[Contribution from the Department of Chemistry of Iowa State College]

THE ELECTRONIC INTERPRETATION OF THE ETHYLENIC LINKAGE

By Henry Gilman and J. Merriam Peterson[1]

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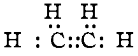
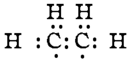
Introduction

The double bond between two carbon atoms, as in ethylene, has been variously interpreted on the basis of current electronic theories. Lewis[2] has suggested three alternative formulas for the structure of ethylene, namely, I, II and III.



$\mathrm{H:\overset{H}{\ddot{C}}::\overset{H}{\ddot{C}}:H}$

I



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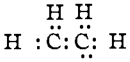
II



$\mathrm{H:\overset{H}{\ddot{C}}:\underset{\cdot\cdot}{\overset{H}{\ddot{C}}}:H}$

III

The first represents ethylene with two non-polar or covalences; the second has one covalence and two odd electrons, one on each carbon atom; and the third is the unsymmetrical and highly polar structure formed by a pair of electrons going over completely to one carbon atom.

At present, it is generally agreed among organic chemists that the ethylenic linkage is polar in one of its several possible equilibrium phases.[3] Apparently, the most preferred structures are those of Lowry[3a] and Carothers.[3b] Lowry's formula depicts the linkage between the carbon atoms in ethylene as a mixed double bond, in the sense that one bond is a covalence and the other an electrovalence. This formula (III) is commonly written thus: $H_2\overset{+}{C}—\overset{-}{C}H_2$. Carothers' formula includes the structure of Lowry as a limiting case. At the same time, he carries over what is a distinctive feature of Lewis' formula, namely, the presence of active (polar) and inactive (non-polar) molecules in an ordinary sample of ethylene. There is, however, a difference between the formulas of

[1] This paper is an abstract of a part of a thesis presented by J. Merriam Peterson in partial fulfilment of the requirements for the degree of Master of Science in Chemistry at Iowa State College.

[2] Lewis, This Journal, **38,** 762 (1916). Also "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., **1923,** p. 124; and *Trans. Faraday Soc.,* **19,** 452 (1923).

[3] (a) Lowry, *J. Chem. Soc.,* **123,** 822 (1923); *Trans. Faraday Soc.,* **19,** 488, 497, 536 (1923). (b) Carothers, This Journal, **46,** 2226 (1924). (c) Robinson and Robinson, *J. Chem. Soc.,* **123,** 532 (1923). (d) Eastman, This Journal, **44,** 438 (1922). (e) Noyes, *ibid.,* **45,** 2959 (1923). (f) Lapworth, *J. Chem. Soc.,* **121,** 416 (1922). (g) Kermack and Robinson, *ibid.,* **121,** 427 (1922). (h) Kolker and Lapworth, *ibid.,* **127,** 307 (1925). (i) Ingold and Weaver, *ibid.,* **125,** 1456 (1924). (j) Hojendahl, *ibid.,* **125,** 1381 (1924).

Objections to a polar ethylenic linkage have been raised by some. See Sidgwick, *Trans. Faraday Soc.,* **19,** 469 (1923). Also, Walker, *ibid.,* **19,** 521 (1923). Sugden, *J. Chem. Soc.,* **123,** 1861 (1923). Farmer, *ibid.,* **123,** 2531 (1923).

Lewis and Carothers. According to Carothers there may be an infinite number of active forms depending on the degree of displacement of electrons. The limits are defined, however, by the undissociated form (I) where no displacement of electrons has occurred and Form III where a pair of electrons has been completely displaced.

Experiment is the only way of deciding, in the present stage of development of the electronic theory, whether there exists an active or polar or dissociated form of ethylene and of compounds having an ethylenic linkage. Obviously a preferred reagent for such a study is a polar compound that can be used under reasonably variable conditions and that makes it possible to estimate with some precision the kind and extent of reaction. The Grignard reagents are among such compounds. Kondyrew[4] is now investigating the conductivity of these compounds.

