washed free of mineral acid and dried, and the solvent was removed. The residue was refluxed for one hour with 0.5 g. of potassium hydroxide in 20 ml. of ethanol; the reaction mixture, after being cooled and acidified, was extracted with ether. The dried ether solution was freed of solvent, leaving a red, oily acid residue (0.73 g., 84%), which was completely soluble in sodium bicarbonate solution but which could not be characterized at this stage because of its instability.

Oxidation of Heliopsin.—To a stirred suspension of 2.0 g. of heliopsin in 200 ml. of water, maintained at 50°, 12.5 g. of finely powdered potassium permanganate (equivalent to 12 moles of oxygen) was added in small portions. As soon as the reaction mixture had become colorless, the manganese dioxide was filtered and washed thoroughly with warm water. The combined aqueous filtrates were concentrated down to 20 ml. and made acid to congo red with sulfuric acid. The solution was steam distilled to remove completely the volatile acids and extracted with ether in a continuous extractor for 66 hours. The ether solution was freed of solvent, and the partly crystalline residue was subjected to sublimation in a micro-sublimator. The colorless solid subliming at 100–110° (15 mm.) weighed 1.18 g. and melted at 185–186° dec.

Anal. Calcd. for $C_2H_2O_4$: neut. equiv., 45. Found: neut. equiv., 43.

The substance (72%, 2.17 moles) was identified as anhydrous oxalic acid by a mixture melting point determination with an authentic specimen (m.p. 186–187° dec.).

The sublimation residue, after recrystallization from ethyl acetate, yielded 0.93 g. of colorless crystals, m.p. 188–189°.

Anal. Calcd. for $C_4H_6O_4$: neut. equiv., 59. Found: neut. equiv., 58.

The substance was identified as succinic acid by a mixture melting point determination, m.p. 188.0–188.5°, and by preparation of the di-*p*-phenylphenacyl ester, m.p. 208°. An additional 190 mg. of succinic acid (total yield 78%, 1.56 moles) was obtained from the ethyl acetate mother liquors, together with a small amount of polymerized material.

The solution of steam-volatile acids obtained above was neutralized with sodium hydroxide solution, concentrated to a small volume on the steam-bath, and acidified to congo red with sulfuric acid. The solution was rapidly steam distilled until all material acid to congo red had distilled over. The distillate was neutralized with sodium hydroxide solution, the neutral solution was evaporated to dryness, and the *p*-phenylphenacyl ester was prepared. It melted at 110°, and a mixed melting point determination with authentic *p*-phenylphenacyl acetate, m.p. 110°, showed no depression.

The distillation residue was neutralized with sodium hydroxide solution, concentrated on the steam-bath to 10 ml., acidified to congo red with sulfuric acid, and extracted with ether in a continuous extractor. The ether solution was dried and freed of solvent. The crystalline residue sublimed completely at 90–95° (15 mm.), and two recrystallizations from petroleum ether (b.p. 60–70°) gave 642 mg. (73%) of colorless feathery needles, m.p. 107°, containing nitrogen.

Anal. Calcd. for $C_6H_{11}NO_3$: N, 9.66; neut. equiv., 145. Found: N, 9.62; neut. equiv., 145.

The substance was identical with a synthetic sample of N-isobutyloxamic acid, m.p. and mixed m.p. 107°.

Exposure of Heliopsin to Ultraviolet Light.—One gram of heliopsin was dissolved in 50 ml. of petroleum ether (b.p. 60–70°)-ethyl ether (9:1) and irradiated with an ultraviolet lamp for 3 hours, during which time the solvent evaporated completely. The resulting orange viscous oil was taken up in a few milliliters of ether, in which a very small quantity remained insoluble, and the solution was evaporated to dryness. The viscous yellow oil remaining showed an infrared spectrum identical with that of heliopsin, and was considered to be unchanged material.

BELTSVILLE, MD.

