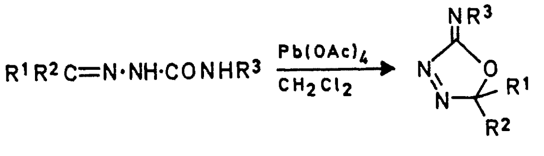
Hydrolysis of 2-Imino-Δ^3-1,3,4-oxadiazolines. Preparation and Properties of Δ^3-1,3,4-Oxadiazolin-2-ones

By S. L. LEE, G. B. GUBELT, A. M. CAMERON, and J. WARKENTIN*
(*McMaster University, Hamilton, Ontario, Canada*)

Summary Acid-catalysed hydrolysis of 2-imino-Δ^3-1,3,4-oxadiazolines affords Δ^3-1,3,4-oxadiazoline-2-ones.

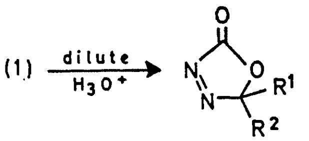
2-IMINO-Δ^3-1,3,4-OXADIAZOLINES (**1**) are readily obtained by oxidative cyclization of semicarbazones.[1] In the synthesis of (**1**; $R^1 = R^2 = R^3 = $ Me) it was found that the crude material obtained following normal work-up with water[1] has an unexpected absorption at 1835 cm^{-1} in the i.r. spectrum. We report that the by-product is a new and novel heterocyclic ring system (**2**), two members of which were prepared by careful acid-catalysed hydrolysis of (**1**). Compounds (**2**), which may be considered as lactones of the unstable azo-carboxylic acids, have spectroscopic and chemical properties quite different from those of $\alpha\beta$-unsaturated lactones.



(1)

Shaking an ether solution of (**1**; $R^1 = R^3 = $ Me, $R^2 = $ Et) with 30% aqueous acetic acid at room temperature for 5 min. gave a 1 : 4 mixture of (**1**) and (**2b**) from which (**2b**), an oil, could be separated only by g.l.p.c. Separation is simplified if the difference between the volatilities of (**1**) and (**2**) is enhanced. Thus (**1**; $R^1 = R^2 = $ Me, $R^3 = CH_2{\cdot}CH_2$-Ph) was partially hydrolysed by treatment with 10% aqueous HCl in methanol. After work-up with water and ether the very volatile (**2a**) was separated from starting material by sublimation to a cold surface (−195°); m.p. 36—37°.

The significant features of the new compounds are: in the i.r. spectrum (CCl_4) a carbonyl stretching frequency at 1835 cm^{-1}; in the u.v. spectrum (hexane) a maximum at 216 nm (ϵ 3495) and a weaker band with fine structure at 365, 373, and 381 nm (ϵ 321, 372, and 241, respectively); and in the ^{1}H n.m.r. spectrum of (**2a**) a singlet at δ 1·63 and in that of (**2b**) a singlet at δ 1·63, a triplet at δ 0·82, and a quartet at δ 2·10 (J 7·5 Hz).†



(2) a; $R^1 = R^2 = $ Me
b; $R^1 = $ Me, $R^2 = $ Et

The carbonyl stretching frequency of (**2**) is remarkably high, about 85 cm^{-1} above that of an $\alpha\beta$-unsaturated-γ-lactone (ν_{CO} 1750 cm^{-1})[2] and only about 14 cm^{-1} below that of an α-lactam.[3] In general the $\alpha\beta$-azofunction appears to enhance a carbonyl stretching frequency.[4] An electron-withdrawing γ-substituent in a γ-lactone also enhances ν_{CO}.[2,5] Oxadiazolinones (**2**) are unique in that both effects

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† Satisfactory elemental analyses have been obtained.

can operate on the carbonyl group to make it unusually electrophilic.

The special structural features of (**2**) result in remarkable reactivity. Dry (**2a**) seems to be stable at 3° in the dark but, at 3° in a bottle that was opened occasionally, it had a half-life of only 3 weeks, at which time 50% had been converted into acetone azine. At room temperature (**2a**) and (**2b**) reacted slowly with distilled water to yield ketone and the corresponding azine. The ready hydrolysis of compounds (**2**) means that their synthesis according to the method described requires caution.

Thermolysis of neat (**2b**) at 83° gave the azine of butan-2-one (52%), butan-2-one (39%), an unidentified product (9%), and gases.‡ In CCl_4 (0·5M-solution) at the same temperature, (**2b**) gave azine (13%), ketone (87%), and a trace of the unidentified product.

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‡ The quoted yields are relative percentages of the non-gaseous products as estimated by g.l.p.c. or n.m.r.

[1] A. M. Cameron, P. R. West, and J. Warkentin, *J. Org. Chem.*, 1969, **34**, 3230.
[2] L. J. Bellamy, "The Infra-Red Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958, pp. 186—187.
[3] H. E. Baumgarten, *J. Amer. Chem. Soc.*, 1962, **84**, 4975.
[4] For examples, see P. R. West and J. Warkentin, *J. Org. Chem.*, 1968, **33**, 2089.
[5] G. B. Gubelt and J. Warkentin, *Canad. J. Chem.*, 1970, **48**, 1391.