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SYNTHESIS OF OXAZOLO- AND IMIDAZOLO-PHANES

Egle M. BECCALLI, Luisella MAJORI, Alessandro MARCHESINI,* and Clara TORRICELLI

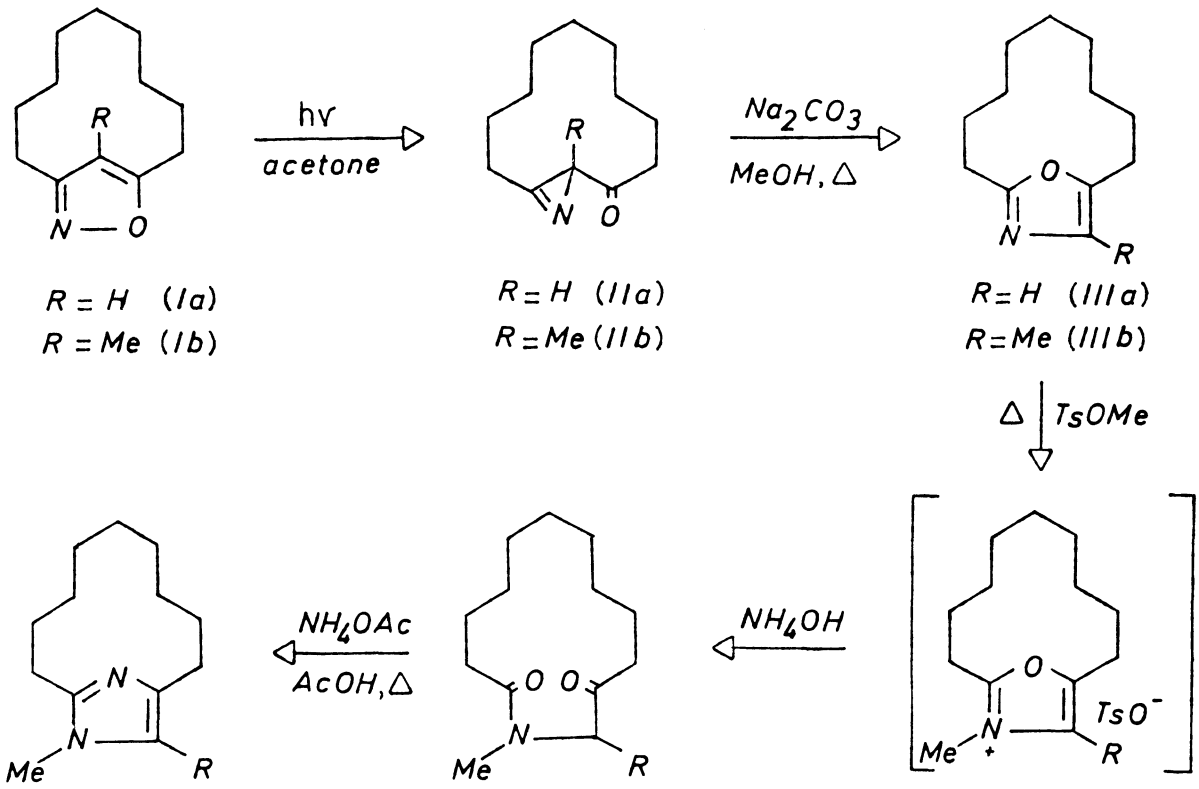
Istituto di chimica industriale dell'Universita'

CNR Centro di studio sulla sintesi e stereochimica di speciali sistemi organici

Via Golgi 19 - 20133 Milano

Irradiation of (3,5)[9]isoxazolophanes (I) afforded the corresponding azabicyclo [10.1.0]tridec-13(1)-en-11-ones (II) from which the [9]oxazolo- (III) and the [9]imidazolo-phanes (V) were obtained.

As a part of our studies in the heterophane field [1] and as synthetic application of the photobehaviour of isoxazolophanes, [2] we now report the synthesis of some hitherto unknown oxazolo- and imidazolo-phanes. The (2,5)[9]oxazolophanes (III) and the (2,4)[9]imidazolophanes (V) were obtained starting from the (3,5)[9]isoxazolophane (Ia) [1a] and the 14-methyl-(3,5)[9]isoxazolophane (Ib) [3,4] according to the following scheme :



R = H (Ia)
R = Me (Ib)

R = H (IIa)
R = Me (IIb)

R = H (IIIa)
R = Me (IIIb)

R = H (Va)
R = Me (Vb)

R = H (IVa)
R = Me (IVb)

Irradiation of the isoxazolophanes (I) in acetone through pyrex with a high pressure Hg lamp (125 W) gave, after silica gel column chromatography, the corresponding azabicyclo-[10.1.0]tridec-13(1)-en-11-ones (II).

The isoxazolophane (Ia) [4.5×10^{-2} M, 53 h] afforded (IIa), (12 %) [5], [bp 135-140 °C/0.7 mmHg ; IR (film) : 1810, 1710 cm^{-1}; NMR (100 MHz, $CDCl_3$, δ) : 2.87(2H, m) 2.71(1H, s) 2.52(2H, m)] and unreacted (Ia), (66 %).