[CONTRIBUTION NO. 980 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Reaction of 1-Alkynes with Organometallic Compounds. VI.[1] The Mechanism of Reactions of Organomagnesium Compounds

BY RAYMOND E. DESSY,[2] J. H. WOTIZ AND C. A. HOLLINGSWORTH

RECEIVED MAY 7, 1956

A mechanism has been postulated for the reaction of Grignard reagents (RMgX) with acetylenes. It is consistent with the deuterium-isotope effect, measured by comparing the rates of reaction of R′—C≡C—H and R′—C≡C—D, with the observed rate laws and agrees with previously reported data on the effects of varying R, R′ and X and the form of the organomagnesium compound according to the Schlenk equilibrium.

An investigation of the reaction

$$\mathrm{RMgX} + \mathrm{R'{—}C{\equiv}C{—}H} \xrightarrow[\text{ether}]{35°} \mathrm{R'{—}C{\equiv}C{—}MgX} + \mathrm{RH} \quad (1)$$

has revealed that the rate of evolution of the hydrocarbon RH is a function of R′,[3] R and X.[4]

A correlation also had been noted between the log (reaction rate) and the decomposition potential (E_d) of the Grignard reagent.[5]

The effect of dioxane upon the rate of reaction 1 has been reported,[6] and the results have been shown to be compatible with the formulation of the Grignard reagent proposed by Schlenk.

$$2\mathrm{RMgX} \rightleftarrows \mathrm{R_2Mg} + \mathrm{MgX_2} \quad (2)$$

The reaction

$$\mathrm{R_2Mg} + 2\mathrm{R'{—}C{\equiv}C{—}H} \xrightarrow[\text{ether}]{35°} (\mathrm{R'{—}C{\equiv}C{—}})_2\mathrm{Mg} + 2\mathrm{RH} \quad (3)$$

has also been investigated,[6] and the effect of magnesium halide upon the rate of reaction reported.[7] The results have been shown to be compatible with the formulation of the Grignard reagent as indicated by equation 2.

The present paper reports the results of substituting a deuterium atom for the active hydrogen atom in the terminal acetylene used in the reactions 1 and 3. The rate laws obeyed by reactions 1 and

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(1) Part V, *J. Org. Chem.*, **21**, 1063 (1956).

(2) National Science Foundation Predoctoral Fellow.

(3) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *J. Org. Chem.*, **20**, 1545 (1955).

(4) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, THIS JOURNAL, **77**, 103 (1955).

(5) R. E. Dessy, C. A. Hollingsworth and J. H. Wotiz, *ibid.*, **77**, 4410 (1955).

(6) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *ibid.*, **78**, 1221 (1956).

(7) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

3 are also reported, and a general mechanism consistent with all of the reported facts is postulated.

Experimental

Organometallic Compounds.—The ethylmagnesium bromide (Br/Mg = 1.08) and diethylmagnesium (Br/Mg = 0) were the same reagents used in references 3 and 6, respectively.

Hexyne-1.—This compound was prepared in the same manner as described in reference 3.

1-Hexyne-d_1.—To a solution of 0.25 mole (5.75 g.) of sodium in 150 cc. of liquid ammonia was slowly added 1-hexyne (approx. 0.3 mole) until the characteristic blue color disappeared. The solvent was removed with a stream of dry nitrogen, and the resulting free-flowing white powder was subjected to a vacuum of 5 mm. for eight hours. The sodiohexyne was stored in sealed ampoules under a nitrogen atmosphere until needed. Yields of about 65%, based on the amount of hexyne-1 used, were obtained.

To 0.22 mole (4.4 cc.) of deuterium oxide (99.5% pure, Stuart Oxygen Co., San Francisco, Calif.) was slowly added 0.184 mole (19.5 g.) of sodiohexyne. An ice-bath was used to moderate the temperature. It was necessary to add 15.0 cc. of n-butyl ether during the course of the reaction in order to maintain fluidity. The mixture was then heated, and the material boiling between 65 and 75° was collected. This was dried over anhydrous magnesium sulfate and redistilled. A total of 9.4 g. of product, b.p. 70-74°, n^{23}_{D} 1.3970, d^{22}_{4} 0.722, was obtained. The infrared spectrum indicated the presence of 1-hexyne-d_1 and 1-hexyne and the absence of any impurities.

