

Carbonyl Oxide Chemistry. Part 3.¹ Regioselectivity of the First [3 + 2] Cycloaddition of Carbonyl Oxides to Phenyl Isocyanate: One-pot Synthesis of 1,2,4-Dioxazolidin-3-ones

M. Rosaria Iesce,^a Flavio Cermola,^a Federico Giordano,^b Rachele Scarpati^{*,a} and M. Liliana Graziano^a

^a Dipartimento di Chimica Organica e Biologica dell'Università di Napoli Federico II, via Mezzocannone 16, 80134 Napoli, Italy

^b Dipartimento di Chimica dell'Università di Napoli Federico II, via Mezzocannone 4, 80134 Napoli, Italy

Carbonyl oxides **3** react with phenyl isocyanate to give the 1,2,4-dioxazolidin-3-ones **4**, providing a potentially useful synthesis of a heterocyclic system which is structurally related to several biologically active products. The crystal structure of the dioxazolidinone **4a** is also reported.

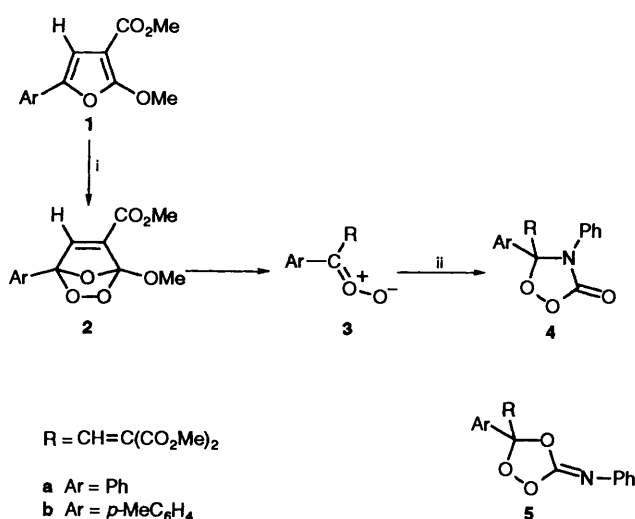
The chemistry of carbonyl oxides has attracted significant attention and stimulated the interest of both the experimental and the theoretical chemical community.² As typical 1,3-dipoles, carbonyl oxides participate in cycloaddition chemistry and represent a method for introducing a COO unit into five-membered rings. However, the classical methods used to produce carbonyl oxides, such as the ozonolysis of alkenes or the oxidation of either diazo compounds or carbenes,^{2a} limit the study of these short-lived 1,3-dipoles towards species which exhibit reduced dipolarophilic activity towards them. We have recently developed an efficient method for the formation of carbonyl oxides **3** by the thermal conversion of suitably substituted 1-methoxy-2,3,7-trioxabicyclo[2.2.1]hept-5-enes **2**, which were both quantitatively and readily obtained by dye-sensitized photooxygenation of the parent 2-methoxyfurans **1**.^{1,3,4} This preparative method has been used to study the behaviour of the carbonyl oxide **3a** towards methyl acrylate as well as towards ethyl vinyl ether. The reversal of regioselectivity in the two cases showed the bidirectionality of the functionalized 1,3-dipole.³ Our interest has now been centred on the 1,3-dipolar cycloadditions of carbonyl oxides to heterocumulenes and we describe here both the capacity of phenyl isocyanate in trapping carbonyl oxides **3** and the application of this cycloaddition in organic synthesis.[†]

Results and Discussion

The tetraphenylporphyrin sensitized photooxygenation of the furan **1a** was carried out at -25°C using phenyl isocyanate as the solvent.[‡] When the reaction was complete (2 h), the ¹H NMR spectrum showed signals for a new product (19%), in addition to those for compounds which were also obtained when the reaction was repeated in unreactive solvents.^{1,3} Rapid column chromatography on silica gel

[†] Isocyanates form cycloadducts with many 1,3-dipolar systems.⁵ Indeed, they add regioselectively to azides giving tetrazolin-5-ones⁶ as well as to nitrones to give 1,2,4-oxadiazolidin-5-ones.⁷ However, when the 1,3-dipoles used were the nitrile ylides, the regioselective reaction afforded the 1,3-oxazolin-5-imines.⁸ In contrast, both the isocyanate double bonds are reactive with nitrile imines, affording mixtures of 1,2,4-triazolin-5-ones and 1,3,4-oxadiazolin-5-imines.⁹

