HETEROCYCLES, Vol. 71, No. 7, 2007, pp. 1529 - 1537. © The Japan Institute of Heterocyclic Chemistry
Received, 28th February, 2007, Accepted, 2nd May, 2007, Published online, 8th May, 2007. COM-07-11040

ON THE PHOTOREACTION OF SOME 1,2,4-OXADIAZOLES IN THE PRESENCE OF 2,3-DIMETHYL-2-BUTENE. SYNTHESIS OF *N*-IMIDOYL-AZIRIDINES

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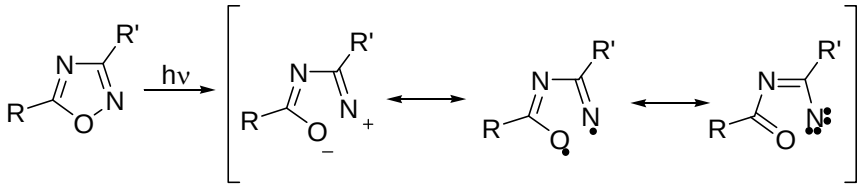
Abstract – The photochemistry of some 3,5-disubstituted 1,2,4-oxadiazoles in the presence of 2,3-dimethyl-2-butene has been investigated. The irradiation in acetonitrile yielded differently substituted *N*-imidoyl-aziridines through an aziridination reaction involving an acyliminonitrene intermediate. Pyrolysis of *N*-imidoyl-aziridines produced the corresponding *N*-allylamidines through a ring opening process.

INTRODUCTION

The 1,2,4-oxadiazole **1** is an interesting heterocycle as it presents many useful applications ranging from pharmaceutical (*e.g.* analgesic, anti-inflammatory, antirhinoviral)[1] to materials science (ionic liquids, liquid crystals, OLED).[2] In the last years the photochemical behaviour of the 1,2,4-oxadiazole system has been the object of several studies that showed the use of this heterocycle as synthon in the construction of different heterocyclic systems such as 1,3,4-oxadiazoles,[3] benzimidazoles,[4,5] benzoxazoles,[4] indazoles,[5] quinolines,[6]quinazolinones,[7] and triazoles.[5,8] In general, the photochemical reactivity of the 1,2,4-oxadiazole ring involves the cleavage of the O-N bond. The photolytic intermediate **2** (Scheme 1), zwitterionic, radicalic or nitrene-like species, will follow different reaction patterns depending on the nature of the substituents of the ring, the kind of solvent and the presence of other reactive species in solution. In many cases the N(2) of the oxadiazolic system acts as electrophilic centre such as in the reactions with an oxygen nucleophile leading to solvolysis products,[3b] in the reaction with sulphur nucleophiles leading to thiadiazoles[9] and in the reaction with nitrogen nucleophiles leading to triazoles.[5,8]



1 **2**

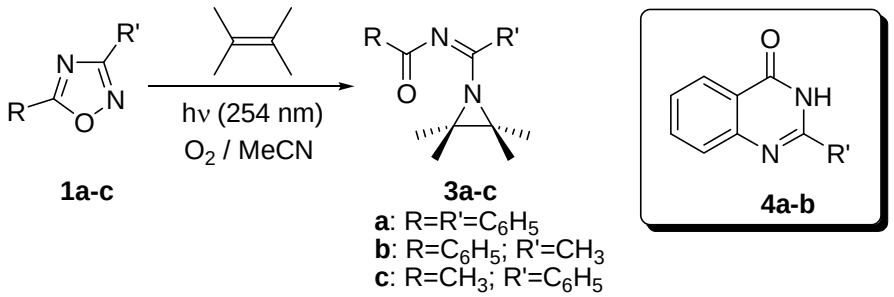
Scheme 1

In the frame of our studies on the photochemical reactivity of 1,2,4-oxadiazoles we decided to explore the use of a mild carbon nucleophile such as an alkene. Considering the *nitrene-like* character of the very reactive intermediate **2** we might expect the occurrence of an olefin aziridination reaction, following the well known cycloaddition mechanism.[10]

RESULTS AND DISCUSSION

Herein we report our results on the photochemical reactivity of 3,5-diphenyl-, 3-methyl-5-phenyl- and 3-phenyl-5-methyl-1,2,4-oxadiazoles (**1a-c**) in the presence of 2,3-dimethyl-2-butene. The choice of 2,3-dimethylbutene is due to its electron-rich character and to its symmetry, that allowed us to avoid any regiochemical issue.

