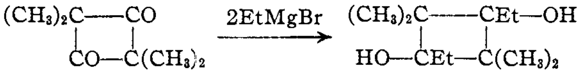
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Ketenes with Grignard Reagents

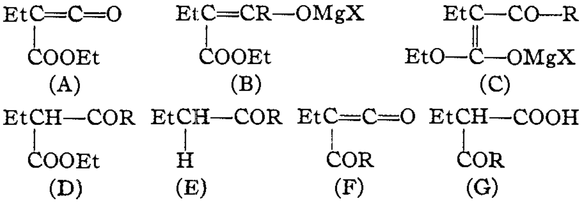
BY CHARLES D. HURD, RALPH N. JONES AND F. H. BLUNCK

Diphenylketene and phenylmagnesium bromide react[1] to produce a derivative of triphenylvinyl alcohol. With ketene[2] itself, the course of the Grignard reaction has not been established because of the vigor and complexity of the process. Toward the dimer of dimethylketene, ethylmagnesium bromide[3] adds to give the cyclic glycol in high yields



$$\begin{array}{l}(CH_3)_2C—CO \\ \;\;|\qquad\;\; | \\ CO—C(CH_3)_2\end{array} \xrightarrow{2EtMgBr} \begin{array}{l}(CH_3)_2C—CEt—OH \\ \qquad\;\;|\qquad\;\; | \\ HO—CEt—C(CH_3)_2\end{array}$$

The present paper extends the Grignard reaction to ethyl ethylketenecarboxylate, (A), and its dimer (K).



$$\underset{(A)}{\begin{array}{l}EtC{=}C{=}O \\ | \\ COOEt\end{array}} \quad \underset{(B)}{\begin{array}{l}EtC{=}CR—OMgX \\ | \\ COOEt\end{array}} \quad \underset{(C)}{\begin{array}{r}EtC—CO—R \\ \| \\ EtO—C—OMgX\end{array}}$$

$$\underset{(D)}{\begin{array}{l}EtCH—COR \\ | \\ COOEt\end{array}} \quad \underset{(E)}{\begin{array}{l}EtCH—COR \\ | \\ H\end{array}} \quad \underset{(F)}{\begin{array}{l}EtC{=}C{=}O \\ | \\ COR\end{array}} \quad \underset{(G)}{\begin{array}{l}EtCH—COOH \\ | \\ COR\end{array}}$$

Three types of addition should be considered, namely, at the ketene carbonyl, at the ester carbonyl, or 1,4 - addition at the C=C—COOEt group. Since the ester group is known[4] to be more sluggish toward Grignards than the aldehyde group the first type should be favored instead of the second but no such basis of comparison is available for the third.

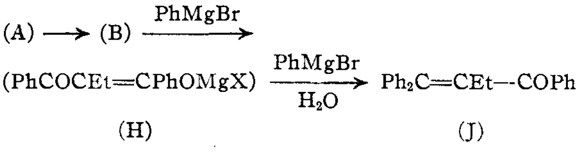
Addition of a Grignard reagent according to type 1 would produce (B), type 2 would produce (F), and type 3 would produce (C). On simple hydrolysis, both B and C would yield the β-keto ester (D), whereas F would yield the ketone E via G. If the reaction went via D, therefore, type 2 would be eliminated.

No satisfactory means of distinguishing between types 1 and 3 was found but the great reactivity of ketene, CH_2CO, toward Grignard reagents makes it appear reasonable that type 1 should be favored. Also, since $>C\begin{smallmatrix}\diagup OR \\ \diagdown OMgX\end{smallmatrix}$ is an unstable configuration, (C) may decompose spontaneously to (F), in which case no (D) would arise.

That (C) may be a stable intermediate is apparent because some unsaturated esters (such as $PhCH{=}CPhCO_2CH_3$ and $PhCH{=}CHCO_2C_6H_5$) react with phenylmagnesium bromide to give saturated esters[5] ($Ph_2CHCHPhCOOCH_3$ and $Ph_2CHCH_2COOC_6H_5$, respectively), evidently by intermediates related to (C).

