ethyl acetate. Removal of the ethyl acetate under vacuum and distillation of the residual brown oil gave 52% of material boiling at 121–127°/0.1 mm., n_D^{25} 1.4755.

Anal. Calcd. for $C_5H_8ClNO_3$: C, 36.3; H, 4.87; N, 8.46. Found: C, 36.3; H, 5.08; N, 8.21.

3-Chloro-N-methylpropionamide. Gaseous methylamine (49.0 g., 1.57 moles) was bubbled into a stirred solution of 3-chloropropionyl chloride (100 g., 0.787 mole) in 300 ml. of ethylene chloride at −15 to −10° for 1.5 hr. The thick white slurry was stirred an additional 2 hr. as it warmed to room temperature. The methylamine hydrochloride (52.2 g., 98%) was filtered off and the filtrate evaporated under vacuum to yield 100 g. of a yellow solid, m.p. 59–62°. Recrystallization from ether gave 86.4 g. (90%) of pale yellow crystals, m.p. 62–64°. The analytical sample (from ether-hexane) had m.p. 65–65.5°.

Anal. Calcd. for C_4H_8ClNO: C, 39.5; H, 6.63; Cl, 29.2; N, 11.5. Found: C, 39.6; H, 6.68; Cl, 28.9; N, 11.4.

3-Bromo-N-methylpropionamide. The same procedure utilized for 3-chloro-*N*-methylpropionamide, with the exception that liquid rather than gaseous methylamine was used, gave the 3-bromoamide from 3-bromopropionyl bromide in 52% yield as a white solid, m.p. 74–75.5°, following two recrystallizations from ethyl acetate-hexane. The analytical sample (from chloroform-hexane) melted at 78.5–79°.

Anal. Calcd. for C_4H_8BrNO: C, 28.9; H, 4.86; N, 8.44. Found: C, 29.8, 29.9; H, 5.03, 5.08; N, 8.52.

N-Chloroacetylphthalimide. The procedure of Evans and Dehn,[40] using phthaloyl chloride (101.5 g., 0.5 mole) and chloroacetamide (46.8 g., 0.5 mole) in 500 ml. of toluene, gave 30 g. (27%) of product, m.p. 170–175°, that settled out on cooling. Recrystallization from toluene, followed by chloroform, gave 10.2 g. of colorless crystals, m.p. 180–182°.

Anal. Calcd. for $C_{10}H_6ClNO_3$: C, 53.71; H, 2.71; Cl, 15.86; N, 6.26. Found: C, 53.38; H, 2.93; Cl, 15.68; N, 6.38.

Acknowledgment. We are indebted to Mrs. Melinda Kozma, who performed much of the synthetic work reported here, as well as to Dr. David Ailman, Mr. Frank Wagner, and Mrs. Ella Swartz Zonas for their contributions. We are also grateful to Dr. John Lancaster for NMR data and interpretation and to Dr. Julius Kuck and Mrs. Lee Grim for microanalyses.

STAMFORD, CONN.

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[40] T. W. Evans and W. M. Dehn, *J. Am. Chem. Soc.*, 51, 3651 (1929).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE ROHM AND HAAS CO.]

The Reaction of Acrylates and Methacrylates with Organomagnesium Compounds[1]

F. H. OWENS, W. L. MYERS, AND F. E. ZIMMERMAN

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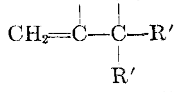
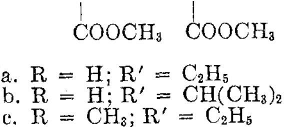
A study of the products of the reaction of methyl methacrylate, isopropyl acrylate, and methyl acrylate with various organomagnesium compounds has shown that these reactions follow a consistent pattern. The products were separated by distillation and chromatography on alumina and were identified by analysis, by infrared, ultraviolet and NMR spectroscopy and gas chromatography. In addition to the expected product (V), produced by 1,4- addition of the organomagnesium compounds to the unsaturated esters, there were products (VI and XI) produced by a combination of a 1,4- followed by a 1,2- addition of the organomagnesium compound to the unsaturated ester. There were, in addition, two unexpected products, the cyclic ketone VIII, resulting from a Dieckmann condensation, and the ketone XII, probably resulting from a combination of 1,4- and 1,2- additions followed by a reversal of the 1,2- addition.

Earlier investigators have studied the reaction of Grignard reagents with acrylic and methacrylic esters.[2–4] Various products were reported, but rarely was an attempt made to isolate and identify all the products. Lebedeva and co-workers[3] reported that the reaction of methyl methacrylate with ethylmagnesium bromide gave Ic and IIc and with isopropylmagnesium bromide gave IId. With methyl acrylate and ethylmagnesium bromide, the products were Ia, IIa, and IIIa, while with isopropyl magnesium bromide and methyl acrylate, IIb and IIIb were the products. These data are presented in Table I.



$$CH_2{=}\overset{R}{\overset{|}{C}}-\underset{R'}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-R'$$

Ia. R = H; R′ = C_2H_5
b. R = H; R′ = $CH(CH_3)_2$
c. R = CH_3; R′ = C_2H_5
d. R = CH_3; R′ = $CH(CH_3)_2$



$$R'CH_2\underset{COOCH_3}{\underset{|}{\overset{R}{\overset{|}{C}}}}\text{——}CH_2\underset{COOCH_3}{\underset{|}{\overset{R}{\overset{|}{C}}}}H$$

IIa. R = H; R′ = C_2H_5
b. R = H; R′ = $CH(CH_3)_2$
c. R = CH_3; R′ = C_2H_5
d. R = CH_3; R′ = $CH(CH_3)_2$

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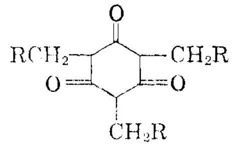
(1) Presented in part before the Division of Organic Chemistry at the 137th Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.

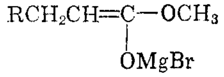
(2) (a) E. E. Blaise and C. Courtot, *Compt. rend.*, 140, 370 (1905); (b) K. A. Ogloblin, *Zhur. Obschei Khim.*, 18, 2153 (1948).

(3) (a) A. I. Lebedeva and E. D. Vainrub, *Zhur. Obschei Khim.*, 22, 1974 (1952); (b) A. I. Lebedeva and E. D. Vainrub, *Zhur. Obschei Khim.*, 24, 1207 (1954); (c) A. I. Lebedeva, L. A. Gavrilova, and T. B. Serdobintseva, *Zhur. Obschei Khim.*, 26, 2436 (1956).

(4) (a) I. N. Nazarov and A. I. Kakhniashvili, *Sbornik Statei Obschei Khim.*, 2, 919 (1954) [*Chem. Abstr.*, 49, 6848 (1955)]; (b) H. Normant and P. Maitte, *Bull. soc. chim. France*, 951 (1956); (c) J. Munch-Petersen, *J. Org. Chem.*, 22, 170 (1957); (d) M. B. Green and W. J. Hickinbottom, *J. Chem. Soc.*, 3262 (1957).



IIIa. R = C_2H_5
b. R = $CH(CH_3)_2$



$RCH_2CH{=}\underset{\displaystyle OMgBr}{\underset{|}{C}}{-}OCH_3$

IV

TABLE I

THE REACTION OF ACRYLIC ESTERS WITH GRIGNARD REAGENTS; DATA OF LEBEDEVA AND CO-WORKERS[3]

Reactants		Products		
Acrylic Ester	Alkyl-magnesium Bromide	Carbinol I, %	Ester II, %	Ketone III, %
Methyl methacrylate	Ethyl	34	12	0
Methyl methacrylate	Isopropyl	0	59	0
Methyl acrylate	Ethyl	11	27	61
Methyl acrylate	Isopropyl	0	80[a]	16

[a] Plus 4.7 g. unidentified material.

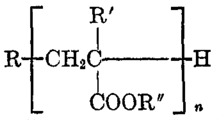
Lebedeva[3b] postulated that compound III resulted from a trimerization of the enolate IV. However, compound III is the keto form of a trisubstituted phloroglucinol, and although the microanalyses and titration data are in accord with the formulation, the ultraviolet absorption at 294 mμ, which Lebedeva attributed to a di-α-substituted ketone, is not in agreement with this structural assignment. Trimethylphloroglucinol absorbs at 271 and 274 mμ,[5] and further substitution on the alkyl group would not be expected to raise the absorption to 294 mμ. Also, in the reaction of methyl acrylate with isopropylmagnesium bromide, a calculation of the yield of all of the products shows that a greater than 100% yield was obtained; therefore, some doubt is cast on the assignment of structure.

