Summary.

1. Di-iodo-acetylene liberates iodine from aqueous solutions of iodides and acetylene is regenerated.

2. Di-iodo-acetylene reacts with ammonia giving acetylene and probably nitrogen iodide, a compound in which the iodine is positive.

3. The conduct of both iodo-acetylene and di-iodo-acetylene is best explained by the assumption that these compounds contain positive iodine, and that the structures are, respectively, $H - C \equiv C - I$ and $I - C \equiv C - I$. These structures seem at present much more probable than the acetylidene structures, $IHC = C<$ and $I_2C = C<$.

4. Biltz has reported that chlorine acts upon di-iodo-acetylene giving hexachloro-ethane. It has been shown that the primary product formed by the action of chlorine upon di-iodo-acetylene is iodochloride-1-chloro-2,2-chloro-iodo-ethylene, $Cl_2I.CCl = CClI$.

5. Iodochloride-1-chloro-2,2-chloro-iodo-ethylene decomposes very easily giving chiefly symmetrical dichloro-di-iodo-ethylene, $CICl = CICl$ and iodine monochloride, also probably a trichloro-iodo-ethylene.

6. The action of iodine trichloride upon acetylene gives iodochloride-2-chloro-ethylene, a compound previously prepared by Thiele and Haakh by the action of chlorine upon 1,2-chloro-iodo-ethylene. This reaction indicates that the iodine atom of chloro-iodo-ethylene is positive in nature. The addition of iodine trichloride to unsaturated linkages should be a ready method for preparing aliphatic iodochlorides having chlorine on the β-carbon.

7. The chief products formed when iodochloride-2-chloro-ethylene decomposes are iodine monochloride and 1,2,2-trichloro-1-iodo-ethane. The observation of Thiele and Haakh that 1-chloro-2-iodo-ethylene and chlorine gas result when iodochloride-2-chloro-ethylene decomposes, appears to be an error.

URBANA, ILL.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF IOWA STATE COLLEGE.]

THE MECHANISM OF THE REACTION BETWEEN KETENES AND THE GRIGNARD REAGENT.

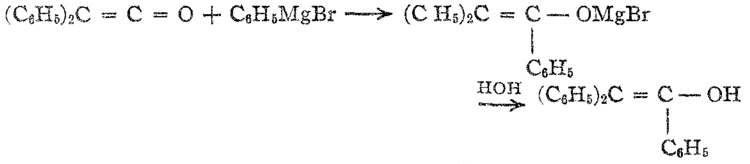
BY HENRY GILMAN AND L. C. HECKERT.

Receiv.d February 6, 1920.

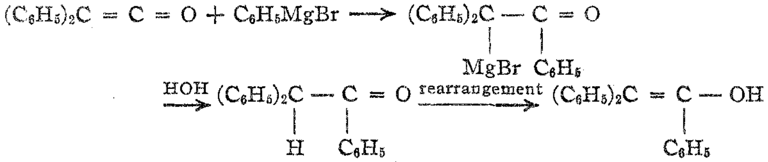
The characteristic grouping of the ketenes is $\overset{|}{\underset{|}{C}} = C = O$. Superficially they may be regarded as unsaturated ketones. However, practically all their reactions are satisfactorily explained as involving primary addition to the ethylenic linkage. A few isolated reactions have been explained by assuming addition to the carbonyl group. Staudinger and his co-workers who have given to chemistry almost all of our present knowledge of ketenes, prefer to regard the carbonyl group in ketenes as essentially unlike the carbonyl group in aldehydes and ketones, and have explained all reactions of the ketenes on the basis of initial addition to the ethylenic linkage.

A search of the literature has disclosed the fact that there are no known cases in which the Grignard reagent combines directly with an ethylenic linkage. The work of Kohler and his co-workers,[1] Reynolds,[2] and Blaise and Courtot[3] on the interaction of the Grignard reagent and unsaturated carbon compounds indicates an apparent addition to the ethylenic linkage. In all these cases, however, we are dealing with 1,4-addition, and the apparent 1,2-addition to the ethylenic linkage is due to the rearrangement of the enol that results when the addition product is decomposed by acids. Attempts by Blaise[4] to bring about a reaction between the Grignard reagent and compounds having an ethylenic linkage but affording no opportunity for 1,4-addition were unsuccessful.

