Action of Methylmagnesium Bromide with Triethylacetyl Chloride (I).—To a solution of 157 g., 0.95 mole, of triethylacetyl chloride in ether was added 2 moles of 1.52 molar methylmagnesium bromide. About 0.5 mole of gas was evolved per mole of Grignard reagent added. The material was worked up as usual. Fractionation gave 45.6 g., 0.32 mole, or 34% of methyl triethylcarbinyl ketone (II), b. p. 90° (60 mm.), n^{20}D 1.4318–9, and 39.9 g., 0.15 mole, or 32% of bis-triethylacetyl-methane (IV), b. p. 135–6° (8 mm.), n^{20}D 1.4769–70. The *2,4-dinitrophenylhydrazone* and the *oxime* of the *monoketone*, both of which were prepared with difficulty, melted at 93–94.5° and 97–101°, respectively. The diketone gave a chelate copper derivative with ammoniacal cupric acetate. The derivative was a brilliant purple compound with m. p. 143–144°. The monoketone gave 94% enolization and no addition when run in the Grignard machine with methylmagnesium bromide.[7]

3-Keto–4,4-diethylhexan-1-ol.—To 16 g., 0.65 gram-atom, of magnesium in 200 cc. of dry ether was added 70 g., 0.65 mole, of ethyl bromide. When the reaction was completed 80 g., 0.56 mole, of methyl triethylcarbinyl ketone was added. The reaction mixture was stirred for twenty-four hours. Formaldehyde gas was then passed into the reaction flask until an excess had been added. The reaction mixture became viscous as the reaction proceeded, and heating was necessary to keep it fluid enough for adequate stirring. The material was worked up as usual. Fractionation gave 37.7 g., 0.22 mole, or 34% of 3-keto-4,4-diethylhexan-1-ol, b. p. 86° (2 mm.), n^{20}D 1.4554–8; alpha-naphthylurethan, m. p. 120–122°.

Mol. wt. Calcd. for $C_{10}H_{20}O_2$: mol. wt., 172. Found: mol. wt. (cryoscopic), 171.

3-Keto-4,4-diethylhexanoic Acid.—To 0.07 mole of ethylmagnesium bromide was added 10 g., 0.07 mole, of methyl triethylcarbinyl ketone. The reaction mixture was stirred three hours. Gas was evolved during the reaction. An excess of carbon dioxide gas was passed into the reaction mixture with continuous stirring. The material was worked up as usual. The oil layer was extracted with dilute sodium carbonate. The alkaline extract was acidified with sulfuric acid and the solid beta-keto acid was filtered off. The yield was 2.5 g., 0.014 mole, or 21%. The acid, m. p. 63–65°, decomposed on heating to give carbon dioxide and methyl triethylcarbinyl ketone.

Anal. Calcd. for $C_{10}H_{18}O_3$: neut. equiv., 186. Found: neut. equiv., 183, 185, 190.

Summary

1. The presence of three ethyl groups on the carbon adjacent to a carbonyl group has been found to have a pronounced influence on the reactions of the carbonyl.

2. The reaction of methyl triethylcarbinyl ketone with a Grignard reagent gives an enolate which reacts as a true Grignard reagent.

3. Methyl triethylcarbinyl ketone is the lowest molecular weight aliphatic ketone found to give only enolization with the methyl Grignard reagent.

STATE COLLEGE, PENNA.   RECEIVED DECEMBER 18, 1941

Grignard Reactions. XV.[1] Sterically Hindered Aliphatic Carbonyl Compounds. V. Enolization Studies. I

BY FRANK C. WHITMORE AND L. P. BLOCK[2]

Methylmagnesium halides have long been used as reagents for the determination of active hydrogen in organic compounds. Early work on such determinations has been reviewed by Courtot,[3] who pointed out that the method is applicable to the study of keto–enol tautomerism.

Kohler and co-workers[4] devised a new type of apparatus with which one can determine the amount of gas evolved with the methylmagnesium halide, and also measure the amount of reagent used in the reaction.

Enolization studies until recently have been confined almost entirely to ketones containing an aromatic group. The reason for this is probably because hindered ketones which would contain conjugated double bonds in the enol form almost invariably give enolization.[5] Thus acetomesitylene and related compounds[6] have been studied rather extensively.

A definite correlation between the branching in aliphatic ketones and the amount of enolization given with the methyl Grignard reagent is not yet entirely clear. The literature indicates that such ketones show little tendency to give enolization with simple Grignard reagents. However, several new aliphatic sterically hindered ketones[7] prepared in this Laboratory give as high as 100%

(1) Whitmore and Lewis, THIS JOURNAL, **64**, 1618 (1942).

(2) Present address: E. I. du Pont de Nemours and Co., Waynesboro, Va.

(3) Courtot, "Le Magnesium en Chemie Organique," 1926.

(4) Kohler, Stone and Fuson, THIS JOURNAL, **49**, 3181 (1927).

(5) (a) Fuson, Fisher and Fugate, *J. Org. Chem.*, **4**, 111 (1939); (b) Fuson, Fugate and Fisher, THIS JOURNAL, **61**, 2362 (1939).

