TABLE II

ALCOHOL ADDITION PRODUCTS FROM ISOBUTYLENE SULFIDE

Alcohol	Formula of product	B. p., °C.	at mm.	$n^{20}\text{D}$	Analyses,[f] % Calcd. C	H	S[a]	Found C	H	S[a]
n-C_4H_9OH	$C_8H_{18}OS^b$	59–61	4.5	1.4493	...	...	19.75	...	...	18.90
n-$C_5H_{11}OH$	$C_9H_{20}OS^b$	58–59	2	1.4543	61.32	11.44	...	61.14	11.15	...
n-$C_6H_{13}OH$	$C_{10}H_{22}OS^b$	73–74	2	1.4536	63.11	11.66	16.85	63.70	11.54	16.34
n-$C_7H_{15}OH$	$C_{11}H_{24}OS^b$	84–86	3	1.4551	64.82	11.87	15.68	65.20	12.10	15.23
n-$C_8H_{17}OH$	$C_{12}H_{26}OS^b$	98–102	3.5	1.4548	...	...	14.68	...	...	14.02
$C_8H_{17}OH^c$	$C_{12}H_{26}OS^b$	75–80	2	1.4550	65.98	12.00	14.68	66.03	12.11	14.00
	$C_{16}H_{34}OS_2{}^d$	119–121	2	1.4831	62.68	11.15	10.46	62.81	11.18	10.25
$C_2H_5OCH_2CH_2OH$	$C_{12}H_{26}O_2S_2{}^{d,e}$	110–125	3	1.5006	54.09	9.84	12.03	54.10	9.71	11.49

[a] Mercaptan sulfur (determined by amperometric analysis). [b] The product contains traces of the tertiary mercaptan. [c] 2-Ethylhexanol. [d] The product from 1 mole of alcohol and 2 of sulfide. [e] Contains 57.4% of tertiary mercaptan. [f] Reference 5.

TABLE III

DERIVATIVES OF ALCOHOL AND MERCAPTAN ADDITION PRODUCTS OF ISOBUTYLENE SULFIDE

Alcohol or mercaptan	Derivative	M. p., °C.	Formula	Analyses, % Calcd. C	H	Found C	H
n-C_4H_9OH	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	62–63	$C_{16}H_{24}O_5N_4S$	50.00	6.29	50.20	6.37
n-$C_5H_{11}OH$	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	52–53.5	$C_{17}H_{26}O_5N_4S$	51.24	6.58	51.21	6.50
n-$C_7H_{15}OH$	RSSR	[a]	$C_{22}H_{46}O_2S_2$	64.96	11.40	64.79	11.49
	$RSCH_2CH_2C_6H_5$	[b]	$C_{19}H_{32}OS$	73.96	10.46	73.85	10.29
n-$C_8H_{17}OH$	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	40–41	$C_{20}H_{32}O_5N_4S$	54.52	7.32	54.79	7.55
$C_8H_{17}OH^c$	$RSCH_2CH{=}NNHC_6H_3N_2O_4$	48–50	$C_{20}H_{32}O_5N_4S$	54.52	7.32	54.38	7.43
n-$C_7H_{15}SH$	RSSR[d]	[d]	$C_{22}H_{46}S_4$	60.61	10.57	60.69	10.74

[a] Liquid boiling at 195–202° (2.5). [b] Liquid boiling at 150–154° (2). [c] 2-Ethylhexanol. [d] The disulfide presumably is related to the primary mercaptan only. [e] Liquid boiling at 185° (2.5 mm.).

phenylhydrazone by means of the procedure of Shriner and Fuson.[10] The ethanol solubility of the derivative is appreciable and in some instances crystallization occurred only after long chilling of the solution. The product was recrystallized from ethanol, methanol or high-boiling petroleum ether.

The derivatives prepared are listed in Table III along with a few of other types which were prepared and analyzed.

Summary

The preparation of a number of mercaptans by the reaction of alcohols or mercaptans with olefin sulfides in the presence of catalysts is described.

URBANA, ILLINOIS RECEIVED MAY 17, 1947

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[10] Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, N. Y., p. 143.