The primary objectives of this work were to establish the nature of the products formed by the reaction of methyl methacrylate with dibutylmagnesium, diphenylmagnesium, butylmagnesium bromide, and phenylmagnesium bromide as well as to determine the relative amounts of these products.

DISCUSSION

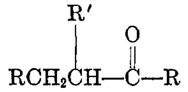
The reactions were conducted under an atmosphere of nitrogen by adding the monomer in diethyl ether dropwise over a period of three hours to the organomagnesium compound in ether so that the temperature did not rise above 5°. The ether-insoluble material was removed by filtration, and the soluble portion was dissolved in petroleum ether. Any petroleum ether-insoluble material was removed by decantation.

The infrared spectra of the petroleum ether-soluble residues were very complex showing carbonyl maxima attributable to ketone, ester, and in some cases, anhydride and lactone. The residues were distilled through a 24″-spinning band column at reduced pressure. The results are shown in the experimental section. Most of the fractions were still mixtures, but several facts could be ascertained from the spectra of these mixtures. In the case of the reaction of methyl methacrylate with dibutylmagnesium or butylmagnesium bromide, in addition to the maximum at 1740 cm.$^{-1}$ attributable to esters of the type Va, there were maxima at 1715 and 1712 cm.$^{-1}$ attributable to saturated ketone, at 908 and 1640 cm.$^{-1}$ attributable to an unsaturated hydrocarbon, at 1810 and 1770 cm.$^{-1}$ attributable to anhydride, and at 1760 cm.$^{-1}$ attributable to lactone. The spectra of the fractions from the reaction of methyl methacrylate with diphenylmagnesium and phenylmagnesium bromide displayed maxima at 1740 cm.$^{-1}$ (Vb), 1665 cm.$^{-1}$ (benzophenone), 1690 cm.$^{-1}$ (conjugated ketone, either VIb or VII), and at 1712 cm.$^{-1}$ (saturated ketone). Since it was felt that the presence of the phenyl group might be a definite aid in determining the nature of the products, most of the identification work was done on the products of the reaction of methyl methacrylate with diphenylmagnesium and phenylmagnesium bromide.



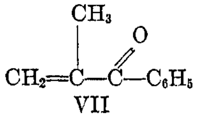
$R\left[CH_2\overset{\displaystyle R'}{\overset{|}{\underset{\displaystyle COOR''}{\underset{|}{C}}}}\right]_n H$

Va. R = $n\text{-}C_4H_9$; R′ = R″ = CH_3
b. R = C_6H_5; R′ = R″ = CH_3
c. R = $CH(CH_3)_2$; R′ = R″ = CH_3
d. R = C_6H_5; R′ = H; R″ = $CH(CH_3)_2$
e. R = $CH(CH_3)_2$; R′ = H; R″ = CH_3



$RCH_2\overset{\displaystyle R'}{\overset{|}{C}}H{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}R$

VIa. R = $n\text{-}C_4H_9$; R′ = CH_3
b. R = C_6H_5; R′ = CH_3
c. R = $CH(CH_3)_2$; R′ = CH_3
d. R = C_6H_5; R′ = H
e. R = $CH(CH_3)_2$; R′ = H



$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}\overset{\displaystyle O}{\overset{/\!/}{C}}{-}C_6H_5$

VII

The saturated ketone, absorbing at 1712 cm.$^{-1}$, could only arise by a Claisen-type condensation, since any ketone formed by reaction of diphenylmagnesium or phenylmagnesium bromide with the ester carbonyl would produce a phenyl-substituted ketone which should have a carbonyl absorption lower than 1712 cm.$^{-1}$ Claisen-type condensations induced by Grignard reagents have been reported by several investigators.[6] In this case, the ketone

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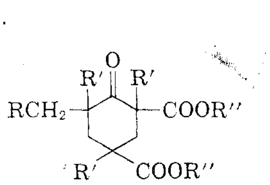
(5) T. W. Compbell and G. M. Coppinger, *J. Am. Chem. Soc.*, **73**, 2708 (1951).

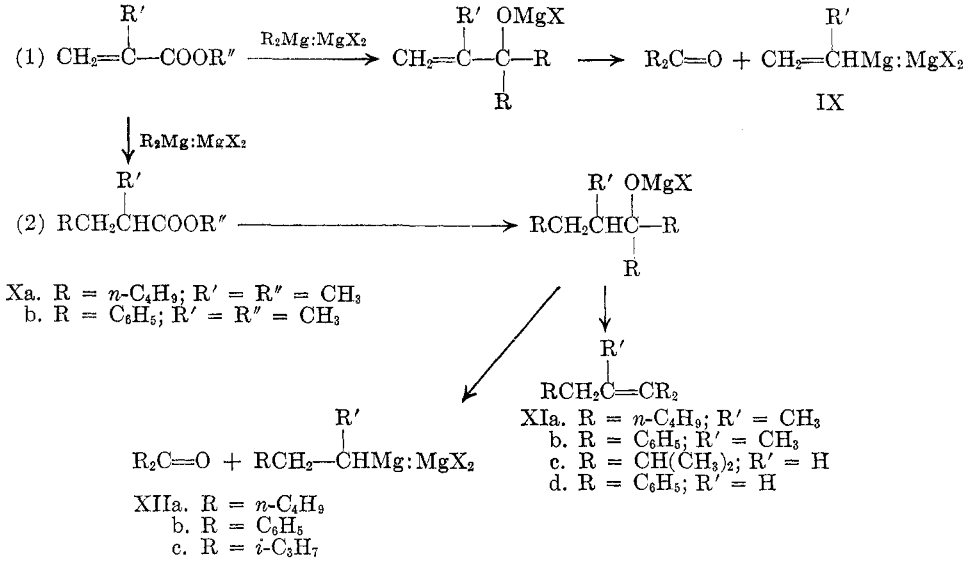
(6) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Non-Metallic Substances*, Prentice-Hall, Inc., New York, 1954, p. 565.

could be formed by an intermolecular condensation giving rise to an acyclic β-keto ester, but an acyclic ketone with five substituents on the adjacent carbon atoms[7] would be expected to absorb nearer 1700 cm.$^{-1}$ Intramolecular condensation would give rise to a substituted cyclic β-keto ester[8] which would be expected to absorb near 1712 cm.$^{-1}$. A fraction rich in the ketone adsorbing at 1712 cm.$^{-1}$ was chromatographed on alumina. The infrared spectrum of the fraction eluted by benzene exhibited carbonyl maxima of equal intensity at 1740 and 1712 cm.$^{-1}$ The microanalysis was consistent with the formula $C_{20}H_{26}O_5$, and the NMR spectrum had one peak at 0.65 (5 protons on benzene), two methyl ester peaks at 2.94 and 3.10, two 2-proton quartets centered at 3.72 and 4.55, a 2-proton doublet at 4.14, and two methyl peaks at 5.23 (intensity, 6) and 5.45 (intensity, 3) p.p.m. from external benzene. Consequently, the ketone having maxima at 1740 and 1712 cm.$^{-1}$ is assigned the structure methyl 5-benzyl-1,3,5-trimethyl-4-oxocyclohexane - 1,3 - dicarboxylate (VIIIb). It was not possible to prepare a 2,4-dinitrophenylhydrazone of this material, probably because of the hindrance of the four substituents *alpha* to the carbonyl group.



VIIIa. R = n-C_4H_9; R′ = R″ = CH_3
b. R = C_6H_5; R′ = R″ = CH_3
c. R = $CH(CH_3)_2$; R′ = R″ = CH_3
d. R = C_6H_5; R′ = H; R″ = $CH(CH_3)_2$
e. R = $CH(CH_3)_2$; R′ = H; R″ = CH_3

The benzophenone could arise by reaction of the organomagnesium compound with adventitious carbon dioxide[9]; however, the organomagnesium compounds were prepared under nitrogen, and the reactions were conducted under nitrogen, so this reason was ruled out. There existed the possibility that the benzophenone might arise as a result of the reversal of the addition of a Grignard reagent to a ketone.