When phenyl- or ethylmagnesium bromides were added to (A), the esters (D) were formed: ethyl α-benzoylbutyrate and ethyl α-propionylbutyrate. Hydrolysis of these esters yielded the ketones (E), namely, phenyl *n*-propyl ketone and ethyl propyl ketone.

When (A) was added to the phenylmagnesium bromide (*i. e.*, the Grignard in excess) phenyl α-ethyl-β,β-diphenylvinyl ketone (J) was one of the reaction products. These steps account for its presence:



$$(A) \longrightarrow (B) \xrightarrow{PhMgBr}$$

$$\underset{(H)}{(PhCOCEt{=}CPhOMgX)} \xrightarrow[H_2O]{PhMgBr} \underset{(J)}{Ph_2C{=}CEt—COPh}$$

This normal type of addition of the Grignard reagent to (H) in producing (J) would probably not have occurred if 1,1-dibenzoylpropane, which would come from (H) by hydrolysis, were taken instead with the Grignard reagent. The analogous case is that of 1,1-dibenzoylethane, which gave[6] no phenyl α-methyl-β,β-diphenylvinyl ketone but yielded (with PhMgBr) propiophenone and triphenylcarbinol.

The structure of (J) is supported by its behavior on ozonization. The products were those predicted, namely, benzophenone, benzoic acid and propionic acid.

In one run with ethylmagnesium bromide the addition product (B) was pyrolyzed instead of hydrolyzed. No evidence for the allene ester, $CH_3CH{=}C{=}CEtCOOEt$, was found. This ester would be anticipated if HOMgBr were detached from (B). Instead, ethyl bromide was evolved in quantity, together with an unidentified, unsaturated liquid boiling at 100–110°. In view of the

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[1] Gilman and Heckert, THIS JOURNAL, **42**, 1010 (1920).

[2] Hurd, Sweet and Thomas, *ibid.*, **55**, 335 (1933).

[3] Wedekind and Miller, *Ber.*, **44**, 3285 (1911).

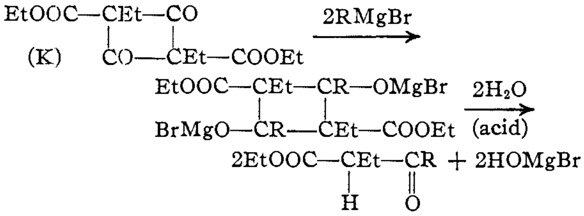
[4] Adams and Noller, THIS JOURNAL, **48**, 1074 (1926); Entemann and Johnson, *ibid.*, **55**, 2900 (1933).

[5] Kohler and Heritage, *Am. Chem. J.*, **33**, 153 (1905); **34**, 568 (1905).

[6] Kohler and Erickson, THIS JOURNAL, **53**, 2306 (1931).

non-production of the desired allene ester, this reaction was not studied further.

Phenyl- and ethylmagnesium bromides were also treated with the dimer (K) of the ketene. As with the ketene, a vigorous reaction resulted and the reaction products were β-keto esters (D) which, on hydrolysis, yielded ketones (E). Here again, practically no reaction occurred at the ester carbonyl. These steps appear probable



The facile, hydrolytic rupture of the C–C bonds in the cyclobutane nucleus is noteworthy, but the reaction of (K) with aniline at 100°, whereby ethyl ethylmalonanilate, $EtO_2CCHEtCONHPh$, is formed,[7] is somewhat analogous. The findings differ in kind from those of Wedekind and Miller[8] who reported direct addition of RMgX to the cyclobutanedione, but resemble those of Kohler and Erickson[6] who reported a C–C split with certain β-diketones.

Direct dehydration of ethyl hydrogen ethylmalonate proved to be an effective means of synthesis: $EtOOCCHEtCOOH + P_2O_5 \longrightarrow EtOOCCEt{=}C{=}O + 2HPO_3$. This saves three steps in the older procedure[9] which also started with ethyl hydrogen ethylmalonate.

Ethyl hydrogen ethylmalonate was synthesized from ethyl ethylmalonate. A method of synthesizing the latter from ethyl sulfate was developed. The older procedure employed ethyl bromide.