Irradiations (for 4 h at $\lambda = 254$ nm) have been carried out in oxygenated acetonitrile and in the presence of a large excess of 2,3-dimethyl-2-butene (alkene/**1** 10/1 molar ratio). In the case of compounds **1a** and **1b** the oxygenated medium had a main role in limiting the formation of quinazolin-4-ones from a photoinduced electron-transfer pathway.[11] In fact, due to the electron-donor character of 2,3-dimethyl-2-butene, the electron transfer process from the alkene (Donor) to the excited oxadiazole (Acceptor) is allowed by a $\Delta G° = -83$ kJmol^{-1}.[12,13] This hypothesis was confirmed by performing analytical irradiations of compounds **1a,b** in the presence of 2,3-dimethyl-2-butene in deoxygenated acetonitrile. Under these conditions, besides the reduction products, benzoylbenzamidine and benzoylacetamidine respectively, quinazolin-4-ones **4a,b** were obtained. As expected, in the case of compound **1c**, where the presence of a methyl group at C(5) does not allow quinazolin-4-one formation, the product distribution was not affected by the presence or the absence of oxygen.

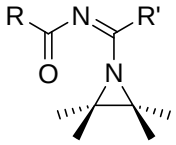
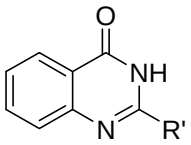


1a-c **3a-c** **4a-b**

a: R=R'=C_6H_5
b: R=C_6H_5; R'=CH_3
c: R=CH_3; R'=C_6H_5

Scheme 2

Table 1. Product distribution for photoreaction of compounds **1** after 4 h irradiation at λ= 254 nm.

Starting Compound (Recovered)		
1a (38 %)	**3a** (20 %)	**4a** (10 %)
1b (42 %)	**3b** (29 %)	**4b** (5 %)
1c (51 %)	**3c** (9 %)	-
1c (56 %)[a]	**3c** (13 %)	-

[a] Irradiation time 1h.

The photoreactions yielded compounds **3** as main products. In the case of irradiations of substrates **1a,b**, quinazolin-4-ones **4a,b** were isolated as minor products (Scheme 2 and Table 1). Compounds **3** were identified as (*Z*)-*N*-[(2,2,3,3-tetramethylaziridin-1-yl)methylene]amides (**3a-c**) from spectroscopic and X-ray (in the case of **3a**) data (Figure 1). Compounds **4a-b** were identified by comparison with authentic samples.[11]

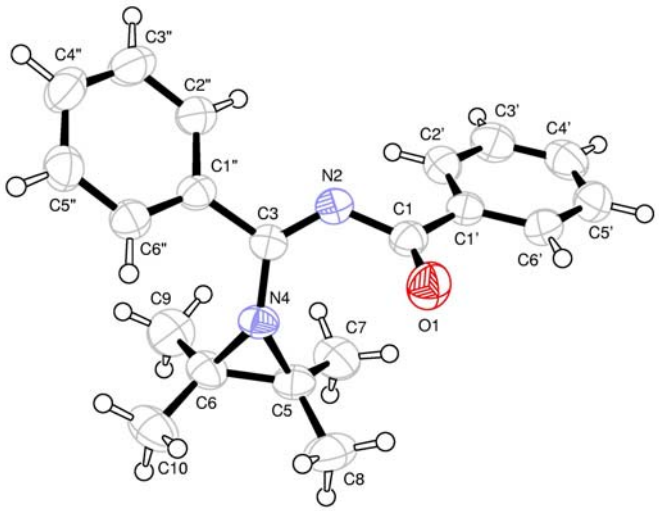
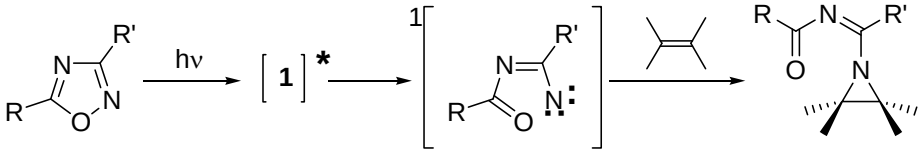


