Table II
Lithium Aluminum Hydride Reduction of Dodecyl Mercaptan

Solvent	Mmol $LiAlH_4$/ mmol RSH	Time, hr	% dodecane
THF	5.4	3.5	0
THF	5.4	21.0	6
THF	5.4	115	53
Dioxane	5.0	2.0	3
Dioxane	5.0	44	47
Dioxane	5.0	71	92
Dioxane	1.1	40	25
Dioxane	1.1	72	83
Dioxane	1.1	96	98

Lithium Aluminum Hydride Reduction of Decyl Dodecyl Sulfide. Approximately 20 ml of dioxane was distilled into a flask containing 1.002 g (2.93 mmol) of decyl dodecyl sulfide,[13] and then 264 mg of cyclododecane and 230 mg (6.0 mmol) of lithium aluminum hydride were added. The stirred slurry was heated at reflux and aliquots were withdrawn periodically, diluted with ether, quenched with water, and acidified with 5% hydrochloric acid. The organic products were extracted with ether and dried. The concentrated ether solution was analyzed using an SE-30 column at 130°. The yields of dodecane follow, time in hours (% dodecane): 2 (0), 15 (0.2), 82 (24), 278 (56), and 472 (64). At no time was there evidence for the presence of decyl or dodecyl mercaptan.

Registry No.—**1**, 13131-58-3; **2**, 54934-37-1; **3**, 54934-38-2; **4**, 54934-39-3; **6**, 13131-57-2; **7**, 54934-40-6; **8**, 54934-41-7; **9**, 54934-42-8; **10**, 54934-43-9; **11**, 54984-43-9; **12**, 54934-44-0; **13**, 38359-42-1; **14**, 54934-45-1; **16**, 54934-46-2; **17**, 54934-47-3; lithium aluminum hydride, 16853-85-3; sodium borohydride, 16940-66-2; dodecyl mercaptan, 112-55-0; decyl dodecyl sulfide, 54934-48-4.

References and Notes

(1) Abstracted in part from the Ph.D. Thesis of R. L. Marhenke, Purdue University, Aug 1970.

(2) J. Wolinsky, D. R. Dimmel, and T. W. Gibson, *J. Org. Chem.*, **32**, 2087 (1967).

(3) J. Wolinsky, R. L. Marhenke, and E. J. Eustace, *J. Org. Chem.*, **38**, 1428 (1973).

(4) For the preparation of sulfinate esters see D. C. Dittmer, R. S. Henion, and N. Takashina, *J. Org. Chem.*, **34**, 1310 (1969); J. F. King, K. Piers, D. J. H. Smith, C. L. McIntosh, and P. DeMayo, *Chem. Commun.*, 31 (1969); E. N. Givens and L. A. Hamilton, *J. Org. Chem.*, **32**, 2857 (1967); R. M. Dodson, P. D. Hammen, and R. A. Davis, *Chem. Commun.*, 9 (1968); K. S. Dhami, *Chem. Ind. (London)*, 1004 (1968); D. N. Harpp and J. G. Gleason, *Tetrahedron Lett.*, 1447 (1969).

(5) It has been suggested[6] that sulfinate esters show characteristic infrared absorption bands at 8.7–9.1 and 10.1–11.0 μ. The sulfinate esters prepared in this study show the first of these peaks. Sulfinates **7** and **14** show a second peak at 10.1 and 10.5 μ, respectively, whereas camphene sulfinate **2** shows only weak absorption in the region 9.1–11.3 μ.

(6) L. F. Field, C. B. Hoelzel, J. M. Locke, and J. E. Lawson, *J. Am. Chem. Soc.*, **83**, 1256 (1961).

(7) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

(8) For the desulfurization of aminothiols see E. L. Eliel and J. Roy, *J. Org. Chem.*, **30**, 3092 (1965), and references cited therein. See B. Franzen and E. I. Snyder, *J. Am. Chem. Soc.*, **87**, 3423 (1965), for the role of a neighoring hydroxyl in the reduction of double bonds by lithium aluminum hydride.