Xa. R = n-C_4H_9; R′ = R″ = CH_3
b. R = C_6H_5; R′ = R″ = CH_3

XIa. R = n-C_4H_9; R′ = CH_3
b. R = C_6H_5; R′ = CH_3
c. R = $CH(CH_3)_2$; R′ = H
d. R = C_6H_5; R′ = H

XIIa. R = n-C_4H_9
b. R = C_6H_5
c. R = i-C_3H_7

In order to check this possibility, methyl methacrylate-1-C^{14} was treated with phenylmagnesium bromide. The reaction was conducted and worked up as before, and the fraction containing the benzophenone was chromatographed on alumina. The fraction eluted by 10 and 25% benzene in petroleum ether was shown to be an unsaturated hydrocarbon. The fraction eluted by 50% benzene was the ketone absorbing at 1690 cm.$^{-1}$, and the fraction eluted by 75% benzene in petroleum ether and by benzene contained the benzophenone. The latter was recrystallized from petroleum ether and twice sublimed, whereupon it melted at 49° both alone and on admixture with pure benzophenone. It gave a 2,4-dinitrophenylhydrazone melting at 242° alone and at 240° on admixture with authentic benzophenone-2,4-dinitrophenylhydrazone. The specific activities of the methyl methacrylate and the benzophenone were identical within experimental error, showing that the carbonyl group of the benzophenone does come from the carboxyl group of the methyl methacrylate.

If the benzophenone arises as shown in equation 1, it should be possible to isolate propylene or the product of the reaction IX with a carbonyl group. In an experiment in which the effluent gas from the

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[7] P. D. Bartlett and M. Stiles, *J. Am. Chem. Soc.*, **77**, 2806 (1955).

[8] L. J. Bellamy and L. Beecher, *J. Chem. Soc.*, 4487 (1954).

[9] H. Gilman and N. B. St. John, *Rec. trav. chim.*, **49**, 1172 (1930); M. Mousseron and R. Granger, *Bull. soc. chim.*, [5], **13**, 251 (1946); G. Schroeter, *Ber.*, **40**, 1584 (1907).

reaction was collected, no propylene was found by mass spectroscopy, and no evidence for the formation of a vinyl ketone was found; therefore, it is believed that the benzophenone arises as shown in equation 2. Although there is no direct evidence for the presence of XII in the reaction mixture, it was possible to identify X in the product mixture by direct comparison of infrared maxima, and evidence is presented later for the presence of XI in addition to the ketone VIb resulting from the addition of one phenylmagnesium bromide to X.

The ketone eluted by 50% benzene in petroleum ether had a carbonyl maximum at 1690 cm.$^{-1}$, melted below 0°, and as pointed out above, could have structure VIb or VII. The empirical formula of the ketone was $C_{16}H_{16}O$ and of its 2,4-dinitrophenylhydrazone was $C_{22}H_{24}N_4O_4$. This ketone is assigned the structure 2-methyl-1,3-diphenylpropan-1-one (VIb). Treatment of methyl 2-methyl-3-phenylpropionate (Xb) with an equivalent of phenylmagnesium bromide yielded a hydrocarbon, 1,1,3-triphenylprop-1-ene (XIb) rather than the expected ketone (VIb). The material eluted by 10 and 25% benzene in petroleum ether had a spectrum identical with this hydrocarbon and an identical melting point, 65–66°, both alone and on admixture. From the infrared spectra of the distillation fractions, it was shown that the remaining material was of the type Vb, with *n* ranging from one to 4800.

On the basis of the above evidence, the products from the reaction of methyl methacrylate with dibutylmagnesium and butylmagnesium bromide were reexamined. The spectra indicated that there were maxima at 1740 and 1712 cm.$^{-1}$ attributable to Va and VIIIa, at 1715 cm.$^{-1}$ attributable to VIa or dibutyl ketone or both, and at 908 and 1635 cm.$^{-1}$ attributable to hydrocarbon XIa. There were also carbonyl maxima at 1810 and 1770 (anhydride) and 1760 (lactone). Unfortunately, chromatography of these materials on alumina did not yield pure fractions, and the material recovered from the columns did not display the maxima attributed to anhydride and lactone. Since the latter could not be identified and since they were there in rather small amounts, the nature of the lactone and anhydride is still in question. Treatment of methyl *n*-valerate with the Grignard reagent from 2-bromoheptane yielded 5-methylundecan-6-one (VIa). By comparison of the positions and intensities of the gas chromatographic peaks for VIa, di-*n*-butyl ketone, and the ketone mixture from the reaction products, it was possible to establish the identity of the two ketones and their relative amounts.

On the basis of the infrared spectra of all these distillation fractions, supported by the structural identifications from alumina and gas chromatography, the semiquantitative data on the reactions of methyl methacrylate with organomagnesium compounds shown in Table II were obtained; however, it must be pointed out that these data are only meant to give an order of magnitude and are subject to the limitations of the infrared method of estimation by comparison of absorbance ratios.[10] A series of reactions in which the organomagnesium compound was added to the methyl methacrylate revealed that much larger amounts of ether-insoluble and petroleum ether-insoluble polymers were obtained. The spectra of the petroleum ether-soluble materials were similar to the spectra of the products where the methyl methacrylate was added to the organomagnesium compound, but because of separation difficulties, quantitative data on these materials were not obtained.

Because the results obtained with methyl methacrylate were at variance with the results reported in the literature, a study of the reaction of isopropyl acrylate with phenylmagnesium bromide was made to determine if the reaction would follow a similar course. Distillation of a portion of the product resulted in extensive decomposition and was abandoned. Chromatography of a portion on alumina achieved little separation, and only 42% of the material was recovered. Although chromatography of a portion of the residue on alumina deactivated with ethyl acetate[12] did not yield pure components, sufficient separation was achieved to enable us to identify the components of the mixtures by comparison with pure materials. In addition to the infrared maximum at 1735 cm.$^{-1}$ (Vd), there were maxima at 1690 cm.$^{-1}$, presumed to be VId by analogy with the results obtained with methyl methacrylate and phenylmagnesium bromide, and at 1712, 1650, and 1615 cm.$^{-1}$ (enolizable β-keto ester) presumed to be VIIId by comparison with the data of Leonard and co-workers[13] and by analogy with the product from the reaction of methyl methacrylate and phenylmagnesium bromide.

In order to furnish unequivocal proof of the structure of these two ketones, they were synthesized and their infrared and ultraviolet spectra were compared. The reduction of benzalacetophenone with zinc in acetic acid[14] gave 1,3-diphenylpropan-1-one (VId). The material was purified by chromatography on alumina followed by sublimation. The infrared spectrum of this material was identical with the spectrum of the ketone absorbing at 1690 cm.$^{-1}$ which was in the reaction mixture from isopropyl acrylate and phenylmagnesium bromide,

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[10] R. N. Jones and C. Sandorfy, Chap. IV in *Technique of Organic Chemistry,* Vol. IX, Interscience Publishers, Inc., New York, 1956, p. 469.

[11] R. E. Dessy and G. S. Handler, *J. Am. Chem. Soc.,* **80**, 5824 (1958).

[12] A. C. Cope, H. L. Dryden, Jr., and C. F. Howell, *Org. Syntheses,* **37**, 73 (1957).

[13] N. J. Leonard, H. S. Gutowsky, N. J. Middleton, and E. M. Petersen, *J. Am. Chem. Soc.,* **74**, 4070 (1952).

[14] W. Schneidewind, *Ber.,* **21**, 1323 (1888).

