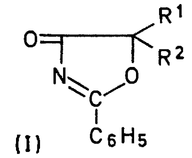
A New Synthesis of a Little Known Heterocyclic System: 4(5*H*)-Oxazolones

By Y. SHYAMSUNDER RAO and ROBERT FILLER*

(*Department of Chemistry, Illinois Institute of Technology, Chicago, Illinois* 60616)

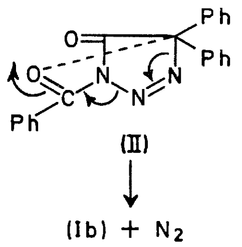
Summary α-Halogeno-imides react with sodium hydride to form 4(5*H*)-oxazolones, this reaction representing a new general route to this class of compounds.

A RECENT report[1] of the reaction of α-halogeno-imides with base prompts us to communicate our results in the synthesis of 4(5*H*)-oxazolones (2-oxazolin-4-ones), as part of our studies of the chemistry of oxazolones.[2] The parent compound (Ia) was first prepared by Sheehan and Izzo[3] by reaction of diazomethane with benzoyl isocyanate. Compound (Ib) was reported by Japp and Findlay[4] to be formed from benzonitrile and benzilic acid in the presence of concentrated H_2SO_4. It has since been shown[5] that the product is not (Ib), but the isomeric 5(4*H*)-oxazolone. 2,5,5-Triphenyl-4(5*H*)-oxazolone (Ib) was finally obtained[6] by cleavage of the oxo-triazoline (II), followed by ring closure with the elimination of nitrogen. More recently, a number of derivatives of 4(5*H*)-oxazolones have been reported.[7,8]



(I)

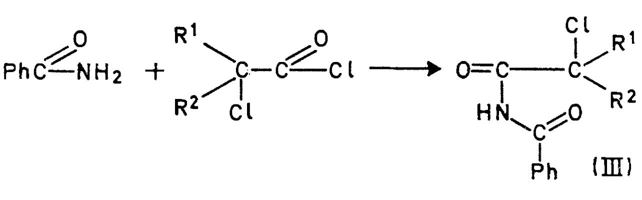
a; $R^1 = R^2 = H$
b; $R^1 = R^2 = Ph$
c; $R^1 = H; R^2 = Ph$



We now report a general method for the synthesis of these 4(5*H*)-oxazolones. α-Chloro-imides (III) are prepared by heating molar equivalent amounts of benzamide and the corresponding α-chloro-acid chlorides.[9] Treatment of (III) with sodium hydride in dry benzene gave the corresponding 4(5*H*)-oxazolones in 50—70% yields.

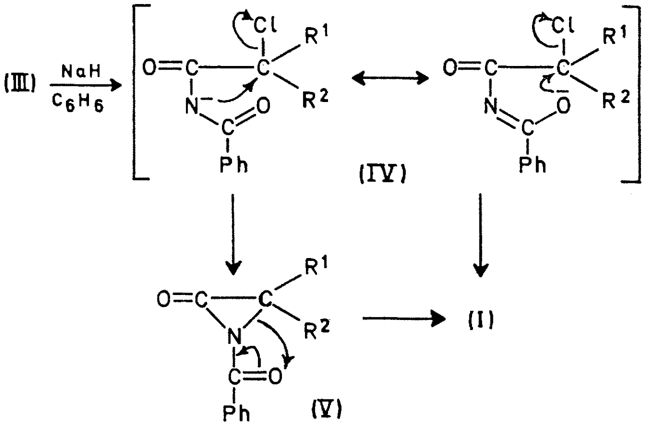
We suggest the mechanism shown in the Scheme for the cyclization reaction.

The ambident anion (IV) could form an α-lactam (V), which would rearrange to the oxazolone (analogous to the Favorskii rearrangement). Alternatively, the oxazolone would be formed directly by *O*-attack on carbon with ready displacement of Cl^-. At present we have no evidence of the intermediacy of α-lactams and we favour the direct displacement mechanism.



a; $R^1 = R^2 = H$ b; $R^1 = R^2 = Ph$ c; $R^1 = H, R^2 = Ph$

Compounds (Ia—c) exhibit strong carbonyl absorption near 1705 cm^{-1}, typical of saturated γ-lactams.[11] Authentic samples of (Ia) and (Ib), prepared by reaction of diazomethane and diphenyldiazomethane,[12] respectively, with benzoyl isocyanate,[13] were identical with the compounds described above (mixed m.p. and i.r. spectra). The diphenyl derivative (Ic) is a new compound, m.p. 161° (uncorrected).



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