The material was analyzed for the light isotope by a one-component analysis, employing the $\equiv$C—H stretching frequency at 3300 cm.$^{-1}$. A Perkin-Elmer model 112 infrared spectrophotometer with calcium fluoride optics was used. This indicated a concentration of 1-hexyne of 10 ± 3%. By difference the concentration of 1-hexyne-d_1 was 90 ± 3%. The yield and composition of product were similar to that found by Rabinovitch and Looney in the production of 1-propyne-d_1.[8]

Determination of Rates.—All determinations were made using 0.0235 equivalent of organometal at 1.0 N concentrations and were measured in the gasometric apparatus previously described.[3] The organometal and the proper amount of ether were added to the reaction vessel and brought to reflux. The terminal acetylene was then added, and the rate of evolution of ethane measured. All reactions and transfers were made in an inert atmosphere of nitrogen, and all transfers were made by hypodermic techniques.

Discussion

Deuterium Isotope Effect.—1-Hexyne-d_1 (C_4H_9—C$\equiv$C—D) was prepared in approximately 90% purity. The only contaminant was 1-hexyne. Its rate of reaction with equivalent amounts of ethylmagnesium bromide or diethylmagnesium was determined employing 1.0 N solutions of reactants in ether at the boiling point of the mixture. Plots of volume of evolved gas *versus* time for these reactions, along with the corresponding reactions of 1-hexyne, are shown in Fig. 1. Relative reactivities were determined from half-lives by assigning a value of 100 to the reaction of 1-hexyne with ethylmagnesium bromide. The results are given in Table I.

TABLE I

RELATIVE RATES OF REACTION OF $C_2H_5MgBr^a$ AND $(C_2H_5)_2Mg^b$ WITH C_4H_9—C$\equiv$CH AND C_4H_9—C$\equiv$CD

Organometal	Acetylene	Relative reactivity
C_2H_5MgBr	C_4H_9—C$\equiv$CH	100
C_2H_5MgBr	C_4H_9—C$\equiv$CD	23
$(C_2H_5)_2Mg$	C_4H_9—C$\equiv$CH	300
$(C_2H_5)_2Mg$	C_4H_9—C$\equiv$CD	107

[a] Br/Mg ratio = 1.08.[1] [b] Br/Mg ratio = 0.[6]

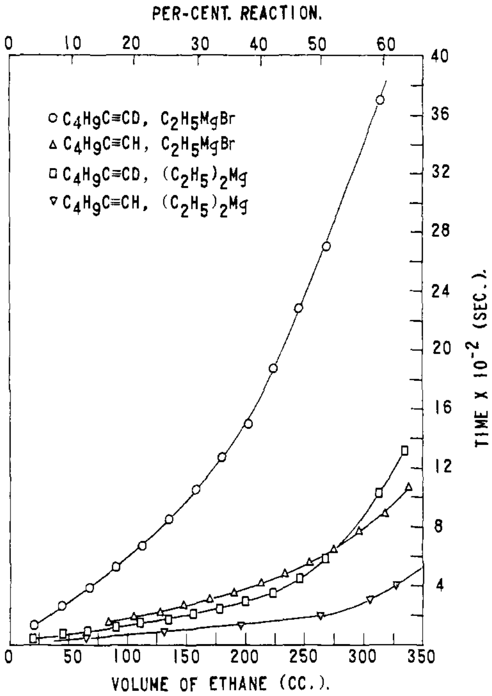

Fig. 1.—Volume of gas evolved and per cent. reaction *versus* time for the reactions of 1-hexyne and 1-hexyne-d_1 with ethylmagnesium bromide and diethylmagnesium.

The substitution of a deuterium atom for the hydrogen atom of a terminal acetylene reduces the reactivity with ethylmagnesium bromide by a factor of at least 4.3.

