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A MILD CYCLIZATION OF 2-AMINOALCOHOLS TO AZIRIDINES USING DIPHOSPHORUS TETRAIODIDE

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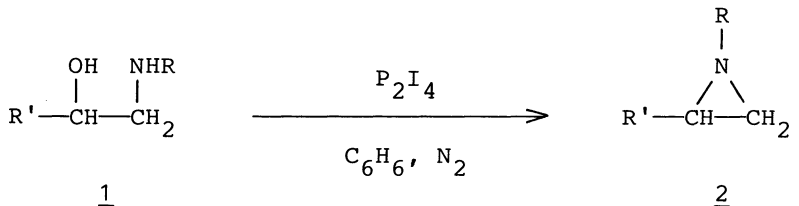
The reaction of 2-aminoalcohols with diphosphorus tetraiodide in benzene at room temperature leads to the corresponding aziridines in good to moderate yields.

Diphosphorus tetraiodide (P_2I_4) is a unique reagent which can effect dehydration of aldoximes,[1] amides,[2] and primary nitroalkanes[3] to nitriles under mild conditions. It can also combine carboxylic acids with amines into amides.[4] In the present paper, we wish to report a further application of this reagent to the dehydrative cyclization of 2-aminoalcohols to aziridines.[5]



1 2

On treatment with P_2I_4 in dry benzene for a day at room temperature, 2-aminoalcohols 1 are cleanly converted to the corresponding aziridines 2 in 45-75% isolated yields (Table 1). The reaction proceeds smoothly under mild conditions with only slight amounts of by-products.

The typical procedure is as follows: Freshly prepared P_2I_4 (1.0 mmol) was added to a solution of 2-t-butylamino-1-phenylethanol (1b: 1.0 mmol) in dry benzene (10 ml) under nitrogen and the mixture was stirred for 20-24 h at room temperature. Dilute aqueous sodium carbonate was then added and organic phase was extracted with ether, dried over sodium sulfate, and evaporated. The residue was purified by distillation through a Kugelrohr apparatus, giving 1-t-butyl-2-phenylaziridine (2b; 62%): ^{1}H NMR (CCl_4) δ=1.02 (9H, s), 1.45 (1H, dd, J=4 and 8), 1.98 (1H, dd, J=4 and 16), 2.47 (1H, dd, J=8 and 16), and 7.10 (5H, s); MS (70 eV) m/e 175 (M^+).

The conversion of 1 to 2 is generally carried out by two-step procedures which involve initial transformation of 1 to 2-halogenoamines (Gabriel method[6]) or 2-aminoethyl hydrogensulfate (Wenker method[7]) and subsequent cyclization of

Table 1. Dehydrative cyclization of 2-aminoalcohols with diphosphorus tetraiodide

	2-Aminoalcohol 1[a]		Reaction	Aziridine 2[b]
	R	R'	time/h	Yield/%
a	$CH_3(CH_2)_3$	C_6H_5	23	75
b	$(CH_3)_3C$	C_6H_5	22	62
c	$CH_2CH_2CH_2CH_2CH_2CH$ (ring)	C_6H_5	20	58
d	$C_6H_5CH_2$	C_6H_5	24	50
e	$C_6H_5CH_2CH_2$	C_6H_5	20	64
f	$C_6H_5CH_2$	CH_3	24	45
g	$C_6H_5CH_2$	CH_3CH_2	24	62

a) Aminoalcohols are prepared from the reaction of amines with epoxides. Substrates and products are all known compounds.

b) Yields refer to isolated compounds and are not optimized.

these intermediates to the corresponding aziridines. Improved one-step methods which were recently reported utilize the reaction of 2-aminoalcohols with triphenylphosphine dibromide in the presence of triethylamine,[8] or triphenylphosphine in the presence of carbon tetrachloride and triethylamine.[9] However, the cyclization procedure described herein has some advantages over the known phosphine-based methods in that triphenylphosphine oxide and piperidines which in some cases complicate the isolation of pure product are not formed, and phosphorus-containing side products are water-soluble and easily removed during aqueous work-up. The mild reaction conditions, simplicity of performance, and good yields make this method a useful addition to the existing methodology for aziridine synthesis.

References

1) H. Suzuki, T. Fuchita, A. Iwasa, and T. Mishina, Synthesis, 1978,905; Nippon Kagaku Kaishi, 1979, 91.
2) H. Suzuki and N. Sato, Nippon Kagaku Kaishi, 1981, 121.
3) J. N. Denis and A. Krief, Tetrahedron Lett., 1979, 3995.
4) H. Suzuki, J. Tsuji, Y. Hiroi, N. Sato, and A. Osuka, Chem. Lett., 1983, 449.
5) For a general survey of aziridine chemistry, see O. C. Dermer and G. E. Ham, "Ethyleneimine and Other Aziridines —— Chemistry and Applications," Academic Press, New York (1969).
6) S. Gabriel, Chem. Ber., 21, 1049, 2669 (1888).
7) H. Wenker, J. Am. Chem. Soc., 57, 2328 (1935).
8) I. Okada, K. Ichimura, and R. Sudo, Bull. Chem. Soc. Jpn., 43, 1185 (1970).
9) R. Appel and R. Kleinstuck, Chem. Ber., 107, 5 (1974).

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