Thoria Aërogel Catalyst: Aliphatic Esters to Ketones

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IN THE first part of this communication[1] it was shown that ketones could be prepared in excellent yield by distilling the corresponding acid over thoria aërogel at atmospheric or under reduced pressures. The size of the ketone which can be conveniently prepared is limited by the volatility of the acid and ketone. In order to extend the scope of the method to higher ketones, the conversion of ethyl esters was studied. The esters have a much lower boiling point than their corresponding acids and, therefore, may often be employed when the use of the free acid is not feasible.

Ethyl laurate was chosen as a typical example. The results of its conversion to laurone are shown in the following table:

RUN NO.	ESTER[a]	RATE OVER CATALYST	TEMP. OF CATALYST	ESTER RECOVERED	KETONE	CONVERSION
	Grams	*Grams/min.*	*° C.*	*Grams*	*Grams*	*%*
1	57	3–4	300	20.0	27	64.8
2	57	3–4	360	4.0	39	92.5
3	57	4–6	360	10.0	34.8	82.5
4	57	8	360	17.0	29.6	70.0

[a] The ethyl laurate was distilled over the catalyst at 150° to 160° C. at 25 to 30 mm. pressure.

[1] IND. ENG. CHEM., **26**, 388–91 (1934).

The ketone was purified by distillation under reduced pressure and by two recrystallizations from ethanol. The melting point was 68° to 69° C.

The best yields of laurone reported in the literature are 10 to 30 per cent from lauric acid over thoria at 400° C. (*3*), from lauric acid with phosphorous pentoxide (*2*), and 91 per cent by heating small quantities of the acid in an iron dish for about 4 hours. The preparation of laurone described in this paper gives better yields than the first two methods and produces laurone at a much higher rate than the third.

Besides laurone, undecylenone, $CH_2 = CH(CH_2)_8CO(CH_2)_8CH=CH_2$ (melting point, 43° C.) was prepared from ethyl undecylenate in 86 per cent yield. This is a new ketone. The microanalysis in per cent is as follows: calculated for $C_{21}H_{33}O$: C = 82.30, H = 12.42; found: C = 82.39, H = 12.47.

This method may be used successfully to prepare in large quantities aliphatic ketones of high molecular weight which were formerly obtained only with difficulty.

The microanalysis was carried out by K. Eder of the Chemistry Department of the University of Illinois.

LITERATURE CITED

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(2) Kipping, F. S., *J. Chem. Soc.*, **57**, 981 (1890).
(3) Pickard, R. H., and Kenyon, J., *Ibid.*, **99**, 57 (1911).

RECEIVED June 9, 1934.