It can be shown[9] that the maximum isotope effect, which corresponds to no bonding to the hydrogen or deuterium in the activated complex, can be calculated from

$$k_H/k_D = \exp\,[E_0(H) - E_0(D)]/RT \qquad (4)$$

where k_H and k_D are the respective rate constants, or relative rates, $E_0(\ )$ is the zero-point energy of the bond to deuterium or hydrogen in the ground state, R is the gas constant, and T is the absolute temperature. The zero-point energies may be estimated from the stretching frequencies of the respective bonds as determined from infrared spectra. At 35° substitution of these values in equation 4 leads to k_H/k_D(max.) = 5.2.

The fact that an isotope effect is observed in the reactions of ethylmagnesium bromide indicates that the cleavage of the $\equiv$C—H is involved in the rate-determining step. Because the observed isotope effect and the maximum theoretical isotope effect are relatively close, the hydrogen must be very weakly bound in the transition state. This could arise only if the $\equiv$C—H was almost completely broken in the transition state and the new bond to the alkyl group of the Grignard reagent had just begun to form. The data indicate then that the reaction of a terminal hydrogen should be considered as at least a three-center process.

The substitution of a deuterium atom for the hydrogen atom of the terminal acetylene reduces the reactivity with diethylmagnesium by a factor of at least 2.8. Figure 1, however, indicates that the

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(8) B. S. Rabinovitch and F. S. Looney, THIS JOURNAL, **75**, 2652 (1953).

(9) K. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

effect is greater in the latter half of the reaction than it is in the initial half.

These data should be compared with those reported in the literature concerning the deuterium isotope effect upon the neutralization of carbanions. No isotope effect was noted when methyl Grignard reagent reacted with a mixture of water and deuterium oxide.[10] Wiberg[11] reports that the hydrolysis of alkyl and aryl Grignard reagents with a mixture of methanol and deuteromethanol indicates a small inverse isotope effect. These results would indicate that in the reaction of Grignard reagents with water or methanol there is essentially no change in the difference in zero-point energy in going to the activated complex.

Kinetics.—Only three investigations concerning the kinetics of Grignard reactions have been reported. In 1946, Brugger[12] showed that the reaction of acetone with methylmagnesium iodide in *n*-butyl ether was first order with respect to the Grignard reagent. In 1947, Swain[13] reported that the reaction of *n*-butylmagnesium bromide and benzonitrile in ether was homogeneous and second order, and Kleinfeller and Lohman,[14] in 1938, were able to show that in the reaction of ethylmagnesium bromide with acetylene the reaction was first order with respect to ethylmagnesium bromide.

It has been shown[4] that in the reaction of 1-alkynes with Grignard reagents (reaction 1) the reaction rate is independent of the concentration of products. By taking into account the relatively high concentrations employed (1 *N*) and, consequently, the non-ideality of the solutions, one may conclude from the rate data[4] that the reaction may be nearly first order with respect to each reactant. With this in mind the reactions discussed in the previous sections were investigated as to the rate laws that they obeyed.

The reactions of hexyne-1 with ethylmagnesium bromide[3] and *equilibrium* mixtures of diethylmagnesium and magnesium bromide[7] were investigated first. The concentration, c, of the hexyne at any given point during the reaction was calculated from the volume of gas evolved. Figure 2 shows plots of $1/c$, as a function of time for these reactions. It will be noted that for Br/Mg ratios greater than unity the curves are very nearly straight lines, suggesting a simple second-order reaction, with specific rate constants, k_2^*, having values of 1.7×10^{-3} and 1.4×10^{-3} liter/mole-second for Br/Mg ratios of 1.08 (Br/basic Mg = 1.15) and 1.34, respectively. For smaller values of Br/Mg the plots show considerable curvature.

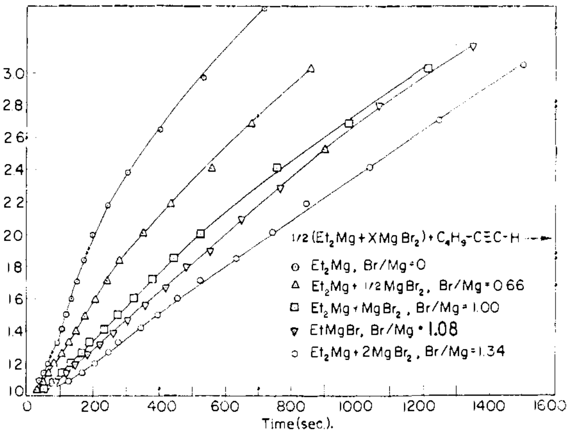

Fig. 2.—$1/c$ *versus* time for the reactions of 1-hexyne with ethylmagnesium bromide and mixtures of diethylmagnesium and magnesium bromide.