(6) (a) Kohler and Baltzly, *ibid.*, **54**, 4015 (1932); (b) Smith and Guss, *ibid.*, **59**, 804 (1937).

(7) (a) Whitmore and Randall, *ibid.*, **64**, 1242 (1942); (b) Whitmore and Lester, *ibid.*, **64**, 1247 (1942); (c) Whitmore and Lewis, *ibid.*, **64**, 1618 (1942).

enolization and no addition with the methyl Grignard reagent.

The present work was undertaken to extend the studies on enolization of branched aliphatic ketones with the methyl Grignard reagent. The compounds studied are not sufficiently branched to prevent the addition reaction entirely. The results of the studies are given in Table I.

The Grignard machine used in this work is essentially the same as the one used by Kohler.[4] The amount of enolization was calculated from the amount of gas evolved by the action of methylmagnesium chloride with the carbonyl compound. The excess methylmagnesium chloride present was determined by observing the amount of gas evolved on the addition of water to the reaction flask. The amount of addition reaction was taken as the difference between the number of moles of methylmagnesium chloride added and the total moles of gas evolved by the enolization reaction and by the decomposition of the excess reagent. This is based on the assumption that the amount of condensation is negligible. The reaction flask was always heated to ensure optimum reaction conditions. The apparatus was enclosed in a case to protect it from changes in temperature caused by air currents. The usual corrections were made for the gas evolved due to the presence of moisture in the reaction flask.

TABLE I

Compound	Percentage Enoliza-tion	Addition
Methyl isopropyl ketone	0	100
Ethyl isopropyl ketone	0	100
Methyl t-butyl ketone	5	86
Ethyl t-butyl ketone	9	86
Pentamethylacetone	0	49
Methyl pinacolyl ketone	48	47
Ethyl pinacolyl ketone	62	33
Methyl s-butyl ketone	32	..
Propyl s-butyl ketone	53	40
2,2-Dimethyl-4-ethyl-3-hexanone	5	19
2,2,4,6,6-Pentamethyl-3,5-heptadione	27/2	129/2

From the above measurements it can be seen that the amount of enolization and addition is dependent upon the steric influence of the groups around the carbonyl. This was first pointed out by Conant and Blatt.[8] The carbonyls of methyl and ethyl isopropyl ketones are not sufficiently hindered to retard the normal addition reaction and allow time for the competing enolization reaction. It is interesting to note that al-

(8) Conant and Blatt, THIS JOURNAL, **51**, 1227 (1929).

though pentamethylacetone gave only 49% addition, no enolization took place. This recalls the failure of phenyl dineopentylcarbinyl ketone to give any enolate.[7b] All of the other ketones investigated gave both enolization and addition.

The steric influence of the ethyl group is shown to be much greater than that of the methyl group. The carbonyls of 2,2-dimethyl-4-ethyl-3-hexanone and 2,2,4,6,6-pentamethyl-3,5-heptadione are sterically hindered to such an extent that the sums of the enolization and addition reactions are 24% and 78%, respectively, of the calculated amount assuming complete reaction. It is thus apparent that steric hindrance in carbonyl compounds may retard, and in some cases prevent, either enolization or addition or both.

We thank R. S. George of this Laboratory for his help.

Experimental

The procedure used in making the enolization measurements has been described above. The compounds run in the Grignard machine were prepared by conventional procedures. The compounds, their physical properties and the method of preparation are given very briefly.

Methyl isopropyl ketone: dichromate oxidation of methylisopropylcarbinol; b. p. 92° (740 mm.) and $n^{20}D$ 1.3886.

Ethyl isopropyl ketone: dichromate oxidation of ethylisopropylcarbinol; b. p. 111–113° (740 mm.) and $n^{20}D$ 1.3975.

Methyl t-butyl ketone: reaction of acetyl chloride with t-butylmagnesium chloride; b. p. 103.5° (735 mm.) and $n^{20}D$ 1.3974.

Ethyl t-butyl ketone: oxidation of olefins; b. p. 124.5° (730 mm.) and $n^{20}D$ 1.4049.

Pentamethylacetone: diisopropyl ketone by reaction with sodamide and dimethyl sulfate; b. p. 135° (735 mm.) and $n^{20}D$ 1.4074.

Methyl pinacolyl ketone: ozonolysis of 3,4,5,5-tetramethyl-2-hexene; b. p. 144° (740 mm.).

Ethyl pinacolyl ketone: reaction of methyl-t-butylacetyl chloride with ethylmagnesium bromide; b. p. 87° (50 mm.) and $n^{20}D$ 1.4221.

Methyl s-butyl ketone: dichromate oxidation of methyl-s-butylcarbinol; b. p. 115.5° (733 mm.) and $n^{20}D$ 1.3988.

Propyl s-butyl ketone: dichromate oxidation of propyl-s-butylcarbinol; b. p. 154° (73 mm.) and $n^{20}D$ 1.4132.

2,2-Dimethyl-4-ethyl-3-hexanone: dichromate oxidation of 2,2-dimethyl-4-ethyl-3-hexanol; b. p. 120° (150 mm.) and $n^{20}D$ 1.4240.

