A Novel Synthesis of 3-Phenyloxaziridines

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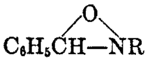
The synthesis of the oxaziridine system,[1] a three-membered ring containing carbon, oxygen, and nitrogen, was independently announced in 1956–1957 by three different groups.[2–4] The most useful preparation of oxaziridines is the oxidation of imines with organic per acids. As part of a study on the spectral properties of three-membered rings, we became interested in the synthesis of 3-phenyl-2-*n*-alkyloxaziridines. Emmons,[2] in his study of the physical properties of oxaziridines, noted that the stability of the oxaziridine ring is markedly influenced by its substituent groups. Attempts of Emmons to prepare 3-phenyloxaziridines other than those with a 2-*t*-alkyl substituent were unsuccessful when peracetic acid was employed as the oxidizing agent. In addition, Emmons found that 2-benzyloxaziridines were also unstable. Emmons suggested that this instability was due to either the extreme sensitivity of the imine to acid-catalyzed hydrolysis or to the facile decomposition of the oxaziridine to benzaldehyde after it was formed.

We speculated that the acid-catalyzed decomposition of either the oxaziridine or the imine could be circumvented by the use of a per acid which, on peroxidation of the imine, would precipitate the parent carboxylic acid from an anhydrous reaction medium. We have found that 3-phenyl-2-*n*-alkyloxaziridines are readily prepared by the addition of *m*-chloroperbenzoic acid in methylene chloride to a solution of the Schiff base in the same solvent. Although no attempts were made to optimize the conditions, yields of >60% were obtained in all cases. The successful preparation of several 3-phenyl-2-*n*-alkyloxaziridines by this procedure demonstrates firstly, the stability of this class of oxaziridines and secondly, that the failure of Emmons to obtain these compounds was indeed due to the acid-catalyzed hydrolysis of either the imine or the oxaziridine.

TABLE I

PHYSICAL PROPERTIES OF OXAZIRIDINES



$C_6H_5CH{-}NR$

R	Imine bp, °C (mm)	Oxaziridine bp, °C (mm)	$n^{20}D$	Carbon, % Calcd	Carbon, % Found	Hydrogen, % Calcd	Hydrogen, % Found	Active oxygen,[i] %
Methyl[a]	69 (10)	45[g] (0.07)	1.5285	71.11	71.16	6.72	7.19	98
Ethyl[b]	81 (9.5)	52 (0.10)	1.5190	72.49	71.96	7.38	7.56	96
Isopropyl[c]	74 (8.0)	52.5 (0.05)	1.5082	73.59	73.46	8.03	8.61	99
t-Butyl[d]	76 (4.0)	61 (0.03)	1.5070	74.54	74.28	8.53	8.76	96
Neopentyl[e]	80 (12)	112 (0.3)	1.4960	75.35	74.92	8.96	8.83	95
Benzyl[f]	140 (1.0)	15–18[h]	1.5805	79.63	79.15	6.20	6.60	95

[a] Reference 4 reported bp 72–73° (13 mm). [b] H. Zauschirn [*Ann.*, **245**, 281 (1888)] reported bp 195° (749 mm). [c] *Anal.* Calcd for $C_{10}H_{13}N$: C, 81.58; H, 8.90. Found: C, 81.70; H, 9.27. [d] Reference 4 reported bp 90–92° (11 mm). [e] *Anal.* Calcd for $C_{12}H_{17}N$: C, 82.23; H, 9.77. Found: C, 81,77; H, 10.04. [f] A. T. Mason and G. R. Winder [*J. Chem. Soc.*, **65**, 191 (1894)] reported bp 200–202° (10–20 mm). [g] Krimm[4] has reported the synthesis of 3-phenyl-2-methyloxaziridine. Attempts to distil the purified material at the temperature and pressure quoted by Krimm led to decomposition. [h] Melting point. [i] Active oxygen was determined by iodometric titration.

Experimental Section

Preparation of Imines.—The imines employed as starting materials were prepared by condensation of the appropriate amine with benzaldehyde at ice-bath temperature. Strong absorption for the C=N stretching at 6.0–6.1 μ was observed in the infrared spectrum of each imine.

Oxaziridine Formation.—*m*-Chloroperbenzoic acid (18.9 g, 0.11 mole) in methylene chloride (200 ml) was added dropwise to a solution (50 ml) of the imine (0.10 mole) in the same solvent. After the addition was complete, the solution was filtered to remove the *m*-chlorobenzoic acid. The filtrate was washed with dilute sodium sulfite solution and dilute sodium carbonate solution and dried over sodium carbonate. After evaporation of the methylene chloride, the oxaziridine was purified by either vacuum distillation or recrystallization. The physical properties of the oxaziridines which were prepared by this procedure are summarized in Table I along with the boiling points of the corresponding imines.

Registry No.—Benzylidenemethylimine, 622-29-7; 2-methyl-3-phenyloxaziridine, 3400-12-2; benzylideneethylimine, 6852-54-6; 2-ethyl-3-phenyloxaziridine, 7771-15-5; benzylideneisopropylimine, 6852-56-8; 2-isopropyl-3-phenyloxaziridine, 7731-32-0; benzylidene-*t*-butylimine, 6852-58-0, 2-*t*-butyl-3-phenyloxaziridine, 7731-34-2, benzylideneneopentylimine, 7731-35-3; 2-neopentyl-3-phenyloxaziridine, 7731-36-4; benzylidenebenzylimine, 780-25-6; 2-benzyl-3-phenyloxaziridine, 7731-37-5.

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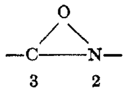
[1] The numbering of the oxaziridine ring is



[2] W. D. Emmons, *J. Am. Chem. Soc.*, **78**, 6208 (1956); **79**, 5739 (1957).

[3] L. Horner and E. Jurgens, *Ber.*, **90**, 2184 (1957).

[4] H. Krimm, *ibid.*, **91**, 1057 (1957).