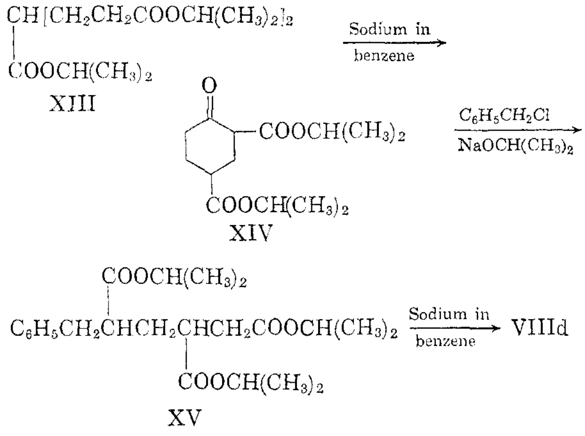
TABLE II

THE REACTION OF ACRYLIC ESTERS WITH ORGANOMAGNESIUM COMPOUNDS

Reactants			Products							
Acrylic[a] ester	Organomagnesium[b] compound	Molar ratio of organomagnesium compound[b] to acrylic ester	Ester V n = 1,2,3, %	Ketone XII, %	Ketone VI, %	Ketone VIII, %	Hydrocarbon XI, %	Lactone, %	Anhydride, %	Polymer[c] V $n > 3$, %
MMA	$(n\text{-}C_4H_9)_2Mg$	0.57	5	1	18	22	2	4	6	42
MMA	$(n\text{-}C_4H_9)_2Mg:MgBr_2$	0.57	36	1	19	10	5	5	1	23
MMA	$(C_6H_5)_2Mg$	0.57	44	8	14	7	1	Trace	Trace	26
MMA	$(C_6H_5)_2Mg$	1.05	43	7	16	15	8	Trace	Trace	11
MMA	$(C_6H_5)_2Mg:MgBr_2$	0.57	70	6	5	6	0	Trace	Trace	13
IPA	$(C_6H_5)_2Mg:MgBr_2$	0.50	50	Trace	3	6	0	0	0	40
MMA	$(i\text{-}C_3H_7)_2Mg:MgBr_2$	1.0	42	Trace	20	13	0	7	0	18
MA	$(i\text{-}C_3H_7)_2Mg:MgBr_2$	1.0	52	1	22	9	0	0	0	16

[a] MMA = Methyl methacrylate; IPA = Isopropyl acrylate; MA = Methyl acrylate. [b] In accordance with the evidence presented by Dessy and Handler,[11] we have adopted the procedure of designating Grignard reagents as $R_2Mg:MgX_2$; thus, 1 mole of $R_2Mg:MgX_2$ is equivalent to 2RMgX. [c] Includes the ether-insoluble and petroleum-ether-insoluble polymer.

allowing for the maxima of the contaminant Vd. The ultraviolet spectrum of VId was identical with that of the material in the reaction mixture. Isopropyl 5-benzyl-4-oxocyclohexane-1,3-dicarboxylate (VIIId) was synthesized by the sequence of reactions shown below. Malonic ester was quantitatively cyanoethylated to give ethyl 1,1-di(2-cyanoethyl)-methane-1,1-dicarboxylate by



the method of Bruson and Riener.[15] The latter was simultaneously hydrolyzed and decarboxylated and was then converted to the triisopropyl ester (XIII) without isolation of the acid. The triester was cyclized by the method of Sengupta[16] with sodium in benzene.

Openshaw and Robinson[17] observed that the addition of an excess of sodium in methanol to a solution of methyl 4-oxocyclohexane-1,3-dicarboxylate and methyl 3-chloropropionate in methanol containing a small amount of sodium iodide gave an 80% yield of methyl heptane-1,3,5,7-tetracarboxylate which, on cyclization with sodium in methanol, gave methyl 5-(2-carbomethoxyethyl)-4-oxocyclohexane-1,3-dicarboxylate in 80% yield. Treatment of a solution of isopropyl 4-oxocyclohexane-1,3-dicarboxylate (XIV), benzyl chloride, and sodium iodide in isopropyl alcohol with sodium in isopropyl alcohol yielded 67% of isopropyl 5-benzylpentane-1,2,4-tricarboxylate (XV) whose infrared spectrum was virtually identical with that of low molecular weight poly(isopropyl acrylate) initiated by phenylmagnesium bromide. Cyclization of triester XV with sodium in benzene gave a 45% yield of isopropyl 5-benzyl-4-oxocyclohexane-1,3-dicarboxylate (VIIId), whose infrared spectrum was identical with that of the ketone having absorption maxima at 1712, 1650, and 1615 cm.$^{-1}$ found in the product of the reaction of isopropyl acrylate with phenylmagnesium bromide. The cyclic ketone VIIId exhibited an ultraviolet maximum at 253 mμ (enolizable β-keto ester) and a shoulder at 208 mμ (phenyl group) but did not obey Beer's law. Bellamy and Beecher[9] have observed that the intensity of the infrared absorption maximum at 1642 cm.$^{-1}$ of ethyl 2-oxocyclohexane-1-carboxylate which they attributed to the chelate form, is independent of concentration, and we find that the intensities of this absorption in both the ultraviolet and infrared spectra do not obey Beer's law.

From the above data and the data obtained from the chromatographic fractions, we were able to determine the amounts of the various products shown in Table II; however, it must be emphasized that these are semiquantitative data because of the reasons given previously and also because not all of the material was recovered from the alumina. Rechromatography of fractions resulted in quantitative recovery, but chromatography of a polymer-containing sample results in a considerable loss of material; therefore, it has been assumed that the difference between the amount of material charged and the amount recovered from the column can be

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(15) H. A. Bruson and T. W. Riener, *J. Am. Chem. Soc.*, 65, 23 (1943).

(16) P. Sengupta, *J. Org. Chem.*, 18, 249 (1953).

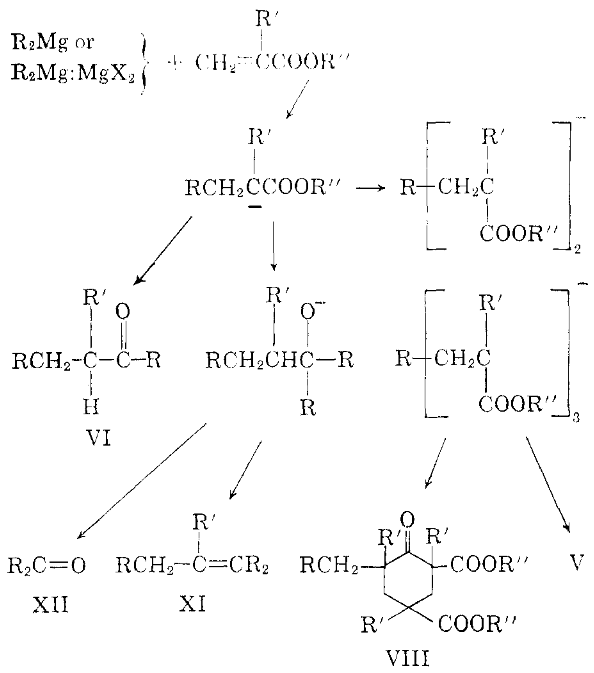
(17) H. T. Openshaw and R. Robinson, *J. Chem. Soc.*, 912 (1946).

considered to be polymer. For these reasons, these data are given only to denote an order of magnitude and are not to be considered quantitative.

The above results seem to indicate that the reactions of isopropyl acrylate and methyl methacrylate with phenylmagnesium bromide follow the same course and that only the amounts of the products differ. However, because of the variance between these data and the data of Lebedeva and collaborators,[3] we have repeated two of their experiments, the reaction of methyl acrylate and of methyl methacrylate with isopropylmagnesium bromide, and analyzed the products by infrared and ultraviolet spectroscopy and by alumina and gas chromatography. The material obtained from the reaction of methyl methacrylate with isopropylmagnesium bromide was distilled. Infrared analysis showed that in addition to the infrared maximum at 1740 cm.$^{-1}$ (Vc), there were maxima at 1715 cm.$^{-1}$ (VIc or diisopropyl ketone or both), at 1712 cm.$^{-1}$ (VIIIc), and at 1760 cm.$^{-1}$ (lactone). As before, the amounts of the different products were determined by infrared analysis of the distillation fractions. Analysis by gas chromatography revealed that there was no diisopropyl ketone, and this result was confirmed by the absence of an infrared maximum at 1025 cm.$^{-1}$ present in the spectrum of diisopropyl ketone. The material obtained from the reaction of methyl acrylate with isopropylmagnesium bromide was chromatographed on deactivated alumina. As was the case with isopropyl acrylate, the separation was incomplete but was sufficient to determine the nature and amounts of the products. There were maxima at 1740 cm.$^{-1}$, attributable to Ve, at 1718 cm.$^{-1}$ attributable to VIe or diisopropyl ketone or both, and at 1712, 1665, and 1612 cm.$^{-1}$ attributable to VIIIe. The ultraviolet spectra of the fractions containing VIIIe had a maximum at 252 mμ but lacked the shoulder at 208 mμ. Gas chromatographic analysis showed the presence of both XVIb and diisopropyl ketone, and this fact was confirmed by the presence of maxima in the infrared spectra of the fractions which were also present in the spectrum of diisopropyl ketone. No evidence could be found for the presence of a trisubstituted phloroglucinol (IIIb). The data on the products of these reactions are shown in Table II.

