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A NEW ONE-STEP SYNTHESIS OF AZIRIDINES FROM OXIRANES

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Recently Appel and Halstenberg[1] reported the conversion of epoxides into oxazaphospholidines by equimolar quantities of N-substituted iminophosphoranes. The five membered heterocyclic compounds undergo thermolysis to give aziridines. We now wish to report a one-step synthesis of aziridines in which oxiranes are simple treated with the sodium salt of an N-substituted amidophosphoric ester in a high boiling solvent.

Typically, 5.73 g (2.5 mmole) of diethyl N-phenylamidophosphate[2] in 20 ml dry xylene was added dropwise to a suspension of sodium hydride in 30 ml of the same solvent. When the evolution of hydrogen ceased 3 g (2.5 mmole) styrene oxide and 20 ml xylene was added and the mixture slowly brought to reflux (within 4 hr). Evaporation of the solvent in vacuo, treatment of the residue with hexane and column chromatography over neutral alumina afforded 2.75 g (62%) 1,2-diphenylaziridine[3] [nmr (CCl_4) δ 2.2-2.5 (m, 2), 2.95 (dd, 1), 6.5-7.4 ppm (m, 10); m/e 195 (M+); no NH absorption in the ir spectrum].

The results of some further experiments are listed in Table I.

While amidophosphoric ester anions react smoothly with carbonyl and thiocarbonyl compounds at room temperature[4] they attack epoxides at reasonable rate only at the boiling temperatures of toluene and xylene. In 1,2-dimethoxyethane (bp 83°) long reaction periods are required and substantial ring opening of the products takes place. Experiments conducted in DMF did not yield any aziridine derivatives, owing to a competing reaction of the amidophosphate anion with the solvent to give $(CH_3)_2N{=}CHNR^1$.

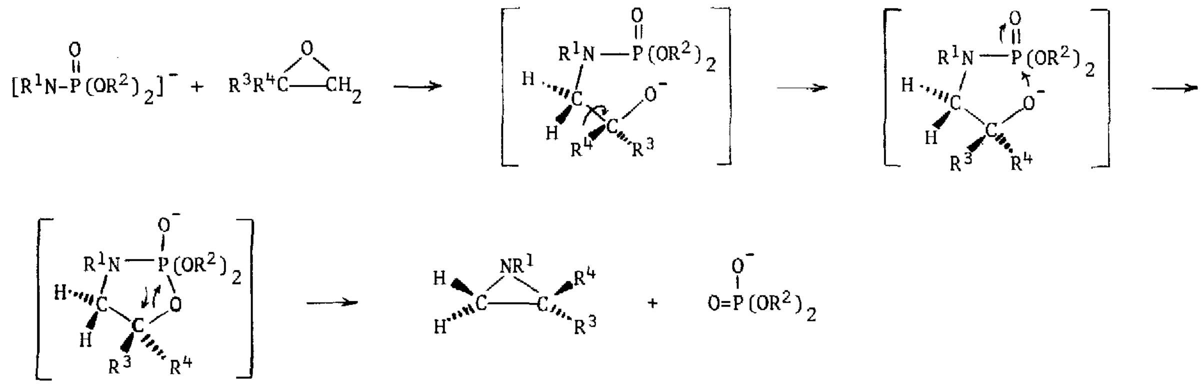
While the aziridine synthesis of Appel and Halstenberg[1] may be regarded as a special Wittig reaction, our method resembles the corresponding Horner modification in which the intermediate needs not to be isolated.

The proposed mechanism involves nucleophilic attack of the amidophosphate ester anion on the less substituted oxiran carbon. The ring closure to the aziridine structure is then accompanied by phosphate ester elimination.

Table I. Examples of Aziridine Synthesis from Amidophosphoric Esters, $R^1NHP(O)(OR^2)_2$ and Epoxides $R^3R^4\overline{C\text{-}O\text{-}C}H_2$

Ester		Epoxide			Reaction	Yield of
R^1	R^2	R^3	R^4	Solvent	time, (hr)	aziridine, (%)[a]
C_6H_5	C_2H_5	C_6H_5	H	toluene	4	38
$C_6H_5CH_2$	C_2H_5	C_6H_5	H	xylene	4	58
$C_6H_5CH_2$	C_2H_5	C_6H_5	H	1,2-dimethoxyethane	10	10
$(CH_3)_3C$	C_6H_5	C_6H_5	H	xylene	4	30
C_6H_5	C_2H_5	C_6H_5	CH_3	1,2-dimethylethane	10	21

[a] The aziridines were identified by direct comparison with authentic samples.



The application of the new synthesis for the preparation of arene imines[5] and the kinetics of the reaction are now under investigation.

References and Notes

1) R. Appel and H. Halstenberg, Chem. Ber., **109**, 814 (1976).

2) The amidophosphoric esters were prepared by the methods of H. McCombie, B.C. Saunders and G.J. Stacey, J. Chem. Soc., 380 (1945), and F.R. Atherton, H.T. Openshaw and A.R. Todol, ibid., 660 (1945).

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5) J. Blum, Y. Ittah and I. Shahak, Tetrahedron Lett., 4607 (1975).