(9) All boiling and melting points are uncorrected. Infrared spectra were recorded with a Perkin-Elmer Infracord spectrometer or with a Perkin-Elmer Model 421 spectrometer. NMR spectra were determined with a Varian A-60A spectrometer. Mass spectra were recorded by the Purdue University Spectral Services Department on a Hitachi RMU-6A instrument using a ionizing energy of 70 eV, an inlet temperature of 185°, and a source temperature of 160°. Microanalyses were performed by Dr. C. S. Yeh and associates.

(10) Prepared by thermal rearrangement of 10-isobornyl sultone (**6**).[2]

(11) The amount of camphene, camphene hydrate, 9-mercaptocamphene, and 9-mercaptocamphene hydrate varied from analysis to analysis, presumably owing to dehydration occurring in the injection port of the gas chromatograph.

(12) O. Dimroth, L. Kraft, and K. Aichinger, *Justus Liebigs Ann. Chem.*, **545**, 124 (1940).

(13) Decyl dodecyl sulfide was obtained by the reaction of dodecyl mercaptan with 1-bromodecane using sodium hydroxide and ethanol. The solid sulfide was purified by distillation, bp 171–173° (0.25 mm), mp 27.5–28.5°, *m/e* 242 (35%).

Reactions of Organolithium Compounds and Grignard Reagents with Lithium Carboxylates

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With the exception of the reaction of equivalents of phenyllithium with lithium acetate for 24 hr, which gives a mixture of acetophenone and diphenylmethylcarbinol, similar reactions involving six other lithium carboxylates give only ketones. The reactions of three lithium carboxylates with phenyllithium for only 0.5 hr give mixtures of ketones and carbinols. These latter results are explained by suggesting that even in the presence of water the unreacted phenyllithium survives for sufficiently long so that it reacts appreciably with the ketone, $RCOC_6H_5$, which arises from the hydrolysis of the intermediate, $R(C_6H_5)C(OLi)_2$. Evidence to support this argument is given. The reactions of two lithium carboxylates with three Grignard reagents give mixtures of ketones and carbinols with the latter products predominating except with methylmagnesium iodide, in which case the reverse is true.

A thorough study of the reactions of carboxylic acids and their lithium salts with phenyllithium has apparently not been reported. In 1933 Gilman and Van Ess[1] made the significant observations that the reaction of benzoic acid (1 equiv) with phenyllithium (2 equiv) gave benzophenone (37.2%) and triphenylcarbinol (14.1%) and that refluxing lithium benzoate (0.136 mol) with phenyllithium (0.1 mol) for 5.5 hr gave benzophenone (70.0%) and no triphenylcarbinol. In contrast to these results Tegnér[2] has shown that the reactions of 2 equiv of methyllithium with 1 equiv of a series of aliphatic and aromatic acids for 1 hr give the corresponding methyl ketones and no tertiary alcohols.

Braude and Coles[3] have also obtained only ketone (30–40%) by stirring a mixture of equivalents of isobutenyllithium and lithium acetate, benzoate, or crotonate for a 24-hr period. Petrov and Sokolova[4] report yields of less than 25% of ketone and no carbinol from the reactions of sodium acetate and sodium *n*-butyrate with primary Grignard reagents in ether.

The present investigation is concerned with a study of the reactions of certain organolithium compounds and Grignard reagents with a series of lithium carboxylates. Refluxing equimolar amounts of phenyllithium and the lithium salts of a number of carboxylic acids (Table I) for 24 hr gave, upon quenching with water, high yields of ketone and usually no tertiary alcohol.

Table I
Reactions of Lithium Carboxylates with Phenyllithium for 24 Hr

Registry no.	Lithium salt[a]	Yields of products[b] % ketone	% carbinol
546-89-4	Acetate	39 (66[c])	35 (5[c])
6531-45-9	Propionate	82	0
21303-03-7	*n*-Butyrate	85	0
25179-23-1	Isobutyrate	79	0
14271-99-9	Pivalate	89[d]	0
16577-51-8	Caproate	84[e]	0
553-54-8	Benzoate	85[f]	0

[a] In each reaction, except as noted below, the lithium carboxylate (1 equiv) was added to phenyllithium (1 equiv) in ether and the mixture was refluxed for 24 hr. [b] In all cases the physical constants of the products agree with the literature values. [c] Reflux time was 72 hr. [d] Pivalic acid (8%) was recovered. [e] Caproic acid (12%) was recovered. [f] Benzoic acid (10%) was recovered.