CONCLUSIONS

From the above data, there emerges a definite, consistent pattern as shown schematically below. In all of these reactions, the predominant product is ester of the type V resulting from successive 1,4-additions to the unsaturated ester, and this result is not surprising in view of the tendency of α,β-unsaturated esters to undergo conjugate addition with Grignard reagents.[18] The ketone VI and the hydrocarbon XI were not unexpected, and the amount of these products are reasonable in view of the data in the literature. It is interesting to note that no products resulting from 1,2- addition of the organomagnesium compound to the *monomer* were found. It is surprising that so much polymer was produced, especially when these results are compared with those of Lebedeva[3] and with those of Munch-Peterson,[4c] but these data do agree with our observations on the ease of polymerization of these monomers with Grignard reagents.



The unexpected products were the ketones VIII and XII. To our knowledge, this is the first example of a Dieckmann cyclization involving a Grignard reagent, although Claisen condensations have been reported,[7] and it is the first example of the reversal of the addition a Grignard to a ketone. It is possible that this reversal occurs on hydrolysis, and it may be a concerted process yielding ketone and hydrocarbon directly.[19] Reversal of the addition of a carbanion to a ketone during hydrolysis has been shown by Hamrick and Hauser.[20]

EXPERIMENTAL[21]

Organomagnesium compounds. The di-*n*-butylmagnesium and diphenylmagnesium were prepared from high purity, sublimed magnesium and the corresponding organomercury compound in ether at reflux under nitrogen by the method of Schlenk.[22] The Grignard reagents were prepared in ether under nitrogen by known techniques.[23]

Methyl methacrylate-1-C^{14}. Sodium bisulfite (26 g., 0.25 mole) in 50 ml. water was stirred and cooled to 10°. To this solution was added acetone (14.5 g., 0.25 mole) during about 1 min., with cooling by an ice water bath. The temperature rose to 35°, and the mixture became a thick slush of crystals of the acetone-bisulfite addition product. A solution of C^{14}-labeled potassium cyanide (0.30 mc./mole) (16.3 g., 0.25 mole) in 25 ml. of water was added during about 5 min. with continued external cooling. The crystals dissolved and the

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(18) M. S. Kharasch and O. Reinmuth, *op. cit.*, pp. 563–564.

temperature fell to 25° during the addition. The mixture was cooled to 5° and held at this temperature for 30 min. The upper oily layer of acetone cyanhydrin was separated from the aqueous layer, which was extracted with three 20-ml. portions of ether. The original organic layer and ether extracts were combined and extracted with two 20-ml. portions of saturated sodium bisulfite solution to remove unchanged acetone, then with four 20-ml. portions of saturated sodium chloride solution to remove traces of bisulfite. The ether solution was concentrated by distillation at reduced pressure; water was removed azeotropically with benzene, and the residue was distilled collecting the product at 72–73°/10.5 mm. The yield was 15.51 g. (73.2%). The activity was 3.5 μc./g.

Concentrated sulfuric acid (27.6 g., 0.27 mole) and 0.1 g. di-β-naphthol were heated to 70° with stirring in a 100-ml. flask having a thermometer, dropping funnel and reflux condenser. The above acetone cyanhydrin (15.35 g., 0.18 mole) was added from the dropping funnel during about 10 min., holding the temperature at 75–85° by external cooling. Following the addition the temperature was raised to 140° for 30 min. The mixture was cooled to 70° and a mixture of water and 17.5 g. of methanol was added from the dropping funnel. The mixture was heated to reflux and held at reflux for 4.5 hr., the temperature falling from 85° to 78.5° during this time. Changing to a downward condenser, distillate consisting of water, methanol and methyl methacrylate was taken off over a range of 70.5–97°, the pot temperature rising from 79 to 140°. The crude distillate (33 g.) was washed with an equal weight of 40% calcium chloride solution to remove water and methanol. The organic layer (16 g.) was treated again with 40% calcium chloride solution, and the combined calcium chloride washes were extracted with ether (3 × 10 ml.). The combined organic layer and ether extracts were dried over anhydrous calcium chloride. The dried ethereal solution was concentrated, and the residue was distilled at 125 mm. pressure through a small column (1 cm. × 16 cm.) with copper packing. The product was collected at 51–52°. The yield was 6.82 g. (39%), activity 3.3 μc./g. This material was diluted with unlabeled methyl methacrylate so that the final activity was 6.7×10^{-3} μc./millimole.

Spectra. The infrared spectra were obtained on a Perkin-Elmer model 21 double beam recording spectrometer equipped with rock salt optics. The slit program was set at 927, and the 2.0 to 15.0 μ scanning time was 15 min. Capillary films between rock salt plates were used except where noted. Identification of the pure products was accomplished by comparison with spectra of samples prepared by alternate routes.

The relative amount of each product in a fraction was determined from the ratio of the absorption of the carbonyl peaks, assuming that the molar absorption coefficients of the various carbonyl maxima were the same. While this assumption is not strictly valid, this method should serve to determine the order of magnitude of the products and should be more accurate for comparison purposes than integrated absorption intensities.[11] In all cases, selected absorption maxima are reported and the letters in parentheses refer to strong, medium, and weak intensities.

The ultraviolet spectra were obtained on a Beckman model DK-2 recording instrument. The samples were examined as solutions in absolute ethanol.

The reaction of methyl methacrylate with organomagnesium compounds. The general procedure for the reaction of methyl methacrylate with organomagnesium compounds is illustrated below in the specific directions for the reaction of methyl methacrylate with diphenylmagnesium.

The reaction of methyl methacrylate with diphenylmagnesium (Expt. 3). To 300 ml. of an ethereal solution containing 0.17 mole of diphenylmagnesium in a 1-l., three-necked flask equipped with a stirrer, addition funnel, reflux condenser, and thermometer was added dropwise with stirring a solution of 32 ml. (30 g., 0.3 mole) of methyl methacrylate over a period of 3 hr. while the temperature was maintained between 0 and 5° by means of an ice bath. On completion of the addition, the mixture was allowed to stir overnight, whereupon it was hydrolyzed with a solution of 150 ml. of concd. hydrochloric acid in 150 ml. of water, the temperature being maintained between 0 and 10°. The solid polymer was removed by filtration and was washed by stirring in a large volume of water for several hours, whereupon it was collected by filtration and dried in a vacuum oven for 48 hr. There was obtained 3.23 g.

The ether layer was separated, and the aqueous layer was extracted with three 150-ml. portions of ether. The combined ether layer was washed with three 150-ml. portions of a saturated salt solution. The ether was dried and was removed at the water pump. Petroleum ether (b.p. 30–78°) (100 ml.) was added to the residue; most of the material dissolved leaving a semisolid residue. The petroleum ether solution was decanted. After drying in a vacuum oven for 24 hr., the petroleum ether-insoluble material amounted to 1.54 g.

The petroleum ether was removed *in vacuo*, and the residue was distilled through a 24″ vacuum-jacketed spinning band column.

Seven fractions were obtained:

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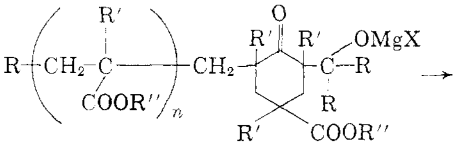
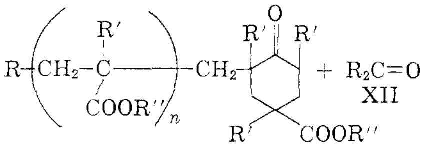
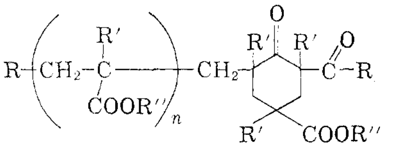
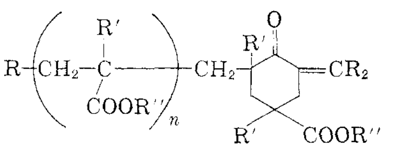
(19) The referee has suggested that ketone XII could arise by a retroaldol reaction of compound XVI to give XVII. There was, however, no evidence for the presence of XVII, XVIII, or XIX in the reaction mixtures. Since it was shown that VI and XI are present, we are inclined toward the reverse Grignard reaction postulated above as an explanation for the origin of the ketone XII.


XVI


XVII


XVIII


XIX

(20) P. J. Hamrick, Jr. and C. R. Hauser, *J. Am. Chem. Soc.*, **81**, 3144 (1959).

(21) All melting points are corrected. All boiling points are uncorrected. The authors are indebted to Miss J. Cronin for technical assistance and to Mr. C. W. Nash for the microanalyses.

(22) W. Schlenk, *Ber.*, **64**, 734 (1931).

