

### 362. *The Dehydration of $\beta$ -Hydroxy-esters.*

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ALTHOUGH many  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated acids have been prepared by the Reformatski reaction and dehydration of the resulting hydroxy-compound, no attempt has yet been made to compare the action of different dehydrating agents.

A few representative examples of open-chain and cyclic  $\beta$ -hydroxy-esters (obtained by the Reformatski reaction from the appropriate ketones; compounds derived from aldehydes have not yet been examined) have now been dehydrated with phosphoric oxide, phosphoryl chloride, potassium hydrogen sulphate, and thionyl chloride in presence of pyridine. Phosphoric oxide and thionyl chloride gave the best yields of the unsaturated ester: the former reagent also gave a maximum, and phosphoryl chloride a minimum, proportion of  $\beta\gamma$ -ester in the product.

A number of the open-chain hydroxy-esters required were obtained by using ethyl chloroacetate in place of the bromoacetate; it was not found necessary to add copper powder as recommended by Nieuwland and Daly (*J. Amer. Chem. Soc.*, 1931, **53**, 1842). *cyclo*Pentanone and *cyclo*hexanone do not react with ethyl chloroacetate either with or without the addition of copper powder, and a condensation product could not be obtained from acetophenone as described by the American authors.

From the properties of  $\beta$ -propyl- $\Delta^{\beta}$ -hexenoic acid, now obtained pure for the first time, it appears that the value for the equilibrium of this acid with its  $\Delta^{\alpha}$ -isomeride given by Kon and May (*J.*, 1927, 1549) is of the right order and it was not deemed necessary to redetermine it exactly.

*Materials.*—Methyl ethyl, diethyl, and dipropyl ketones condensed with ethyl chloroacetate diluted with  $C_6H_6$  (300 c.c. per g.-mol.) in presence of Mg powder and a trace of  $I_2$ , giving yields of 40—48% of hydroxy-ester. *cyclo*-Hexanone gave only 15%, much *cyclo*hexenyl*cyclo*hexanone being produced. The sole product formed from *cyclo*pentanone was *cyclo*pentylidene*cyclo*-pentanone: a good deal of this ketone was also produced in the reaction with

ethyl bromoacetate and necessitated a special purification of the hydroxy-ester.

*Dehydration of the Hydroxy-esters.*—(1) *With phosphoric oxide or phosphoryl chloride.* The ester (1 mol.) was diluted with 3 vols. of  $C_6H_6$  and boiled under reflux for 3 hrs. with  $P_2O_5$  (1.25 mols.) or  $POCl_3$  (slight excess);  $H_2O$  was then added, and the ester isolated in the usual way. Distillation with  $P_2O_5$  under reduced press. in absence of  $C_6H_6$  was less satisfactory.

(2) *With thionyl chloride.* Darzens's instructions (*Compt. rend.*, 1911, **152**, 1601) were followed exactly.

(3) *With potassium hydrogen sulphate.* Equal wts. of  $KHSO_4$  and ester were heated at  $160-180^\circ$ ,  $H_2O$  added to the cooled product, and the ester isolated by extraction with  $Et_2O$ ; in some cases it was distilled in steam before extraction.

*Analysis of the Product.*—The proportion of  $\alpha\beta$ - and  $\beta\gamma$ -unsaturated isomerides in the dehydration product, which was purified by distillation under reduced press., was determined by Linstead and May's iodometric method (J., 1927, 2565), the reaction time being 1 hr. and the solvent  $CHCl_3$ . Reference curves for the iodine addition ( $J$ ) were constructed from data already available or obtained from the pure esters. The physical properties of the mixtures of esters were determined in every case as a check but are not recorded.

The proportion of unchanged hydroxy-ester in the product was insignificant except when  $KHSO_4$  was the dehydrating agent.

*Ethyl  $\beta$ -Hydroxy- $\beta$ -methylvalerate.*—Pure solid  $\beta$ -methyl- $\Delta^a$ -pentenoic ( $\beta$ -methyl- $\beta$ -ethylacrylic) acid (Fichter and Gisiger, *Ber.*, 1908, **41**, 4707) was esterified through its Ag salt, prepared in the cold; the ester had b. p.  $68^\circ/14$  mm.,  $d_4^{20.0^\circ}$  0.91375,  $n_D^{20.0^\circ}$  1.4424,  $[R_L]_D$  41.15 (calc., 40.33). The  $\beta\gamma$ -ester was a pure specimen, prepared by the partial esterification of the  $\beta\gamma$ -acid (Kon and Linstead, J., 1925, **127**, 616); its properties will shortly be described. The reference curve was constructed from the following values :

Mixture, % $\alpha\beta$ .....	0	10	25	50	75	90	100
$J$ , % .....	78.5	72.8	65.9	46.9	24.3	11.5	3.4

*Dehydrations.*

Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.	Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.
$P_2O_5$	82	55.2	39.5	$SOCl_2$	77	44.2	53.5
$POCl_3$	80	36.6	62.0	$KHSO_4$	50	40.1	57.5