[‡] Control experiments showed that phenyl isocyanate is unreactive at -25°C with both singlet oxygen and with dimethyl 1-methoxy-4-phenyl-2,3,7-trioxabicyclo[2.2.1]hept-5-ene-5,6-dicarboxylate; the latter is an *endo*-peroxide which does not open into the corresponding carbonyl oxide and was stable at the temperature of the experimental conditions used.¹⁰ Hence, possible side-reactions could be excluded.



Scheme 1 Reagents: i, ¹O₂; ii, PhNCO

followed by HPLC led to the isolation of the new product (10%) as a solid. Analytical and spectroscopic data for the new compound confirmed it to be a cycloadduct formed between the carbonyl oxide **3a** and phenyl isocyanate. However, conventional spectroscopic techniques were unable to distinguish between the two possible structures **4a** and **5a** (Scheme 1), although the absorption band at 1776 cm^{-1} did indicate that structure **4a** was probably correct.[§] Confirmation of the 1,2,4-dioxazolidinone structure **4a** was eventually obtained by X-ray crystallographic analysis. The molecular structure is shown in Fig. 1 and relevant bond lengths and angles are presented in Table 1.

The tetraphenylporphyrin-sensitized photooxygenation of the furan **1b** in phenyl isocyanate under similar conditions as those used for the furan **1a** led to a crude mixture which contained compound **4b** in 23% yield. Purification as reported above for compound **4a** yielded the pure cycloadduct **4b** (11%) as an oil. In addition, the products **6b–9b** were also isolated and were identical with the products formed when the photooxygenation was performed using inert solvents (see Experimental section).

Compounds **4**, which in the pure state are stable at room

[§] 4-Phenyl-3-(2,4,6-trimethylphenyl)-1,2,4-oxadiazolidin-5-one possesses a carbonyl absorption at 1770 cm^{-1} .¹¹

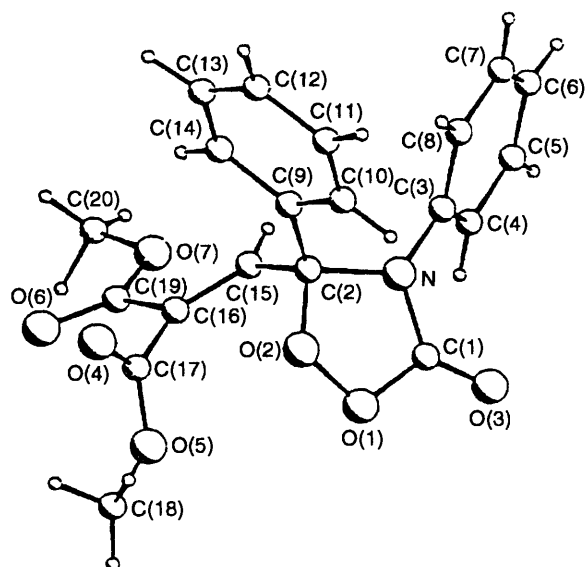
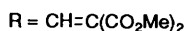
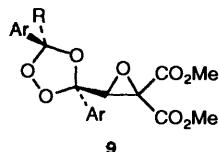
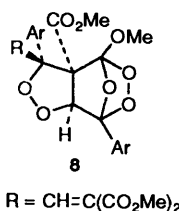
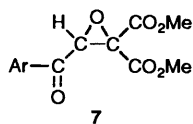
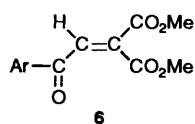


Fig. 1 X-Ray molecular structure of compound 4a

Table 1 Selected bond lengths and angles with their e.s.d.s in parentheses for compound 4a

