TABLE II

SPECTROPHOTOMETRIC ANALYSES OF MIXED TRIGLYCERIDES

Acyl radical	Conjugation, %[a] Diene	Triene
1-Linoleyl-2,3-diacyl Glycerols		
Caprylyl	0.55	<0.06
Capryl	.89	< .07
Lauryl	1.18	< .07
Myristyl	1.35	< .08
Palmityl	0.89	< .08
Stearyl	.71	< .08
1-Acyl-2,3-dilinoleins		
Lauryl	1.45	<0.06
Myristyl	0.91	< .18
Palmityl	.57	< .14
Stearyl	.84	< .08

[a] Calculated as per cent. of 18-carbon conjugated acid. Where no absorption peaks were observed values are indicated as maximal.

In the instance of both conjugated diene and triene absorption peaks for these compounds, the maxima were shifted to wave lengths shorter than those expected from consideration of the absorption curves for 9,11-linoleic acid or isomerized 9,12-linoleic acid. The absorption curves, represented in Figs. 1 and 2, are typical for the triglycerides reported in this investigation.

Brode, *et al.*,[13] found as much as 0.46% conjugated diene material in their crystallization linoleic acid and 1.2% in their debromination acids. However, Wood, *et al.*,[6] obtained a debromination linoleic acid which after distillation had less than 0.1% of diene material. The preparation of linoleyl chloride from this acid increased the percentage of conjugated diene to only 0.34%. The conjugation in each of the triglycerides reported in this paper did not increase significantly beyond the percentage reported by Wood, *et al.*, considering the extensive manipulation necessary in their preparation.

Summary

Physical and chemical data are reported for a series of 1-linoleyl-2,3-disaturated triglycerides and 1-monosaturated-2,3-dilinoleins.

[13] Brode, Patterson and Brown, *Ind. Eng. Chem.*, *Anal. Ed.*, **16**, 77 (1944).

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Ester Interchange by Means of the Grignard Complex

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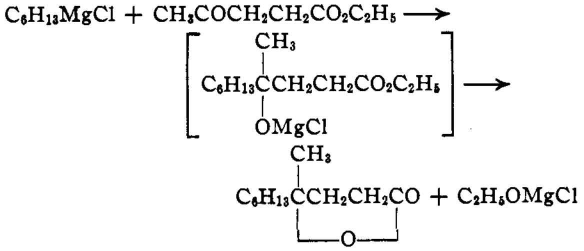
A recent investigation in this Laboratory involved the preparation of γ-methyl-γ-decanolactone by the addition of *n*-hexylmagnesium chloride to ethyl levulinate.[1] It was remarkable that the peach-like fragrance of the lactone was noticed as soon as the Grignard reagent was added to the keto ester. It was subsequently found that the lactone could be isolated directly from the reaction mixture without intermediate saponification, which indicates the reaction



$$C_6H_{13}MgCl + CH_3COCH_2CH_2CO_2C_2H_5 \longrightarrow \left[C_6H_{13}\overset{CH_3}{\underset{OMgCl}{C}}CH_2CH_2CO_2C_2H_5 \right] \longrightarrow C_6H_{13}\overset{CH_3}{\underset{\llcorner O \lrcorner}{C}}CH_2CH_2CO + C_2H_5OMgCl$$

Examination of the literature showed that this type of reaction was known to Grignard[2] and that it is also known to take place intermolecularly as follows:

$$RCO_2R' + R''OMgX \longrightarrow RCO_2R'' + R'OMgX$$

Stadnikoff[3] has studied the intermolecular reaction and obtained such esters as menthyl acetate, menthyl propionate and menthyl benzoate in high yields.

Further study of Stadnikoff's method has provided a practical means of preparing certain esters which are not otherwise easy to obtain. The method is particularly applicable for the preparation of acrylates and substituted acrylates of primary and secondary alcohols, higher alkyl carbonates and higher esters of malonic acid, as shown in the accompanying table. It was not successful, however, for the preparation of cyclohexyl acetoacetate from ethyl acetoacetate, probably due to chelation of the enol form of the acetoacetate. Unsuccessful attempts also were made to prepare *t*-butyl acetate, *t*-butyl methacrylate, phenyl acrylate, furfuryl formate and *s*-butyl γ-hydroxyvalerate.