It is suggested that the reason for obtaining only ketone in all of the reactions except that with lithium acetate for a 24-hr reaction time may be due to the stability of the dilithium salts.[1] $RR'C(OLi)_2$, which might resist further substitution with a second mole of organolithium reagent or loss of lithium oxide to give the ketone, $RR'C{=}O$, which could then react with an additional mole of organolithium reagent. The following suggestion might possibly account for the formation of a mixture of ketone (39%) and carbinol (35%) in the 24-hr lithium acetate–phenyllithium reaction. The stability of the initially formed adduct between lithium acetate and phenyllithium, $CH_3C(C_6H_5)(OLi)_2$, may be such that it decomposes to some extent during the reaction to give some free ketone, $CH_3COC_6H_5$, which reacts with more phenyllithium to give the carbinol, $(C_6H_5)_2C(CH_3)OH$. Alternatively, the steric requirements of the adduct may be sufficiently favorable so what may be described as a nucleophilic attack on carbon by the phenyllithium may occur to some extent to give the carbinol.

It was somewhat unexpected to find that the interaction of equivalents of phenyllithium and three typical lithium carboxylates, with a reflux time of only 30 min, gives mixtures of ketones and tertiary alcohols. Thus, lithium propionate gave propiophenone (40%) and diphenylethylcarbinol (25%); lithium *n*-butyrate gave *n*-butyrophenone (39%) and diphenyl-*n*-propylcarbinol (30%); and lithium benzoate gave benzophenone (8%) and triphenylcarbinol (22%). Furthermore, in the case of lithium *n*-butyrate, for example, when the reflux time is increased by increments, from 0.5 to 24 hr, increasing amounts of ketone and decreasing amounts of tertiary alcohol are obtained (Table II). It was also found that the interaction of equivalents of lithium benzoate and *n*-propyllithium for 24 hr gave only *n*-butyrophenone (85.8%) while a similar reaction for a 30-min reaction time gave a mixture of *n*-butyrophenone (11.7%) and di-*n*-propylphenylcarbinol (17.6%).

The formation of substantial amounts of carbinol during a short reaction time appears to be the result of a *slow* reaction between the lithium carboxylate and the organolithium compound combined with a *slow* hydrolysis of the reaction intermediate. It is suggested that at short reaction times there is considerable unreacted organolithium compound present which reacts during the hydrolysis with part of the ketone which is formed by the hydrolysis of the intermediate adduct, $RR'C(OLi)_2$.

$$RR'C(OLi)_2 \xrightarrow{H_2O} RCOR' \xrightarrow{R'Li} RR'R'C(OLi) \xrightarrow{H_2O} RR'R'COH$$

Table II
Reactions of Lithium *n*-Butyrate with Phenyllithium[a] for Varying Reaction Times

Reflux time, hr	Products, % yield Ketone[b]	Carbinol[b]
0.5	39	30
1.0	42	28
2.0	46	30
3.0	61	21
4.0	70	10
5.0	79	5
10.0	90	0
24.0	85	0

[a] Equivalents of lithium *n*-butyrate and phenyllithium were used. [b] The physical constants of the *n*-butyrophenone [C. R. Hauser, W. J. Humphlett, and M. J. Weiss, *J. Am. Chem. Soc.*, **70**, 426 (1948)] and diphenyl-*n*-propylcarbinol [H. Masson, *C. R. Acad. Sci.*, **135**, 534 (1902)] agree with the literature values.

A somewhat comparable mechanism has been suggested by Jorgenson[5] in a review on the preparation of ketones from the reaction of organolithium reagents with carboxylic acids. It is of interest to note that when House and Bare[6] treated a mixture of the stereoisomeric 4-*tert*-butylcyclohexanecarboxylic acids with methyllithium and processed the reaction by removing aliquots from the mixture and adding them dropwise, with vigorous stirring, to fresh portions of ice and dilute hydrochloric acid, only 4-*tert*-butylcyclohexyl methyl ketone (94.8%) and no dimethyl-4-*tert*-butylcyclohexylcarbinol were obtained. Under less controlled hydrolytic conditions often a mixture of ketone and carbinol is obtained.[5]

