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Studies of the Isomerization of Unsaturated Carboxylic Acids. III.⁽¹⁾ Thermal Rearrangement of Dimethyl Methylenesuccinate to Dimethyl Mesaconate

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Dimethyl methylenesuccinate (**1**) was found to equilibrate with dimethyl mesaconate (**3**) at elevated temperatures. Thermal rearrangements of **1** and **3** were studied kinetically and a plausible mechanism is proposed.

The rearrangement[2] and isomerization[2] of unsaturated esters in thermal[3–5] and photochemical[6–8] reactions have received much attention. In the preceding paper of this series, it was reported that some unsaturated dicarboxylic acids exhibited unique equilibrium composition during thermal reactions[2] and a plausible mechanism was proposed.[1]

On the other hand, it has been found that the corresponding unsaturated esters behave quite differently from the free acids. The present paper deals with the interconversion between dimethyl methylenesuccinate (**1**), dimethyl citraconate (**2**), and dimethyl mesaconate (**3**), and the mechanism for this interconversion will be discussed.

Experimental

All the boiling points are uncorrected.

Materials. Dimethyl methylenesuccinate (dimethyl methylenebutanedioate) (**1**), bp 105 °C/22 Torr, dimethyl citraconate (dimethyl (*Z*)-2-methyl-2-butenedioate) (**2**), bp 104 °C/25 Torr, and dimethyl mesaconate (dimethyl (*E*)-2-methyl-2-butenedioate) (**3**), bp 96 °C/20 Torr, were prepared according to the literature.[9] Organic solvents were purified by the standard methods. Other reagents were commercial materials and were used without further purification.

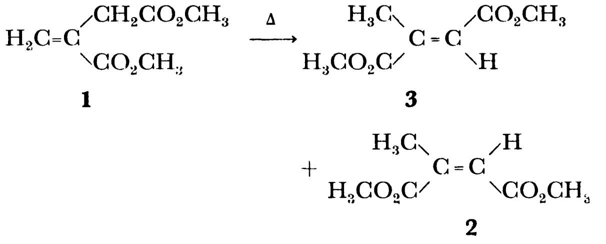
Procedure. A mixture of 0.30 g (1.9 mmol) of an unsaturated ester, 0.60 g of methanol, and a small amount of hydroquinone was sealed at atmospheric pressure in a glass tube, which was heated to an appropriate temperature in an autoclave filled with aqueous methanol. After cooling the autoclave, the tube was opened and the mixture was analyzed by GLC as described in a preceding paper.[1] When the reaction was carried out in the presence of iodine, the cooled reaction mixture was treated with aqueous sodium thiosulfate, and then the products were extracted with benzene. The benzene solution was subjected to GLC.

Reaction in Methanol-d. A mixture of 0.40 g of **1** and 1.30 g of methanol-*d* was sealed in a glass tube. After the reaction, the mixture of esters was recovered by distillation under reduced pressure. The distillate diluted with CCl_4 was subjected to NMR analysis. The deuterium content was calculated from the relative intensities of the NMR signals (in CCl_4, TMS) at δ 6.26 (=CH_2), 5.70 (=CH_2), and 3.28 (–CH_2–) for **1**, and 6.83 (=CH) and 2.24 (–CH_3) for **3**. The NMR spectra were recorded on a Varian T-60A spectrometer.

Kinetics. A mixture, consisting of 0.30 g of ester and 0.60 g of methanol, in a sealed tube was placed in an autoclave. The temperature was raised at a rate of 5 °C/min. After maintaining the mixture at an appropriate temperature for a desired period of time, the vessel was cooled immediately to room temperature. The cooled mixture was analyzed using GLC. Each run correctly followed first-order kinetics. The results at 250 °C were analyzed using equilibrium kinetics.[10]

Results

It was confirmed by GLC that the reaction mixture contained three isomers of the esters and no by-product was detected. The reaction was carried out in methanol, since thermal reaction without a solvent brought about the polymerization of **1** and the decomposition of the esters. In benzene, practically no reation occurred.