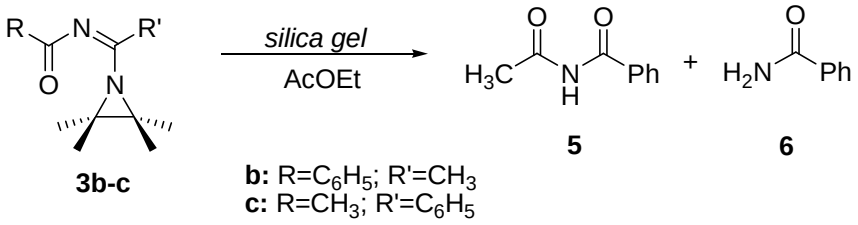
Figure 1. Drawing of the crystal structure of **3a**. Ellipsoids enclose 50% probability.

The formation of the aziridines **3** can be explained through the initial cleavage of the O-N bond of the oxadiazole followed by the nucleophilic attack of the alkene on the singlet nitrene intermediate **2** through a typical [1+2] cheletropic cycloaddition mechanism (Scheme 3).[10]



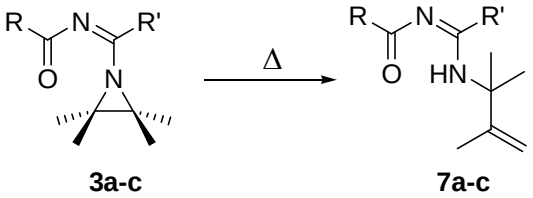
Scheme 3

In all the cases, small amounts of hydrolysis products were isolated from the photochemical mixture. These compounds are not primary photochemical products since they take origin from a silica-mediated decomposition of the aziridines during the chromatographic purification. This was confirmed by a separate experiment performed on aziridines **3b,c** which, after being absorbed on silica gel, yielded *N*-acetylbenzamide **5** and benzamide **6** (Scheme 4).



Scheme 4

Since aziridines are known to undergo ring-opening processes leading to useful synthons, we also explored the reactivity of our *N*-acyl-imidoylaziridines towards thermal rearrangements. Pyrolysis of compounds **3** (in a sealed tube at 150 °C) produced the corresponding *N*-acyl-*N'*-allylamidines (**7a-c**) (41-57 %) (Scheme 5) which were identified by spectroscopic characterization and, in the case of compound **7a**, by X-ray diffraction (Figure 2).



Scheme 5

The formation of these *N*-acyl-*N*'-allylamidines **7** is in agreement with previous reports on the reactivity of acyl-aziridines,[14] and can be explained as a ring-opening rearrangement involving an intramolecular proton abstraction from the methyl group (Scheme 5).