Experimental

The experimental procedure was essentially the same for the synthesis of each ester, a typical example of which, the preparation of *s*-butyl methacrylate, is here described in detail:

A 500-cc., three-necked, round-bottomed flask was fitted with a reflux condenser, a 125-cc. dropping funnel and a mechanical stirrer. Calcium chloride tubes were placed on the end of the condenser and on the top of the dropping funnel. An ethylmagnesium bromide solution was prepared in the flask in the usual manner from 6.08 g. (0.25 g. atom) of magnesium turnings, 19.0 cc. (27.2 g.; 0.25 mole) of freshly-distilled ethyl bromide and 100 cc. of dry ether. A solution of 23.0 cc. (18.5 g., 0.25 mole) of anhydrous *s*-butyl alcohol in 50 cc. of dry ether was then

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[1] Frank, Arvan, Richter and Vanneman, THIS JOURNAL, **66**, 4 (1944).

[2] Grignard, *Compt. rend.*, **135**, 627 (1902); *Bull. soc. chim.*, **39**, 1304 (1926).

[3] Stadnikoff, *J. Russ. Phys.-Chem. Soc.*, **46**, 887 (1914); **47**, 1113, 1122, 2037, 2115 (1915); *C. A.*, **9**, 1755, 3051, 3052 (1915); **10**, 1355 (1916).

TABLE I

ESTER INTERCHANGE BY MEANS OF THE GRIGNARD COMPLEX

The microanalyses reported herein were carried out by Miss Dorothy Schneider and Miss Theta Spoor.

Starting ester	Ratio $\frac{\text{moles alc.}}{\text{moles ester}}$	Products	Yield, %	B. p., °C.	Mm.	n^{20}D	d^{20}_4
Ethyl acrylate	1.00	*l*-Menthyl acrylate[a]	55	90–95	4	1.4591	
Methyl methacrylate	1.00	*n*-Butyl methacrylate[b]	71	82–83	50	1.4230	
Methyl methacrylate	1.00	*s*-Butyl methacrylate[c]	65	70–71	50	1.4179	0.886
Methyl α-bromoacrylate	0.81	*s*-Butyl α-bromoacrylate[d]	59	78–81	24	1.4587	1.305
Methyl α-bromoacrylate	1.18	Cyclohexyl α-bromoacrylate[d]	78	81–85	3	1.4956	1.346
Methyl α-bromoacrylate	0.93	*l*-Menthyl α-bromoacrylate[e]	65	100	3	1.4859	1.199
Methyl α-chloroacrylate	1.04	*s*-Butyl α-chloroacrylate[d]	79	67–69	18	1.4362	1.046
Methyl α-chloroacrylate	1.00	Cyclohexyl α-chloroacrylate[d]	73	111	18	1.4751	1.112
Methyl α-chloroacrylate	0.80	*l*-Menthyl α-chloroacrylate[f]	65	96–98	3	1.4712	1.031
Ethyl carbonate	2.64	*n*-Butyl carbonate[g]	27	94–96	16	1.4115	
Ethyl carbonate	2.64	*s*-Butyl carbonate[h]	30	73–76	18	1.4039	0.917
Ethyl carbonate	2.64	Ethyl cyclohexyl carbonate[i]	31	99	18	1.4393	1.015
		Cyclohexyl carbonate[j]	14	(m. p. 41–42°)			
Ethyl carbonate	8.00	Ethyl cyclohexyl carbonate	33				
		Cyclohexyl carbonate	18				
Ethyl malonate	2.00	*s*-Butyl malonate[k]	46	120	18	1.4213	0.973
Ethyl malonate	2.00	Cyclohexyl malonate[l]	29	153	1	1.4736	1.068
Ethyl butyrate	1.00	*n*-Butyl butyrate[m]	31	164	760	1.4053	
Methyl acetate	1.00	*l*-Menthyl acetate[n]	85	115–118	22	1.4472	