Bond distances (Å)		Bond angles (°)	
O(1)–O(2)	1.472(2)	O(2)–O(1)–C(1)	106.0(2)
O(2)–C(2)	1.442(3)	C(1)–N–C(2)	109.7(2)
N–C(1)	1.367(3)	C(2)–N–C(3)	124.0(2)
N–C(3)	1.436(3)	O(1)–C(1)–N	108.7(2)
C(2)–C(15)	1.508(3)	O(2)–C(2)–N	100.2(2)
O(1)–C(1)	1.375(3)	O(1)–O(2)–C(2)	105.2(2)
O(3)–C(1)	1.194(3)	C(1)–N–C(3)	121.7(2)
N–C(2)	1.476(3)	O(1)–C(1)–O(3)	120.6(2)
C(2)–C(9)	1.506(3)	O(3)–C(1)–N	130.7(3)



temperature, were found to undergo decomposition and hydrolysis on contact with the chromatographic adsorbent.*

No evidence for any regioisomer was observed in either case. However, since the total yield of reaction products of ca. 70–75%, it would be inappropriate to view this reaction as completely regioselective.

The structures of the new products were assigned on the basis of elemental analyses and spectroscopic data. For compound 4a, the structure was confirmed by X-ray analysis. The previously known compounds were identified by straightforward

* Approximately half the amount of each of the compounds 4 estimated to be present in the reaction mixture was ever isolated after chromatographic separation.

comparison of their IR and ¹H NMR spectra with those of authentic samples.

Conclusion

The reaction presented above is the first ever reported [3 + 2] cycloaddition of a carbonyl oxide to a heterocumulene and provides a potentially useful one-pot synthesis of 1,2,4-dioxazolidin-3-ones† which, in consequence of their cyclic peroxy-carbamate structure, are expected to exhibit interesting biological properties. Indeed, it is well known that carbamates constitute an important class of insecticides¹⁴ and useful pharmacological agents.¹⁵ On the other hand, applications of dioxazoles both as agrochemicals and as pharmaceuticals have been suggested.^{13b} Moreover, cyclic peroxides isolated from marine organisms have been shown to exhibit cytotoxic activity,¹⁶ encouraging research into the synthesis of related compounds.¹⁷

Experimental

IR spectra were recorded on a Perkin-Elmer 1760 X-FT spectrophotometer with chloroform as solvent. ¹H and ¹³C NMR spectra were recorded with Bruker AC-270 or AM-400 spectrometers, using deuteriochloroform as the solvent and tetramethylsilane as the internal standard. *J* Values are given in Hz. DEPT techniques were employed to determine the multiplicity in the ¹³C spectra. HPLC was performed on a Shimadzu LC-9A instrument equipped with a Beckman UV detector using a Merck Lichrosorb Si-60 (10 μm) column with 5 cm³ min⁻¹ flow rate of elution. Carbon tetrachloride used in the photo-oxygenation reaction of the furan 1b was anhydrous. Silica gel 0.06–0.20 mm (Merck) and light petroleum (b.p. 40–70 °C) were used for column chromatography. TLC was performed on silica gel layers (Watman PK6F). Phenyl isocyanate (Fluka) was freshly distilled. Tetraphenylporphyrin (TPP) (Fluka) was used without purification.

The furan 1b was prepared according to a procedure reported previously for different furans,¹⁸ starting from methyl propiolate and 5-methoxy-4-methyl-2-(*p*-tolyl)oxazole. Silica gel chromatography of the reaction mixture, using light petroleum–diethyl ether (9:1) as the eluent, gave the furan 1b (19%): m.p. 109–110 °C (from diethyl ether–hexane) (Found: C, 68.1; H, 5.6. C₁₄H₁₄O₄ requires C, 68.28; H, 5.73%); $\nu_{\max}/\text{cm}^{-1}$ 1704; δ_{H} 2.34 (3 H, s, Me), 3.82 and 4.18 (6 H, 2 × s, 2 × OMe), 6.78 (1 H, s, CH), 7.16 (2 H, d, *J* 8.3, ArH) and 7.42 (2 H, d, *J* 8.3, ArH). 5-Methoxy-4-methyl-2-(*p*-tolyl)oxazole was obtained by cyclization of the methyl 2-(*p*-toluylamino)propionate with phosphorus pentachloride¹⁸ and isolated (82%) by silica gel chromatography eluting with light petroleum–diethyl ether (4:1): oil (Found: C, 70.8; H, 6.4; N, 6.8. C₁₂H₁₃NO₂ requires C, 70.91; H, 6.45; N, 6.89%); δ_{H} 2.13 (3 H, s, 4-Me), 2.36 (3 H, s, Me-C₆H₄), 3.96 (3 H, s, OMe), 7.19 (2 H, d, *J* 8.1, ArH) and 7.79 (2 H, d, *J* 8.1, ArH).