Accordingly, a quantitative study has been made of the reaction between some substituted ethylenic compounds and the Grignard reagent. Previously, Gilman and Crawford[5] in a corresponding study showed that there was no reaction between ethylenic hydrocarbons and ethylmagnesium iodide. Then Gilman and Shumaker[6] showed that ethylmagnesium bromide and ethylmagnesium iodide do not add to several typical disubstituted acetylenic hydrocarbons.

The results of the present study show that various organomagnesium halides do not add to some selected substituted ethylenic compounds where the substituents are insensitive to RMgX compounds.[7]

Experimental Part

The technique used in the gas analysis was essentially identical with that employed by Gilman and Crawford.[5] One improvement was made in the method of sweeping out the apparatus with dry ether. In each experiment a 50cc. Erlenmeyer flask containing about 40 cc. of ether over fresh sodium wire was connected to a small condenser that in turn was connected directly to G (see diagram on p. 555 of Ref. 5). The ether was then boiled through the condenser which was jacketed with steam. Without the use of the steam superheater it was almost impossible to prevent some cloudiness appearing at the surface of the standard solution in the tube. This cloudiness indicated moisture and was probably responsible for some of the earlier irregular results. When nearly all of the ether was boiled away, the ether-generator flask was disconnected and a

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[4] Kondyrew, *Ber.*, **58**, 459, 464 (1925). Also, Nelson and Evans, THIS JOURNAL, **39**, 82 (1917). Conant, *ibid.*, **43**, 1705 (1921).

[5] Gilman and Crawford, *ibid.*, **45**, 554 (1923).

[6] Gilman and Shumaker, *ibid.*, **47**, 514 (1925).

[7] An article has just appeared by Sugden and Whittaker [*J. Chem. Soc.*, **127**, 1868 (1925)] on the relationship between chemical constitution and some physical properties. They determined that all the ethylenic compounds examined by them contained nonpolar double bonds.

Wieland and Krause [*Ann.*, **443**, 129 (1925)] have very recently shown that no reaction takes place between the very active ethylenic linkage of biphenylene-ethylene and phenylmagnesium bromide and methylmagnesium iodide.

closed short piece of rubber tubing was used to cap the end of the delivery tube. A further precaution was observed in replacing immediately the generator flask so that only ether vapor might be drawn through any small leak in the cap during hydrolysis. A single glass tube joined the generator and the flask, thereby reducing possible leaks to a minimum.

The inverted test-tube arrangement used for testing the complete displacement of air by ether was dispensed with. This was possible when it was found that all of the air was displaced by the vapor from about 40 cc. of ether solution.

TABLE I

REACTION BETWEEN ETHYLENIC COMPOUNDS AND ETHYLMAGNESIUM BROMIDE

The *corrected* average percentage reaction is 1% lower than the listed average percentage reaction.[a]

	Av. corr. vol. of		
Ethylenic compound	C_2H_6 from 20 cc. of C_2H_5MgBr soln., cc.	C_2H_6 after reaction, cc.	Av. % reaction
Trimethylene and propylene[b]	170.2	168.7	0.8
Styrene[c]	178.9	169.8	5.0
unsym.-Diphenyl-ethylene[d]	165.4	157.5	4.8
Tetramethyldiamino-diphenyl-ethylene[e]	178.9	172.8	3.4
Tetramethyldiamino-diphenyl-propylene[e]	178.9	171.7	4.0
Allyl bromide[f]	148.8	90.0	39.6
sym.-Dichloro-ethylene[c]	148.8	145.5	2.2
Trichloro-ethylene[g]	165.4	152.7	7.7
Styryl ethyl ether[h]	165.4	156.7	5.3
β-Naphthyl ethyl ether[i]	146.8	142.3	3.0
Furan[j]	215	219.5	0
Styryl-dimethyl-amine	196.3	192.1	2.1
Allyl sulfide[c]	178.9	169.6	5.2
Thiophene[c]	178.9	169.5	5.3
Di-*p*-tolyl-dithio-ethylene[k]	165.4	151.0	8.65
Di-*p*-tolyl-disulfonethylene[l]	165.4	0.0	100
Pyridine[c]	165.4	159.1	3.8
Quinoline[m]	190.5	174.9	8.2

[a] Two cc. of pure dry ether when refluxed for 30 minutes (the time used in all of the experiments) with an aliquot part of ethylmagnesium bromide gave 147.2 cc. as the average corrected volume of ethane. Since the average volume from a corresponding aliquot part of standard ethylmagnesium bromide solution was 148.8 cc., then 1% reaction took place. The difference is very probably due to the decidedly small but equally significant amount of moisture contained in the supposedly dry pipet.

