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A New Synthetic Route to 2-Oxazolidones

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Summary 2-Oxazolidones were obtained in good yield from the reaction of carbon dioxide and aziridine compounds in the presence of iodine.

AZIRIDINE reacts at low temperatures with carbon dioxide to give the crystalline homopolymerization product, m.p. -10 °C.¹ We have previously reported² that aziridine and 2-methylaziridine copolymerize with carbon dioxide to give polyurethane copolymers in the absence of a catalyst. We now report that aziridine and 2-methylaziridine react with carbon dioxide to give the corresponding 2-oxazolidones in the presence of iodine.

Carbon dioxide, iodine, and 2-methylaziridine (or aziridine) were heated in a solvent in a 50 ml stainless steel vessel (Table). In the case of 2-methylaziridine, the reaction mixture was distilled under reduced pressure to give 4-methyl-2-oxazolidone [liquid, b.p. 129·5—130·0 °C at 3 mmHg (lit.³ 155—160 °C at 11 mmHg); ν_{max} 1735 and 1240 cm⁻¹; δ (CDCl₃) 1·3 (3H, d, Me), 4·0 (2H, m, CH₂ and CH), 4·5 (1H, m, CH₂), and 6·7 (1H, br s, NH); *M ca.* 100 (vapour pressure osmometry)].[†]

The reaction with aziridine produced a polymer which was separated by precipitation with diethyl ether. After filtration and removal of the bulk of the solvent by evaporation, the remaining solution was cooled to room temperature to give a white crystalline solid which recrystallized from chloroform to afford 2-oxazolidone as white needles [m.p. $86\cdot0-88\cdot0$ °C (lit.³ 87-89 °C); ν_{max} 1735, 1256, 1085, 1023, 970, and 920 cm^-1, δ (D2O) 4.16 (2H, t, CH2) and 5.02 (2H, t, CH2)].†

TABLE. Reaction of carbon dioxide with 2-methylaziridine^a

Temp.	CO2	I,	Solventb	Time	4-Methyl- 2-oxazolidone	
(°C)	(mmol)	(mmol)		(h)	(mmol)	(%)°
60	150	0.04	CH ₂ Cl ₂	24	9.1	80.5
80	125	0.04	CHCl,	24	$6 \cdot 1$	54.0
,,	83	0.06	CH2Cl2	24	8.8	77.9
"	150	0.06	EtOH	21	5.0	$44 \cdot 2$
,,	150	0.04	Me ₂ SO	24	$2 \cdot 8$	$24 \cdot 8$
"	150	0.04	$n-\bar{C_6}H_{14}$	24	$1 \cdot 1$	9·0
"	150	0.04	C ₆ H ₆	24	0.6	$5 \cdot 0$

 $^{\rm a}$ 11.3 mmol of 2-methylaziridine was used in each case. $^{\rm b}$ 30.0 mmol of solvent was used in each case. $^{\rm c}$ Based on 2-methylaziridine.

The effects of solvent, temperature (25-80 °C) and the ratios of the reactants on the yields were investigated. The optimum yield $(21\cdot5\%)$ of 2-oxazolidone was obtained from aziridine $(14\cdot9 \text{ mmol})$, carbon dioxide (150 mmol), and iodine $(0\cdot06 \text{ mmol})$ in CH₂Cl₂ (30 mmol) which was a little better than that in CHCl₃. The optimum yield from 2-methylaziridine was also obtained in CH₂Cl₂ and the effect of other solvents is shown in the Table.

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[†] Satisfactory elemental analyses were obtained for these compounds.

¹ A. Seher, Annalen, 1952, 575, 153.

² K. Soga, S. Hosoda, and S. Ikeda, Makromol. Chem., 1974, 175, 3309.

⁸ M. E. Dyen and D. Swern, Chem. Rev., 1967, 67, 197.