Experimental Part

Ethyl Ethylmalonate, $EtCH(COOEt)_2$

From Ethyl Bromide.[9]—A 62% yield was obtained by the ethyl bromide method in a 3-mole run. This method is economical because the sodium bromide which separates is so readily recoverable.

Careful fractional distillation was required in the purification. Unused ethyl malonate was collected at 88–91° (12 mm.), only 10° below that of the desired homolog. A 60-cm. Vigreux column was employed. The ethyl ethylmalonate taken possessed these constants: b. p. 96–99° (12 mm.), d^{20}_4 1.005, n^{20}_D 1.4171. The density is a convenient criterion of purity for the d^{20}_4 value for ethyl malonate is 1.054. In order to demonstrate the absence of ethylmalonate in the ethyl ethylmalonate used, some of the ester was hydrolyzed to ethylmalonic acid and the latter pyrolyzed to butyric acid. Duclaux values on this material were correct for pure butyric acid.

From Ethyl Sulfate.—In a 2-liter, three-necked, round-bottomed flask which is fitted with a mechanical stirrer, dropping funnel and reflux condenser, 29 g. (1.25 moles) of sodium was dissolved in 300 cc. of absolute alcohol. While still warm (60–75°), 200 g. (1.25 moles) of technical ethyl malonate was added slowly to it. To this solution, which was well stirred, was added 155 g. (1 mole) of ethyl sulfate without cooling. The addition should be fast enough to keep the alcohol boiling, but under control. The time for the addition was 25 minutes, after which the solution was refluxed for one hour on a hot plate. The alcohol was then distilled off and the residual solution heated for one hour at 160–165°, and for three hours at 145–150°. After cooling, water was added to the residue, the ester layer removed, washed with dilute alkali, then with water and dried with calcium chloride. On vacuum distillation, the ethyl ethylmalonate was collected at 100–103° (14 mm.); yield, 200 g. (1.07 moles). This is an 86% yield based on the ethyl malonate or a 54% yield based on the ethyl sulfate (assuming the reaction $Et_2SO_4 + 2CH_2(COOEt)_2 + 2Na \longrightarrow 2EtCH(COOEt)_2 + Na_2SO_4$). No better yield of ethyl ethylmalonate was obtained when 2 moles each of ethyl malonate and sodium were taken instead of 1.25 moles, even when the hot reaction period was extended to twenty hours.

When exactly molar quantities of the three reactants were taken and refluxed in alcohol for two to three hours (without subsequent heating at 145–165°) the yield was 0.80–0.88 mole. This is an 80–88% yield based on the ethyl malonate or a 40–44% yield based as above on the ethyl sulfate.

Synthesis of other Reagents.—Staudinger and Bereza's[9] directions were followed and confirmed for the syntheses of ethyl hydrogen ethylmalonate,[10] its acid chloride (α-carbethoxybutyryl chloride),[11] and α-bromo-α-carbethoxybutyryl chloride. The reported yields in the conversion of the last substance into ethyl diethylcyclobutanedicarboxylate (K) and its depolymerization into (A) were 61 and 80%, respectively, whereas our experience was 50 and 15–30%.

Ethyl Ethylketenecarboxylate from Ethyl Hydrogen Ethylmalonate.—One hundred grams of dried sand and 50 g. of phosphorus pentoxide were mixed in a liter flask which was placed in an oil-bath at 180–200°. The flask was connected to an upright condenser containing water at 75–85°, hot enough to force over the ketene, but cool enough to keep back impurities. Another cold water condenser and a receiver held at −78° were used to condense the ketene. The system was evacuated to 15 mm. and 30 g. of the acid was added rapidly through an attached dropping funnel. In this process the effort was made to cover the entire surface of the dehydrating mixture. Nine grams (34%) of distillate accumulated in thirty minutes. This, on redistillation, gave 6 g. (23%) of the

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(7) Staudinger and Bereza, *Ber.*, **42**, 4916 (1909).

(8) Wedekind and Miller, *ibid.*, **44**, 3285 (1911).