General Procedure for the Photosensitized Oxygenation of the 2-Methoxyfurans 1 in Phenyl Isocyanate.—A solution of the furan 1 (5 × 10⁻² mol dm⁻³; 0.5 mmol) in phenyl isocyanate was irradiated with a halogen-superphot lamp (Osram 650 W) in the presence of TPP (1.8 × 10⁻⁴ mmol). During the irradiation, dry oxygen was bubbled through the solution, which was maintained at –25 °C. Progress of the reaction was checked by periodically monitoring the disappearance of the furan (¹H NMR). When each reaction was complete (2 h), the excess of phenyl isocyanate was removed at room temp. and under reduced pressure, using a solid CO₂–acetone trap.

† Only one example of this heterocyclic system is reported in the chemical literature.^{12,13}

Inspection of the ^1H NMR spectrum of the crude reaction mixture of the furan **1a** showed, in addition to the products **6a–9a** and the polymeric material obtained when the photooxygenation of compound **1a** had been performed in carbon tetrachloride,^{3b} only the presence of the cycloadduct **4a** (ca. 19%).* Rapid chromatography on a silica gel column, eluting with light petroleum–diethyl ether (17:3), gave the alkene **6a** (23 mg) and a fraction (45 mg) containing the alkene **6a**, the adduct **4a** and the epoxide **7a** in ca. 1.1:1.2:1 molar ratio (^1H NMR). Elution with light petroleum–diethyl ether (4:1–1:0:1) gave the tricyclic compound **8a** (13 mg), the trioxolane **9a** (10 mg) and polymeric material, successively. HPLC Chromatography of the fraction containing compounds **6a**, **4a** and **7a** was performed using *tert*-butyl methyl ether–hexane (1:4) as mobile phase and yielded successively the alkene **6a** (R_t 15 min) (12 mg), the adduct **4a** (R_t 22 min) (20 mg) and the epoxide **7a** (R_t 28 min) (12 mg). The yields of the products **4a**, **6a**, **7a**, **8a** and **9a** were 10, 28, 9, 9 and 7%, respectively. The products **6a**,¹⁹ **7a**,¹⁹ **8a**^{3b} and **9a**^{3b} were identified by straightforward comparison of their IR and ^1H NMR spectra with those of authentic samples. The physical, analytical and spectroscopic data of the dioxazolidinone **4a** are as follows: m.p. (decomp.) 84.5 °C (from diethyl ether–hexane) (Found: C, 62.5; H, 4.4; N, 3.5; O_{act} 3.7.† $\text{C}_{20}\text{H}_{17}\text{NO}_7$ requires C, 62.66; H, 4.47; N, 3.65; O_{act} 4.17%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1776, 1736 and 1660; δ_{H} 3.79 and 3.86 (6 H, 2 × s, 2 × OMe), 7.07 (2 H, m, ArH), 7.26 and 7.20–7.60 (s + m, 9 H, CH and ArH); δ_{C} 52.8 and 53.3 (2 × q, 2 × OMe), 100.5 (s, C-5), 125.7, 128.2, 128.5, 129.1, 129.5 and 131.7 (6 × d, CH of two Ar), 131.6, 132.9 and 133.1 (3 × s, 2 × C-1 of two Ar and olefinic C), 136.5 (d, olefinic CH), 154.1 (s, C-3), 162.9 and 164.7 (2 × s, 2 × CO_2).