(23) M. S. Kharasch and O. Reinmuth, *op. cit.*, Chapter II.

Fraction Number	B.P.	Mm.	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
1	51–68	92	0.50	1740 (s), 1690 (m), 1635 (m)
2	84–86	2.7	3.32	1740 (s), 1665 (w)
3	83–99	0.05	6.69	1740 (s), 1690 (s), 1665 (m)
4	99–103	0.05	7.74	1740 (s), 1690 (s)
5	100–104	0.05	4.08	1740 (s), 1712 (m), 1690 (w)
6	110–118	0.05	2.38	1810 (w), 1770 (m), 1740 (s), 1712 (s)
Residue			6.90	1810 (w), 1770 (m), 1740 (s), 1712 (s), 1690 (w)

The reaction of methyl methacrylate with dibutylmagnesium (Expt. 1). The ether-insoluble polymer amounted to 2.12 g., and 2.34 g. of the petroleum ether-insoluble polymer was obtained. From the distillation there were obtained nine fractions:

Fraction Number	B.P.	Mm.	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
1	52–63	97	1.36	1740 (s), 1715 (s)
2	76–93	4.95	1.52	1740 (w), 1715 (s)
3	46–50	0.10	2.58	1715 (s), 1640 (w)
4	61–66	0.10	1.50	1740 (s), 1715 (s)
5	68–72	0.025	1.79	1740 (s), 1712 (s)
6	102–116	0.075	8.88	1810 (m), 1770 (s), 1740 (s), 1712 (s)
7	117–120	0.10	3.51	1760 (s), 1740 (s), 1712 (s)
8	120–124	0.10	0.92	1810 (w), 1770 (s), 1740 (s), 1712 (s)
Residue			3.47	1810 (m), 1770 (s), 1740 (s), 1712 (s)

The reaction of methyl methacrylate with butylmagnesium bromide (Expt. 2). The ether-insoluble polymer amounted to 2.39 g., and the petroleum ether-insoluble fraction weighed 0.53 g.

Nine fractions were obtained on distillation:

Fraction Number	B.P.	Mm.	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
1	42–46	100	0.58	1740 (s), 1640 (w)
2	65–66	4.55–4.85	0.67	1740 (s), 1715 (s), 1640 (w)
3	82–98	5.00	3.66	1740 (w), 1715 (s)
4	106–108	4.70	2.55	1715 (s)
5	70–73	0.1–0.05	3.49	1740 (s), 1715 (s)
6	74.5–77	0.05	7.16	1740 (s)
7	84–103	0.05	4.28	1740 (s), 1712 (s)
8	116–127	0.10	4.13	1760 (s), 1740 (s), 1712 (s)
Residue			4.14	1760 (s), 1740 (s), 1712 (s)

The reaction of methyl methacrylate with phenylmagnesium bromide (Expt. 5). There was obtained 1.00 g. of ether-insoluble polymer and 0.87 g. of petroleum ether-insoluble polymer. Distillation gave eight fractions:

Fraction Number	B.P.	Mm.	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
1	100–106	3.90	1.01	1740 (s)
2	53–59	0.10	0.81	1740 (s)
3	83–91	0.10	2.49	1740 (s), 1665 (s), 1635 (w)
4	94–101	0.025	3.56	1740 (s), 1690 (w), 1665 (m)
5	102–104	0.025	12.40	1740 (s), 1690 (w)
6	104–108	0.025	3.69	1740 (s)
7	112–124	0.10	3.79	1740 (s), 1712 (s)
Residue			3.90	1810 (w), 1770 (m), 1740 (s), 1712 (m)

The reaction of methyl methacrylate with diphenylmagnesium (Expt. 4). Three hundred milliliters of an ethereal solution containing 0.315 mole of diphenylmagnesium was used. No insoluble polymer was obtained. Distillation gave eleven fractions.

Four grams of fraction 9 was chromatographed on a 33-mm. bore column packed with three 100-g. portions of alumina separated by 1" glass wool plugs. There was eluted with 75% benzene in petroleum ether and with pure benzene 0.89 g. of material having infrared maxima at 1740 (s) and 1712 (s) cm.$^{-1}$ This material did not crystallize, and it was not possible to prepare a 2,4-dinitrophenylhydrazone.

Anal. Calcd. for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.34; H, 7.47.

Fraction Number	B.P.	Mm.	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
1	47–57	99	0.75	1690 (m), 1665 (m), 1635 (w)
2	75–78	98	4.29	1740 (s), 1690 (m), 1665 (m), 1635 (w)
3	87–110	98	1.54	1740 (s), 1665 (m), 1635 (w)
4	107–111	3.50	1.06	1740 (s), 1665 (w)
5	126–136	4.00	0.34	1740 (s), 1712 (m), 1665 (s)
6	70–79	0.05	0.93	1750 (w), 1712 (w), 1655 (s), 1635 (w)
7	88–94	0.05	4.03	1740 (s), 1712 (m), 1690 (m), 1665 (s), 1635 (w)
8	98–104	0.10	20.68	1740 (s), 1690 (m)
9	114–118	0.10	6.64	1810 (m), 1770 (m), 1740 (m), 1712 (s)
10	121–136	0.10	3.22	1810 (m), 1770 (s), 1740 (s), 1712 (s)
Residue			4.10	1810 (s), 1770 (m), 1740 (s), 1712 (s)

The NMR data, determined by Varian Associates, are given in the discussion section. This material was assigned the structure methyl 5-benzyl-4-oxo-1,3,5-trimethylcyclohexane-1,3-dicarboxylate (VIIIb).

The reaction of methyl methacrylate-1-C^{14} with phenylmagnesium bromide. No polymer was obtained. Distillation gave three fractions and a residue of 24.47 g.: 1. b.p. 48–69° (0.5–0.3 mm.), 0.60 g.; 2. 69–72° (0.3–0.25), 1.50 g.; 3. 80–122° (0.15 mm.), 7.43 g. Fractions 2 and 3 were combined and dissolved in 15 ml. of petroleum ether. The petroleum ether solution was placed on a 30-mm. bore column packed with five 100-g. portions of alumina separated by 1″ plugs of glass wool. The material from fractions 7–14 was sublimed *in vacuo* and was shown to have a spectrum identical with that of the material obtained from the reaction of phenylmagnesium bromide with methyl 2-methyl-3-phenylpropionate (*vide infra*) and the melting point was 65–66° both alone and on admixture; therefore it was assigned the structure 2-methyl-1,1,3-triphenylprop-1-ene (XIb).

Fraction Number	Eluent	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
7–14	10 and 25% benzene in petroleum ether	2.18	1740 (w), 1635 (w), 910 (m)
17–20	50% benzene in petroleum ether	1.62	1740 (w), 1690 (s)
22–28	75% benzene in pet. ether and benzene	2.22	1665 (s), 1690 (w)

The material from fractions 17–20 melted below 0° and could not be recrystallized. It was dried in a desiccator at 0.1 mm.

Anal. Calcd. for $C_{16}H_{16}O$: C, 85.68; H, 7.19. Found: C, 85.45; H, 7.07.

A *2,4-dinitrophenylhydrazone* was prepared, m.p. 136°, after three recrystallizations from ethanol–ethyl acetate.

Anal. Calcd. for $C_{22}H_{20}N_4O_4$: C, 65.34; H, 4.99; N, 13.85. Found: C, 65.73; N, 4.80; N, 13.89.

This material was assigned the structure 2-methyl-1,3-diphenylpropan-1-one (VIb).

The material from fractions 22–28 was recrystallized once from petroleum ether, m.p. 48°. Two subliminations *in vacuo* gave material melting at 49° both alone and on admixture with pure benzophenone. The activity was 6.6 × 10^{-3} μc./mmole. The 2,4-dinitrophenylhydrazone after three recrystallizations from ethanol melted at 242° alone and at 240° on admixture with the 2,4-dinitrophenylhydrazone of benzophenone.

2-Bromoheptane. Hydrogen bromide gas was passed into 232 g. (2 moles) of heptanol-2, prepared by the reduction of heptanone-2, until the alcohol was saturated. The mixture was heated at 83° for 6.5 hr. while a slow stream of hydrogen bromide was passed through it. On cooling, the reaction mixture was diluted with an equal volume of ether, was washed with two 250-ml. portions of a 10% aqueous solution of sodium carbonate and three 250-ml. portions of a saturated aqueous solution of sodium chloride. The ether solution was dried with anhydrous magnesium sulfate, and the ether was removed *in vacuo*. The residue was distilled through a 30 cm. helices-packed column. Two fractions were obtained: 1. b.p. 75–77° (36 mm.), 13.5 g.; 2. b.p. 77° (37 mm.), 248.8 g., n_D 1.4478 (25°) [reported[24] b.p. 85 (50 mm.), n_D 1.4450 (25°)], 70% yield.