[CONTRIBUTION FROM THE BUREAU OF ENTOMOLOGY AND PLANT QUARANTINE, AGRICULTURAL RESEARCH ADMINISTRATION, UNITED STATES DEPARTMENT OF AGRICULTURE]

The Synthesis of Some β-Keto Esters

BY S. B. SOLOWAY AND F. B. LAFORGE

For the synthesis of dihydrocinerone (2-butyl-3-methyl-2-cyclopenten-1-one)[1] by a procedure of Hunsdiecker,[2] β-oxocaprylic acid ester is required as the starting material. Hauser and Hudson[3] list three methods which have been used for the synthesis of this β-keto ester: (1) the acylation of ethyl acetoacetate with caproyl chloride and the subsequent ammonolysis of the product (yield "excellent"); (2) the hydration of 2-octynoic acid and esterification (yield, 50–80%); and (3) the forced condensation of 2-heptanone with ethyl carbonate by the agency of sodium ethoxide (yield, 65%). Recently, Anderson and co-workers[4] have employed a modification of the third method, developed by Levine and Hauser,[5] which substitutes sodium amide as the condensing agent (yield, 57%).

Under the first method Hauser and Hudson[3] mention the alcoholysis of the acylacetoacetic ester but without giving references. Hunsdiecker[2] has employed the alcoholysis procedure successfully (yield, 65–70%), and in our hands good yields were likewise obtained with the employment of commercial sodium methoxide and commercial anhydrous methanol. The procedure

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(1) LaForge and Barthel, *J. Org. Chem.*, **10**, 222 (1945).

(2) Hunsdiecker, *Ber.*, **75B**, 447, 455, 460 (1942).

(3) Hauser and Hudson, "Organic Reactions," Adams, editor-in-chief, vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, chap. 9, p. 266.

(4) Anderson and co-workers, THIS JOURNAL, **67**, 2197 (1945).

(5) Levine and Hauser, *ibid.*, **66**, 1768 (1944).

is outlined in the experimental part of this paper.

With the availability of commercial sodium hydride, we have devised a more convenient and direct procedure than those previously described for the synthesis of ethyl β-oxocaprylate. The essential feature of the method was found to involve the very slow addition of 2-heptanone to a refluxing solution of ethyl carbonate in ethyl ether in the presence of sodium hydride. The yields in a number of experiments were 75–79%. The introduction of the carbethoxy group on the methyl carbon of the ketone is proved by the subsequent reactions leading to dihydrocinerone, although some methylene–carbon substitution may have occurred to produce ethyl α-butylacetoacetate.

The sodium hydride condensation procedure has also been applied to dihydrocinerone itself,[6,7] and the reaction is probably of general applicability.

Sodium hydride has also found application by us for the introduction of the ethoxalyl group in ethyl caproate, yielding ethyl β-carbethoxy-α-oxoenanthate. This compound has been prepared recently by Adickes and Andresen[8] by a procedure employing sodium ethoxide as the condensing agent and requiring two eight-hour periods of reflux for completion (yield of crude product, 80%).

A simple fractionating column of the concentric-tube type was employed for the distillation of the products.

Experimental

Methyl β-Oxocaprylate.—To a solution of 30 g. (0.55 mole) of commercial sodium methoxide in 350 ml. of commercial methanol at room temperature was added 110 g. (0.48 mole) of ethyl α-acetyl-β-oxocaprylate (b. p. 142° (15 mm.), n^{25}D 1.4600). The resulting solution was allowed to stand overnight, becoming orange in color. It was then poured into about 1200 ml. of water containing sufficient hydrochloric acid to render the aqueous phase acid to congo red. The separated oil was taken up in petroleum ether, and the organic layer was washed free of acid and dried. After removal of the solvent, fractional distillation from a modified Claisen flask yielded 73 g. (88%) of product, b. p. 108–116° (14 mm.), n^{26}D 1.4315. Hunsdiecker[2] gives a b. p. of 109° (11 mm.).