To obtain evidence in support of the scheme shown above, two experiments were performed. A mixture of equivalents of lithium propionate and phenyllithium, A, was refluxed for 24 hr. Hydrolysis of such a mixture had given (see Table I) an 82% yield of propiophenone and no carbinol. In another flask, phenyllithium, B (1 equiv), was prepared. Simultaneously, rapidly and with vigorous stirring, A and B were poured down the opposite sides of a beaker containing crushed ice and water. Processing gave propiophenone (58.1%) and diphenylethylcarbinol (28.3%). In the second experiment equivalents of propiophenone, C, in an equal volume of ether and phenyllithium, B, were treated with ice and water as described above to give diphenylethylcarbinol (44.8%) and some material which appeared to be self-condensed derivatives of propiophenone. These experiments lend some support to the proposed origin of diphenylalkylcarbinols (vide supra).

It was not surprising to find that when lithium *n*-butyrate (1 equiv) and phenyllithium (2 and 3 equiv) were allowed to react for 24 hr, the yields of ketones dropped to 63.5 and 48.0% and the yields of carbinol increased to 34 and 52%, respectively, as contrasted with the yields of products, ketone (85.0%) and carbinol (0%), which were obtained when equivalents of the reagents were allowed to react for 24 hr.

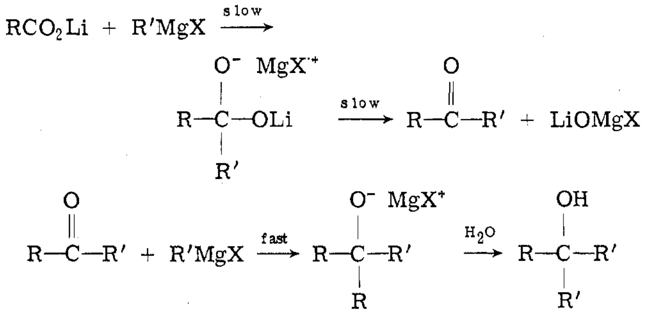
In contrast with what was observed in the reaction of the lithium carboxylates with organolithium compounds, lithi-

Table III
Reactions of Grignard Reagents with Lithium Carboxylates

Grignard reagent[a]	Products[b]	Yield, %
	Lithium n-Butyrate[a]	
CH_3MgI	n-$C_3H_7COCH_3$	24
	n-$C_3H_7C(CH_3)_2OH$	12
n-C_4H_9MgBr	n-$C_3H_7COC_4H_9$-n	11
	n-$C_3H_7C(n\text{-}C_4H_9)_2OH$	43
C_6H_5MgBr	n-$C_3H_7COC_6H_5$	7 (14[c])
	n-$C_3H_7C(C_6H_5)_2OH$	70 (58[c])
	Lithium Benzoate[a]	
CH_3MgI	$C_6H_5COCH_3$	33
	$C_6H_5C(CH_3)_2OH$	15
n-C_4H_9MgBr	$C_6H_5COC_4H_9$-n	12
	$C_6H_5C(n\text{-}C_4H_9)_2OH$	61
C_6H_5MgBr	$(C_6H_5)_2CO$	10
	$(C_6H_5)_3COH$	61

[a] In each reaction the lithium carboxylate (1 equiv) was slowly added to the Grignard reagent (1 equiv) and the mixture was refluxed for 24 hr. [b] The physical constants of the products agreed with the literature values. [c] This reaction was refluxed for 2.5 hr.

um salts of carboxylic acids (1 equiv) reacted exothermally with an ether solution of Grignard reagent (1 equiv) to give mixtures of both ketone and tertiary alcohol with the tertiary alcohol usually the major product, even in a 24-hr reaction time. The results obtained from the reactions of lithium n-butyrate and lithium benzoate with methyl, n-butyl, and phenylmagnesium halides are found in Table III. The results obtained in the lithium carboxylate–Grignard reagent experiments (Table III) when coupled with those in Table II suggest that in the former reactions (Table III) the formation of free ketone may occur slowly prior to the hydrolysis of the intermediate adduct, RR′C(OMgX)(OLi), and the ketone may then be rapidly converted to the halomagnesium salt of the tertiary alcohol by reaction with more Grignard reagent.