2,2,4,6,6-Pentamethyl-3,5-heptadione: oxidation of triisobutylene; b. p. 91° (16 mm.) and $n^{20}D$ 1.4320.

Summary

1. Eleven aliphatic ketones have been analyzed in the Grignard machine with methylmagnesium chloride.

2. Pentamethylacetone gave no enolization and 49% addition with the methyl Grignard reagent.

3. It has been confirmed that steric hindrance around the carbonyl retards both the enolization and addition reactions. Thus 2,2-dimethyl-4-ethyl-3-hexanone gave 5% enolization and 19% addition with the methyl Grignard reagent.

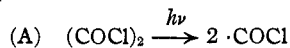STATE COLLEGE, PENNSYLVANIA
RECEIVED DECEMBER 24, 1941

Carboxylation. III. The Peroxide-catalyzed Reaction of Oxalyl Chloride with the Side-chains of Aralkyl Hydrocarbons. A Preliminary Study of the Relative Reactivity of Free Radicals
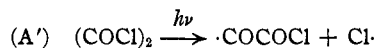
BY M. S. KHARASCH, STEPHEN S. KANE[1] AND HERBERT C. BROWN

It has been suggested that the photochemical carboxylation[2] of the paraffin hydrocarbons with oxalyl chloride proceeds in the following manner.
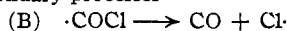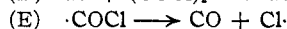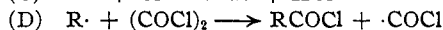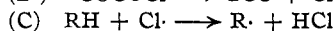
Primary process

$$(A) \quad (COCl)_2 \xrightarrow{h\nu} 2 \cdot COCl$$

and/or

$$(A') \quad (COCl)_2 \xrightarrow{h\nu} \cdot COCOCl + Cl\cdot$$

Secondary processes

$$(B) \quad \cdot COCl \longrightarrow CO + Cl\cdot$$

and/or

$$(B') \quad \cdot COCOCl \longrightarrow 2CO + Cl\cdot$$
$$(C) \quad RH + Cl\cdot \longrightarrow R\cdot + HCl$$
$$(D) \quad R\cdot + (COCl)_2 \longrightarrow RCOCl + \cdot COCl$$
$$(E) \quad \cdot COCl \longrightarrow CO + Cl\cdot$$
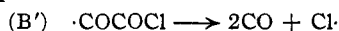
The experimental evidence upon which this mechanism is based has already been discussed.[3]

Study of the carboxylation of a number of representative hydrocarbons indicates that this reaction is general for the paraffins, the cycloparaffins and their halogen derivatives. However, attempts to extend this photochemical reaction to the carboxylation of the side chains of representative aralkyl hydrocarbons have thus far met with little success.

This observation can be interpreted in either of two ways: (1) the aromatic hydrocarbons containing side-chains are opaque to the radiation necessary for the chain-initiating step, which is the photolysis of the oxalyl chloride (A); or (2) the aralkyl free radicals which are formed (C) require a relatively high energy of activation to break the carbon-to-carbon bond in oxalyl chloride (D).

Considerable support for the belief that the first of these interpretations is of importance in the photochemical carboxylation reaction was furnished by a study of the carboxylation of cyclohexane in the presence of various diluents. Carbon tetrachloride, chloroform, and similar inert diluents exert but small effects upon the rate of carboxylation of cyclohexane. The slight decrease observed, approximately 20%, can easily be accounted for by decreased concentration of the reactants. On the other hand, the presence of comparable quantities of benzene in the reaction mixture causes a five-fold drop in the rate. It is evident, therefore, that in the *photochemical* carboxylation of the aralkyl hydrocarbons, the poor yields are largely due to the effect of the aromatic nucleus upon the radiation required to initiate the carboxylation reaction.

It is noteworthy, however, that this interpretation does not eliminate the second of the two possibilities mentioned above: namely, that the low degree of reactivity[4] of the aralkyl free radicals might also contribute to the sluggishness of the aralkyl hydrocarbons in the photochemical carboxylation reaction under discussion. The observation that the carboxylation reaction could be initiated thermally in the dark by the addition of several mole per cent. of an organic peroxide[3] offered a means of investigating this question.

Accordingly, a study of the peroxide-catalyzed carboxylation of a number of aralkyl hydrocarbons was undertaken. It is significant that low yields (about 5–10%) of the corresponding acid chlorides were obtained with such representative aralkyl hydrocarbons as toluene, *m*-xylene, and mesitylene. In these reactions, the inhibitory ef-

(1) This paper is part of a dissertation submitted by Stephen S. Kane to the Faculty of the Division of Physical Sciences of the University of Chicago in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) The authors have adopted the term carboxylation to describe the introduction of the chloroformyl (—COCl) group; see the first paper of this series (reference in footnote 3).

(3) Kharasch and Brown, THIS JOURNAL, 64, 329 (1942).

(4) That is, low compared with the highly reactive normal alkyl free radicals.