(9) Staudinger and Bereza, *ibid.*, **42**, 4909 (1909).

(10) The use of 95% alcohol for the alcoholic potassium hydroxide also gave satisfactory results.

(11) In this synthesis, it was found more convenient to add the acid to the phosphorus pentachloride than *vice versa*.

ketene, b. p. 45–55° at 11–12 mm. The ketene was kept at −78° to retard polymerization effects.

Distillation of the residue gave a small fraction at 89–91° (11 mm.), $n^{23}\mathrm{D}$ 1.4171 which was ethyl ethylmalonate. At a still higher temperature a small fraction of butyric acid was collected, evidently a decomposition product of ethylmalonic acid. The butyric acid was identified by its odor, solubility in water and Duclaux constants. Although most of the ethyl hydrogen ethylmalonate underwent dehydration, a small, concurrent disproportionation was also encountered.

The ketene (0.5 g.) reacted with pure aniline to produce ethyl ethylmalonanilate (yield, 0.8 g.) as stated by Staudinger and Bereza[9] but no reaction was found between the ketene and β-naphthylamine (in benzene).

Reactions with Grignard Reagents

Phenylmagnesium Bromide and (A). First Experiment.—Twenty-five cc. of absolute ether (distilled from a Grignard preparation) and 8.5 g. (0.06 mole) of the ketene were mixed. Then 0.06 mole of phenylmagnesium bromide was dropped into it. Following the vigorous reaction, the solution was refluxed for one-half hour, then stirred with dilute sulfuric acid. The ether layer was removed, washed with dilute sodium carbonate and dried over calcium chloride and distilled. Vacuum distillation (11 mm.) of the residue gave these fractions: (1) 70–120°, 3 g.; (2) 120–170°, 7 g. Redistillation of the 3 g. fraction revealed no constant-boiling material. It distilled between 90–120° (11 mm.). The 7-g. fraction was chiefly ethyl α-benzoylbutyrate.[12] Six grams of it was collected at 159–162° (11 mm.). Its identity was established as follows: (1) its saponification number was 215 (calcd. 210); (2) it was refluxed for 2.5 hours with a 5% solution of potassium hydroxide, then ether extracted, the extract dried and the ether removed. The 2 g. of residue contained some diphenyl but it was largely phenyl *n*-propyl ketone. It gave a semicarbazone, m. p. 184–185° after one crystallization. The recorded value[13] is 188°.

Second Experiment.—In this run, 0.077 mole (11 g.) of the ketene was dropped into a solution of 0.2 mole of phenylmagnesium bromide. By adding the ketene rather than the Grignard reagent, the latter was in great excess throughout.

The reaction product was hydrolyzed with cold, dilute acid. After separation and removal of ether the residue was distilled at 15 mm. There was 0.3 g. of diphenyl and 5.0 g. of liquid collected between 100–140°. The residue from the distillation was taken up in alcohol. On cooling, 2.5 g. of white crystals, m. p. 126–127°, separated. Five cc. of liquid, presumably ethyl α-benzoylbutyrate, was left on evaporation of the alcohol.

A small quantity of the same crystalline material was obtained by interaction of α-bromo-α-carbethoxybutyryl chloride (8 g.) and the Grignard reagent from 13 g. of bromobenzene. Only 0.1 g. was isolated when the former was added to the latter. The reverse type of addition, which should have given better yields, was not tried.

The crystalline material was phenyl α-ethyl-β,β-diphenylvinyl ketone (J). It was non-volatile in steam. It was unaffected by acetic anhydride and did not undergo hydrolysis by refluxing with dilute sulfuric acid or concd. sodium hydroxide solutions. A mixed melting point determination with triphenylcarbinol showed a depression to 109–115°, which showed the virtual absence of the latter.

Anal. Calcd. for $C_{23}H_{20}O$: C, 88.4; H, 6.45. Found: C, 87.7, 87.6; H, 6.28, 6.44.