Experimental Section

Lithium Carboxylates. These were prepared by the interaction of equivalents of lithium carbonate and the appropriate carboxylic acids in aqueous solution followed by evaporation and thorough drying under vacuum, e.g., lithium isobutyrate. Anal. Calcd for $C_4H_7O_2Li$: Li, 7.38. Found: Li, 7.16.

General Procedure for the Reaction of Lithium Carboxylates with Organolithium Compounds. The dry lithium carboxylate was added all at once to the organolithium compound in ether (100 ml of ether was used per 0.1 mol of lithium reagent). The ether does not reflux during the addition of the lithium salts. The reaction mixture was then refluxed for the appropriate length of time and the reaction was then quenched by pouring the mixture onto crushed ice and water. The phases were separated and the aqueous phase was extracted with several portions of ether. The combined basic, ether phases were dried over Drierite, the solvent and low boilers were removed at atmospheric pressure, and the residue was fractionated under vacuum. The aqueous phase was acidified with concentrated hydrochloric acid and extracted with several portions of ether. The combined acidic, ether phases were processed in the same manner as the basic ether phases.

Reaction of Equivalents of Lithium Propionate and Phenyllithium for 24 and 0.5 Hr. From the interaction of phenyllithium [0.4 mol, prepared from lithium ribbon (0.8 mol, 5.6 g, in 400 ml of ether) and bromobenzene (0.4 mol, 62.8 g)] and lithium propionate (0.4 mol, 32.0 g) there was obtained, after a 24-hr reaction time, propiophenone [43.7 g, 82.0%, bp 84–85° (8 mm)] (see first reference in Table II), 2,4-dinitrophenylhydrazone mp 187.0–188.0, alone and when mixed with an authentic sample. When this reaction was repeated using phenyllithium (0.2 mol) and lithium propionate (0.2 mol) except that the reaction time was 0.5 hr, there was obtained a mixture of propiophenone [10.8 g, 40.3%, bp 104–107° (20 mm)] and diphenylethylcarbinol [5.2 g, 24.5%, bp 183–185° (21 mm), mp 93.2–94.6° (see second reference in Table II)].

Reaction of Equivalents of Lithium n-Butyrate and Phenyllithium for 0.5 and 3 Hr. From the interaction of phenyllithium (0.3 mol) and lithium n-butyrate (0.3 mol, 28.2 g) there was obtained a mixture of n-butyrophenone [17.4 g, 39.0%, bp 104–108° (11 mm) (see first reference in Table II)] and diphenyl-n-propylcarbinol [10.1 g, 29.7%, bp 176–177° (10 mm) (see second reference in Table II)]. When this reaction was repeated except that the reflux time was 3 hr, there was obtained n-butyrophenone [27.0 g, 60.6%, bp 96–98° (8 mm)] and diphenyl-n-propylcarbinol [7.2 g, 21.2%, bp 173–175° (8 mm)].[8]

Reaction of Lithium Benzoate (1 Equiv) with n-Propyllithium (1 Equiv) for 0.5 and 24 Hr. From 0.26 mol of n-propyllithium [prepared in 75% yield from lithium (0.7 mol, 4.9 g)], n-propyl bromide (0.35 mol, 43.1 g), and lithium benzoate (0.26 mol, 33.3 g), there were obtained 4.5 g (11.7%) of n-butyrophenone and 4.4 g (17.6%) of di-n-propylphenylcarbinol.

The total yields of n-butyrophenone and di-n-propylphenylcarbinol were determined by the hydroxylamine hydrochloride titration method.[7] The distilled material consisted of three fractions. The lowest boiling fraction consisted of pure ketone and the highest boiling fraction consisted of pure carbinol. Aliquots of the intermediate boiling fraction, consisting of a mixture of ketone and carbinol, were titrated with hydroxylamine hydrochloride in order to determine the ketone content. The amount of carbinol in this intermediate fraction was calculated by subtracting the amount of ketone from the total weight of the fraction. The yields of ketone and carbinol indicated above represent, within experimental error, the total amounts of ketone and carbinol obtained. The lowest boiling fraction, n-butyrophenone, bp 108.0–111.0° (14 mm), gave a 2-4-dinitrophenylhydrazone, mp 189.0–189.8°, alone and when mixed with an authentic sample.