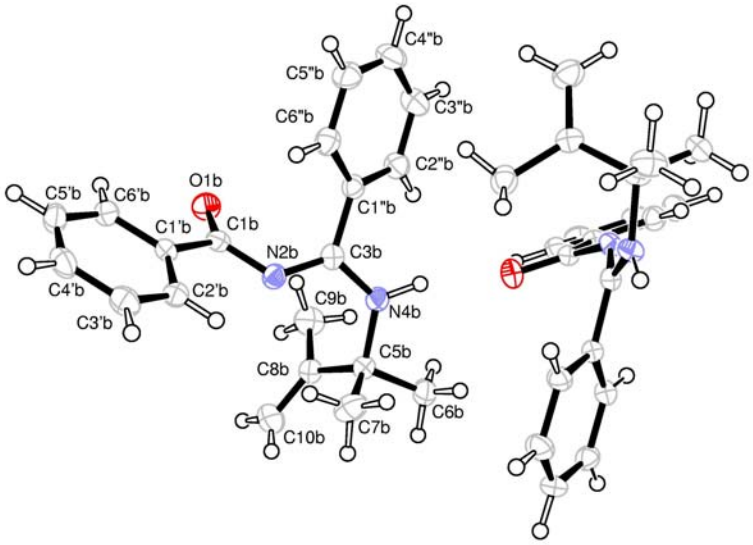


Figure 2. View of the asymmetric unit of **7a**. Ellipsoids enclose 50% probability.

In conclusion, despite the low yields, the use of 1,2,4-oxadiazoles **1** as nitrogen atom source, allows the construction of *N*-imidoyl-aziridines under mild conditions. Besides their pharmacological applications,[15] these compounds represent also useful synthons for heterocycles[16] and biologically active targets.[17]

EXPERIMENTAL

General. Melting points were determined on a REICHART-THERMOVAR hot-stage apparatus and are uncorrected. FT-IR spectra (Nujol) were determined with a SHIMADZU FTIR-8300 instrument. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 Avance spectrometer by using residual peak of the solvent ($CDCl_3$ or DMSO-d_6) as reference. Electrospray mass (ESI-MS) spectra have been obtained in positive mode by a Thermo LCQ Deca instrument. GC/MS determinations were carried out on a VARIAN STAR 3400 CX/SATURN 2000 system. Flash chromatography was performed using silica gel (200-400 mesh) and mixtures of EtOAc and light petroleum (fraction boiling in the range 40-60 °C) in various ratios. Oxadiazoles **1a-c** were prepared as reported.[18]

General Procedure for Photochemical Reactions

Photochemical reactions were carried out by using a Rayonet RPR-100 photoreactor fitted with 16 Hg lamps irradiating at λ = 254 nm (RPR-2537Å) (Quartz vessels) and equipped with a merry-go-round apparatus. A solution of compound **1** (10 mmol) in dry MeCN (400 mL), was partitioned in nine quartz tubes and purged with oxygen (10 min). An excess of 2,3-dimethyl-2-butene (molar ratio alkene/oxadiazole = 10/1) was added and the solution was irradiated for 4 h. The solvent was evaporated and the residue chromatographed.

Photochemical Reaction of 3,5-diphenyl-1,2,4-oxadiazole 1a.

Chromatography of the residue gave recovered **1a** (38%), 2-phenylquinazolin-4-one **4a** (10%, mp 232-234 °C, lit.,[11] 233-234 °C) and (*Z*)-*N*-[(2,2,3,3-tetramethylaziridin-1-yl)(phenyl)methylene]-benzamide **3a** (20%).

Compound **3a** had mp 132-135 °C (decomp.) (H_2O/EtOH). FT-IR (Nujol) (ν): 1636 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) (δ ppm): 8.12-8.22 (m, 2H), 7.82-7.79 (m, 2H), 7.51-7.40 (m, 6H), 1.23 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) (δ ppm): 177.3 (Cq), 168.8 (Cq), 137.6 (Cq), 136.5(Cq), 132.5 (CH), 131.5 (CH), 129.9 (2CH), 128.6 (2CH), 128.5 (2CH), 128.2 (2CH), 46.6 (2Cq), 20.5 (4CH_3). ESI-MS (m/z): 307 ([M+H]$^+$, 100%). Anal. Calcd for $C_{20}H_{22}N_2O$**:** C, 78.40; H, 7.24; N, 9.14. Found: C, 78.40; H, 7.25; N, 9.10.