For the reaction of diethylmagnesium with hexyne[6] the data can be explained by a competitive, consecutive second-order reaction.[15] Undoubtedly more complex mechanisms would also be suitable, but a competitive, consecutive second-order mechanism is the simplest and most plausible, under the given conditions. The integrated rate law for such a reaction is

$$P_{(\text{calcd.})} = \frac{a}{k_1 - k_2}\left[(2k_2 - k_1)e^{-k_1\theta} - k_1e^{-k_2\theta}\right] + 2a \qquad (5)$$

wherein k_1 and k_2 are the specific rate constants for the first and second steps, P is the amount of gas evolved (amount of hexyne reacted), a is the initial concentration of diethylmagnesium, and the time variable θ is given by

$$\theta = \int_0^t [b - P_{(\text{expt.})}]\mathrm{d}t \qquad (6)$$

where b is the initial concentration of hexyne. θ was obtained as a function of t by graphical integration of the experimental data. Figure 3 shows, along with the experimental points, a theoretical curve for P as a function of time according to equation 5 when $k_1 = 1.3 \times 10^{-2}$ and $k_2 = 2.5 \times 10^{-3}$ liter/mole-second, using an induction period of 25 seconds.[16]

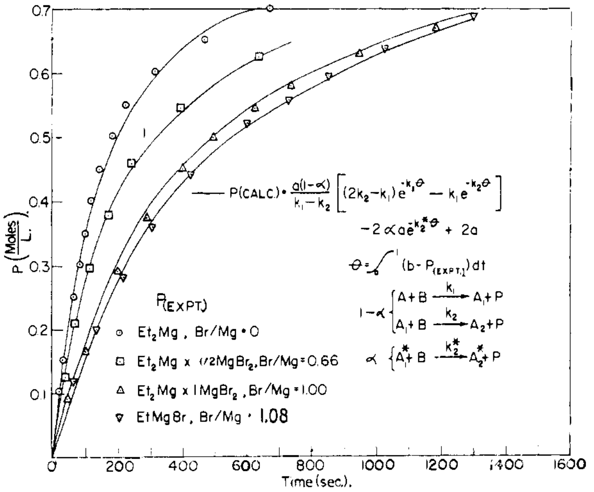

Fig. 3.—Theoretical curves and experimental points for the reactions of 1-hexyne with ethylmagnesium bromide and mixtures of diethylmagnesium and magnesium bromide.

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[10] M. Orchin, I. Wender and R. A. Friedel, *Anal. Chem.*, **21**, 1073 (1949).

[11] K. Wiberg, THIS JOURNAL, **77**, 5987 (1955).

[12] J. E. Brugger, M.S. Thesis, Pennsylvania State College, 1946.

[13] C. G. Swain, THIS JOURNAL, **69**, 2307 (197).

[14] H. Kleinfeller and H. Lohman, *Ber.*, **71**, 2608 (1938).

[15] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953.

[16] In almost all cases an induction period was noted. This was apparently due to a slight solubility of the evolved gas and to the period required for complete mixing of the reactants.

