

## References

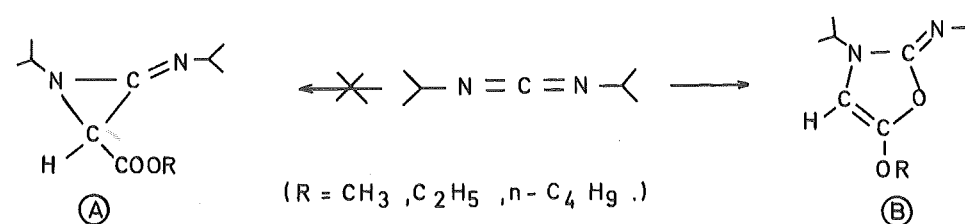
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(Received in UK 4 December 1978)

NOVEL IMINOXAZOLINES FROM REACTIONS OF  
DIAZOACETATES WITH CARBODIIMIDES ( A REVISION )<sup>1</sup>

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In a previous article<sup>2)</sup>, four of us reported that alkyl diazoacetates react with N,N'-diisopropylcarbodiimide in the presence of transition metal salts ( copper triflate or rhodium(II) acetate ) to give 1-isopropyl-2-alkoxycarbonyl-3-isopropylimino-aziridine (A).



A revision of the structure<sup>3)</sup> and a reinterpretation of the spectral data in the light of an X-ray diffraction analysis<sup>4)</sup> showed that our compounds are in fact 2-isopropylimino-3-isopropyl-5-alkoxy-4-oxazolines (B).

The crystallographical data<sup>4)</sup> as well as the results reported below were obtained on highly purified B ( R=CH<sub>3</sub>, m.p.=51.5 - 52°C ).

The i.r. spectrum (KBr) is best explained by attributing the 1725 and the 1665 cm<sup>-1</sup> bands respectively to the exocyclic (C=N-) imino group and the endocyclic (C=C) bond.

The <sup>1</sup>H n.m.r. spectrum in CDCl<sub>3</sub> (100 MHz, TMS as reference) shows singlets at δ(ppm) = 5.33 (4H oxazoline) and 3.71 (CH<sub>3</sub>-O), two heptuplets (CH isopropyl) at 4.14 (<sup>3</sup>J=6.7 Hz) (N-CH) and 3.64 (<sup>3</sup>J=6.3 Hz) (C=N-CH) and two doublets (CH<sub>3</sub> isopropyl) at 1.16 (<sup>3</sup>J=6.7 Hz) and 1.03 (<sup>3</sup>J=6.3 Hz).

The  $^{13}\text{C}$  n.m.r. spectrum in  $\text{CDCl}_3$  (TMS as reference) gives signals at  $\delta$  (ppm) = 150.9 and 147.0 (ring  $\underline{\text{C}}^2$  and  $\underline{\text{C}}^5$ ), 84.6 ( $^1J=194.1$  Hz) ( $\underline{\text{C}}^4\text{H}$ ), 46.7 ( $^1J=131.0$  Hz) and 45.2 ( $^1J=138.5$  Hz) ( $\underline{\text{C}}\text{H}$  isopropyl), 25.0 ( $^1J=122.7$  Hz) and 20.7 ( $^1J=125.0$  Hz) ( $\underline{\text{C}}\text{H}_3$  isopropyl) and 58.6 ( $^1J=143.7$  Hz) ( $\text{O}-\underline{\text{C}}\text{H}_3$ ).

The mass spectrum of (B,  $\text{R}=\text{CH}_3$ ) exhibits signals at  $m/e$  (relative intensity) (70 eV): 198 (25, molecular peak), 183 (9,  $\text{M}-\text{CH}_3$ ), 169 (8), 156 (11,  $\text{M}-\text{C}_3\text{H}_6$ ), 155 (14,  $\text{M}-\text{C}_3\text{H}_7$ ), 141 (23,  $\text{M}-\text{C}_3\text{H}_7\text{N}$ ), 114 (25,  $\text{M}-2\text{C}_3\text{H}_6$ ), 113 (100,  $\text{M}-\text{C}_3\text{H}_7\text{NCO}$ ), 99 (40), 97 (20), 82 (22), 70 (50,  $\text{M}-\text{C}_3\text{H}_7\text{NCO}-\text{C}_3\text{H}_7$ ), 58 (50,  $\text{CH}_2\text{N}_2\text{O}$  from 114), 56 (8,  $\text{CH}=\text{COCH}_3$  from 114) and 43 (69,  $\text{C}_3\text{H}_7^+$ ).