Inspection of the ^1H NMR of the crude reaction mixture of the furan **1b** showed, in addition to the products **6b–9b** and polymeric material obtained when the photooxygenation of the furans **1b** was performed in carbon tetrachloride (see below), only the presence of the cycloadduct **4b** (ca. 23%).* Rapid chromatography on a silica gel column, by elution with light petroleum–diethyl ether (4:1), gave the alkene **6b** (31 mg) and a fraction (54 mg) containing the alkene **6b**, the adduct **4b**, the epoxide **7b** and the tricyclic compound **8b** in ca. 3:3:1.3:1 molar ratio (^1H NMR). Elution with light petroleum–diethyl ether (7:3) and diethyl ether gave a fraction (8 mg) composed of the epoxide **7b** and the trioxolane **9b** in ca. 1:1 molar ratio (^1H NMR) and polymeric material, successively. HPLC chromatography of the fraction containing compounds **6b**, **4b**, **7b** and **8b**, performed as reported, yielded successively the alkene **6b** (R_t 15 min) (15 mg), the adduct **4b** (R_t 19 min) (22 mg), the epoxide **7b** (R_t 31 min) (7 mg) and the tricyclic compound **8b** (R_t 36 min) (10 mg). TLC Chromatography of the fraction composed of compounds **7b** and **9b** (eluent benzene–diethyl ether 19:1) gave the epoxide **7b** (3 mg) and the trioxolane **9b** (5 mg). The yields of the products **4b**, **6b**, **7b**, **8b** and **9b** were 11, 37, 7, 4 and 2%, respectively. The products **6b**, **7b**, **8b** and **9b** were identified by comparison of their IR and ^1H NMR spectra with those of authentic samples obtained in the photooxygenation of the furan **1b** in CCl_4 (see below). The physical, analytical and spectroscopic data of the dioxazolidinone **4b** are as follows: oil (Found: C, 63.3; H, 4.6; N, 3.4; O_{act} 3.5.† $\text{C}_{21}\text{H}_{19}\text{NO}_7$ requires C, 63.47; H, 4.82; N, 3.53; O_{act} 4.02%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1774, 1737 and 1667; δ_{H} 2.40 (3 H, s, Me), 3.79 and 3.86 (6 H, 2 × s, 2 × OMe), 7.09 (2 H, m, ArH), 7.24 and 7.20–7.50 (s + m, 8 H, CH and ArH).

* Quantification was based on the relative areas of the signal at δ 3.86 (one OMe of **4a**) and the methoxy signals of all the products present in the mixture (400 MHz).

† See ref. 20.

Photosensitized Oxygenation of the 2-Methoxyfuran 1b in CCl_4 .—A solution of the furan **1b** (2×10^{-2} mol dm^{-3} ; 1 mmol) in CCl_4 was photooxygenated in the presence of TPP (3.6×10^{-4} mmol) at -25 °C according to the procedure reported above for the phenyl isocyanate solutions and reported previously for the furan **1a**.^{3b} When inspection of the ^1H NMR spectrum showed the complete conversion of the furan **1b** (90 min), the lamp was removed and the oxygen flow was stopped. After a further 3 h, the solvent was removed at room temperature under reduced pressure and the residue analysed by ^1H NMR spectroscopy. The composition of the reaction mixture, deduced on the basis of the ^1H NMR spectrum, was confirmed by isolation of the products by silica gel chromatography. Elution with light petroleum–diethyl ether (17:3–4:1–7:3–0:1) gave, successively, the alkene **6b** (14%), the epoxide **7b** (9%), the tricyclic compound **8b** (40%), the trioxolane **9b** (22%) and polymeric material. The physical, analytical and spectroscopic data for compounds **6b**, **7b**, **8b** and **9b** are as follows.

Compound 6b: m.p. 86–87 °C (from diethyl ether–hexane) (Found: C, 64.3; H, 5.5; $\text{C}_{14}\text{H}_{14}\text{O}_5$ requires C, 64.11; H, 5.38%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1735 and 1670; δ_{H} 2.42 (3 H, s, Me), 3.81 and 3.88 (6 H, 2 × s, 2 × OMe), 7.31 (2 H, d, J 8.0, ArH), 7.86 (2 H, d, J 8.0, ArH) and 7.87 (1 H, s, CH).

Compound 7b: oil (Found: C, 60.2; H, 5.15. $\text{C}_{14}\text{H}_{14}\text{O}_6$ requires C, 60.43; H, 5.07%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1757 and 1693; δ_{H} 2.44 (3 H, s, Me), 3.74 and 3.91 (6 H, 2 × s, 2 × OMe), 4.69 (1 H, s, CH), 7.23 (2 H, d, J 8.3, ArH) and 7.90 (2 H, d, J 8.3, ArH).