[b] The mixture of gases was obtained according to the method of Gustavson [*J. prakt. Chem.*, [2] **36**, 300 (1887)] by heating trimethylene bromide with zinc dust and 75% alcohol at 50–60°. It was purified by bubbling through phenylmagnesium bromide solution before it was passed into the refluxing standard solution of ethylmagnesium bromide. It was shown that some of the gas, after passing through the phenylmagnesium bromide solution, was cyclopropane, by the preparation of 1,3-dibromopropane.

[c] Purified by a preliminary treatment with phenylmagnesium bromide. This consisted in refluxing in ether with about three equivalents of phenylmagnesium bromide for about one hour. The mixture was then hydrolyzed by ammoniacal ammonium chloride and worked up in the customary manner.

[d] *unsym.*-Diphenyl-ethylene was prepared from benzophenone and an *excess* of methylmagnesium iodide to avoid contamination with benzophenone (Ref. 5).

[e] Prepared by F. Schulze according to the method of Freund and Mayer, *Ber.*, **39**, 1118 (1906).

When tetramethyldiamino-diphenyl-ethylene was refluxed with ethylmagnesium bromide for three hours the average percentage reaction (uncorrected) was 3.8.

[f] The considerable reaction observed with allyl bromide is undoubtedly due to the highly reactive halogen that forms magnesium bromide and an R-R compound with ethylmagnesium bromide. Späth, *Monatsh.*, **34**, 1965 (1913). Also, Gilman and King, THIS JOURNAL, **47**, 1136 (1925), and André, *Bull. soc. chim.*, [4] **9**, 192–195 (1911).

[g] It is probable that some reaction took place with the chlorine atoms. Compounds having several halogens on a carbon atom undergo ready reaction with RMgX compounds.

[h] Prepared according to the method of Erlenmeyer, *Ber.*, **14**, 1868 (1881).

[i] The β-naphthyl ethers have more reactive ethylenic linkages than the alpha derivatives.

[j] This unusual result may be due to a small amount of the low boiling furan that was not removed by the concd. sulfuric acid and so came over with ethane. The sulfuric acid was very black and contained a black precipitate, indicating charring of furan. When furan was added to the ethylmagnesium bromide a white precipitate formed that was appreciably soluble in ether. This was the only evidence of reaction and it may indicate merely the formation of an etherate with the Grignard reagent.

[k] Prepared by W. B. King according to the method of Fromm and Siebert, *Ber.*, **55**, 1014 (1922).

[l] Prepared by J. B. Shumaker according to the method of Fromm and Siebert, *Ber.*, **55**, 1014 (1922).

Unqualifiedly a complete reaction took place between the di-*p*-tolyl-disulfonethylene and ethylmagnesium bromide. The nature of this reaction is as yet unknown. It must be remembered that we are dealing here with a conjugated system and that RMgX compounds add with ease to such systems. However, in all such cases the addition to the ethylenic linkage is only apparent because it has been shown to involve preliminary 1,4 addition and then rearrangement of the enol formed on hydrolysis. (See Ref. 5.) Studies are now in progress on the reaction of such unsaturated sulfones with the Grignard reagent.

[m] The quinoline used was apparently not pure. When twice as much quinoline was added in corresponding runs to the same amount of ethylmagnesium bromide used in the 8.2% reaction, the observed reaction was 17.3%.

