Thermal Dimerization of Alkali-metal Salts of Crotonic Acid in the Solid State

Kiyoshi Naruchi * **and Masatoshi Miura**
Department of Synthetic Chemistry, Faculty of Engineering, Chiba University, Yayoicho, Chiba-shi 260, Japan

---

The thermal reaction of sodium crotonate (Na-crotonate) in the solid state gave a nearly quantitative yield of hex-1-ene-3,4-dicarboxylate (**1**). Potassium crotonate (K-crotonate), on the other hand, afforded three isomeric dimers, *i.e.* (**1**), 4-methylpent-2-ene-3,5-dicarboxylate (**2**), and 2-methylene-3-methylbutane-1,4-dicarboxylate (**3**). In the case of Na-crotonate, *X*-ray analysis suggests the formation of a solid solution crystal during dimerization. K-Crotonate yielded predominantly (**3**) at the early stage of the reaction at 295 °C with formation of a solid solution crystal. At a higher temperature, *i.e.* 320 °C, (**1**) and (**3**) were gradually converted into (**2**), resulting in the decay of the crystal structure.

We have previously reported on the thermal reaction of alkaline-earth metal methacrylates in the solid state, leading to formation of dimers, trimers, and tetramers.[1-4] In the solid-state reaction the structure of the oligomer formed depends upon whether or not the crystal structure of the monomer is maintained in the course of oligomerization. We have also reported on the solid-state thermal reaction of sodium crotonate (Na-crotonate): Na-crotonate should have little tendency to polymerize at 300 °C but afforded hex-1-ene-3,4-dicarboxylate (**1**) in a nearly quantitative yield.[5]

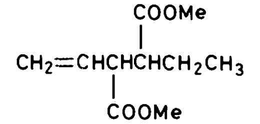
We report here that the solid-state dimerization of potassium crotonate (K-crotonate) yields three isomeric dimers. Changes of the crystalline state during dimerization were examined by *X*-ray diffraction analysis so as to explain the difference in product formation between the two alkali-metal crotonates.

Results

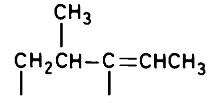
Differential Scanning Calorimetry and Thermogravimetric Analysis of Na- *and* K-*Crotonate.*—Thermogravimetric analysis of Na- and K-crotonate showed sudden weight loss without melting, at 450 and 410 °C, respectively. Below these temperatures no weight loss was observed with both salts. Differential thermal analysis of Na-crotonate showed a small exothermic peak at *ca.* 330 °C, which is presumably due to the heat of polymerization. K-Crotonate exhibited no corresponding peak. Both salts showed massive exothermic peaks at temperatures where major weight loss is observed on thermogravimetric analysis.

Structures of Dimers obtained from K-*Crotonate.*—K-Crotonate was heated for 4 h at 320 °C under reduced pressure. The products were treated with diazomethane to obtain the corresponding methyl esters. G.c. analysis of the methyl esters showed three peaks corresponding to three isomeric dimers. Separation of the dimer fraction, b.p. 100 °C at 6—135 °C at 6 mmHg, was carried out by fractional distillation and preparative g.c. The structures of the isomeric dimers were elucidated by ^{1}H n.m.r., mass, and i.r. spectroscopy.

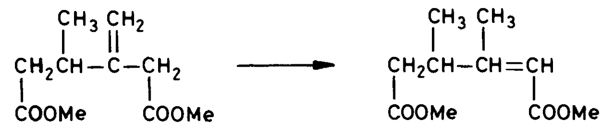
One isomer was identified as dimethyl hex-1-ene-3,4-dicarboxylate (**1a**) which had previously been shown to be the sole product from Na-crotonate.[5] The ^{1}H n.m.r., mass, and i.r. spectra were in good agreement with those of an authentic sample of (**1a**).