The highest boiling fraction, which was pure di-n-propylphenylcarbinol, bp 128.0–131.0° (14 mm),[8] and did not give a positive hydroxylamine test, was dehydrated to 4-phenyl-3-hexene by refluxing a sample (1.8 g) with acetic anhydride (5 ml) and glacial acetic acid (10 ml) for 2 hr. The resulting olefin was extracted with ether and oxidized with potassium permanganate in acetone (according to the procedure of Adkins and Roebuck)[9] to give propionic acid (identified as propionamide, mp 78.0–78.5°, alone and when mixed with an authentic sample) and n-butyrophenone (2,4-dinitrophenylhydrazone, mp 189.0–189.8°, alone and when mixed with an authentic sample). In addition, 23.7 g (74.5%) of benzoic acid was recovered. When the reaction was repeated using a 24-hr reaction time there was obtained n-butyrophenone [33.0 g, 85.8%, bp 119–120° (23 mm), 2,4-dinitrophenylhydrazone, mp 89.0–189.8°].

Reaction of the 1:1 Adduct of Lithium Propionate and Phenyllithium, Phenyllithium, and Water. In flask A, lithium propionate (0.1 mol, 8.0 g) and phenyllithium (0.1 mol in 100 ml of ether) were refluxed for 24 hr. In another flask, B, phenyllithium (0.1 mol in 1.00 ml of ether) was prepared. Simultaneously and with rapid stirring the contents of flasks A and B were poured down the opposite sides of a beaker containing 250 g of crushed ice. The customary processing gave propiophenone [7.8 g, 58.1%, bp 84–85° (8 mm) (see first reference in Table II); 2,4-dinitrophenylhydrazone mp 187.0–188.0° alone and when mixed with an authentic sample] and diphenylethylcarbinol (3.0 g, 28.3%, mp 94.0–95.0°[10] alone and when mixed with an authentic sample).

Reaction of Equivalents of Propiophenone, Phenyllithium, and Water. Using a procedure similar to that described in the last experiment, phenyllithium (0.1 mol, 70 ml of 1.4 *M* commercial material in 30% ether and 70% benzene) and propiophenone (0.1 mol, 13.4 g in 12 ml of anhydrous ether) were added with rapid stirring to 300 g of ice and water to give diphenylethylcarbinol [9.0

g, 44.8% (8 mm), mp 94–95°[10] alone and when mixed with an authentic sample] and 5.7 g of material, bp 108–125° (20 mm), which appeared to consist of propiophenone and its self-condensed products.

Registry No.—Phenyllithium, 591-51-5; propiophenone, 93-55-0; propiophenone 2,4-dinitrophenylhydrazone, 3375-37-9; diphenylethylcarbinol, 5180-33-6; *n*-butyrophenone, 495-40-9; diphenyl-*n*-propylcarbinol, 5331-17-9; *n*-propyllithium, 2417-93-8; di-*n*-propylphenylcarbinol, 4436-96-8; methyl iodide, 74-88-4; *n*-butyl bromide, 109-65-9; phenyl bromide, 108-86-1.

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Action of Grignard Reagents on the Esters of Propiolic Acid

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When methyl propiolate (1) was treated with an excess of ethylmagnesium bromide, no ethane was evolved and the expected tertiary alcohol, diethylethinylcarbinol, was obtained in only 10% yield. The primary reaction product proved to be an unsaturated 3,4-epoxy ester (2) whose formation required two alkyl groups, ✱, from the Grignard reagent and a third, x, from a second mole of the original ester. Catalytic hydrogenation yielded the saturated analog (5) which upon mild hydrolysis underwent simultaneous loss of carbon dioxide and fissure of the epoxide ring to form an identifiable ethyl ketone (8). Several combinations of Grignards and esters were employed to show in each case analogous reaction products. A mechanism to account for the products obtained is presented.