The oxazolines (B) are weak bases, soluble in dilute acids, and can be titrated potentiometrically in methanol with  $\text{HClO}_4$  0.1 N in dioxane (equivalent weight for (B),  $\text{R}=\text{CH}_3$ : found 210; calcd. 198).

They react with picric acid in aqueous solution to give a monoadduct. For example, (B),  $\text{R}=\text{CH}_3$ , gives the corresponding salt as yellow needles after crystallization from benzene. Mp:  $125^\circ\text{C}$ . Calcd for  $\text{C}_{16}\text{H}_{21}\text{N}_5\text{O}_9$ : C, 44.95; H, 4.95; N, 16.4%. Found: C, 45.0; H, 4.9; N, 16.3%.  $m/e$  (70 eV): 427 (calcd 427).

The mechanism of the formation of (B) involves most probably a 1,3-dipolar addition of the carbalkoxycarbene onto a  $\text{C}=\text{N}$ -group of the cumulene, and is in fact similar to the cycloaddition of carbalkoxycarbenes onto nitriles<sup>5</sup>.

**Conclusion:** The reported reaction, which illustrates the difficulty to obtain exocyclic methylene aziridines, is a new straightforward method for the preparation of novel 4-oxazolines which are not easily accessible by other methods.

**Acknowledgements:** we are particularly indebted to the FNRS (Belgium) for a grant (HPLC equipment) and to SPSS (Belgium) for financial support. We thank Professor Charette (Université Catholique de Louvain-la-Neuve) for high resolution MS measurements; the analyses were performed by Miss Crismer, and we acknowledge the skilful collaboration of MM R. Antoine and M. Lalmand.

- 1) Part I of the series, part II will be devoted to the chemical properties of the reported oxazolines.
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(Received in UK 3 November 1978)

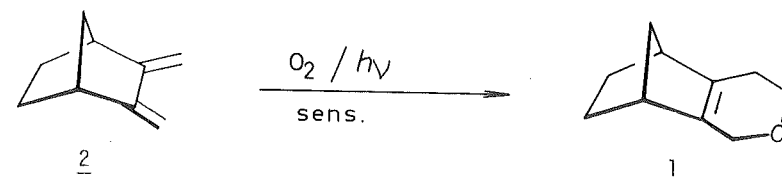
THE CONFORMATIONAL ANALYSIS AND THE REARRANGEMENTS OF  
(NORBORN-2-ENO)[d](3,6-DIHYDRO-1,2-DIOXINE)

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A recent communication of KONDO et al.<sup>1</sup> on the microwave and nmr studies of the structure and conformational isomerization of 3,6-dihydro-1,2-dioxine prompts us to disclose our results on the conformational analysis of the peroxide 1, as well as preliminary results on its thermal, photochemical, base, acid and  $\text{Rh}^I$  promoted rearrangements<sup>2</sup>.



The diene 2 is highly reactive towards strong dienophiles<sup>3</sup>. As expected for a diene blocked in the *s-cis* conformation<sup>4</sup>, 2 added  $^1\text{O}_2$  (0.5 M in  $\text{CCl}_4$ , tetraphenylporphine, Pyrex vessel, Iodine 250 W lamp,  $-10^\circ$ ,  $\text{O}_2$ ) rapidly, yielding the peroxide 1 (86%, after distillation). This 3,6-dihydro-1,2-dioxine is of special interest for at least 3 reasons: (1) distinction between the half-chair ( $\text{C}_1$ ) and boat ( $\text{C}_s$ ) conformations of the peroxide will be possible by  $^1\text{H}$ -nmr, (2) variable temperature  $^{13}\text{C}$ -nmr will allow an easy evaluation of the activation parameters of its ring inversion and (3) the stereochemistry of the thermal and photochemical peroxide  $\rightarrow$  diepoxide rearrangement<sup>1,5</sup> can be established by product analysis.

The  $^1\text{H}$ - and  $^{13}\text{C}$ -nmr spectra of 1 at  $30^\circ$  were consistent either with the fast equilibrating half-chair conformers or with the degenerate or near-degenerate equilibrium of the boat conformers 1i and 1j. At  $-100^\circ$ , the  $^{13}\text{C}$ - $\{^1\text{H}\}$ -FT-nmr spectrum<sup>6</sup> showed splitting of all signals except