Ethyl β-Oxocaprylate.—In view of the mechanism of carbethoxylation by the agency of sodium amide postulated by Levine and Hauser,[5] the molar ratio of 1:2:2 for 2-heptanone, ethyl carbonate and sodium hydride was adopted. However, when the reaction of 2-heptanone with the sodium hydride was followed by the addition of ethyl carbonate, yields were poor. They were improved when a mixture of the ketone and ethyl carbonate was added to ether refluxing over sodium hydride, but decidedly better results were obtained when the ketone was added very slowly to a refluxing mixture of ethyl carbonate in ether over sodium hydride. The following is a typical experiment:

Sodium hydride, 48 g. (2 moles), was weighed under nitrogen and transferred to a nitrogen-swept three-necked flask equipped with reflux condenser. mercury-sealed stirrer and dropping funnel. The hydride was covered with 250 ml. of ether, and 236 g. (2 moles) of ethyl carbonate was added. With stirring and refluxing, 114 g. (1 mole) of 2-heptanone, dissolved in 250 ml. of ether, was added dropwise over a period of seven hours. The following day the stirring and heating were resumed for an additional hour. The reaction mixture was then cooled with ice water and the sodium compound was decomposed by the gradual addition of 125 ml. of glacial acetic acid. Upon the addition of water the separated sodium acetate was dissolved and the two phases separated. The aqueous phase was extracted with ether, the ethereal extracts were combined, washed free of acid with sodium bicarbonate and dried, and the solvent was removed. After 114 g. of ethyl carbonate had been distilled off from a Claisen flask at the water pump, the residue was distilled through a concentric-tube column, yielding the following fractions.

TABLE I

Fraction	B. p., °C.	p, mm.	Wt., g.	n^{25}D
1	88–102	11	5	1.4196
2	102–108	11	11	1.4283
3	108–110	11	72	1.4312
4	110–112	11	74	1.4340

Yield for fractions 3 and 4 = 79%.

Anal. Calcd. for $C_{10}H_{18}O_3$: C_2H_5O, 24.2. Found: C_2H_5O, 24.2.

The refractive index reported by Wallingford, Homeyer and Jones[9] for ethyl β-oxocaprylate is n^{20}D 1.4315, whereas an authentic specimen of ethyl α-butylacetoacetate, the isomer obtainable by methylene-carbon carbethoxylation of 2-heptanone, boiled at 99° (10 mm.), n^{26}D 1.4260.

The product was converted to its sodium enolate, which is soluble in ether, and it reacted with bromoacetone. The crude reaction product was then cyclized by dilute aqueous sodium hydroxide to 2-butyl-3-methyl-2-cyclopenten-1-one in an over-all yield of 55%.[2]

Ethyl β-Carbethoxy-α-oxoenanthate.—To a mixture of 48 g. (2 moles) of sodium hydride and 292 g. (2 moles) of diethyl oxalate in 200 ml. of refluxing ether 144 g. (1 mole) of ethyl caproate was added with stirring. The procedure was the same as that just described, except that the period of addition of ethyl caproate was reduced to three and one-half hours, followed by one hour of reflux. The reaction mixture was worked up in the same manner, and the product distilled, yielding 218 g. (90%), b. p. 91–99° (0.4 mm.), n^{30}D 1.4321 (lit. b. p. 118–122° (2 mm.).[8]

Anal. Calcd. for $C_{12}H_{20}O_5$: $2C_2H_5O$, 36.9%. Found: C_2H_5O, 36.6%.

The product yielded a 2,4-dinitrophenylhydrazone, m. p. 85–86° (lit. m. p. 84–85°).[8]

Summary

The synthesis of ethyl β-oxocaprylate, from a methyl ketone, 2-heptanone, and ethyl carbonate with sodium hydride as the condensing agent, is described.

Sodium hydride has also been employed to introduce the ethoxalyl group into ethyl caproate to prepare ethyl β-carbethoxy-α-oxoenanthate.

BELTSVILLE, MARYLAND RECEIVED JUNE 5, 1947

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(6) LaForge and Soloway, THIS JOURNAL, **69**, 186 (1947).

(7) LaForge and Soloway, *ibid.*, to be published.

(8) Adickes and Andresen, *Ann.*, **555**, 41 (1943).

(9) Wallingford, Homeyer and Jones, THIS JOURNAL, **63** 2252 (1941).