$CH_2{=}CHCH(COOMe)CH(COOMe)CH_2CH_3$

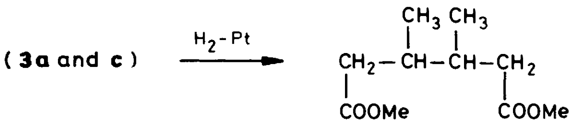
(**1a**)


$CH_2(COOMe)CH(CH_3)\text{-}C(COOMe){=}CHCH_3$

(**2a**)


$CH_2(COOMe)CH(CH_3)\text{-}C({=}CH_2)\text{-}CH_2COOMe \longrightarrow CH_2(COOMe)CH(CH_3)\text{-}CH{=}C(CH_3)COOMe$

(**3a**) (**3c**)


$(\mathbf{3a}\ \text{and}\ \mathbf{c}) \xrightarrow{H_2\text{-}Pt} CH_2(COOMe)\text{-}CH(CH_3)\text{-}CH(CH_3)\text{-}CH_2COOMe$

(**3b**)

The ^{1}H n.m.r. spectrum of the second isomer showed two methyl protons, both doublets, at δ 1.05 and 2.15. The methyl proton attached to a double bond appeared at δ 5.50 as a quartet and two methoxy protons as singlets at δ 3.61 and 3.62, respectively. Based upon these data, the isomer was identified as dimethyl 4-methylpent-2-ene-3,5-dicarboxylate (**2a**). The mass and i.r. spectra confirmed the structure.

The ^{1}H n.m.r. spectrum of the third isomer revealed two broad singlets, at δ 5.63 and 5.89, corresponding to terminal methylene protons. Two methylene protons and a methyne proton were observed as a multiplet at δ *ca.* 2.22. This isomer was found to be thermally unstable. Several hours of heating at 170—180 °C resulted in complete disappearance of the terminal methylene protons and simultaneous emergence of a new methyne proton at δ 6.73. Hydrogenation of this isomer and its rearrangement product gave the same product, which showed two methyl protons as a doublet at δ 1.00, two methyne protons as a multiplet at δ 1.44, and two methylene protons as a doublet at δ 2.20, indicative of a symmetrical structure (**3b**). The isomer was thus elucidated as (**3a**), which was converted into (**3c**) through double-bond migration.

Dimer Formation of Na- *and* K-*Crotonate in Relation to Heating Time.*—Conversion of Na- and K-crotonate into dimers as a function of heating time is shown in Figures 1—3. As shown in Figure 1, Na-crotonate is converted into (**1**) even at 250 °C and its yield reached 90% in 4 h at 300—320 °C. K-Crotonate, on the other hand, afforded no dimer at 250 °C. At

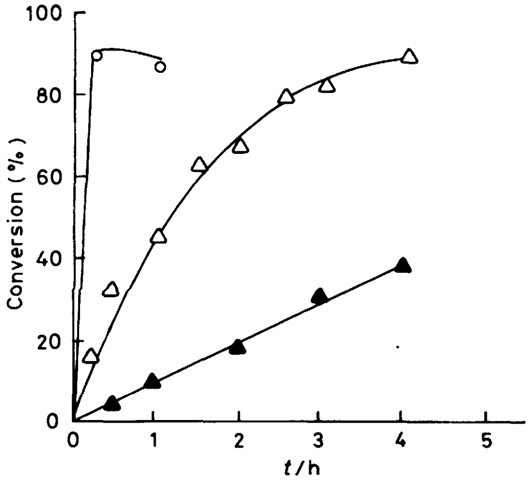


Figure 1. Effect of heating temperature on conversion of sodium crotonate into dimer: ○, 320; △, 300; ▲, 250 °C

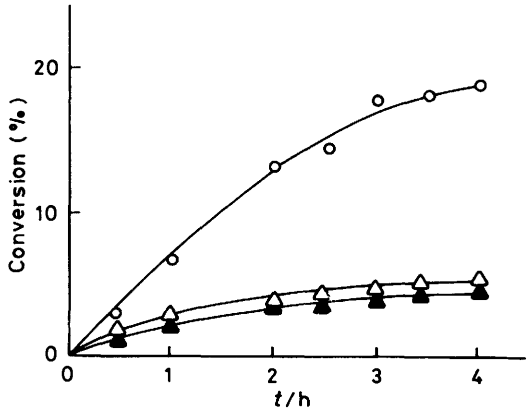


Figure 2. Conversion of potassium crotonate into dimers at 295 °C: ▲, (**1a**); △, (**2a**); ○, (**3a**)