Photochemical Reaction of 3-methyl-5-phenyl-1,2,4-oxadiazole 1b.

Chromatography of the residue gave recovered **1b** (42%), 2-methylquinazolin-4-one **4b** (5%, mp

236-238 °C, lit.,[11] 236-238 °C), *N*-acetylbenzamide **5** (12%, mp 116-118 °C, lit.,[19] 116-118 °C), benzamide **6** (10%), and (*Z*)-*N*-[1-(2,2,3,3-tetramethylaziridin-1-yl)ethylidene]benzamide **3b** (29%).

Compound **3b** is an Oil. FT-IR (Nujol) (ν): 1660 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) (δ ppm): 7.97-7.96 (m, 2H), 7.61-7.49 (m, 3H), 2.10 (s, 3H), 1.36 (s, 12H). ^{13}C NMR (75 MHz, DMSO-d_6, proton decoupled) (δ ppm): 176.9 (Cq), 164.5 (Cq), 135.9 (Cq), 132.5(CH), 129.3 (2CH), 128.8 (2CH), 45.7 (2Cq), 20.9 (CH_3), 20.1 ($4CH_3$). ESI-MS (m/z): 245 ($[M+H]^+$, 100%). Anal. Calcd for $C_{15}H_{20}N_2O$**:** C, 73.74; H, 8.25; N, 11.47. Found: C, 73.80; H, 8.20; N, 11.50.

Photochemical Reaction of 3-phenyl-5-methyl-1,2,4-oxadiazole 1c.

Chromatography of the residue gave recovered **1c** (51%), *N*-acetylbenzamide **5** (5%, mp 115-118 °C, lit.,[19] 116-118 °C) and (*Z*)-*N*-[(2,2,3,3-tetramethylaziridin-1-yl)(phenyl)methylene]acetamide **3c** (9%).

Compound **3c** is an Oil. FT-IR (Nujol) (ν): 1668 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) (δ ppm): 7.60-7.57 (m, 2H), 7.41-7.22 (m, 3H), 2.10 (s, 3H), 1.17 (s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$, proton decoupled) (δ ppm): 183.3 (Cq), 160.8 (Cq), 137.3 (Cq), 131.2 (CH), 128.7 (2CH), 128.3 (2CH), 46.4 (2Cq), 26.3 (CH_3), 20.5 ($4CH_3$). ESI-MS (m/z): 245 ($[M+H]^+$, 100%). Anal. Calcd for $C_{15}H_{20}N_2O$**:** C, 73.74; H, 8.25; N, 11.47. Found: C, 73.70; H, 8.10; N, 11.50.

Pyrolysis of aziridines 3a-c. General Procedure

1 mmol of aziridine **3** in a sealed tube was heated to 150 °C for 2 h. The resulting residue was chromatographed giving amidines **7**.

Pyrolysis of aziridine 3a.

Chromatography of the residue gave recovered starting material (10%) and (*Z*)-*N*-[(2,3-dimethylbut-3-en-2-ylamino)(phenyl)methylene]benzamide **7a** (50%), mp 94-97 °C (H_2O/EtOH). FT-IR (Nujol) (ν): 3274, 3063, 1611 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) (δ ppm): 8.20 (s, 1H, exchangeable with D_2O), 8.10-8.00 (m, 2H), 7.60-7.32 (m, 8H), 4.95 (bs, 1H), 4.90 (bs, 1H), 1.90 (s, 3H), 1.60 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6, proton decoupled) (δ ppm): 174.4 (Cq), 161.7 (Cq), 150.2 (Cq), 137.60 (Cq), 135.3 (Cq), 131.7 (CH), 130.3 (CH), 129.2 (2CH), 128.5 (2CH), 128.5 (2CH), 128.0 (2CH), 109.6 (CH_2), 57.9 (Cq), 27.4 ($2CH_3$), 19.6 (CH_3). ESI-MS (*m/z*): 307 ($[M+H]^+$, 100%). Anal. Calcd for $C_{20}H_{22}N_2O$**:** C, 78.40; H, 7.24; N, 9.14. Found: C, 78.35; H, 7.25; N, 9.15.