Compound 8b: m.p. 151–153 °C (from diethyl ether–hexane) (Found: C, 60.5; H, 5.2. $\text{C}_{28}\text{H}_{28}\text{O}_{12}$ requires C, 60.43; H, 5.07%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1742 and 1654; δ_{H} 2.31 and 2.40 (6 H, 2 × s, 2 × Me), 3.35, 3.67, 3.79 and 3.93 (12 H, 4 × s, 4 × OMe), 5.64 (1 H, s, CH), 7.10–7.60 (8 H, m, ArH) and 7.79 (1 H, s, olefinic CH).

Compound 9b: oil (Found: C, 60.3; H, 5.3. $\text{C}_{28}\text{H}_{28}\text{O}_{12}$ requires C, 60.43; H, 5.07%); $\nu_{\text{max}}/\text{cm}^{-1}$ 1746 and 1655; δ_{H} 2.38 (6 H, 2 × s, 2 × Me), 3.48, 3.64, 3.74 and 3.76 (12 H, 4 × s, 4 × OMe), 4.02 (1 H, s, epoxide CH), 7.08 (1 H, s, olefinic CH) and 7.15–7.65 (8 H, m, ArH).

X-Ray Crystallography.—Crystal data and relevant details of the structure determination for compound **4a** are presented in Table 2.

X-Ray data were collected at room temperature on an Enraf-

Table 2 Crystal data and refinement conditions for compound **4a**

Formula	$\text{C}_{20}\text{H}_{17}\text{NO}_7$
<i>M</i>	383.34
Crystal system	Monoclinic
Space group	$P2_1/c$
<i>a</i> /Å	9.460(2)
<i>b</i> /Å	25.141(4)
<i>c</i> /Å	15.702(3)
β /°	149.92(1)
<i>V</i> /Å ³	1872(1)
<i>Z</i>	4
<i>D_c</i> (g cm ⁻³)	1.360
Crystal size/mm	0.07 × 0.17 × 0.40
λ (Cu-K α) (Å)	1.5418
<i>F</i> (000)/e	800
θ_{max} (°)	72
μ (cm ⁻¹)	8.36
No. indep. refl.	3677
No. refl. with $I > 3\sigma(I)$	2644
No. refined parameters	321
<i>R</i> ^a	0.045
<i>R_w</i> ^b	0.054
Goodness of fit ^c	0.910

^a $R = \Sigma(|F_o - K|F_c|)/\Sigma F_o$; ^b $R_w = [\Sigma w(F_o - K|F_c|)^2/\Sigma wF_o^2]$; ^c Goodness of fit = $[\Sigma w(F_o - K|F_c|)^2/(N_o - N_r)]$ where N_o and N_r are the number of observations and refined parameters, respectively.

Nonius CAD-4F diffractometer on line with a MicroVax Digital computer using graphite-monochromated Cu-K α radiation operated in the ω/θ scan mode. The unit-cell parameters were obtained by a least-squares fitting of the setting values of 25 strong reflections in the range $24 < \theta < 29^\circ$. Three standard reflections, monitored every 250, showed a regular crystal decay which was about 14% at the end of the data collection. A linear correction was applied for this effect. The intensities were corrected for Lorentz and polarization factors, but not for absorption effect. The structure was solved by direct methods (MULTAN82)²¹ and the non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from a ΔF map and refined isotropically.

The refinement was by full-matrix (on F) least-squares with $1/w = [\sigma^2(F_o) + (0.02 \times F_o)^2 + 1]$. The absolute value of the highest positive or negative peaks in the final difference Fourier map was not larger than $0.23 \text{ e } \text{\AA}^{-3}$ and final Δ/σ was 0.05.

Throughout the crystallographic work the Enraf-Nonius package of computer programs (SDP) was used and the atomic coordinates, bond lengths and angles and thermal parameters have been deposited as supplementary material with the Cambridge Crystallographic Data Centre.*

Acknowledgements

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* For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, 1994, Issue 1.