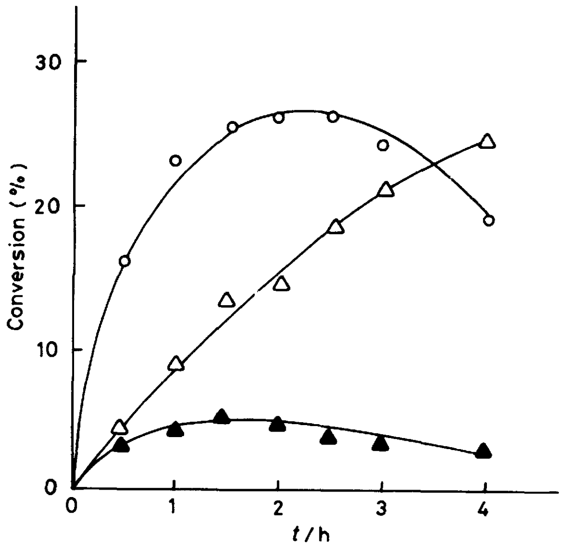


Figure 3. Conversion of K-crotonate into dimers at 320 °C: ▲, (**1a**); △, (**2a**); ○, (**3a**)

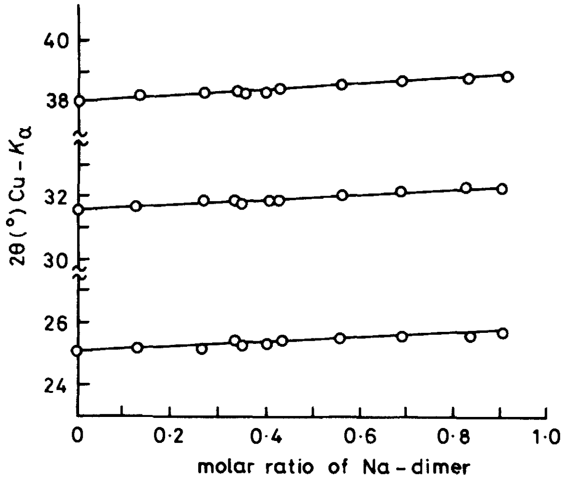


Figure 4. Relation between the molar ratio of Na-dimer and the peak (2θ) shift on X-ray diffraction. Dimerization at 300 °C

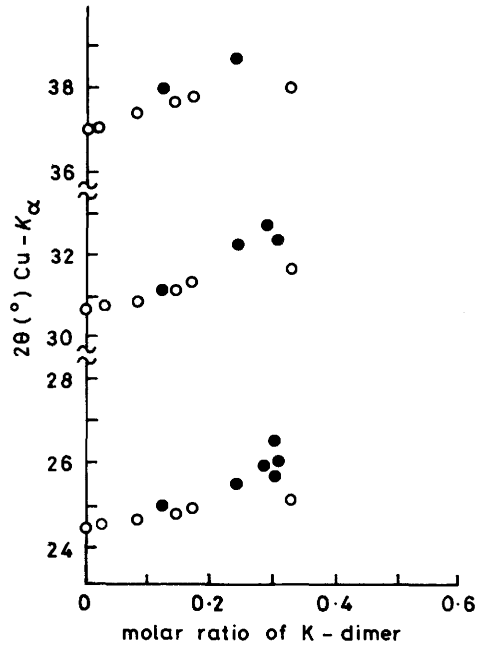
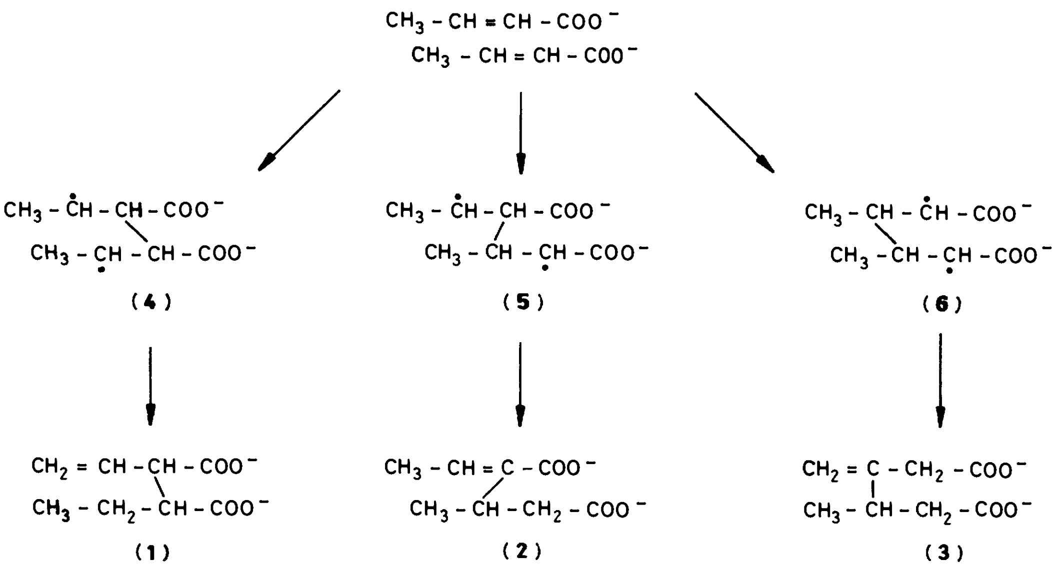