Ozonolysis of (J).—The sample (1.85 g.) was dissolved in 80 cc. of carbon tetrachloride and 5.4 liters of ozonized oxygen was passed through. The ozonide was insoluble. Eighty cc. of water was added and the mixture distilled until all the carbon tetrachloride and much of the water had been removed. The residue contained about 0.5 g. of benzophenone, present as a yellow oil. When treated with hydroxylamine, 0.6 g. of benzophenone oxime, m. p. 143°, was formed.

The carbon tetrachloride layer was separated from the distillate and evaporated. The oily residue was taken up in hot water. On cooling, 0.7 g. of benzoic acid separated, m. p. 121°. No attempt was made to determine the propionic acid content of the carbon tetrachloride layer.

The water layer was neutralized with 49.10 cc. of 0.053 *N* sodium hydroxide, then evaporated to a volume of 5 cc. Ten cc. of alcohol and 0.5 g. of *p*-bromophenacyl bromide were added and the mixture refluxed for one hour. On cooling, the more insoluble *p*-bromophenacyl benzoate, m. p. and mixed m. p. 118° (yield, 0.3 g.), separated. By concentrating the filtrate, crystals were obtained which melted about 39°. After two recrystallizations, the melting point was raised to 59°, which is characteristic of *p*-bromophenacyl propionate.

Phenylmagnesium Bromide and the Dimer of (A).—When phenylmagnesium bromide solution was dropped into an ice-cold solution of 25 g. of (K) in 50 cc. of absolute ether, a vigorous reaction occurred until nearly the calculated quantity had been introduced. Then the mixture was refluxed for an hour and worked up as in the preceding "first experiment." On distillation at 30 mm., these fractions were obtained (°C., g.): 107–111, 7; 115–120, 8; 120–130, 3; 150–165, 5; 170–175, 15; some residue. The first two fractions appeared to be a mixture of the ketene and its dimer (A and K). Similar material was produced in the distillation of the dimer (K) to produce (A). Thus, distillation of 50 g. of (K) at 25 mm. gave: 50–100°, 20 g. of (A); 109–112°, 13 g.; 125–127°, 2 g.; 140–150°, 5 g.; some residue. The 107–120° portions from both experiments, on alkaline hydrolysis, yielded ethylmalonic acid of neutral equivalent 67 and m. p. 100–105°. (Values, if pure, would be 66 and 112°, respectively.) Carbon dioxide was detached (as shown by lime water test) from this acid by pyrolysis and the butyric acid residue yielded *p*-bromophenacyl butyrate of m. p. 59–60° (literature, 62°) with *p*-bromophenacyl bromide.

The 15-g. fraction (b. p. (30 mm.) 170–175°) was chiefly ethyl α-benzoylbutyrate. Six grams of it gave rise to 4 g. of phenyl *n*-propyl ketone, b. p. 200–210°; semicarbazone, m. p. 185–186°.

Ethylmagnesium Bromide and (A). First Experiment.—The calculated quantity of ethylmagnesium bromide in dry ether was added dropwise with stirring into 4 g. of the ketene (also in ether and cooled by ice). An-

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[12] Hope and Perkin, *J. Chem. Soc.*, **95**, 2047 (1909).

[13] Sorge, *Ber.*, **35**, 1074 (1902).

other 4-g. portion of the ketene was added to the solution and the process repeated till 17.5 g. of the ketene had been used. Then the mixture was refluxed for a half hour, cooled and mixed with ice and dilute sulfuric acid. The ether layer was removed, washed with water, with 5% sodium carbonate solution and dried with calcium chloride. There was 15 g. of residue after removal of the ether. Most of it distilled at 97–100° (18 mm.) but there were higher (100–110°) and lower boiling fractions. The latter, which was collected at 65–70° (40 mm.) and which weighed about 1 g. possessed a mol. wt. of 147–156. The quantity at hand was insufficient for definite characterization.

The mol. wt. of the 97–100° (18 mm.) fraction was 162, 172 (calcd. for $C_8H_{16}O_3$, 172). This material was largely ethyl α-propionylbutyrate. In another similar run (from 5 g. of the ketene) the product was hydrolyzed by stirring with dilute alkali until dissolved and then acidified with 50% sulfuric acid. Ethyl propyl ketone was extracted from it with ether and characterized as the semicarbazone. The latter melted at 107–108° after two crystallizations from water. Michael[14] lists 111° as the m. p. for this semicarbazone.