References

- Part 2, M. R. Iesce, F. Cermola, M. L. Graziano and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1994, 147.
- (a) W. H. Bunnelle, *Chem. Rev.*, 1991, **91**, 335; (b) R. D. Bach, A. L. Owensby, J. L. Andrés and H. B. Schlegel, *J. Am. Chem. Soc.*, 1991, **113**, 7031; (c) R. L. Kuczkowski, *Chem. Soc. Rev.*, 1992, 79; and references therein.
- (a) M. L. Graziano, M. R. Iesce, F. Cermola, F. Giordano and R. Scarpati, *J. Chem. Soc., Chem. Commun.*, 1989, 1608; (b) M. R. Iesce, M. L. Graziano, F. Cermola, G. Cimminiello and R. Scarpati, *Gazz. Chim. Ital.*, 1990, **120**, 629.
- M. L. Graziano, M. R. Iesce, F. Cermola, G. Cimminiello and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1991, 1479.
- 1,3-Dipolar Cycloaddition Chemistry*, ed. A. Padwa, Wiley, New York, 1984, vol. 1 and vol. 2.
- J. M. Vandensavel, G. Smets and G. L'abbé, *J. Org. Chem.*, 1973, **38**, 675; G. Denecker, G. Smets and G. L'abbé, *Tetrahedron*, 1975, **31**, 765.
- A. M. T. Bell, J. Bridges, R. Cross, C. P. Falshaw, B. F. Taylor, G. A. Taylor, I. C. Whittaker and M. J. Begley, *J. Chem. Soc., Perkin Trans. 1*, 1987, 2593; D. S. C. Black, R. F. Crozier and I. D. Rae, *Aust. J. Chem.*, 1978, **31**, 2013.
- B. Jackson, N. Gakis, M. Marky, H. J. Hansen, W. von Philipsborn and H. Schmid, *Helv. Chim. Acta*, 1972, **55**, 916.
- R. Huisgen, R. Grashey, H. Knupfer, R. Kunz and M. Seidel, *Chem. Ber.*, 1964, **97**, 1085.
- M. L. Graziano, M. R. Iesce, G. Cimminiello and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1989, 241; M. R. Iesce, F. Cermola, M. L. Graziano, G. Cimminiello and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1992, 1855.
- K. Bast, M. Christl, R. Huisgen and W. Mack, *Chem. Ber.*, 1972, **105**, 2825.
- E. Hoeft and S. Ganschow, *J. Prakt. Chem.*, 1972, **314**, 145.
- (a) W. Edl and H. Kropf in Houben-Weyl, *Methoden der Organischen Chemie, Organische Peroxo-Verbindungen*, ed. H. Kropf, Georg Thieme Verlag, Stuttgart, 1988, vol. E 13/1, pp. 905-917; (b) M. P. Sammes, in *Comprehensive Heterocyclic Chemistry*, eds. A. R. Katritzky and C. W. Rees, Pergamon, Oxford, 1984, vol. 6, pp. 897-946.
- R. J. Kuhr and H. W. Dorough, *Carbamate Insecticides: Chemistry, Biochemistry, and Toxicology*, CRC Press, Cleveland, 1976.
- H. E. Brezenoff and R. Giuliano, *Annu. Rev. Pharmacol. Toxicol.*, 1982, **22**, 341.
- B. S. Davidson, *J. Org. Chem.*, 1991, **56**, 6722; S. Sakemi, T. Higa, U. Anthoni, C. Christophersen, *Tetrahedron*, 1987, **43**, 263; E. Quinoa, E. Kho, L. V. Manes, P. Crews, G. J. Bakus, *J. Org. Chem.*, 1986, **51**, 4260.
- B. B. Snider and Z. Shi, *J. Org. Chem.*, 1990, **55**, 5669.
- H. Gotthardt, R. Huisgen and H. O. Bayer, *J. Am. Chem. Soc.*, 1970, **92**, 4340.
- M. L. Graziano, M. R. Iesce, G. Cimminiello and R. Scarpati, *J. Chem. Soc., Perkin Trans. 1*, 1988, 1699.
- Active oxygen (O_{act}) analysis was performed according to a literature procedure: J. D. Pasto and C. R. Johnson, *Organic Structure Determination*, Prentice Hall International, London, 1969, p. 409.
- P. Main, S. J. Fiske, S. E. Hull, L. Lessinger, G. Germain, J.-P. Declercq and M. M. Woolfson, MULTAN82. *A System of Computer Programs for the Automatic Solutions of Crystal Structures from X-ray Diffraction Data*, Univs. of York (England) and Louvain (Belgium), 1982.

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