Figure 5. Relation between the molar ratio of K-dimer and peak (2θ) shift on X-ray diffractions: ○, dimerization at 295 °C (molar ratio of the components derived from Figure 2); ●, dimerization at 320 °C (molar ratio of the components derived from Figure 3)

295—320 °C K-crotonate gave three dimers as shown in Figures 2 and 3. But the combined yield of the three dimers was less than of (**1**) from Na-crotonate at each temperature. The dimerization of K-crotonate is thus less selective and requires higher heating temperatures.

X-*Ray Diffraction Study of Structural Changes of Crystals*.—The change in crystal structure of Na- and K-crotonate during dimerization was examined by X-ray diffraction analysis. Figure 4 shows the shifts of peaks at $2\theta = 25.16, 31.65$, and 38.17° in Na-crotonate crystal with conversion into the dimer. The three peaks shifted linearly towards higher angles, suggesting the formation of a solution crystal of Na-crotonate and the sodium salt of (**1**): the crystal structure is maintained though the face distance of the crystal gradually decreases with conversion.



Scheme.

In the case of K-crotonate (Figure 5) a similar linear relationship was maintained only until the conversion into dimers reached *ca.* 20%, and further conversion results in lowering of refractive intensities and broadening of the refractive peaks, suggesting destruction of the crystal structure.

Discussion

While dimerization of Na-crotonate gave exclusively (**1**) in high yield, that of K-crotonate gave three dimers (**1**)—(**3**) in much lower yield. With Na-crotonate, the crotonate anions may be in the best arrangement to form (**1**), and this crystal structure appears to be maintained up to high conversion of the monomer, resulting in high selectivity and high yield of the dimer. On the other hand, the crotonate anions in the crystal of K-crotonate may be separated from one another because of the larger ionic radius of potassium (1.33 Å) compared with that of sodium (0.95 Å). This is confirmed by the smaller refractive angles of K-crotonate crystal than those of Na-crotonate. Therefore, dimer formation requires larger thermal activation, resulting in low selectivity of the product and destruction of the crystal structure. In fact, while Na-crotonate dimerizes at 250 °C, K-crotonate does not give any dimers at that temperature.

The mechanism of dimer formation is assumed to proceed through biradicals as shown in the Scheme. The α-carbons of crotonate anions are bonded to each other to form a biradical dimer (**4**). Subsequent hydrogen migration and double bond formation will give (**1**). By similar mechanisms, dimer biradicals (**5**) and (**6**) will afford (**2**) and (**3**), respectively. However, other reaction mechanisms are also possible for dimer formation. Studies are now under way to elucidate these mechanisms.

Experimental

Materials.—Alkali-metal crotonates were prepared by neutralizing crotonic acid with alkali-metal hydroxides in aqueous solution using phenolphthalein as an indicator. Water was slowly distilled off, and the crystals were collected and vacuum-dried at 50—60 °C over P_2O_5.

Thermal Reaction and Analysis of Products.—A sample (*ca.* 1 g) of K-crotonate was placed in a Pyrex tube (6 mm i.d. × 200 mm) and heated in a metal bath maintained at a constant temperature. The tube was evacuated through the reaction. After a given time the reaction tube was taken out of the bath and allowed to cool to room temperature. The heat-treated salt was weighed and dissolved in aqueous hydrochloric acid solution and extracted with ether. The ether extract was treated with diazomethane. The methyl ester derivatives of the products were subjected to analysis by g.c. using diethyl maleate as internal standard.

