	1.459(5)		
C1-O1-C3	105.5(2)	C4-N2-C5	121.2(3)
O1-C1-O2	119.6(3)	C5-N2-C6	114.9(3)
O1-C1-C2	103.9(3)	C3-C7-C8	120.1(3)
C2-C1-O2	136.5(3)	C3-C7-O3	119.0(3)
C1-C2-C4	122.4(3)	O3-C7-C8	120.8(3)
C1-C2-N1	110.1(3)	C7-C8-C13	122.4(3)
N1-C2-C4	127.5(3)	C7-C8-C9	118.6(3)
C2-N1-C3	105.3(2)	C9-C8-C13	118.9(3)
O1-C3-N1	115.2(2)	C8-C9-C10	121.0(3)
N1-C3-C7	128.0(3)	C9-C10-C11	119.3(4)
O1-C3-C7	116.8(3)	C10-C11-C12	121.6(4)
C2-C4-N2	129.6(3)	C11-C12-C13	119.0(4)
C4-N2-C6	123.9(3)	C8-C13-C12	120.2(3)

Table 2

Positional Parameters ($\times 10^4$) and Equivalent or Isotropic Thermal Parameters ($\times 10^3$)

Atom	x/a	y/b	z/c	U_{eq}
O(1)	2729(2)	5180(2)	3494(1)	46(1)
C(1)	2682(3)	4020(4)	3960(2)	41(2)
C(2)	3325(2)	2895(3)	3733(1)	35(2)
N(1)	3684(2)	3332(3)	3140(1)	36(1)
C(3)	3331(2)	4645(3)	3030(2)	36(2)
O(2)	2152(2)	4167(3)	4411(1)	58(2)
C(4)	3510(2)	1563(4)	4067(2)	36(2)
N(2)	4048(2)	403(3)	3909(1)	40(2)
C(5)	4145(4)	-914(5)	4330(2)	56(3)
C(6)	4547(4)	290(5)	3293(2)	59(3)
C(7)	3530(2)	5655(3)	2492(2)	38(2)
O(3)	3510(2)	6996(2)	2592(1)	54(2)
C(8)	3722(2)	5063(3)	1833(2)	36(2)
C(9)	4113(3)	6006(4)	1385(2)	46(2)
C(10)	4209(3)	5555(4)	744(2)	55(2)
C(11)	3928(3)	4129(5)	551(2)	55(2)
C(12)	3553(3)	3151(4)	983(2)	49(2)
C(13)	3453(3)	3611(4)	1630(2)	42(2)

single crystal of appropriate size (0.6 x 0.5 x 0.2 mm) was employed. Determination of the cell parameters was performed by least-square refinement of 25 accurately centered reflections. The intensities of two standard reflections were monitored periodically during data collection. Intensity data were corrected for Lorentz and polarization effects. The absorption corrections was made using the DIFABS program [4] after the isotropic refinement. The compound crystallizes in the monoclinic system, space group C2/c with $a = 12.745(3)$, $b = 9.057(1)$, $c = 20.127(6)$ Å, $\beta = 97.88(2)$; $Z = 8$; $V = 2301.3(9)$ Å³; $\mu = 8.04$ cm⁻¹; $D_c =$

1.410 g⁻³; 2312 reflections were collected in the range $5 < 2\theta < 140^\circ$, using CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) θ - 2θ scan mode. The structure was solved by direct methods using SIR88 [5] and refined by full-matrix least-squares to $R = 0.059$ and $R_w = 0.053$ ($w = 1/\sigma^2$), by using the 1710 observed reflections having $I > 3\sigma(I)$ for 211 parameters refined. Anisotropic thermal parameters were used for non-hydrogen atoms, whereas the hydrogen atoms were refined isotropically. A final Fourier difference did not show any interesting feature. All calculation were performed with the SHELX-76 [6] set of programs which use the analytical approximation for the atomic scattering factors and anomalous dispersion corrections for all the atoms from the International Tables [7]. The molecular plot was produced by ORTEP [8] program. Bond distances and angles are reported in Table 1. Table 2 shows the final parameters of non-hydrogen atoms with estimated standard deviations. Further data are available on request from the authors.

REFERENCES AND NOTES

- [1] H. H. Lau and U. Schöllkopf, *Liebigs Ann. Chem.*, 2093 (1982).
- [2] R. Bossio, S. Marcaccini and R. Pepino, *J. Chem. Res.*, (S), in press.
- [3a] P. Hofmann, D. Marquarding, H. Kliemann and I. Ugi, in *The Chemistry of the Cyano Group*, S. Patai and Z. Rappoport, eds, Interscience, London, 1970, p 860-861; [b] I. Ugi and U. Fetzer, *Chem. Ber.*, **94**, 1116, (1961); [c] E. Kühle, *The Chemistry of the Sulfenic Acids*, Georg Thieme Publishers, Stuttgart, 1973, p 57.
- [4] N. Walker and D. D. Stuart, *Acta Crystallogr. Sect. A*, **39**, 158 (1983).
- [5] M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, G. Polidori, R. Spagna and D. Viterbo, *J. Appl. Crystallogr.*, **22**, 389 (1989).
- [6] G. M. Sheldrick, SHELX 76, Program for Crystal Structure Determination, University of Cambridge, 1976.
- [7] International Tables for X-Ray Crystallography, Kynoch Press, Birmingham, 1974, Vol 4.
- [8] C. K. Johnson, ORTEP, Report ORNL 3794, Oak Ridge National Laboratory, TN, 1971.