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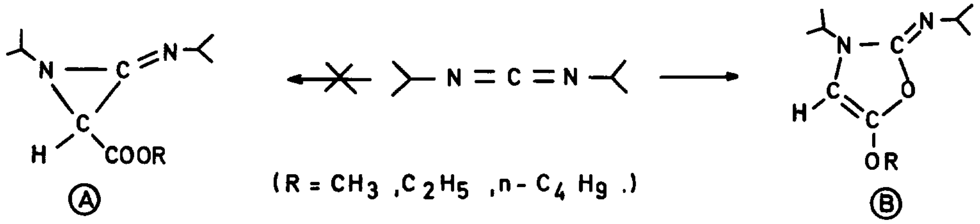
NOVEL IMINOOXAZOLINES FROM REACTIONS OF DIAZOACETATES WITH CARBODIIMIDES (A REVISION)[1]

By Julien Drapier, Alain Feron, Roger Warin, André J. Hubert* and Ph. Teyssié
Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman, B-4000 Liège, Belgium.

In a previous article2), 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 structure3) and a reinterpretation of the spectral data in the light of an X-ray diffraction analysis4) showed that our compounds are in fact 2-isopropylimino-3-isopropyl-5-alkoxy-4-oxazolines (B).

The crystallographical data4) as well as the results reported below were obtained on highly purified B (R=CH_3, m.p.=51.5 - 52°C).

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

The ^1H n.m.r. spectrum in $CDCl_3$(100 MHz, TMS as reference) shows singlets at δ(ppm) = 5.33 ($4\underline{H}$ oxazoline) and 3.71 ($C\underline{H}_3$-O), two heptuplets ($C\underline{H}$ isopropyl) at 4.14 (^3J=6.7 Hz) (N-$C\underline{H}$) and 3.64 (^3J=6.3 Hz) (C=N-CH) and two doublets ($C\underline{H}_3$ isopropyl) at 1.16 (^3J=6.7 Hz) and 1.03 (^3J=6.3 Hz).

The ^{13}C n.m.r. spectrum in $CDCl_3$(TMS as reference) gives signals at δ(ppm)= 150.9 and 147.0 (ring $\underline{C}^2$and $\underline{C}^5$), 84.6 (^1J=194.1 Hz) ($\underline{C}^4$H), 46.7 (^1J=131.0 Hz) and 45.2 (^1J=138.5 Hz) ($\underline{C}$H isopropyl), 25.0 (^1J=122.7 Hz) and 20.7 (^1J=125.0Hz) ($C\underline{H}_3$ isopropyl) and 58.6 (^1J=143.7 Hz) ($O-C\underline{H}_3$).

The mass spectrum of (B, R=CH_3) exhibits signals at M/e (relative intensity) (70 eV) : 198 (25, molecular peak), 183 (9, M-CH_3), 169 (8), 156 (11, M-C_3H_6), 155 (14, M-C_3H_7), 141 (23, M-C_3H_7N), 114 (25, M-2C_3H_6), 113 (100, M-C_3H_7NCO), 99 (40), 97 (20), 82 (22), 70 (50, M-C_3H_7NCO-C_3H_7), 58 (50, CH_2N_2O from 114), 56 (8, CH=$COCH_3$ from 114) and 43 (69, $C_3H_7^+$).

The oxazolines (B) are weak bases, soluble in dilute acids, and can be titrated potentiometrically in methanol with $HClO_4$ 0.1 N in dioxane (equivalent weight for (B), R=CH_3: found 210; calcd. 198)

They react with picric acid in aqueous solution to give a monoadduct. For example, (B), R=CH_3, gives the corresponding salt as yellow needles after crystallization from benzene. Mp : 125°C. Calcd for $C_{16}H_{21}N_5O_9$: 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 C=N- group of the cumulene, and is in fact similar to the cycloaddition of carbalkoxycarbenes onto nitriles$^{5)}$.

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.

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1) Part I of the series, part II will be devoted to the chemical properties of the reported oxazolines.

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3) We are grateful to Prof. L'Abbé for having brought to our attention some spectral discrepancies militating against structure (A) and for helpful discussions while this work was in progress.

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