

[CONTRIBUTION FROM THE LABORATORY OF ORGANIC CHEMISTRY OF THE UNIVERSITY OF WISCONSIN]

## Hydroxy and Bromo Esters Derived from the Hydrogenation of Certain Omega-Acetyl Esters

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Several years ago it was noted in this Laboratory that the hydrogenation of acetoacetic ester with Adams platinum oxide catalyst proceeded at a considerably slower rate than that of a simple ketone, such as acetone. The most apparent reason for this behavior was the close proximity of the carboxy group to the carbonyl group in the acetoacetic ester molecule.

Since a series of bromo esters of the type  $\text{CH}_3\text{CHBr}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$  were needed for some other work, it seemed advisable to prepare them from the corresponding hydroxy esters derived from the hydrogenation of a series of  $\omega$ -acetyl esters of the type  $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ . This would

make possible the determination of the effect of increasing the number of methylene groups between the carboxy and carbonyl group on the rate of hydrogenation of the latter group.

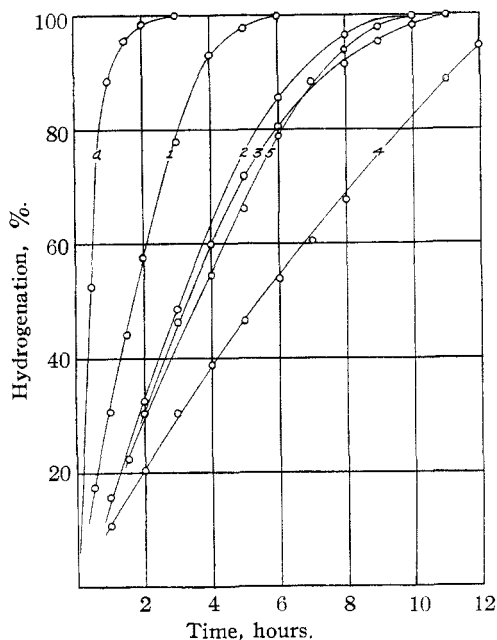


Fig. 1.—Rate of hydrogenation of  $\omega$ -acetyl esters: Curve a, acetone; the number on each of the other curves is the value of  $n$  in the formula  $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ .

The results which were obtained with such a series of keto esters are illustrated in Fig. 1. A curve showing the rate of hydrogenation of acetone under similar conditions is included for comparison. In each instance 0.3 mole of the keto compound and 0.3 g. of Adams platinum oxide catalyst were used. These hydrogenations were made in alcohol solution, but the relative rates were practically the same when the hydrogenations were carried out without a solvent. It is seen from these curves that rate of hydrogenation of the

keto esters does not approach that of acetone but continues, in general, to decrease as the value of  $n$  increases. The only explanation for the variation of the positions of Curves 4 and 5 from the regular order is that the keto

ester in which  $n$  is 4 was prepared through a cyanide and may have contained a small amount of an impurity which lowered the rate of hydrogenation.

**$\omega$ -Acetyl Esters.**—Acetoacetic ester was carefully distilled before use. Acetyl-succinic ester and acetylglutaric ester were prepared by the method described by Isbell, Wojcik and Adkins.<sup>1</sup>

Acetylpinelic ester was prepared by a similar procedure from acetoacetic ester and  $\delta$ -bromovaleric ester.<sup>2</sup> This diester was not purified by distillation, but was used directly after it was freed from lower boiling associated products. These acetyl diesters were converted into the corresponding keto acids  $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COOH}$  by hydrolysis with dilute hydrochloric acid.<sup>3</sup> The acids so obtained were esterified in carbon tetrachloride solution.<sup>4</sup> The over-all yield of ethyl  $\omega$ -acetylcaproate from ethyl  $\delta$ -bromovalerate was 20% of the theoretical. The keto ester in which  $n$  is 4 was prepared by esterification of  $\omega$ -acetylvaleric acid.<sup>5</sup> The properties of these esters are summarized in the table. The esters in which  $n$  is 4 and 5 have not been described previously in the literature.

TABLE I  
I. KETO ESTERS,  $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$

$n$ is	B. p., °C. (9 mm.)	$d_{25}^{25}$	$n_D^{25}$	Analyses, %			
				Calcd.		Found	
				C	H	C	H
1	64–65	...	....	...	...	...	...
2	82–83	...	....	...	...	...	...
3	94–95	...	....	...	...	...	...
4 <sup>a</sup>	107–108	0.9795	1.4305	62.79	9.30	62.51	9.16
5	121–122	.9708	1.4375	64.52	9.68	64.26	9.62

II. HYDROXY ESTERS,  $\text{CH}_3\text{CHOH}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$

1 <sup>b</sup>	70–71 (9 mm.)	0.9496	1.4195	...	...	...	...
2 <sup>c</sup>	85–86 (2 mm.)	.9532	1.4265	57.54	9.59	57.51	9.62
3	94–95 (2 mm.)	.9832	1.4315	60.00	10.00	59.62	9.98
4	103–104 (2 mm.)	.9714	1.4329	62.07	10.35	61.55	10.24
5	111–113 (2 mm.)	.9621	1.4387	63.83	10.64	63.70	10.41

<sup>a</sup> This ester was used in a condensation by Blaise and Koehler, *Compt. rend.*, **148**, 1401 (1909) but no description of its properties was given.