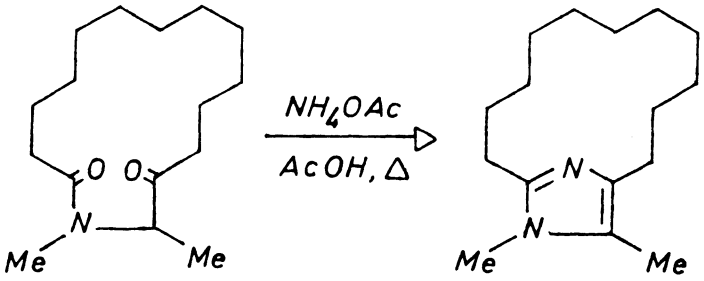
The isoxazolophane (Ib) [9×10^{-2} M, 15 h] afforded (IIb), (37 %), [bp 115-120 °C/0.5 mmHg ; IR (film) : 1795, 1700 cm^{-1}; NMR (100 MHz, $CDCl_3$, δ) : 2.95(2H, m) 2.5(2H, m)] and unreacted (Ib), (40 %).

Upon heating in methanol solution and in the presence of a catalytic amount of Na_2CO_3, [6] (IIa) and (IIb) gave quantitative yields of the (2, 5)[9]oxazolophane (IIIa) and the 11-methyl-(2, 5)[9]oxazolophane (IIIb), respectively, [(IIIa), bp 105-110 °C/0.5 mmHg ; IR (film) : 1620, 1580 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 6.67(1H, s) 2.7(4H, m) 1.8(4H, m) 1.4-0.75 (10H, m) ; λ_{max}^{EtOH} : 217 nm (5200) ; m/e : 193(M^+)(68), 96(100)]; [(IIIb), bp 105-110 °C/0.5 mmHg ; IR (film) : 1640, 1590 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 2.7(4H, m) 2.05(3H, s) 1.8(4H, m) 1.4-0.7(10H, m) ; λ_{max}^{EtOH} : 224 nm (5180) ; m/e : 207(M^+)(73), 110(100)].

The oxazolophanes (IIIa) and (IIIb) by treatment with methyl tosylate [10 min, 125-130 °C] and subsequent ring opening with NH_4OH solution [pH 8.5-9] [7] afforded the 2, 12-dioxo-1-methylazacyclotridecane (IVa) and the 3, 13-dioxo-1, 2-dimethylazacyclotridecane (IVb), respectively, [(IVa), mp 85-86 °C from CH_2Cl_2-Et_2O ; IR (nujol) : 1725, 1640 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 4.12(2H, s) 3.1(3H, s) 2.4(4H, m) ; m/e : 225(M^+)(75), 41(100)]; [(IVb), bp 130-135 °C/0.3 mmHg ; IR (film) : 1730, 1650 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ): 5.42(1H, q, J = 6 Hz) 2.88(3H, s) ; m/e : 239(M^+)(3), 58(100)].

From (IVa) and (IVb) the corresponding 12-methyl(2, 4)[9]imidazolophane (Va) and the 11, 12-dimethyl(2, 4)[9]imidazolophane (Vb) were obtained by refluxing in acetic acid and in the presence of NH_4OAc [8] [(Va), bp 115-120 °C/0.5 mmHg ; IR (film) : 1575 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 6.5(1H, s) 3.51(3H, s) 2.7(2H, m) 2.5(2H, m) 1.8(4H, m) 1.2(8H, m) 0.5(2H, m) ; λ_{max}^{EtOH} : 217 nm (6000) ; m/e : 206(M^+)(92), 177(100)] ; [(Vb), mp 53 °C from pentane ; IR (nujol) : 1580 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 3.43(3H, s) 2.7(2H, m) 2.5(2H, m) 2.13(3H, s) 1.8(4H, m) 1.2(8H, m) 0.5(2H, m) ; λ_{max}^{EtOH} : 227 nm (5600) ; m/e : 220(M^+)(100)].

In the same way the 13, 14-dimrthyl(2, 4)[11]imidazolophane (VI) was prepared from the 3, 15-dioxo-1, 2-dimethylazacyclopentadecane [2] [(VI), mp 50-51 °C from pentane ; IR (nujol) : 1595 cm^{-1}; NMR (100 MHz, $CDCl_3$, δ) : 3.43(3H, s) 2.65(2H, m) 2.44(2H, m) 2.06 (3H, s) 1.7(4H, m) 1.22(14H, m) ; λ_{max}^{EtOH} : 226 nm (4500) ; m/e : 248(M^+)(81), 138(100)].



(VI)

The inspection of the NMR spectra of the heterophanes (III) and (V) shows that some protons of the saturated chain are appreciably shielded. The largest shielding effect is observed in the case of the imidazolophanes (V), where two protons give rise to an apparent quintet centered at 0.5 δ. As expected, in the case of the imidazolophane (VI), the saturated chain length does not allow shielding to be observed.

A study of the low temperature NMR spectroscopy of the above compounds (III) and (V) is in progress as well as the study of the photobehaviour of the bicyclic azirines (II).

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REFERENCES AND NOTES

* Address inquiries to this author.

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2. S. Albanesi, A. Marchesini, and B. Gioia, Tetrahedron Lett., 1875 (1979).
3. All new products gave correct elemental analyses.
4. The 14-methyl(3, 5)[9]isoxazolophane (Ib) was prepared (85 % yield) by reaction of the methyl-2-cyclododecan-1, 3-dione with hydroxylamine and acidic cyclisation of the intermediate monooxime [(Ib), bp 140-145 °C/1.5 mmHg ; IR (film) : 1645, 1615 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 2.68(4H, m) 2(3H, s)].

   The methyl-2-cyclododecan-1, 3-dione was obtained (90 % yield) by methylation of the cyclododecan-1, 3-dione [9] by the method of Clark and Miller [10] [bp 135-140 °C/1.5 mmHg ; mp 45 °C ; IR (nujol) : 1715 cm^{-1}; NMR (90 MHz, $CDCl_3$, δ) : 3.7(1H, q, J = 6 Hz) 2.5(4H, m) 1.7(4H, m)].
5. Yields refer to isolated pure products.

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