The reactions for which the ratio Br/Mg is less than unity were fitted by assuming that two independent reactions are involved, one a competitive, consecutive second-order reaction and the other a simple second-order reaction. In this case the integrated rate law for the evolution of gas becomes

$$P = \frac{a(1 - \alpha)}{k_1 - k_2} [(2k_2 - k_1)e^{-k_1\theta} - k_1e^{-k_2\theta}] - 2\alpha a e^{-k_2^*\theta} \tag{7}$$

where α is a parameter which indicates the fraction of the over-all reaction that takes place by the simple second-order reaction, a is the initial concentration of organometallic expressed as diethylmagnesium, and the other symbols are as previously described. Figure 3 also shows the experimental points and the theoretical curves according to equation 7 with $k_1 = 1.3 \times 10^{-2}$, $k_2 = 2.5 \times 10^{-3}$, $k_2^* = 1.4 \times 10^{-3}$ (liter/mole-second), and $\alpha = 0.35$ for Br/Mg = 0.66 and $\alpha = 0.65$ for Br/Mg = 1.0, with induction periods of 35 seconds.

The plot for ethyl Grignard reagent in Fig. 2 is nearly linear with a slope corresponding to $k_2^* = 1.7 \times 10^{-3}$ liter/mole-second, indicating simple second-order kinetics. This is in agreement with the previously mentioned data in which it was shown that variations in the initial concentrations indicated that the reaction was approximately first order with respect to each reactant. Slightly better fits of these data are obtained, however, with equation 7 with $k_1 = 1.3 \times 10^{-2}$, $k_2 = 2.5 \times 10^{-3}$, $k_2^* = 1.4 \times 10^{-3}$ (liter/mole-second) and $\alpha = 0.75$, with an induction period of 50 seconds. Thus, all runs can be fit to equation 7 with the same set of rate constants by choosing the proper value of α for each run.

The reaction of 1-hexyne-d_1 with ethylmagnesium bromide followed approximate second-order kinetics with $k_2^* = 0.4 \times 10^{-3}$ liter/mole-second (*cf.* hexyne, where $k_2^* = 1.7 \times 10^{-3}$). The reaction of 1-hexyne-d_1 with diethylmagnesium was fit to a competitive, consecutive second-order reaction with $k_1 = 0.6 \times 10^{-2}$ and $k_2 = 0.65 \times 10^{-3}$ liter/mole-second and an induction period of 35 seconds (*cf.* hexyne, where $k_1 = 1.3 \times 10^{-2}$, $k_2 = 2.5 \times 10^{-3}$). The substitution of the deuterium for hydrogen in the reaction with diethylmagnesium apparently affects the second step of the reaction to a greater extent than the first.

The relative reactivities of various terminal acetylenes with ethylmagnesium bromide and of various Grignard reagents with hexyne-1 have been previously reported,[4,3] and plots of $1/c$. *vs.* t for these reactions do not differ significantly from that of ethylmagnesium bromide with hexyne-1, indicating that the same mechanism is involved in all of the reactions of this type.

Mechanism.—A possible mechanism for the competitive, consecutive second-order reaction considered in the previous section corresponds to

$$(C_2H_5)_2Mg + C_4H_9{-}C{\equiv}CH \xrightarrow{k_1} C_4H_9{-}C{\equiv}C{-}Mg{-}C_2H_5 + C_2H_6 \tag{A}$$

$$C_4H_9{-}C{\equiv}C{-}Mg{-}C_2H_5 + C_4H_9{-}C{\equiv}CH \xrightarrow{k_2} (C_4H_9{-}C{\equiv}C{-})_2Mg + C_2H_6$$

The simple second-order reaction might correspond to

$$C_2H_5MgBr + C_4H_9{-}C{\equiv}CH \xrightarrow{k_2^*} C_4H_9{-}C{\equiv}C{-}MgBr + C_2H_6 \tag{B}$$

Simple second-order kinetics, however, can also result from a competitive, consecutive second-order reaction when the rate contant for the first step is approximately twice that of the second step. This can be seen by taking $k_1 = 2k_2$ in equation 5. This introduces the possibility that the simple second-order reaction might result from a mechanism such as

$$(C_2H_5)_2Mg{\cdot}MgBr_2 + C_4H_9{-}C{\equiv}CH \xrightarrow{k'_1} C_4H_9{-}C{\equiv}C{-}Mg{-}C_2H_5{\cdot}MgBr_2 + C_2H_6 \tag{C}$$

$$C_4H_9{-}C{\equiv}C{-}Mg{-}C_2H_5{\cdot}MgBr_2 + C_4H_9{-}C{\equiv}CH \xrightarrow{k'_2} (C_4H_9{-}C{\equiv}C{-})_2Mg{\cdot}MgBr_2 + C_2H_6$$

where $k_1' = 2k_2' = 2k_1^*$. This would involve a formulation of the Grignard reagent as proposed by Jolibois, *e.g.*, $R_2Mg{\cdot}MgX_2$.[17]