The Reaction between 1,1-Diphenyl-ethylene and Compounds with an -MgX Group Attached to Oxygen, Sulfur and Nitrogen.—The gas analysis obviously could not be used with these organomagnesium halides. However, very good approximation of any reaction could be made by standardizing another method with ethylmagnesium bromide which does not react with 1,1-diphenyl-ethylene.

It was previously[5] shown that a relative analysis of 1,1-diphenyl-ethylene in ether could be made by a rapid titration with standard bromine-benzene or bromine-carbon tetrachloride solution. First, check analyses were made of a mixture of ethylmagnesium bromide and 1,1-diphenyl-ethylene after three hours of refluxing. The average volume of standard bromine solution required for an aliquot part of the dry ether solution after hydrolysis was 26.2 cc. Under identical conditions the volume of bromine solution required after an aliquot part of ethylmagnesium bromide had been refluxed with butoxymagnesium iodide (n-C_4H_9OMgI) was 26 cc. Accordingly, the average percentage reaction here was 0.75.

In like manner, the average percentage reaction with p-tolylmercaptomagnesium iodide ($CH_3C_6H_4SMgI$) was 4.8; and the average percentage reaction with methylaniline magnesium bromide ($C_6H_5N(CH_3)(MgBr)$) was zero.

Admittedly the method is only approximate, because despite all extra precautions it is difficult to preclude some bromination of the hydrolysis products of the organomagnesium halides. However, the absence of reaction with these compounds was confirmed in another way. Large quantities of the reactants were used and then after the refluxing, the 1,1-diphenyl-ethylene was recovered in large part, even though a liberal excess of RMgX compound was taken.

The Reaction between 1,1-Diphenyl-ethylene and Ethylzinc Iodide.—Fifteen g. of 1,1-diphenyl-ethylene was refluxed for three to four hours with two molecular equivalents of ethylzinc iodide. After hydrolysis by water, the ether extracts were dried and then distilled. Eight g. of 1,1-diphenyl-ethylene was recovered. In a corresponding run, 7.5 g. was recovered.

A blank run was then made in which 15 g. of 1,1-diphenyl-ethylene was refluxed in ether with a very small quantity of zinc dust corresponding to that present in the ethylzinc iodide solutions used previously. On treatment of the product in the same manner, 8.8 g. of 1,1-diphenyl-ethylene was recovered.

Conclusions

The results show that there is no polar form of the ethylenic linkage in so far as a reaction with organomagnesium halides is concerned.[5] A number of objections immediately suggest themselves.

First, is the method sufficiently sensitive to detect a small concentration of active molecules? Lewis[2] has said that no one of his three formulas expresses the average state of ethylene and that "the great majority of molecules must be nearest to the first structure"—the undissociated form (I). Carothers[3b] expresses a like idea when he says that the dissociated forms "are assumed to be capable of only momentary existence so that the actual concentration of the active forms is always small." However, if we agree with Carothers that an equilibrium exists between the active and inactive forms, then an appreciable reaction should be observed with extensive refluxing since there is no basis for a belief that dissociation will take place between the carbon-carbon linkage formed when the RMgX compound adds to the ethylenic linkage. When tetramethyl-diamino-diphenyl-ethylene was refluxed for 30 minutes with sufficient ethylmagnesium bromide to react with all of it, the uncorrected average percentage of reaction was 3.4. Under corresponding conditions the reaction was 3.8% after refluxing had been continued for three hours. Also, Gilman and Crawford[5] found no apparent reaction when 1,1-diphenyl-ethylene was refluxed for 35 hours with 6 equivalents of ethylmagnesium iodide.

Second, are the compounds studied sufficiently representative to warrant the conclusion that an ethylenic linkage will not add the Grignard reagent? Robinson and Robinson[3c] say that ethylene should be represented after Formula I with covalences. However, they state that "If the symmetrical character of ethylene is disturbed by substitution, the induced polar effects may become so considerable that the unsaturated group simulates the behavior of the carbonyl group of a ketone. The bond is then clearly polarized but, if chemical behavior counts for anything, the extent to which the covalences are replaced by electrovalences is variable." It might be impracticable to carry out fully this suggestion. Admittedly, the critical test would rest with a substituted ethylenic compound such that the substituents on one carbon induced a maximum repulsion of electrons and the substituents on the other carbon atom induced a maximum attraction of electrons.