Methyl 2-methylheptanoate (Xa). To 200 ml. of ether and 15 g. of magnesium metal in a 500 ml., three-necked, steam-jacketed flask, equipped with a stirrer, Dry Ice condenser, addition funnel, and a stopcock in the bottom attached to a 2-l., 3-necked flask equipped with a stirrer and a Dry Ice condenser, was added dropwise a solution of 80 g. (0.45 mole) of 2-bromoheptane in 80 ml. of ether. On completion of the addition, the solution was heated at reflux by means of steam for 3 hr., whereupon it was allowed to stand overnight. The ether solution of the Grignard reagent was then added during 45 min. through the stopcock in the bottom of the flask to a mixture of 100 g. of powdered Dry Ice and 250 ml. of ether in the lower flask. The mixture was stirred for 1 hr.; the mixture was hydrolyzed with 75 ml. of concd. hydrochloric acid in 75 ml. of water. The layers were separated, and the aqueous portion was extracted with three 150-ml. portions of ether. The combined ether layer was washed with three 150-ml. portions of a saturated aqueous salt solution, was dried with anhydrous magnesium sulfate, and the ether was removed *in vacuo*. Distillation through a 24″, vacuum-jacketed, spinning band column gave two fractions: 1. 73–101° (0.7 mm.), 7.46 g.; 2. 101–103° (0.7 mm.), 25.8 g., n_D 1.4239 (25°), 40% yield.

A solution of 25 g. (0.17 mole) of the above acid, 100 ml. of methanol, 600 ml. of benzene, and 1 g. of *p*-toluenesulfonic acid was heated at reflux for 65 hr. The solvent was removed *in vacuo* at room temperature; ether (150 ml.) was added to the residue, and the ether solution was washed with two 100-ml. portions of a 5% aqueous solution of sodium carbonate and three 100-ml. portions of saturated aqueous salt solution. The ether was dried and was removed on a water pump. The residue was distilled through the spinning band column. After a 0.35-g. forerun, the methyl 2-methylheptanoate distilled at 78–80° (21–24 mm.). There was obtained 15.8 g. (56%) of material having an infrared maximum at 1740 cm.$^{-1}$ This material was shown to be pure by gas chromatography.

6-Methylundecan-5-one (VIa). To 200 ml. of ether and 15 g. of magnesium metal in a 500 ml., three-necked, steam-jacketed flask, equipped with a stirrer, Dry Ice condenser, addition funnel, and a stopcock in the bottom attached to a 1-l., three-necked flask equipped with a stirrer and a Dry Ice condenser, was added dropwise a solution of 80 g. (0.45 mole) of 2-bromoheptane in 80 ml. of ether. On completion of the

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[24] L. M. Ellis, Jr., and E. E. Reid, *J. Am. Chem. Soc.*, **54**, 1863 (1932).

addition, the solution was heated at reflux by means of steam for 3 hr., whereupon it was allowed to stand overnight. The ether solution of the Grignard reagent was then added during 90 min. through the stopcock to a solution of 39 g. (0.3 mole) of ethyl *n*-valerate in 100 ml. of ether. The solution was allowed to stir for 1 hr. and was then hydrolyzed with 75 ml. of concd. hydrochloric acid in 75 ml. of water. The ether layer was separated; the aqueous portion was extracted with three 150-ml. portions of ether; the combined ether layer was washed with three 150-ml. portions of saturated sodium chloride solution, was dried with anhydrous magnesium sulfate, and the ether was removed at the water pump. The residue was distilled through the spinning band column. Three fractions were obtained: 1. b.p. 69–73° (0.75 mm.), 1.52 g.; 2, 73–76° (0.75–0.80 mm.), 2.05 g.; 3. 76–78° (0.8 mm.) 4.25 g. Fraction 3 had an infrared maximum at 1715 cm.$^{-1}$

Attempted preparation of 2-methyl-1,3-diphenylpropen-1-one (VIb). To 28.2 g. (0.16 mole) of methyl 2-methyl-3-phenylpropionate (Xb) in 250 ml. of ether at 0° was added dropwise 0.08 mole of phenylmagnesium bromide in 100 ml. of ether solution. The mixture was stirred for 4 hr. and was allowed to stand overnight. The mixture was hydrolyzed with 75 ml. of concd. hydrochloric acid in 75 ml. of water. The ether was separated, and the aqueous portion was extracted with three 150-ml. portions of ether. The combined ether layer was washed with three 150-ml. portions of aqueous saturated salt solution. The ether solution was dried, and the ether was removed *in vacuo*. The residue was distilled through the spinning band column. Four fractions were obtained: 1. b.p. 30–72° (0.1 mm.), 1.6 g.; 2.72° (0.1 mm.), 10.1 g.; 3. 55° (0.05 mm.), 1.8 g.; 4. 120–138° (0.1–0.15 mm.) 15.2 g. Fraction 2 was starting material; fraction 3 was a mixture of fractions 2 and 4; and fraction 4 solidified on standing, m.p. 63.5–65°, and exhibited infrared maxima at 1635 and 910 cm.$^{-1}$ indicative of an olefinic, aromatic hydrocarbon. Four grams of fraction 4 was dissolved in 15 ml. of petroleum ether and placed on a 19 mm.-bore column containing four 20 g. portions of alumina separated by glass wool plugs. Five and ten per cent (by volume) benzene in petroleum ether solution eluted 3.9 g. of material, m.p. 65–66°, having infrared maxima at 1635 and 910 cm.$^{-1}$.

Anal. Calcd. for $C_{22}H_{20}$: C, 92.91; H, 7.09. Found: C, 92.76; H, 7.09. The material was assigned the structure 2-methyl-1,1,3-triphenylprop-1-ene (XIb).

The reaction of isopropyl acrylate with phenylmagnesium bromide. To 50 ml. of an ether solution containing 0.144 mole of phenylmagnesium bromide in a 1-l., three-necked flask equipped with a stirrer, addition funnel, reflux condenser, and thermometer was added dropwise with stirring a solution of 42.5 ml. (38 g., 0.33 mole) of isopropyl acrylate in 100 ml. of ether over a period of 90 min. while the temperature was maintained between 0 and 4°. Stirring was continued for 3 hr., and the mixture was hydrolyzed with 150 ml. of concd. hydrochloric acid in 150 ml. of water. The ether was separated, and the aqueous layer was extracted with three 100-ml. portions of ether. The combined ether solution was washed with three 100-ml. portions of a saturated solution of sodium chloride and was dried. The ether was removed *in vacuo*. Attempted distillation of a 10-g. portion of the residue resulted in extensive decomposition in the pot and was discontinued. A portion of the residue (10 g.) was dissolved in 75 ml. of petroleum ether and this solution was placed on a 37-mm. bore column packed with five 150-g. portions of alumina separated by 1″ plugs of glass wool. There was eluted by 50% benzene 0.52 g. of material having an infrared maximum at 1735 cm.$^{-1}$; by 10% ether in benzene 1.37 g. of the same material; and by 10, 25, 50, and 75% methanol in chloroform 2.54 g. of material having infrared maxima at 1735 (s) and 1650 (m) cm.$^{-1}$

A 10-g. portion of the residue was dissolved in a mixture of 40 ml. of benzene and 60 ml. of petroleum ether, and this solution was placed on a 37-mm. bore column packed with five 150-g. portions of deactivated[12] alumina separated by 1″ plugs of glass wool. The following fractions were obtained:

Fraction Number	Eluent	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
6–10	25% benzene in pet. ether	2.12	1735 (s), 1690 (w)
11–15	50% benzene in pet. ether	2.24	1735 (s), 1690 (w)
16–21	75% benzene in pet. ether	1.33	1735 (s), 1690 (w)
22–25	Benzene	0.25	1735 (s), 1690 (m)
26–30	10% ether in benzene	0.31	1735 (s), 1712 (w), 1690 (m), 1650 (m), 1615 (m)
31–35	25% ether in benzene	0.17	1735 (s), 1712 (w), 1650 (m), 1615 (m)
36–39	75% ether in benzene	0.08	
71–72	Chloroform	1.04	
80–95	10% Methanol in chloroform	0.40	1735 (s)

Fractions 6–25 had a maximum in the ultraviolet at 240 mμ, with a shoulder at 280 mμ. Fractions 31–72 had a minimum in the ultraviolet at 253 mμ with a shoulder at 208 mμ.