*Ethyl  $\beta$ -Hydroxy- $\beta$ -ethylvalerate.*— $\beta\beta$ -Diethylacrylic acid (Kon, Leton, Linstead, and Parsons, J., 1931, 1411) was converted through its Ag salt into the ethyl ester, b. p.  $77^\circ/14$  mm.,  $d_4^{20.0^\circ}$  0.90432,  $n_D^{20.0^\circ}$  1.4440,  $[R_L]_D$  45.82 (calc., 44.95). The  $\beta\gamma$ -isomeride was prepared as described by those workers and had the properties recorded by them. A reference curve was constructed from the following values :

Mixture, % $\alpha\beta$ .....	0	10	25	50	75	90	100
$J$ , % .....	77.5	68.8	62.1	47.0	27.3	14.2	4.6

*Dehydrations.*

Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.	Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.
$P_2O_5$	65	62.6	23.5	$SOCl_2$	70	47.1	50.0
$POCl_3$	65	32.6	68.0	$KHSO_4$	60	36.1	63.5

*Ethyl  $\beta$ -Hydroxy- $\beta$ -propylhexoate.*— $\beta\beta$ -Dipropylacrylic acid (Kon and May, *loc. cit.*) was purified by two partial esterifications for 12 and 24 hrs. respectively. It then had b. p.  $132^\circ/14$  mm.,  $d_4^{20.0^\circ}$  0.94859,  $n_D^{20.0^\circ}$  1.4670,  $[R_L]_D$

45.63 (calc., 44.84), and  $J$  1.1. The Et ester prepared through the Ag salt had b. p. 96—97°/14 mm.,  $d_4^{20.0}$  0.89537,  $n_D^{20.0}$  1.4470,  $[R_L]_D$  54.91 (calc., 54.19).

Crude  $\beta$ -propyl- $\Delta\beta$ -hexenoic acid (Kon and May, *loc. cit.*) was partially esterified for 3 hrs.; the ester obtained had b. p. 98—100°/17 mm.,  $d_4^{20.0}$  0.89050,  $n_D^{20.0}$  1.4366,  $[R_L]_D$  54.09,  $J$  71.5. Its purity was proved by hydrolysing it in the cold with 5% alc. KOH to the pure  $\Delta\beta$ -acid, b. p. 135°/15 mm.,  $d_4^{20.0}$  0.93577,  $n_D^{20.0}$  1.4505,  $[R_L]_D$  44.80 (calc., 44.84). When this was re-esterified for 3 hrs., an ester with  $J$  70.9 was obtained. The reference curve was constructed from the following values:

Mixture, % $\alpha\beta$ .....	0	10	35	50	75	90	100
$J$ , % .....	71.5	68.7	61.8	46.6	26.4	12.8	3.1

*Dehydrations.*

Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.	Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.
P <sub>2</sub> O <sub>5</sub>	80	61.9	24.0	SOCl <sub>2</sub>	78	52.1	31.5
POCl <sub>3</sub>	60	45.5	51.5	KHSO <sub>4</sub>	68	45.7	51.0

*Ethyl  $\beta$ -Hydroxy- $\alpha\beta$ -dimethylvalerate.*—The reference curve given by Kon, Linstead, and MacLennan (preceding paper) was employed.

*Dehydrations.*

Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.	Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.
P <sub>2</sub> O <sub>5</sub>	75	56.3	28.0	SOCl <sub>2</sub>	79	53.4	33.0
POCl <sub>3</sub>	65	47.5	43.0	KHSO <sub>4</sub>	65	56.0	28.0

*Ethyl cycloHexanolacetate.*—The reference curve given by Kon and Linstead (*J.*, 1929, 1269) was employed.

*Dehydrations.*

Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.	Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.
P <sub>2</sub> O <sub>5</sub>	68	70.2	19.0	SOCl <sub>2</sub>	70	62.8	32.0
POCl <sub>3</sub>	64	55.0	43.0	KHSO <sub>4</sub> *	60	54.0	45.0

\* The product in this case evidently contained some unchanged hydroxy-ester.

*Ethyl cycloPentanolacetate.*—This hydroxy-ester always contains an appreciable quantity of *cyclopentylidenecyclopentanone*, from which it cannot be separated by fractionation. The crude ester was therefore hydrolysed to the acid, and the latter recrystallised; on esterification of the acid by boiling for 3 hrs. with alc.-HCl, a product consisting almost entirely of the two unsaturated esters was obtained. It had  $J$  57.4 ( $d_4^{15.0}$  0.98686,  $n_D^{15.0}$  1.4603) and was practically unchanged by further treatment with P<sub>2</sub>O<sub>5</sub>. The hydroxy-acid was therefore esterified through the Ag salt, and the pure ester, b. p. 108°/14 mm.,  $d_4^{20.0}$  1.0343,  $n_D^{20.0}$  1.4515, used for dehydration experiments, in conjunction with the reference curve given by Kon, Linstead, and MacLennan (preceding paper).

*Dehydrations.*

Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.	Reagent.	% Yield.	$J$ .	% $\alpha\beta$ -Ester.
P <sub>2</sub> O <sub>5</sub>	72	67.2	30.0	SOCl <sub>2</sub>	66	45.0	50.0
POCl <sub>3</sub>	70	42.6	58.0	KHSO <sub>4</sub>	66	59.7	38.0

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