What has been done is to take ordinarily accessible compounds, the substituents of which should induce some polar effects. The range of compounds for a study of this kind is circumscribed because of the extraordinary reactivity of the Grignard reagent towards practically all groups in organic molecules. Furthermore, it must be remembered that not a single case has been found in the literature where the Grignard reagent has been proved to add to an ethylenic linkage. Many ethylenic compounds with an unusual variety of substituents have been treated with the Grignard reagent. The apparent absence of a proof of the addition of RMgX to the ethylenic linkage of these many compounds merits citation as supplementary proof.

Third, have the RMgX compounds been sufficiently varied? There are inherent limitations to the kind of Grignard reagents that can be used in a quantitative study involving gas analysis.[8] Ethylmagnesium bromide and ethylmagnesium iodide have been used.[5,6] In addition, phenylmagnesium bromide, in liberal excess and with protracted digestion, was used actually to purify some of the compounds in the way of removing hydroxyl and carbonyl compounds.[5] The compounds having an -MgX group attached to oxygen, nitrogen and sulfur also showed no reaction. Ethylzinc iodide, a typical reactive organometallic compound, showed no reaction. It is doubtful whether there are any organometallic halides more reactive than those of magnesium and zinc. There would be no object in trying other Grignard reagents in the sense that all organomagnesium halides are held to be completely polar.[4]

[8] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45**, 150 (1923).

Fourth, have the conditions been sufficiently varied? Carothers[3b] says, "The extent of dissociation under any given set of conditions is assumed to be determined..... for any given compound by the temperature, concentration, nature of the medium, etc." The temperature and concentration have been varied.[5] The highly reactive nature of the Grignard reagent permits of limited variations in the kind of medium. Ethers, sulfides, hydrocarbons and tertiary amines are the chief media that can be employed. It is undoubtedly true that RMgX compounds are polarized in solvents other than ether, but they are polarized in ether.[4] Of more serious moment is the effect of ether as a medium on the concentration of the active forms of the ethylenic compounds. A recent pertinent illustration is the work of Kolker and Lapworth.[3h] They have made the noteworthy observation that bisulfites will add to ethylenic hydrocarbons. Hitherto such addition has only been held to be possible when the ethylenic linkage was in the alpha position with respect to a carbonyl, cyano or like group. They stress the importance of very intimate contact by emulsifying with the aid of purified diatomaceous earth. In the present work, the factor of solubility is of little import because of the ready solubility of both ethylenic and RMgX compounds in ether. It is possible that some catalysts might increase a low concentration of active molecules. Catalytic effects were not studied.[9]

A study is in progress of the reaction between organomagnesium halides and variously substituted anils to determine if it is possible to "invert" the polarities of carbon and nitrogen, so that the –MgX group will add to the carbon of the =C=N— linkage instead of to nitrogen.

Summary

It has been shown that organomagnesium halides do not add in ether solution to substituted ethylenic compounds. Under the conditions of the experiments, there appear to be no active or polar forms of the ethylenic linkage, or the concentration of active forms is extremely small, or the active forms are not sufficiently active to add RMgX compounds.

AMES, IOWA

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[9] In an article that has just appeared, Job and Reich [*Bull. soc. chim.*, **37**, 817–818 (1925); see also *Compt. rend.*, **179**, 330–332 (1924); **177**, 1439–1441 (1923)] have found that nickel chloride does act catalytically to cause phenylmagnesium bromide to react with ethylene. The mode of reaction is not clear. They attribute the formation of one of their products to the addition of the hypothetical HMgBr to the double bond in ethylene. They do not explain any of the other products as being due to the addition of phenylmagnesium bromide to the double bond in ethylene.

Some time ago B. Toubes and C. H. Meyers showed in this Laboratory that ethylene when passed through a very powerful silent electric discharge directly into phenylmagnesium bromide underwent no reaction.