1,3-Diphenylpropan-1-one (VId). Benzalacetophenone was reduced with zinc in acetic acid by the procedure of Schneidewind.[14] The ether-soluble material was dissolved in 100 ml. of petroleum ether and placed on a 30-mm. bore column packed with five 100-g. portions of alumina separated by 1″ plugs of glass wool. The fractions eluted by 10% benzene in petroleum ether amounted to 6.33 g. and had an infrared maximum at 1690 cm.$^{-1}$ After one sublimation *in vacuo* the melting point was 71–72° (reported[14] m.p. 72°).

Anal. Calcd. for $C_{15}H_{14}O$: C, 85.68; H, 6.71. Found: C, 85.44; H, 6.73.

Ethyl 1,1-di(2-cyanoethyl)methane-1,1-dicarboxylate was prepared according to the procedure of Bruson and Riener,[15] m.p. 61.5–62° (reported[15] m.p. 62°) after one recrystallization from ethanol.

Isopropyl pentane-1,3,5-tricarboxylate (XIII). Pentane-1,3,5-tricarboxylic acid was prepared from the above nitrile by the method of Sengupta.[16] The crude acid was esterified without purification. To the crude acid in a 3-l., two-necked flask, connected to a 30-cm. column packed with Cannon packing, was added 800 ml. of isopropyl alcohol, 1-l. of benzene, and 30 ml. of concd. sulfuric acid. A Barrett-type water separator was connected to the top of the column, and the mixture was heated at reflux for 30 hr. at which time no more water separated. A total of 180 ml. of aqueous phase was collected. The solvent was removed *in vacuo* at room temperature. Ether (1.5 l.) was added, and the ether solution was washed with three 750-ml. portions of a 10% aqueous solution of sodium carbonate which was saturated with sodium chloride. The ether solution was then washed with three 750-ml. portions of saturated salt solution, was dried, and the ether was removed *in vacuo*. The residue was distilled through the spinning band column. The fraction boiling at 124° (0.2 mm.) was shown to be pure by infrared absorption and by gas chromatography. There was obtained 223 g., 70% yield based on the nitrile.

Isopropyl 4-oxocyclohexane-1,3-dicarboxylate (XIV). To 500 ml. of benzene in a 1-l., three-necked, Morton flask equipped with a Labline high speed stirrer, a condenser, and an addition funnel was added 9 g. (0.39- g.-atom) of sodium metal. The benzene was heated at reflux, and the sodium was pulverized with the high speed stirrer. With continued heating and stirring, 0.5 ml. of isopropyl alcohol was added, and 82.5 (0.25 mole) of isopropyl pentane-1,3,5-tricarboxylate was added dropwise during 90 min. Heating and stirring were continued for 6.5 hr., and the mixture was allowed to cool to room temperature. A solution of 50 ml. of acetic acid in 50 ml. of benzene was added followed by 500 ml. of water. The benzene was separated, and the aqueous layer was washed with three 50-ml. portions of benzene. The combined benzene layer was washed with three 200-ml. portions of water saturated with sodium chloride. The benzene solution was dried with magnesium sulfate, and the benzene was removed *in vacuo*. The residue was distilled through the spinning band column. The fraction boiling at 118–121° (0.45 mm.) amounted to 50.6 g., 75% yield, and had infrared maxima at 1735, 1712, 1655, and 1615 cm.$^{-1}$ and an ultraviolet maximum at 250 mμ (ϵ = 9300).

Anal. Calcd. for $C_{14}H_{22}O_5$: C, 62.20; H, 8.20. Found: C, 62.05; H, 8.22.

Isopropyl 5-benzyl-4-oxocyclohexane-1,3-dicarboxylate (VIIId). To a stirred solution of 27 g. (0.1 mole) of isopropyl 4-oxocyclohexane-1,3-dicarboxylate, 11.5 ml. of benzyl chloride, and 0.25 g. of sodium iodide in 100 ml. of isopropyl alcohol was added a solution of 2.5 g. of sodium metal in 250 ml. of isopropyl alcohol dropwise over a period of 2 hr. The solution was allowed to stand at room temperature for 48 hr., whereupon the solvent was removed on a water pump and finally at 0.5 mm. at room temperature. Ether (250 ml.) was added, and the solution was washed with three 150-ml. portions of water and was dried. On removal of the ether, there remained 28 g. of residue having infrared maxima at 1735, 745, and 705 cm.$^{-1}$ but lacking the maxima at 1712, 1655, and 1615 cm.$^{-1}$ found in the cyclohexanonedicarboxylate.

To 500 ml. of toluene in a 1-l., three-necked, Morton flask equipped with a high speed stirrer, reflux condenser, and dropping funnel was added 4 g. (0.17 g.-atom) of sodium metal. The toluene was heated at reflux, and the sodium was dispersed with the high speed stirrer. Isopropyl alcohol (0.5 ml.) was added followed by 25 g. of the above residue dropwise during 90 min. Heating and stirring were continued for 6 hr. The flask was cooled in an ice bath and a solution of 11 ml. of acetic acid in 10 ml. of benzene was added, followed by 100 ml. of water. The toluene was separated; the aqueous layer was extracted with two 50-ml. portions of toluene; the combined toluene layer was washed with two 100-ml. portions of water, and the toluene was dried with anhydrous magnesium sulfate. Removal of the toluene *in vacuo* left 21 g. of residue, 20 g. of which was dissolved in a mixture of 40 ml. of benzene and 40 ml. of petroleum ether. The benzene-ether solution was placed on the top of a 19-mm. bore column packed with four 20-g. portions of deactivated[12] alumina separated by glass wool plugs. There was eluted with 50:50 (v:v) benzene-petroleum ether 10.6 g. (34% based on isopropyl 4-oxocyclohexane-1,3-dicarboxylate) of material having infrared maxima at 1735, 1712, 1650, 1615, 745, and 705 cm.$^{-1}$

Anal. Calcd. for $C_{21}H_{28}O_5$: C, 69.98; H, 7.83. Found: C, 70.08; H, 7.83. This material had an ultraviolet maximum at 253 mμ (ϵ = 8160) and a shoulder at 208 mμ.

The reaction of methyl methacrylate with isopropylmagnesium bromide. The procedure of Lebedeva and Vainrub[3a] was repeated exactly. Distillation through the spinning band column gave six fractions:

Fraction Number	B.P.	Mm.	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
1	92–100	2.25	0.61	1740 (s), 1715 (s)
2	102–114	3.00	1.50	1740 (s), 1715 (s)
3	64.5–67	0.10	1.28	1740 (s), 1715 (w)
4	67–68	0.15	4.22	1740 (s), 1715 (m)
5	66	0.10	0.87	1740 (s), 1712 (s)
Residue			4.22	1760 (m), 1740 (s), 1712 (m)

The reaction of methyl acrylate with isopropylmagnesium bromide. The procedure of Lebedeva and Vainrub[3a] was repeated exactly, except that the material was not distilled but was placed on a 37-mm. bore column packed with five 150-g. portions of deactivated[12] alumina separated by 1″ plugs of glass wool. The following fractions were obtained:

Fraction Number	Eluent	Fraction Weight, G.	Infrared Maxima, Cm.$^{-1}$
5–7	10% Benzene in pet. ether	0.51	1740 (s), 1718 (s), 1025 (w)
8–16	25% Benzene in pet. ether	2.15	1740 (s), 1718 (m), 1025 (w)
17–21	50% Benzene in pet. ether	1.06	1740 (s), 1718 (m), 1025 (w)
22–26	75% Benzene in pet. ether	0.75	1740 (s), 1718 (m)
27–31	Benzene	0.34	1740 (s), 1718 (s), 1665 (w), 1622 (w)
32–37	10% Ether in benzene	0.23	1740 (s), 1718 (s), 1665 (w), 1622 (w)
53–58	Ether	0.47	1740 (s), 1718 (s), 1712 (w), 1665 (m), 1622 (m)
74–79	Chloroform	0.43	1740 (s), 1665 (w), 1622 (w)
80–89	50% Methanol in chloroform	3.10	1740 (s)
90–102	Methanol	0.26	1740 (s)

Fractions 27–29 had a maximum in the ultraviolet at 250 mμ.

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