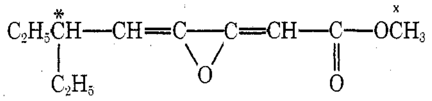
The investigation presented in this paper originated from the observation that methyl propiolate (1), HC≡C–COOCH$_3$, on treatment with methylmagnesium iodide in the Zerevitinov machine yielded no methane but did undergo a vigorous reaction which consumed 3 mol of Grignard reagent. The failure to form methane was particularly puzzling since the acidity of the acetylenic hydrogen is increased by its conjugation with the carbomethoxy group to such an extent that it not only forms a silver and copper salt, but also undergoes Claisen condensation with ethyl oxalate and Michael condensation with ethyl fumarate.[1]

Addition of Grignard reagents of higher molecular weight such as phenyl-, naphthyl-, or triphenylvinylmagnesium bromide[2] and the reagent prepared by the action of phenylmagnesium bromide on α-bromo-β-phenylbenzalacetophenone[3] produced immediate and vigorous reaction, but decomposition of the reaction mixtures yielded only heavy, intractable oils. Gilman and Robinson[4] reported similar difficulties when they added phenylmagnesium bromide to the ethyl ester of acetylenedicarboxylic acid.

The action of lighter Grignards such as methyl- and ethylmagnesium bromide on methyl propiolate yielded distillable oils from which definite compounds could be obtained by fractionation under vacuum. Thus, when methyl propiolate (1) was added to an excess of ethylmagnesium bromide, two pure liquids were isolated from the reaction mixture.

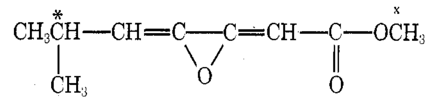
The first, a colorless, low-boiling oil, was identified as diethylethinylcarbinol through the formation of a silver salt and by catalytic hydrogenation to the known triethylcarbinol. The acetylenic alcohol was present only to the extent of 8–10% and its formation may be regarded as a secondary reaction in which the Grignard reagent undergoes the expected 1,2 addition to the ester carbonyl.

The primary reaction product 2, a pale yellow oil, was shown by analytical methods to be dimolecular product of empirical formula $C_{11}H_{16}O_3$, containing one methoxy group. All tests for the functional groups –HC=O, >C=O, and HC≡C– were negative, but catalytic hydrogenation consumed 2 mol of hydrogen, indicating the presence of two double bonds or one triple bond of the type RC≡CR.



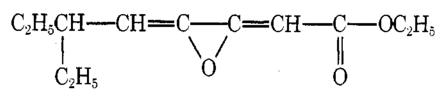
$C_2H_5\overset{*}{C}H(C_2H_5)-CH=\underset{\diagdown O \diagup}{C-C}=CH-C(=O)-\overset{x}{O}CH_3$

2



$CH_3\overset{*}{C}H(CH_3)-CH=\underset{\diagdown O \diagup}{C-C}=CH-C(=O)-\overset{x}{O}CH_3$

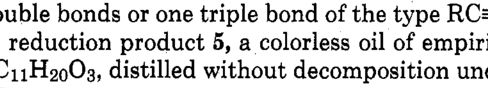
3



$C_2H_5CH(C_2H_5)-CH=\underset{\diagdown O \diagup}{C-C}=CH-C(=O)-OC_2H_5$

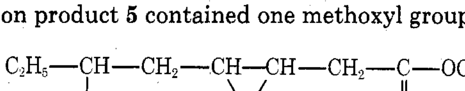
4

The reduction product 5, a colorless oil of empirical formula $C_{11}H_{20}O_3$, distilled without decomposition under vacuum. Because of its greater physical and chemical stability it was selected to elucidate the ultimate structure of 2. The reduction product 5 contained one methoxyl group, formed a crystalline amide, $C_{10}H_{19}O_2N$, with concentrated ammonia, and gave no test for aldehydic or ketonic carbonyl groups. In the Zerevitinov machine no gas was evolved but 2 mol of Grignard was consumed.



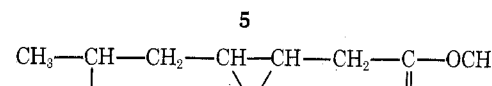
$C_2H_5-CH(C_2H_5)-CH_2-\underset{\diagdown O \diagup}{CH-CH}-CH_2-C(=O)-OCH_3$

5



$CH_3-CH(CH_3)-CH_2-\underset{\diagdown O \diagup}{CH-CH}-CH_2-C(=O)-OCH_3$

6



$C_2H_5-CH(C_2H_5)-CH_2-\underset{\diagdown O \diagup}{CH-CH}-CH_2-C(=O)-OC_2H_5$

7