[a] $[\alpha]^{33}$D −89.9° (no solvent); Marvel and Frank, THIS JOURNAL, **64**, 1675 (1942). [b] Imperial Chemical Industries, Ltd. and Crawford, English Patent 405,699 (Aug. 3, 1934). [c] *Anal.* Calcd. for $C_8H_{14}O_2$: C, 67.57; H, 9.93. Found: C, 67.36; H, 10.10. [d] Marvel, Dec, Cooke and Cowan, THIS JOURNAL, **62**, 3495 (1940). [e] $[\alpha]^{27}$D −74.1° (1.275 g. in 25 cc. of carbon tetrachloride solution, α −7.56°); *Anal.* Calcd. for $C_{13}H_{21}O_2Br$: Br, 27.68. Found: Br, 27.92. [f] $[\alpha]^{27}$D −80.7° (2.388 g. in 25 cc. of dioxane solution, α −15.42°); *Anal.* Calcd. for $C_{13}H_{21}O_2Cl$: Cl, 14.51. Found: Cl, 14.30. [g] Lieben and Rossi, *Ann.*, **165**, 109 (1873). [h] *Anal.* Calcd. for $C_9H_{18}O_3$: C, 62.04; H, 10.41. Found: C, 61.93; H, 10.67. [i] *Anal.* Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.69; H, 9.39. [j] *Anal.* Calcd. for $C_{13}H_{22}O_3$: C, 68.99; H, 9.80. Found: C, 69.20; H, 10.04. [k] *Anal.* Calcd. for $C_{11}H_{20}O_4$: C, 61.08; H, 9.32. Found: C, 61.11; H, 9.49. [l] *Anal.* Calcd. for $C_{15}H_{24}O_4$: C, 67.14; H, 9.01. Found: C, 67.07; H, 9.20. [m] Linnemann, *Ann.*, **161**, 195 (1872). [n] $[\alpha]^{27}$D −74.0° (no solvent); Stadnikoff, *J. Russ. Phys.-Chem. Soc.*, **47**, 1113 (1915).

added slowly. As the alcohol was added, a white solid formed on the sides of the flask above the ether layer, and after the last of the alcohol solution had been added, the flask was shaken gently a few times to remove this solid, which dissolved readily in the ether solution. A mixture of 26.7 cc. (25.0 g., 0.25 mole) of methyl methacrylate and an equal volume of dry ether was next added all at once through the dropping funnel. No heat of reaction could be detected during this addition and no precipitate formed immediately, but when the mixture was refluxed, a white, granular precipitate formed after thirty minutes. This remained until the Grignard complex was decomposed (such a precipitate does not form in every case, however). The mixture was refluxed overnight with stirring, after which it was poured into 300 cc. of cold dilute hydrochloric acid. The ethereal and aqueous layers were separated and the aqueous layer, after saturation with sodium chloride, was extracted with three 50-cc. portions of ether. These extracts were combined with the original ether layer and, after drying with anhydrous magnesium sulfate, fractionally distilled in a modified Widmer column. *s*-Butyl methacrylate was collected in a yield of 23.2 g. (65%) at 70–71° (50 mm.).

Methyl α-Bromoacrylate and Methyl α-Chloroacrylate.—These esters were prepared by the method of Marvel and Cowan.[4] The former was obtained from 123 g. (0.50 mole) of methyl α,β-dibromopropionate and the yield was 70 g. (85%), boiling at 57–59° (24 mm.). The latter was prepared from 70 g. (0.445 mole) of methyl α,β-dichloropropionate, and the product in this case weighed 32 g. (60%), b. p. 41–44° (28 mm.); n^{20}D 1.4420.

Summary

A practical method is presented for preparing certain esters by *trans*-esterification involving the Grignard complex. It is especially suitable for the preparation of acrylates and substituted acrylates of primary and secondary alcohols.

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[4] Marvel and Cowan, THIS JOURNAL, **61**, 3156 (1939).

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