It can be shown also that a simple second-order rate law would be obtained from a combination of mechanisms B and C if $k_1' \cong 2k_2' \cong 2k_2^*$. This would be true regardless of whether or not an equilibration such as

$$(C_2H_5)_2Mg{\cdot}MgBr_2 \rightleftarrows 2C_2H_5MgBr \tag{8}$$

exists during the reaction with hexyne. It appears that it would be extremely difficult to distinguish the species in equation 8 by kinetic methods.

One is strongly tempted to interpret $(1 - \alpha)$ as the fraction of organometallic compound that is in the form of diethylmagnesium. It must be pointed out, however, that equation 7 is based on the assumption that mechanism A is independent of mechanism B and/or C. This assumes that such reactions as

$$2C_4H_9{-}C{\equiv}C{-}Mg{-}C_2H_5 \rightleftarrows (C_4H_9{-}C{\equiv}C{-})_2Mg + (C_2H_5)_2Mg \tag{9}$$

do not occur to a significant extent during the reaction with hexyne and that equilibria such as

$$2C_2H_5MgBr \rightleftarrows (C_2H_5)_2Mg + MgBr_2 \tag{10}$$

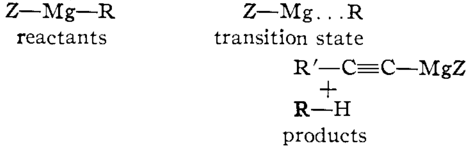
do not shift appreciably during the reaction. It may be, therefore, that α is nothing more than an empirical parameter without simple significance.

Despite the fact that the exact species reacting in the Grignard reagent has not been determined, it is possible to propose a mechanistic picture which is consistent with all of the facts.

The Grignard reagent may be most simply represented as

$$R_2Mg + MgX_2 \rightleftarrows R_2Mg{\cdot}MgX_2 \rightleftarrows 2RMgX \tag{11}$$

The exact position of these equilibria is not known. The reaction of the organometallic compound with an acetylene may be diagrammed as



$$\underset{\text{reactants}}{\begin{matrix} R'{-}C{\equiv}C{-}H \\ + \\ Z{-}Mg{-}R \end{matrix}} \rightleftarrows \underset{\text{transition state}}{\begin{matrix} R'{-}C{\equiv}C\ldots H \\ \vdots \quad\ \vdots \\ Z{-}Mg\ldots R \end{matrix}} \longrightarrow \underset{\text{products}}{\begin{matrix} R'{-}C{\equiv}C{-}MgZ \\ + \\ R{-}H \end{matrix}} \tag{12}$$

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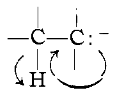
[17] P. Jolibois, *Compt. rend.*, **155**, 353 (1912).

in which the bond breaking is more important to the formation of the transition state than is bond making.[18]

This concept is in agreement with the known facts concerning the reaction: 1. **Effect of Changing R.**—It has been shown that in the reactions of various Grignard reagents with hexyne-1,[4] the rate of reaction is proportional to the number of β-hydrogens of R. It has been proposed that this represents a stabilization of the incipient carbanion, R:$^-$, by anionic hyperconjugation[19]



2. **Effect of Changing R′.**—In the reactions of ethylmagnesium bromide with various terminal acetylenes,[3] the rate of reaction is dependent upon the electron-withdrawing power (inductive effect) of R′ when steric factors are not important. Such inductive effects would render the terminal acetylenic hydrogen more labile, increasing the rate of reaction. However, when R′ is capable of preventing the "close approach" of the two reactants, because of steric factors, the formation of the transition state would be more difficult, thus decreasing the observed rate of reaction.