Equilibria. The reactions in methanol for **1**, **2**, and **3** were studied at 250 °C and the results are summarized in Table 1. The equilibrium composition in methanol at 250 °C were found to be 41% for **1**, 5% for **2**, and 54% for **3**. For the corresponding diethyl

TABLE 1. EQUILIBRIUM AT 250 °C[a)]

Starting ester	Time, h	Composition, %			Total yield, %
		1	**3**	**2**	
1	2	90.8	9.2	—	90.5
3	2	15.2	84.5	0.3	89.6
1	4	77.5	22.1	0.5	81.3
3	4	23.6	76.4	—	86.6
1	7	64.7	34.4	0.8	78.7
3	7	27.1	72.0	0.9	88.9
1	10	61.8	37.3	1.1	80.9
3	10	39.0	54.3	6.7	87.0
1	26	42.2	53.7	4.1	67.1
3	26	41.6	53.5	5.1	74.1
1	44	41.5	53.9	4.6	53.3
1:**3**=1:2	44	40.3	54.4	5.3	46.3
1:**3**=1:2	44	41.4	54.5	4.1	56.0
3	44	40.3	54.2	5.5	47.5
2	44	37.0	47.1	16.0	62.5

a) Ester, 0.3 g; methanol, 0.6 g.

Table 2. *cis-trans* Isomerization in the presence of I_2[a)]

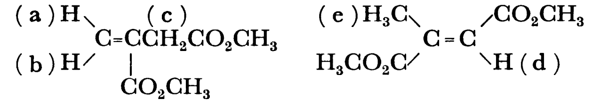
Starting ester	Temp, °C	Time, h	I_2, mmol	Composition, %			Total yield, %
				1	**3**	**2**	
2	200	6	0	0.2	0.4	99.4	86.6
2	200	6	0.76	0.4	90.1	9.5	83.7
3	200	6	0.76	0.4	90.6	9.6	83.0
1	200	6	0.76	98.8	1.2	—	53.7
1	250	2	0	99.4	0.6	—	84.8
1	250	2	0.19	78.5	15.7	6.0	48.8
3	250	2	0	0.2	99.8	—	97.7
3	250	2	0.19	7.3	82.5	10.2	64.8
2	250	2	0	0.6	0.4	99.0	100.0
2	250	2	0.19	7.3	82.0	10.7	65.9

a) Ester, 0.3 g; benzene, 0.6 g.

Table 3. NMR data for the reaction[a)]

Starting ester	Solvent	Relative area[b)]				
		H_a (δ 6.26)	H_b (5.70)	H_c (3.28)	H_d (6.83)	H_e (2.24)
1	Methanol	1.0	1.1	2.1	1.1	3.1
1	Methanol-*d*	1.0	1.1	0.98	0.30	1.5
3	Methanol	1.0	1.1	2.1	1.3	4.0
3	Methanol-*d*	1.0	1.1	1.1	0.61	2.1

a) Ester, 0.4 g; solvent, 1.3 g; temp, 250 °C; reaction time, 26 h. b) The relative area of terminal methylene of **1** (δ 6.26) is estimated to be 1.0.



$$\text{(a)H(b)H}C{=}C(CO_2CH_3)\overset{(c)}{C}H_2CO_2CH_3 \qquad \text{(e)}H_3C(H_3CO_2C)C{=}C(CO_2CH_3)H\text{(d)}$$

esters, the values were 27, 3, and 70%, respectively.

The addition of iodine to the reaction mixture dramatically accelerated the isomerization, whereas the rate of rearrangement remained unaffected. The results are shown in Table 2.

The results of the reactions of the esters in methanol-*d* are shown in Table 3. When **1** was heated in methanol-*d*, deuterium atoms were incorporated into the α-methylene group of **1** recovered and into the methyl group of **3** produced.

Kinetics. Kinetic studies were undertaken in the temperature range from 200 to 280 °C. In methanol, the esters were recovered in good yield even after prolonged heating. The reaction was unaffected by the presence of hydroquinone. The first-order rate constants for the disappearance of **1**, **2**, and **3** were measured at appropriate temperature. The results are listed in Table 4. It should be noted that the initial rate constants, *k*, obtained from an analysis using first-order kinetics (the sum of the rate constants for the forward and reverse reactions) do not differ markedly from the rate constants, *k'*, obtained on the basis of equilibrium kinetics[10)] (the rate constants for the forward reaction only). The linearity of $\ln[C]_0/[C]$ plotted against time was observed up to a conversion of about 30%. The Arrhenius plot for the rate of disappearance of **1** was correctly linear (r=0.995), from which ΔH^* and ΔS^* were calculated to be 77.8 kJ mol^{-1} and 184 J K^{-1} mol^{-1}, respectively.