<sup>b</sup> Curtius and Müller, *Ber.*, **37**, 1277 (1904), report this ester b. p. 170; *cf.* also Tschitschenko, *Chem. Centr.*, [II] 1310 (1906).

<sup>c</sup> Both Neugebauer [*Ann.*, **227**, 101 (1885)] and Thomas, Schuette and Cowley [THIS JOURNAL, **53**, 3861 (1931)] report that this ester is converted by distillation into valerolactone. It was found, however, in the present work that no appreciable amount of this lactone is formed if the hydroxy ester is distilled rapidly from a Claisen flask with a short side arm.

**Hydroxy Esters,  $\text{CH}_3\text{CHOH}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ .**—A solution of 0.3 mole of the keto ester in 35 cc. of absolute alcohol was shaken with hydrogen under 2–3 atmospheres of pressure in the presence of 0.3 g. of Adams platinum oxide catalyst until the theoretical amount of hydrogen was absorbed. After decantation from the catalyst, the alcoholic solution was distilled under diminished pressure from a Claisen flask without a fractionat-

(1) Isbell, Wojcik and Adkins, THIS JOURNAL, **54**, 3685 (1932).

(2) Merchant, Wickert and Marvel, *ibid.*, **49**, 1828 (1927).

(3) Fittig and Wolff, *Ann.*, **216**, 129 (1883).

(4) "Organic Syntheses," 1923, Vol. III, p. 51.

(5) Derick and Hess, THIS JOURNAL, **40**, 551 (1918).

ing column. The yields of the hydroxy esters were 82-88%. Their properties are summarized in Table I.

**Bromo Esters,  $\text{CH}_3\text{CHBr}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ .**—To a solution of 0.3 mole of the hydroxy ester in 30 cc. of benzene was added slowly 0.1 mole of phosphorus tribromide. The flask containing the reactants was placed in an ice-bath and allowed to remain for half an hour. After this time the reaction mixture was gradually warmed to 60° and kept at this temperature for thirty minutes. It was then cooled, treated with 50 cc. of water, the layers separated and the aqueous layer extracted with an equal volume of benzene. The benzene extracts were combined, washed with water, dried over anhydrous sodium sulfate and distilled. The yields were 61-74% of the theoretical. The properties of these bromo esters are listed in Table II.

TABLE II  
BROMO ESTERS,  $\text{CH}_3\text{CHBr}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$

$n$ is	B. P., °C. (2 mm.)	$d_{25}^{25}$	$n_D^{25}$	Analyses, %					
				C	Calcd. H	Br	C	Found H	Br
1 <sup>a</sup>	41-42	1.3103	1.4445	36.92	5.64	41.02	37.00	5.70	40.77
2	52-54	1.2330	1.4497	40.19	6.22	38.28	40.21	6.29	37.97
3	69-71	1.1943	1.4525	43.05	6.73	35.88	43.25	6.67	35.03
4	85-87	1.2028	1.4550	45.57	7.17	33.75	45.51	7.05	33.00
5	95-96	1.1660	1.4564	47.81	7.57	31.87	47.68	7.39	31.21

<sup>a</sup> Lespiau, *Chem. Centr.*, I, 24 (1905), notes this ester as boiling at 183 (755 mm.).

### Summary

The hydrogenation of a series of  $\omega$ -acetyl esters,  $\text{CH}_3\text{CO}(\text{CH}_2)_n\text{COOC}_2\text{H}_5$ , in which  $n$  varies from 1 to 5, has been described. The resulting hydroxy esters have been converted into the corresponding bromo esters.

The properties of the following compounds, not previously listed in the literature, are described: ethyl  $\omega$ -acetylvalerate, ethyl  $\omega$ -acetylcaproate, ethyl  $\gamma$ -hydroxyvalerate, ethyl  $\delta$ -hydroxycaproate, ethyl  $\epsilon$ -hydroxyheptate, ethyl  $\zeta$ -hydroxycaprylate, ethyl  $\gamma$ -bromovalerate, ethyl  $\delta$ -bromocaproate, ethyl  $\epsilon$ -bromoheptate and ethyl  $\zeta$ -bromocaprylate.

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