Apparently, then, we are concerned here with a so-called impossible reaction. On the one hand, the general reactions of ketenes demand that the Grignard reagent add to the ethylenic linkage. On the other hand, the Grignard reagent has not been known to add to an ethylenic linkage. Staudinger[5] carried out the reaction between diphenyl ketene and phenyl magnesium bromide, and obtained triphenyl-vinyl alcohol. The formation of this compound, however, throws no light on the mechanism of the reaction. The Grignard reagent may have added either to the carbonyl group, as in the case of aldehydes and ketones, or, as Staudinger prefers to explain the reaction, to the ethylenic linkage.



$$(C_6H_5)_2C = C = O + C_6H_5MgBr \longrightarrow (C H_5)_2C = \underset{C_6H_5}{\underset{|}{C}} - OMgBr \xrightarrow{HOH} (C_6H_5)_2C = \underset{C_6H_5}{\underset{|}{C}} - OH \qquad (I).$$



$$(C_6H_5)_2C = C = O + C_6H_5MgBr \longrightarrow (C_6H_5)_2\underset{MgBr}{\underset{|}{C}} - \underset{C_6H_5}{\underset{|}{C}} = O$$

$$\xrightarrow{HOH} (C_6H_5)_2\underset{H}{\underset{|}{C}} - \underset{C_6H_5}{\underset{|}{C}} = O \xrightarrow{\text{rearrangement}} (C_6H_5)_2C = \underset{C_6H_5}{\underset{|}{C}} - OH \qquad (II).$$

Obviously the formation of triphenyl-vinyl alcohol can be explained satisfactorily by either mode of addition. It is pertinent to remark at this point, that Staudinger obtained the same product by the use of 2 or 3 molecules of phenyl magnesium bromide and the application of heat.

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[1] *Am. Chem. J.*, 31, 642 (1904), etc.

[2] *Ibid.*, 46, 198 (1911).

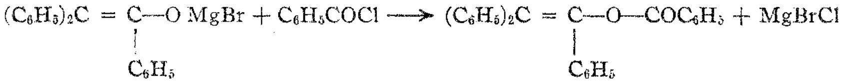
[3] *Compt. rend.*, 140, 370 (1905).

[4] *Ibid.*, 132, 38 (1901).

[5] *Ann.*, 356, 122 (1907).

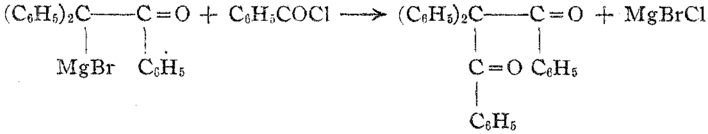
The purpose of this work was to prove conclusively the mode of addition. This has been done by treating the compound resulting from the addition of diphenyl ketene and phenyl magnesium bromide with benzoyl chloride, and identifying the resulting compound.

If addition takes place as represented in (I) the magnesium addition product should give with benzoyl chloride, the benzoate of triphenyl-vinyl alcohol.



$$(C_6H_5)_2C = \underset{\underset{C_6H_5}{|}}{C}—O\,MgBr + C_6H_5COCl \longrightarrow (C_6H_5)_2C = \underset{\underset{C_6H_5}{|}}{C}—O—COC_6H_5 + MgBrCl$$

If addition takes place as represented in (II) the magnesium addition product should give with benzoyl chloride a 1,3-diketone, diphenyl-dibenzoyl-methane.



$$(C_6H_5)_2\underset{\underset{MgBr}{|}}{C}——\underset{\underset{C_6H_5}{|}}{C}=O + C_6H_5COCl \longrightarrow (C_6H_5)_2\underset{\underset{\underset{\underset{C_6H_5}{|}}{C=O}}{|}}{C}——\underset{\underset{C_6H_5}{|}}{C}=O + MgBrCl$$

The product actually obtained and identified was the benzoate of triphenyl-vinyl alcohol, thereby proving that the Grignard reagent adds to the carbonyl group and not to the ethylenic linkage of ketenes. Deakin and Wilsmore[1] obtained very small amounts of acetone from the reaction between ketene and methyl magnesium iodide. Undoubtedly this reaction is to be explained by the addition of the Grignard reagent to the carbonyl group.

In view of the marked similarity in chemical behavior between ketenes and isocyanates, and because the Grignard reagent will add to a —N = C = linkage, it is of interest to know the mode of addition of the Grignard reagent to isocyanates. This reaction is now being studied in this laboratory.

Experimental.

Reaction between Diphenyl Ketene and Phenyl Magnesium Bromide.

Diphenyl ketene was prepared after the method of Schroeter.[2] An ethereal or petroleum ether solution of the ketene was freshly prepared for each of the several runs, the concentration being determined in the usual manner, namely, by running a measured volume of the solution into an ethereal or petroleum ether solution of aniline, and weighing the diphenyl-acetanilide formed. Because of the sparing solubility of the magnesium compounds, particularly in petroleum ether, it was found desirable to carry out the reaction in absolute ether, to use a rather dilute solution of ketene (about 0.1 *N*), and to maintain vigorous stirring throughout.

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[1] *J. Chem. Soc.*, **97**, 1968 (1905).

[2] *Ber.*, **42**, 2336 (1909). See also Staudinger, *ibid.*, **44**, 1619 (1911).