Table 4. Temperature dependence of the rate constants for the disappearance of the esters[a)]

Starting ester	Temp,[b)] °C	Rate constant	
		$k\times10^5\,s^{-1}$ [c)]	$k'\times10^5\,s^{-1}$ [d)]
1	200	0.228	
1	230	0.984	
1	250	1.58	1.76
1	280	4.96	
3	250	1.50	1.35
2	250	1.14	1.15

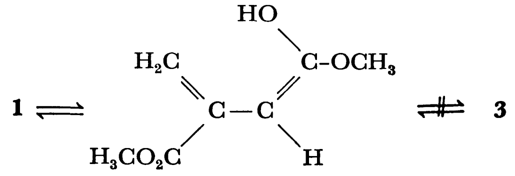
a) Ester, 0.3 g; methanol, 0.6 g. b) ±1 °C. c) The error in *k* is expected to be in the range of 5—10%. d) First-order rate constants calculated for equilibrium systems.[10)]

Discussion

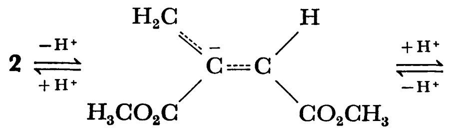
The equilibrium composition of the esters is completely different from that of the corresponding acids, for which methylenesuccinic and mesaconic acids are the most and the least abundant materials, respectively.[1)] This fact appears to indicate that the factor which governs the relative stability of the esters in equilibrium is different from that for free acids.

A free-radical mechanism may be disregarded in the rearrangement of the esters, because the addition of iodine as a radical source accelerated isomerization at low temperature (200 °C), whereas little rearrangement occurred. In addition, it was found that hydroquinone affected neither the equilibrium composition nor the rate constants.

For thermal rearrangement of unsaturated esters, a mechanism has been proposed which involves enolization followed by the intramolecular rearrangement of the enol-proton to the terminal methylene group.[4] However, an inspection of the Dreiding model of enol-methylenesuccinate, a possible common intermediate of the rearrangement, reveals that the orbital of the terminal methylene is not arranged in a position suitable for accepting the enol-proton intramolecularly. In the reverse process, the intramolecular abstraction of a methyl-proton in **3** by the carbonyl-oxygen must produce a twisted enolate of **1**, in which conjugative stabilization of diene is hardly conceivable. Thus, from a consideration of the orbital arrangement, it is predicted that cyclic intramolecular process for the rearrangement is unfavorable.



Consequently, another plausible mechanism is the intervention of a carbanion, which has been proposed for the corresponding free acids:[1)]



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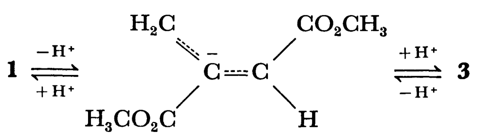

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The rate-determining reaction for the formation of carbanions, **4** and **5**, under the general-base catalysis of methanol, is supported by the facile hydrogen-deuterium exchange at the position expected for these species and by first-order kinetics for the rearrangement of the esters. If the reaction proceeds for the carbonium ion under the general-acid catalysis of methanol, the protons of the terminal methylene group in **1** must be replaced by deuterium atoms faster than those of the α-methylene group, because protonation to **1** is expected to take place at the terminal methylene group. Similarly, for general-acid catalysis, the α-methylene protons in **1** formed should be replaced by deuteriums faster than the methyl protons in **3**. This is, however, is not the case. The general-base catalysis of methanol is also confirmed by preliminary results for triethylamine-catalyzed reactions of the esters.[11)] Since it was observed that the addition of triethylamine accelerated both the rearrangements of **1** and **3**, the mechanism involving carbanion intermediates is the more reasonable for this reaction. Furthermore, the formation of **1** from **2** is not interpreted using the intramolecular mechanism. Once again the intramolecular mechanism appears doubtful.

The fact that the thermodynamically least-stable ester (**2**) has the smallest rate constant is compatible with the carbanion mechanism. The rate for the formation of **2** is slower than that of **3**, because carbanion **5** is more stable than **4**. It is interesting to note that **1** predominated over **3** at the initial stage of the rearrangement of **2**. Direct interconversion between carbanions, **4** and **5**, may be negligible, since the rate constant for the disappearance of **1** is larger than that of **3** and since **1** is less abundant than **3** at equilibrium. The above results show that it is unreasonable to expect facile direct isomerization between **2** and **3**.[12)]

The difference between the compositions resulting from the rearrangement of the free acids and the rearrangement of the esters is accounted for as follows. Equilibrium between citraconic and methylenesuccinic acids is interpreted using the intermediate *cis*-carbanion, whose configuration is fixed by intramolecular hydrogen bonding.[1)] However, the esters are free from intramolecular hydrogen bonding and the *trans*-carbanion favors the rearrangement of the esters. Consequently, **3** appears as the most abundant product.

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2) Rearrangement is defined as the migration of a double bond, whereas isomerization is used to mean *cis-trans* interconversion. A reaction is any transformation including both rearrangement and isomerization.

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