Pyrolysis of aziridine 3b.

Chromatography of the residue gave (*Z*)-*N*-[1-(2,3-dimethylbut-3-en-2-ylamino)ethylidene]benzamide **7b** (57%), mp 126-128 °C (H_2O/EtOH). FT-IR (Nujol) (ν): 3271, 3104, 1610 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) (δ ppm): 7.97-7.94 (m, 2H), 7.84 (s, 1H, exchangeable with D_2O), 7.47-7.36 (m, 3H), 4.87 (bs, 1H), 4.84 (bs, 1H), 2.13 (s, 3H), 1.73 (s, 3H), 1.46 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6, proton

decoupled) (δ ppm): 174.7 (Cq), 162.4 (Cq), 150.1 (Cq), 137.8 (Cq), 131.2 (CH), 128.9 (2CH), 127.9 (2CH), 108.9 (CH_2), 56.9 (Cq), 27.1 ($2CH_3$), 19.3 (CH_3), 19.2 (CH_3). GC/MS (m/z): 243 ($[M-H]^+$, 16%), 139 (20%), 105 (100%), 77 (52%), 42 (40%). Anal. Calcd for $C_{15}H_{20}N_2O$**:** C, 73.74; H, 8.25; N, 11.47. Found: C, 73.70; H, 8.30; N, 11.40.

Pyrolysis of aziridine 3c.

Chromatography of the residue gave (*Z*)-*N*-[(2,3-dimethylbut-3-en-2-ylamino)(phenyl)methylene]-acetamide **7c** (41%), mp 108-110 °C (H_2O/EtOH). FT-IR (Nujol) (ν): 3224, 3045, 1615 cm^{-1}. ^1H NMR (300 MHz, DMSO-d_6) (δ ppm): 7.60 (bs, 1H, exchangeable with D_2O), 7.50-7.40 (m, 5H), 4.90 (bs, 1H), 4.84 (bs, 1H), 1.86 (s, 3H), 1.83 (s, 3H), 1.52 (s, 6H). ^{13}C NMR (75 MHz, DMSO-d_6, proton decoupled) (δ ppm): 180.7 (Cq), 157.8 (Cq), 150.1 (Cq), 135.9 (Cq), 130.4 (CH), 128.6 (2CH), 128.1 (2CH), 109.5 (CH_2), 57.4 (Cq), 27.5 (CH_3), 27.3 ($2CH_3$), 19.5 (CH_3). GC/MS (m/z): 243 ($[M-H]^+$, 33%), 201 (53%), 145 (50%), 104 (100%), 84 (42%), 77 (33%), 43 (83%). Anal. Calcd for $C_{15}H_{20}N_2O$**:** C, 73.74; H, 8.25; N, 11.47. Found: C, 73.75; H, 8.25; N, 11.50.

X-Rray Crystallography. Single crystals of **3a** and **7a** were submitted to X-ray data collections. A Siemens P4 four-circle (for **3a**) and a Bruker-Nonius FR591 rotating anode diffractometers (for **7a**) with graphite monochromated Mo-*K*α radiation (λ =0.71073Å) were used for data collections. The structures were solved by direct methods implemented in the SHELXS-97 program.[20] The refinements were carried out by full-matrix anisotropic least-squares on F^2 for all reflections for non-H atoms by using the SHELXL-97 program.[21]

The crystallographic data of both these structures have been deposited at the Cambridge Crystallographic Data Centre with deposit numbers CCDC-633320 (**3a**) and CCDC-633321 (**7a**). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

ACKNOWLEDGEMENTS

Financial support through University of Palermo and Siena is gratefully acknowledged.

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