In a typical run the diphenyl ketene prepared in an atmosphere of carbon dioxide, was dissolved in absolute ether to make a solution of 500 cc. Using the pressure of the carbon dioxide, a measured volume of the ethereal solution was brought into immediate reaction with aniline to determine the concentration, and the remainder forced into a reaction flask. The reaction flask was a 2-liter filtering flask, immersed in a freezing mixture, and provided with a separatory funnel, mechanical stirrer, and entry tube for dry and purified hydrogen. An ethereal solution of 1.5 molecules of phenyl magnesium bromide was gradually added to the cold, vigorously stirred ethereal solution of ketene kept in a fresh atmosphere of hydrogen.

A flocculent, white precipitate soon formed and in a few runs the mixture became reddish colored. In an initial experiment the reaction mixture was directly treated with a slight excess of benzoyl chloride in absolute ether. On working up the reaction products of this run there was obtained, prior to the crystallization of the benzoate of triphenyl-vinyl alcohol, a small quantity of a sparingly soluble compound melting at 248°.[1] It was at first thought that this compound was a polymerization product of diphenyl ketene: namely, tetraphenyl-diketo-cyclobutane, a compound melting at 244–245°. The formation of this polymer with another was found by Staudinger to be accelerated by carbonyl containing compounds like benzoyl chloride. In consequence, the reaction mixture in subsequent runs was allowed to warm up to room temperature in the course of one hour, meanwhile being well stirred. In one of the runs, a portion of the mixture, prior to the addition of benzoyl chloride, was treated directly with dil. sulfuric acid, and triphenyl-vinyl alcohol was obtained and verified by a mixed melting-point determination.

Reaction of the Addition Compound of Diphenyl Ketene and Phenyl Magnesium Bromide with Benzoyl Chloride.—The addition compound of ketene and Grignard reagent was again cooled in a freezing mixture. To it was gradually added, with stirring, a small excess of benzoyl chloride in absolute ether. This reaction mixture, still reddish colored and containing a flocculent, white precipitate, was allowed to warm up to room temperature in the course of one hour, and then refluxed on a water-bath for 4 hours. The red color disappeared during the first half hour of heating. The ethereal mixture was cooled, treated with an excess of hydrochloric acid, and on shaking in a separatory funnel the white precipitate dissolved. The clear, slightly yellow ethereal solution was thoroughly washed, first with dil. ammonium hydroxide and then with water, dried with calcium chloride, and distilled on a water bath to drive off the ether. The resulting oil was dissolved in hot ethyl alcohol and the solution so formed allowed to cool slowly. In a few hours the solution

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[1] The temperatures recorded in this paper are uncorrected.

was completely filled with white crystals melting at 143°. A single recrystallization from ethyl alcohol gave 14.7 g. of a compound melting sharply at 153°. This substance was identified as the benzoate of triphenyl-vinyl alcohol; first, by a mixed melting point determination with some of the same compound synthesized after the manner described by Biltz,[1] and second, by saponification with alcoholic potash and identification of the triphenyl-vinyl alcohol and benzoic acid so formed.

Yield of the benzoate of triphenyl-vinyl alcohol based on 10.2 g. of diphenyl ketene, 79%.

Compound Melting at 248°.—The very sparingly soluble compound formed in small quantities was crystallized from hot ethyl alcohol. It contained neither magnesium nor halogen. The compound was found to undergo no change when refluxed for 8 hours with alcoholic potash. This proved that the compound was not the supposed polymer of diphenyl ketene, tetraphenyl-diketo-cyclobutane. Staudinger and Göller[2] found their compound melting at 244–245° to hydrolyze on even milder treatment to tetraphenyl acetone and diphenyl acetic acid.

Likewise, this proved that the compound is not diphenyl-dibenzoyl methane. This compound would be expected if the Grignard reagent had added to the ethylenic linkage of the ketene. 1,3-Diketones are readily hydrolyzed under these conditions to acids and monoketones.

Summary.

The benzoate of triphenyl-vinyl alcohol was obtained when the addition compound of diphenyl ketene and phenyl magnesium bromide was treated with benzoyl chloride. This proves that the Grignard reagent adds to the carbonyl group and not to the ethylenic linkage in ketenes.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF CASE SCHOOL OF APPLIED SCIENCE.]

THE CONSTITUTION OF THE ORGANIC NITROGEN BASES OF CALIFORNIAN PETROLEUM.

BY C. F. MABERY AND L. G. WESSON.

Received February 10, 1920.

The acid washings of crude Californian petroleum contain a mixture of organic nitrogen bases. By neutralization of the diluted acid these may be made to separate as a heavy, dark brown oil which possesses an odor closely resembling that of an empty cigar box. Californian crudes, according to Engler and Höfer,[3] have the highest nitrogen content of any known petroleum, 2.39%. Japanese oil follows closely with 2.25%

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[1] *Ber.*, 32, 655 (1899).

[2] *Ibid.*, 44, 530 (1911).

[3] "Das Erdöl," 1, 1913.