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Preparation of Novel Mesoionic Compounds: A Reversible Photochromic Process

Fructuoso Barba* and Belén Batanero

Departamento de Química Orgánica, Universidad de Alcalá de Henares, Madrid, Spain

Abstract: The *3,7*-diaryl-*2H*-imidazo*[*2,1-b*][*1,3,4*]*oxadiazines **1** in sunlight undergo a reversible transformation into mesoionic imidazole compounds **2**.

In a previous paper we described the synthesis of *3,7*-diaryl-*2H*-imidazo*[*2,1-b*][*1,3,4*]*oxadiazines in very good yield by electrochemical methods[1]. We have also described some of the chemical reactivity of these compounds for example their facile conversion into *3*-aryl-*7,8*-dimethoxycarbonyl-*2H*-pyrrolo*[*2,1-b*][*1,3,4*]*oxadiazines by a Diels-Alder reaction[2].

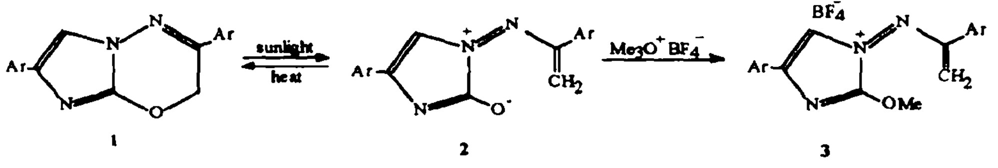
Our present work shows a photoreversible reaction under sunlight of the imidazo-oxadiazines, which was previously observed[3] but until now the nature of the product had not been determined.

The irradiation of the *3,7*-diphenyl-*2H*-imidazo*[*2,1-b*][*1,3,4*]*oxadiazine was performed in solid state under sunlight during few minutes changing its pale yellow colour to an orange colour. When the exposure was carried out in solution the rate of the process was increased. So, 0.2 g (0.727 mmol) of **1** in $CHCl_3$ or MeOH was quantitatively transformed into **2**. By refluxing the orange compound **2** in the dark, the imidazo-oxadiazine was regenerated.

All these changes were followed by IR and HPLC.

Evidence is presented here for the formation of a mesoionic product which was trapped by reaction with $Me_3O^+ BF_4^-$. The product was isolated, crystallized and identified by spectroscopic methods†.

The photochromic and the methylation processes are summarized in the Scheme.



1
yellow

2
orange

3

^{1}H NMR of **2** showed two doublets at 5.94 and 5.66 ppm with *J*= 1.5Hz giving an integral of 1 H for each signal, and a singlet at 8.44 ppm, corresponding to the terminal methylene and unsaturated =CH- respectively. When the mesoionic product reacts with the trimethyloxonium salt, the signals corresponding to the =CH- and CH_2= are shifted down field and the *J* corresponding to the doublets of =CH_2 undergoes an appreciable change from 1.5 to 2.6Hz. The singlet at 9.4 ppm, is in agreement with other similar protons on cationic structures described in the literature[4].

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REFERENCES AND NOTES.

† The following physical and spectroscopical properties were observed for **2** when the aryl group was phenyl:
IR (KBr): υ[cm^{-1}]: 3057, 1685, 1591, 1573, 1306, 1284, 773, 691. UV-VIS ($CHCl_3$): λ*max.*[nm]: 248, 298, 360. ^{1}H NMR (300MHz, $CDCl_3$): δ[ppm]: 8.44 (s, 1H, =CH-), 8.22-7.53 (m, 10Harom.), 5.94 (d, 1H, *J*= 1.5Hz), 5.66 (d, 1H, *J*= 1.5Hz). ^{13}C NMR (75.4MHz, $CDCl_3$): δ[ppm]: 164.14, 152.3, 146.7, 134.3, 133.3, 132.4, 130, 128.98, 128.86, 128.4, 128.23, 125.31, 113.93. MS (EI): *m/z*: 275 (*M*$^+$).

0.1 g (0.363 mmol) of **2** was dissolved in dry CH_2Cl_2 (25 mL) and added to a equimolecular amount of Me_3O^+ F_4B^- (47 mg, 0.364 mmol) under an argon atmosphere. The mixture was stirred for 24 h. The solvent was then evaporated to give crude **3**, which was resolved into $CHCl_3$-Et_2O (1:1) and the solution was crystallized in this medium. The compound **3** showed the following physical and spectroscopical properties:

M.p.: 107-109 °C. IR (KBr): υ[cm^{-1}]: 3062, 2935, 1682, 1592, 1570, 1308, 1286, 1082 (BF_4^-), 774, 696. ^{1}H NMR (300MHz, $CDCl_3$): δ[ppm]: 9.4 (s, 1H, =CH-), 8.45-7.37 (m, 10Harom.), 6.08 (d, 1H, *J*= 2.6Hz), 6.04 (d, 1H, *J*= 2.6Hz), 4.38 (s, 3H). MS (EI) *m/z*: 290 (*M*$^+$).

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