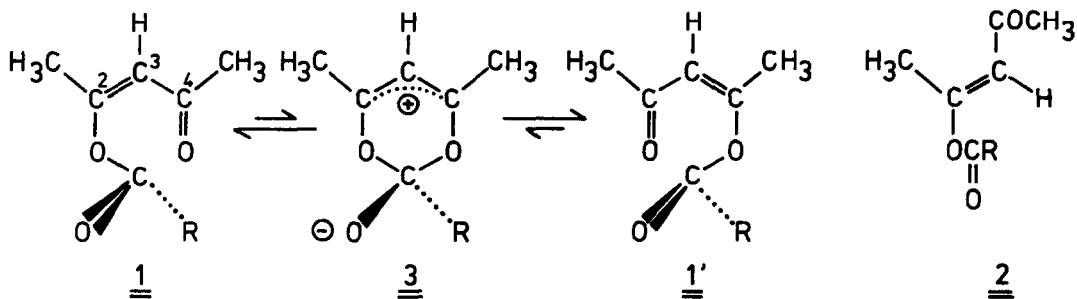


THERMAL ACYL SHIFT IN 2-ACYLOXY-2-PENTEN-4-ONES<sup>1)</sup>Albrecht Mannschreck and Hans DvorakFachbereich Chemie, Universität Regensburg,  
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O-Acyl transfer has been detected for a number of 2-acyloxy-2-alken-4-ones, i.e. carboxylic esters of enols of 2,4-diones<sup>2-4)</sup>. Formula 1 exemplifies this type of compounds, although acyl transfer was not known for this particular example. These observations<sup>2-4)</sup> apparently do not permit safe conclusions about the intra- or intermolecular nature of these processes and whether they occur thermally, i.e. without extramolecular assistance. Two recent investigations show that in O-acetylnaphthazarins<sup>5)</sup> and in 3-acetyl-2-acyloxy-indenes<sup>6)</sup> a thermal intramolecular acyl shift is at least predominant and report kinetic data for this process. Such results are described in the present communication for much simpler systems, i.e. (Z)-2-acyloxy-2-penten-4-ones (1).

a. R = CH<sub>3</sub>b. R = C(CH<sub>3</sub>)<sub>3</sub>c. R = C<sub>6</sub>H<sub>5</sub>d. R = C<sub>6</sub>H<sub>4</sub>-p-NO<sub>2</sub>

We prepared the enol acetate from acetylacetone and acetylchloride in the presence of pyridine according to a known general procedure<sup>4,7</sup>). The properties of the product were in agreement with the literature data<sup>8,9</sup>). However, it turned out to be a mixture of the (Z)-isomer 1a ( $\approx 40\%$ ) and the (E)-isomer 2a ( $\approx 60\%$ ) which were completely separated by column chromatography on silica gel, distilled, and characterized by elemental analyses, refractive indices, as well as uv, ir<sup>10</sup>), <sup>1</sup>H nmr, and mass spectra. The isomer with the higher retention in a petroleum ether/diethyl ether mixture (1:1) was assigned<sup>11</sup>) configuration 1a because of the higher shielding ( $\delta = 5.92$ , CDCl<sub>3</sub>, 35°C) of its alkene proton compared to that of 2a ( $\delta = 6.15$ ). The isomers interconverted very slowly (half-life > 45 hours) in d<sub>5</sub>-nitrobenzene at 121°C, but in the presence of a trace of Cl<sub>2</sub>CCOOH, starting from both pure isomers, an equilibrium of 47% 1a and 53% 2a was attained after 4 days at 35°C in CCl<sub>4</sub>.

