Thermal Cross-coupled Dimerisation of Alkali and Alkaline Earth Metal Salts of Methacrylic–Crotonic Acid Binary Systems in the Solid State

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Thermal reaction of sodium and potassium salts of methacrylic-crotonic acids in the solid state selectively affords a cross-coupled dimer, dimethyl hex-1-ene-2,4-dicarboxylate.

We have reported on the thermal oligomerisation reaction of alkali and alkaline earth metal salts of unsaturated carboxylic acids in the solid state. The orientation of double bond in dimerisation, whether head to head or head to tail, was controlled by their crystal lattice. In the case of alkaline earth metal salts of methacrylic acid (MA), under the circumstances where the crystal lattic collapsed as a result of the formation of the oligomer, then dimethyl hex-1-ene-2,5-dicarboxylate 1, a head to head type oligomer, was obtained, whereas if the crystal structure altered to another one during oligomer formation, then dimethyl 4-methylpent-1-ene-2,4-dicarboxylate 2, a head to tail type oligomer, was obtained together with 1.^{1–3} The sodium salt of crotonic acid (CA) afforded almost quantitatively dimethyl hex-1-ene-3,4-dicarboxylate 3.^{4,5}

Binary systems, containing either calcium or barium salts of MA-acrylic acid gave a mixture of dimers comprising binary acid moieties and homodimers of each acid.^{6,7} We report here an alkali and alkaline earth metal dependent selective cross dimerisation of the corresponding MA–CA binary salts in their solid state thermal reaction. The metal salts were dried *in vacuo* at 50–60 °C to anhydrous salts. The thermal reaction

was conducted with 2–3 g of the metal salts by heating at 200, 230 and 250 °C for 3 h under reduced pressure. The reaction mixture was acidified with aqueous hydrochloric acid to liberate carboxylic acids, which were extracted with diethyl ether, and then converted to the methyl ester through treatment with diazomethane. The amount of each dimer was analysed by gas chromatography with an internal standard. For a preparative run, 20 g of the metal salt was heated, the products obtained were fractionated by distillation. Seven metals were used to prepare the corresponding salts (the alkali metals Li, Na, K and the alkaline earth metals Mg, Ca, Sr and Ba). The results are summarised in Table 1.



Scheme 1

methacrylic_crotonic acids in the solid state

Metal salts	Heating		Dimer conversion (%) ^a			
	T/°C	t/h	1	2	3	4
Li	200	3	9.5			
	230	3	17.7			
	250	3	17.0			<u></u>
Na	200	3		5.2		24.4
	230	3		6.8	9.6	48.1
	250	3	1.2	15.9	9.6	59.0
К	200	3	_			
	230	3		0.5		3.8
	250	3		2.1		19.5
Mg	200	3	13.1	_		
	230	3	23.5		8.6	_
	250	3	22.6			
Ca	200	3	16.1			
	230	3	13.5		6.6	
	250	3	35.7	—		—
Sr	200	3	26.5	_		—
	230	3	17.0		10.9	
	250	3	32.6		-	
Ba	200	3	21.5	3.7		5.7
	230	3	10.6	20.5		14.6
	250	3	35.4	21.5	0.3	19.0

^{*a*} 1 =dimethyl hex-1-ene-2,5-dicarboxylate; 2 =dimethyl 4-methylpent-1-ene-2,4-dicarboxylate; 3 =dimethyl hex-1-ene-3,4-dicarboxylate; 4 =dimethyl hex-1-ene-2,4-dicarboxylate.

Dimers 1 and 2 were derived from the dimerisation of MA, and 3 from that of CA, respectively. The spectra of these dimers were identical to those previously reported.^{2,5} The

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structure of **4** was elucidated based on its mass, NMR and IR spectra.[†] The formation of **4** is assumed to proceed by a biradical mechanism as shown in Scheme 1.

Out of the seven metal salts examined, only three, namely Na, K and Ba salts, afforded 4 selectively upon heating the others gave 1, 2 and 3, which were derived from two molecules of MA, or CA, respectively, with no formation of 4.

The selective formation of 4 from Na and K salts is closely related to their crystal lattice which was maintained, even after reaction, as the crystal structure of these salts is such as to allow it.

Further study on the relation between the cross dimerisation and the crystal state of the binary salt mixture by X-ray diffraction analysis, is in progress.

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[†] Mass spectrum m/z 200 (M^{+·}), 169 (– OMe). ¹H NMR δ 0.91 (3H, s) 1.61 (2H, m), 2.52–2.60 (3H, m), 3.64 (3H, s), 3.76 (3H, s), 5.57 (1H, s), 6.17 (1H, s). ¹³C NMR δ 11.63 (-CH₃), 25.47 (-CH₂-), 34.57 (-C-), 46.23 (-CH₂-), 51.33 (-OCH₃), 51.89 (-OCH₃), 126.76 (=CH₂), 138.07 (=C), 167.21 (C=O), 175.78 (C=O). IR v/cm⁻¹ 1726 (C=O).