3. **The Deuterium Isotope Effect.**—A large deuterium isotope effect is noted in such reactions, indicating that the cleavage of the $\equiv$C—H bond is involved in the rate-determining step and that bond breaking is more important than bond making in determining the activation energy.

4. **The Kinetic Picture.**—The rate laws obeyed by the various reactions are in agreement with the proposed reaction mechanism and with the equilibrium picture illustrated by equation 11.

5. **The Effect of Dioxane.**—The results obtained by adding dioxane to solutions of ethylmagnesium bromide[6] are in agreement with equation 11, indicating a shift in the equilibrium to the left. It was found that the rate of reaction of hexyne-1 with ethylmagnesium bromide in the presence of dioxane was dependent upon both the concentration of dioxane used and the time of contact between the Grignard reagent and the dioxane. The reactivity of such mixtures eventually approached that of diethylmagnesium.

6. **The Effect of Magnesium Bromide.**-The results obtained by adding magnesium bromide to solutions of diethylmagnesium[7] are in agreement with equation 11, indicating a shift in equilibrium to the right. It was found that the rate of reaction of hexyne-1 with diethylmagnesium in the presence of magnesium bromide was dependent upon the concentration of magnesium bromide used and on the time of contact between the Grignard reagent and the magnesium bromide. The reactivity of solutions with Br/Mg ratios of unity eventually approached that of ethylmagnesium bromide.

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[18] It should be noted that the present information does not exclude a three-center reaction, in which the first products are the alkane and an ion pair, provided that the collapse of the latter to give a covalent bond takes place rapidly, and is not in any way rate determining.

[19] The term hydridization was suggested for such resonance by J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, Abstracts of Papers, American Chemical Society Meeting, Kansas City, Mo., 1954, page 11N. Recently Seubold [*J. Org. Chem.*, **21**, 156 (1956)] has published a paper on the infrared absorption spectra of some sodium alkoxides, in which he describes some additional evidence for such anionic hyperconjugation.

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Organic Sulfur Derivatives. I. Addition of Mercaptoacetic Acid to Long-chain Monounsaturated Compounds

BY N. H. KOENIG AND DANIEL SWERN

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Sulfides are formed by the free-radical addition of mercaptoacetic acid to oleic acid, methyl oleate, methyl ricinoleate or 10-undecenoic acid. Diesters have been prepared by esterifying the product from oleic acid, 9(10)-(carboxymethylthio)-stearic acid and by treating *n*-butyl oleate with ethyl mercaptoacetate. The addition products are centrally branched long-chain molecules, except for 11-(carboxymethylthio)-undecanoic acid, and can be purified by separating the unreacted linear starting materials as urea complexes. In developing optimum reaction conditions, the yield of urea complexes serves as a key method of determining the extent of reaction. Supporting evidence for the structure of the products is provided by molecular refraction, infrared and X-ray data.

The patent literature contains many references to reactions of fats and their long-chain derivatives with sulfur, hydrogen sulfide, mercaptans, sulfur halides and phosphorus sulfides. The products have commercial value as lubricant additives, coatings and rubber substitutes, but little is known about their structure and chemistry. The aim of this program is to prepare and study clearly defined sulfur derivatives, starting with well characterized fatty compounds. The reaction selected for initial study is the addition of a reactive mercaptan (mercaptoacetic acid) to the olefinic linkage of monounsaturated fatty acids or their esters. The addition of mercaptans to olefins is a well known reaction and generally follows a free-radical mechanism.[2]

Present Investigation.—Oleic acid reacts with mercaptoacetic acid to give a sulfide (thioether),

[1] A laboratory of the Eastern Utilization Research Branch, Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

[2] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940); J. I. Cunneen, *J. Chem. Soc.*, 36 (1947); J. T. Hackmann and R. Berkenbosch, *Rec. trav. chim.*, **68**, 745 (1949); M. S. Kharasch, W. Nudenberg and G. J. Mantell, *J. Org. Chem.*, **16**, 524 (1951); B. Smith and S. Hernestam, *Acta Chem. Scand.*, **8**, 1111 (1954).