The <sup>1</sup>H nmr spectrum of 1a in CDCl<sub>3</sub>/CCl<sub>4</sub> (1:1) at -42°C shows a narrow multiplet for C=CH ( $\delta = 5.94$ ), singlets for OCOCH<sub>3</sub> (2.30) and CCOCH<sub>3</sub> (2.22), as well as a doublet for C=CCH<sub>3</sub> (2.05, <sup>4</sup>J = 1.0 Hz). The CCOCH<sub>3</sub> and C=CCH<sub>3</sub> absorptions coalesce at T<sub>c</sub> = +18°C (100 MHz) and give rise to a sharp average singlet ( $\delta = 2.08$ ) at 53°C. We interpret this behavior as an O-acetyl shift 1a  $\rightleftharpoons$  1'a ( $\Delta G_c^\ddagger = 14.5 \pm 0.3$  kcal/mole at +18°C)<sup>12</sup>) which we assume to be an intramolecular one, because its barrier is not changed by a fourfold change of concentration in CDCl<sub>3</sub>/CCl<sub>4</sub> nor by the addition of a trace of 1,4-diazabicyclo[2.2.2]octane to a solution in d<sub>6</sub>-acetone. A dipolar, six-membered intermediate<sup>13</sup>) (or transition state) 3a is proposed<sup>14</sup>).

The corresponding (E)-isomer 2a in CDCl<sub>3</sub> at 35°C shows, besides a narrow multiplet for C=CH ( $\delta = 6.15$ ) and a singlet for OCOCH<sub>3</sub> (2.18), another singlet (2.22, CCOCH<sub>3</sub>), and a doublet (2.33, <sup>4</sup>J = 1.0 Hz, C=CCH<sub>3</sub>) which do not coalesce or broaden up to 95°C in d<sub>5</sub>-nitrobenzene. Consequently, the barrier of a corresponding O-acetyl shift, if any, must be higher than 19.5 kcal/mole. The different behavior of 1a and 2a gives support to the above assignment of (E) and (Z) configurations at the C=C-bond.

We obtained very similar results concerning the preparation, separation, characterization, and acyl shift of the enol acylates 1b/2b, 1c/2c, and 1d/2d<sup>15</sup>). Recently, the benzoyl shift in 1c was demonstrated independently by another group<sup>17</sup>). Our kinetic results<sup>12,13</sup>) obtained by <sup>1</sup>H nmr are given in the table.

	Solvent	$\delta$			$T_c^*)$	$\Delta G_c^\ddagger, \pm 0.3$
		$C=CCH_3$	$CCOCH_3$	$T [^\circ C]$	$[^\circ C]$	$[kcal/mole]$
<u>1a</u>	$CDCl_3/CCl_4(1:1)$	2.05	2.22	-42	+18	14.5
	$C_6D_5CD_3$	1.55	1.72	-40	+22	15.0
<u>1b</u>	$CDCl_3/CCl_4(1:1)$	2.00	2.20	-40	+11	14.3
	$C_6D_5CD_3$	1.55	1.75	-40	+17	14.7
<u>1c</u>	$C_6D_5CD_3$	1.62	1.77	-44	+55	16.9
<u>1d</u>	$C_6D_5CD_3$	1.62	1.66	-5	+24	15.7

\*) Coalescence temperatures for all solutions were determined at 60 MHz, except for 1a in  $CDCl_3/CCl_4$  and for 1d in  $C_6D_5CD_3$  which were measured at 100 MHz.

The above barriers may contain contributions from three processes moving the (Z) enol acylates into a conformation (formula 1) prone to O-acyl shift. These motions are: rotation (or inversion) about the  $C^2-O$  bond, rotation about the  $O-C_{acyl}$  bond, and rotation<sup>10)</sup> about the  $C^3-C^4$  bond. Perhaps these energy requirements represent one of the reasons for the observation that our  $\Delta G_c^\ddagger$ -values for the shift of the groups -COR do not show precisely the same order as the rate constants<sup>18)</sup> for alkaline hydrolysis of the corresponding alkyl acylates. Clearly, all activation parameters for the transfer of different acyl groups should be measured. These parameters might contribute to a quantitative knowledge of the reactivity of carboxylic acid derivatives towards nucleophiles.

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