Isolation and spectral analysis of the dimers. K-Crotonate (100 g) was heated at 320 °C for 4 h and subsequently treated as described above. The methyl ester (42 g), b.p. 100—135 °C at 6 mmHg, were fractionally distilled to give three components: *dimethyl hex-1-ene-3,4-dicarboxylate* (**1a**), b.p. 97 °C at 8 mmHg, ν 1 745 and 1 645 cm^{-1}, δ (60 MHz; CCl_4) 0.89 (3 H, t, CH_3), 1.48 (2 H, q, CH_2), 2.70 (1 H, q, CH), 3.20 (1 H, t, =CH–CH), 3.60 (3 H, s, OCH_3), 3.65 (3 H, s, OCH_3), 5.10 (2 H, m, =CH_2), and 5.75 (1 H, q, =CH–), *m/e* 169.0885 (M^+ – OCH_3) (Calc. for $C_9H_{13}O_3$: *M*, 169.0865); *dimethyl 4-methylpent-2-ene-3,5-dicarboxylate* (**2a**), b.p. 118 °C at 5 mmHg, ν 1 775 and 1 660 cm^{-1}, δ (60 MHz; CCl_4) 1.05 (3 H, d, CH_3), 2.15 (3 H, dd, =CH–CH_3), 2.68 (1 H, t, CH_2–C*H*), 2.90 (2 H, d, CH_2), 3.61 (3 H, s, OCH_3), 3.62 (3 H, s, OCH_3), and 5.50 (1 H, q, =CH–), *m/e* 169.0866 (M^+ – OCH_3); *dimethyl 2-methylene-3-methylbutyl-1,4-dicarboxylate* (**3a**), b.p. 129 °C at 8 mmHg, ν 1 745 and 1 645 cm^{-1}, δ (60 MHz; CCl_4) 1.04 (3 H, bs, CH_3), 2.22 (5 H, m, CH_2–CH–CH_2), 3.62 (3 H, s, OCH_3), 3.68 (3 H, s, OCH_3), 5.63 (1 H, bs, =CH^a_2), and 5.89 (1 H, bs, =CH^b_2), *m/e* 169.008 73 (M^+ – OCH_3).

Dimethyl 2,3-dimethylbut-1-ene-1,4-dicarboxylate (**3c**) had δ (60 MHz; CCl_4) 1.04 (3 H, bs, CH_3), 2.22 (6 H, m, CH_2, CH, =CH–CH_3), 3.67 (6 H, s, OCH_3), and 6.73 (1 H, m, =CH–).

Spectral Analysis of Hydrogenation Products of Dimer Methyl Esters.—Each of the isolated dimer methyl esters (**3a** and **c**) was dissolved in methanol and hydrogenated under an atmospheric pressure of hydrogen in the presence of platinum black. ^1H N.m.r. and mass spectra were taken to identify the hydrogenation products.

Dimethyl 2,3-dimethylbutane-1,4-dicarboxylate (**3b**) had ν 1 750 cm^{-1}, δ (60 MHz; CCl_4) 1.00 (6 H, d, CH_3), 1.44 (2 H, m, CH), 2.20 (4 H, d, CH_2), and 3.66 (6 H, s, OCH_3), *m/e* 202 (M^+) (Calc. for $C_{10}H_{18}O_4$: 202).

X-*Ray Data*.—*X*-Ray measurements were conducted on a powder *X*-ray diffractometer (Rigaku; horizontal-type goniometer). Conditions were as follows: target Cu-K_α, voltage 25 kV, current 10 mA, time constant 1 s, scanning speed 1° min^{-1}, slit SS 1°, RS 0.3 mm, DS 1°. Although the accuracy of 2θ was not checked as to its absolute value using an internal standard, errors due to sample setting were considered to be within ±0.05°.

References

1 K. Naruchi, O. Yamamoto, M. Miura, and K. Nagakubo, *Nippon Kagaku Kaishi*, 1976, 1794.

2 K. Naruchi, M. Miura, and K. Nagakubo, *Nippon Kagaku Kaishi*, 1977, 871.

3 K. Naruchi and M. Miura, *Polymers*, 1981, **22**, 1716.

4 K. Naruchi, S. Tanaka, M. Higuma, M. Yamamoto, and K. Yamada, *Polymers*, 1982, **23**, 152.

5 K. Naruchi, S. Tanaka, M. Yamamoto, and K. Yamada, *Nippon Kagaku Kaishi*, 1983, 1291.

Received 3rd *January* 1986; *Paper* 6/015