



Fig. 3.

can be changed if it breaks or becomes defected during use. Part (d) acts also as a stop for the piston on its way up.

- (e) Piston.
- (f) Spring which brings the piston up automatically, once the hole has been made. This movement allows a more perfect function of the apparatus because it cleans the terminal and narrowest part of the cylinder (b).
- (g) Movable part (attached to the piston by a screw) which acts as a stop for the piston on its way down. It permits adjustment of the effective length of the piston thereby bringing the ends of the helical conveyer into the most favourable working position.
- (h) Knob.
- (i) Wiper to remove the pieces of agar attached to the shaft by making them fall into cylinder (a).

**Procedure.** The apparatus is placed on the agar plate and pushed down vertically to cut the agar. The piston is pushed down and turned simply by rotating the knob

between the thumb and the forefinger. In this way the piece of agar is taken up by the helical conveyer. On releasing the downward pressure on the screw-cap the piston readily slides up into its initial position.  
Capacity. 100–120 holes/min.

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## Conjugate Additions of Grignard Reagents to $\alpha$ , $\beta$ -Unsaturated Esters IV. Cuprous Chloride Catalysed Additions to Ethyl Esters

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Additions of Grignard reagents to *sec*-butyl esters of  $\alpha$ ,  $\beta$ -unsaturated acids, such as crotonic, tiglic and cinnamic acids, have been found to usually take place at the double bond (1,4-addition)<sup>1</sup> whereas, in general, additions to the corresponding ethyl esters take place predominantly at the carbonyl group (1,2-addition). However, in certain cases 1,4-addition to *sec*-butyl esters does not occur to any appreciable extent. This is for instance the case in some recently described<sup>2</sup> additions of methylmagnesium bromide, but it was found<sup>2,3</sup> that the presence of cuprous chloride during the addition of the esters to the Grignard reagent would secure fair to good yields of 1,4-addition products. It was further found that these yields were obtained not only with *sec*-butyl esters but also with ethyl esters. Crotonic esters thus gave the corresponding *isovaleric* esters, whereas tiglic and cinnamic esters gave saturated ketones as results of both 1,4- and 1,2-addition.

The present investigation was carried out as a consequence of the above-mentioned findings in order to establish if 1,4-addition products would also with higher Grignard reagents be the major products from ethyl esters in the presence of cuprous chloride, thus avoiding the use of *sec*-butyl esters. As model reactions the additions

of *n*-butylmagnesium bromide to ethyl crotonate, tiglate and cinnamate have been tried. The results are given in Table 1.

In the case of crotonic esters a good yield of simple 1,4-addition product was indeed obtained, and it appears as if in

In the case of the cuprous chloride catalyzed reaction with ethyl tiglate, the simple 1,4-addition product ( $\alpha,\beta$ -dimethyl-substituted ester) was not formed, but the saturated ketone (resulting from both 1,4- and 1,2-addition) was produced, as was the

Table 1. Additions of *n*-butylmagnesium bromide to ethyl esters of  $\alpha,\beta$ -unsaturated acids.

Ethyl ester	Product	Yield %	b. p. °C	Refractive index
Crotonic	ethyl 3-methylheptanoate a	70—74	89— 90/20 mm 81/15 »	$n_D^{20}$ 1.4186
Tiglic	6,7-dimethylundecanone-5 b	45	118—119/15 »	$n_D^{25}$ 1.4370
Cinnamic	ethyl 3-phenylheptanoate c	15	113°/1 mm	$n_D^{25}$ 1.4879

a Calc. for  $C_{10}H_{20}O_2$  (172.26): Sap.equiv. 172.26. Found: 172.0.

b Calc. for  $C_{13}H_{26}O$  (198.34): C 78.72; H 13.21. Found: C 78.15; H 13.14 (microanalysis by Mr. Preben Hansen, The Chemical Laboratory, University of Copenhagen). Infra-red spectrum (recorded in this laboratory by Mrs. Susanne Refn, M.Sc.) shows the presence of a ketone group and the absence of hydroxyl groups.

c Calc. for  $C_{15}H_{22}O_2$  (234.33): Sap.equiv. 234.33. Found 234.2.

this case the two alternative procedures to prepare  $\beta$ -methylsubstituted fatty acids are equally good. In fact, when the conditions of the procedure previously described<sup>1,2</sup> were otherwise observed, it was found that no particular precautions with respect to the quality of cuprous chloride and the cooling of the reaction mixture were necessary: cooling in ice-water and the use of commercial cuprous chloride (Merck, p.a., without any previous reduction or drying) were sufficient to secure the same yield as was obtained in the non-catalyzed reaction with *sec*-butyl crotonate.

Methyl crotonate, with *n*-butylmagnesium bromide in the presence of cuprous chloride, has previously<sup>3</sup> been found to give 1,4-addition, although, in this case, the primarily produced ester self-condensed to give an acetoacetic ester.

When no cuprous chloride is used, ethyl crotonate has been found to give a mixture of different compounds, including large amounts of high-boiling material.

case when methylmagnesium bromide<sup>4</sup> was used. Only a 45 % yield was obtained.

With ethyl cinnamate and *n*-butylmagnesium bromide a 15 % yield of the simple 1,4-addition product, 3-phenylbutyric ester, was obtained.

It may be concluded that, as a practical procedure for preparing substituted fatty acids from  $\alpha,\beta$ -unsaturated acids (by the conjugate addition of Grignard reagents), the cuprous chloride catalyzed reaction with ethyl esters is not as generally applicable as the use of *sec*-butyl esters; although 3-methyl-substituted acids (from crotonic esters) do arise in equally good yields by the two methods.

1. Munch-Petersen, J. *Acta Chem. Scand.* **12** (1958) 967.
2. Munch-Petersen, J. *Acta Chem. Scand.* **12** (1958) 2007.
3. Munch-Petersen, J. *J. Org. Chem.* **22** (1957) 170.

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