Second Experiment.—Twenty-two grams (0.15 mole) of the redistilled ketene (b. p. 50–53° (11 mm.)) in 10- and 12-g. portions was treated as before with 0.16 mole of ethylmagnesium bromide. After the half-hour period of refluxing, the ether was distilled away and the temperature of the oil-bath progressively raised to 200°. A drop of paraffin lessened the tendency of the residue to foam. A distillate was obtained near 200°. The temperature was increased to 300° and finally a free flame was used. The 6 g. of liquid obtained was redistilled into two fractions: (1) 37–45°, 3 g.; (2) 45–110°, 2 g. The mol. wt. determination, high bromine content, and b. p. of fraction (1) confirmed its identity as ethyl bromide. Over half of fraction (2), on redistillation, boiled at 100–110°. The substance was unsaturated and 0.0034 mole of it (0.4265 g.) absorbed 0.0032 mole of bromine solution, indicative of one double bond. The mol. wt. values found were 113.7 and 117.4.

Ethylmagnesium Bromide and the Dimer of (A).—Fifteen grams of the dimer, diluted with 50 cc. of dry ether, was taken. Into it (ice cold) was dropped the calculated amount of ethylmagnesium bromide. The reaction mixture was worked up as with the ketene. These fractions were obtained at 12 mm.: 95–97°, 5 g.; 97–145°, 2 g.; 145–155°, 2 g.

The identity of the higher boiling fractions was not established but the 95–97° fraction was ethyl α-propionylbutyrate, the same as from the ketene itself. Hydrolysis yielded ethyl propyl ketone as before; semicarbazone, m. p. 108.5–109°.

Summary

Ethyl ethylketenecarboxylate was prepared by direct dehydration of ethyl hydrogen ethylmalonate with phosphorus pentoxide. The behavior was studied of this ketene and its dimer toward phenyl- and ethylmagnesium bromides. Addition was found to occur preferentially at the ketene carbonyl, giving β-keto esters. No allene type was produced when the addition product of the ketene and ethylmagnesium bromide was pyrolyzed. Instead, ethyl bromide and an unsaturated compound were formed.

Ethyl malonate was converted to ethyl ethylmalonate by the use of ethyl sulfate and sodium ethoxide.

EVANSTON, ILLINOIS RECEIVED JUNE 24, 1935

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[14] Michael, THIS JOURNAL, **41**, 393 (1919).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Reaction between Ethylene and Chlorine in the Presence of Chlorine Acceptors. The Photochlorination of Ethylene

BY T. D. STEWART AND BERNHARDT WEIDENBAUM

This work was instigated by the concept of the reaction between ethylene and chlorine being a chain reaction, similar to the photochemical formation of benzene hexachloride from benzene and chlorine, which has been shown to have a quantum efficiency of the order of 100. That these two reactions have a common intermediate was shown by Stewart and Hanson[1] when they found that ethylene passed into a solution of chlorine in benzene in the dark yielded benzene hexachloride, in the ratio of about ten moles of chlorine reacting with benzene for each one reacting with ethylene, or an induction factor of ten.[2]

These photochlorinations are now commonly considered to involve chlorine atoms or possibly the complex Cl_3, with no clear way as yet of distinguishing their relative importance.[3] The chlorinations of hydrogen and of saturated hydrocarbons involve the same variables.

The Photochlorination of Gaseous Ethylene.—To ascertain that this addition reaction, normally

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[1] Stewart and Hanson, THIS JOURNAL, **53**, 1121 (1931).

[2] Two years ago, Mr. Harold Pitt, in this Laboratory, succeeded occasionally in obtaining an induction factor of 70–100. Rigid exclusion of oxygen and low partial pressures of ethylene permitted the longer benzene–chlorine chains.

[3] Dickinson and Carrico, THIS JOURNAL, **56**, 1478 (1934).