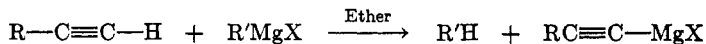


THE REACTION OF 1-ALKYNES WITH ORGANOMETALLIC COMPOUNDS. III.¹ THE REACTIVITY OF ETHYLMAGNESIUM BROMIDE TOWARD SOME MONOSUBSTITUTED ACETYLENES

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An investigation of the reaction



revealed that the rate of evolution of gaseous R'H is dependent upon the nature of R' and X (1). The relative reactivity of 100 was assigned to the rate of the reaction of equimolar quantities of ethylmagnesium bromide with hexyne-1 at the boiling point of their ether solution (1). This paper reports the relative reactivities, based on half-lives, of ethylmagnesium bromide toward some substituted terminal acetylenes. The quantity of reagents was usually 0.02 mole; concentrations were 1 molar. Values were obtained with a precision of $\pm 2.5\%$ (average deviation from the mean) and are listed in Table I. The effect of some co-solvents on the relative reactivity of hexyne with ethylmagnesium bromide was also observed.

EXPERIMENTAL

All acetylenic compounds were freshly re-distilled or recrystallized. If after the purification the relative reactivity was greater than 100, the purity of the acetylenic compound was rechecked spectroscopically, and it was found that even traces of other sources of an active hydrogen were absent. Thus, spectroscopically (infrared) pure alkynes were used.

Hexyne-1 (2), b.p. 71°, n_D^{25} 1.3968. *Heptyne-1* (2), b.p. 98°, n_D^{25} 1.4061. *Octadiyne-1,7* (2), b.p. 138°, n_D^{24} 1.4455. *5-Chloropentyne-1* (3), b.p. 113°, n_D^{25} 1.4412. *Butoxyacetylene* (4), b.p. 47° at 86 mm., n_D^{25} 1.4030. *Methyl propargyl ether* (5), b.p. 61°, n_D^{25} 1.3947. *3-Ethoxy-3-methylbutyne-1*,³ b.p. 92°. *Tertiarybutylacetylene* (6), b.p. 37°, n_D^{24} 1.3724. *Isopropenylacetylene*,³ b.p. 33°. *Propargyl bromide*,⁴ b.p. 82°, n_D^{25} 1.4912. *Phenylacetylene* (7), b.p. 50° at 27 mm., n_D^{25} 1.5464. *p-Tolylacetylene* (8), b.p. 64° at 18 mm., n_D^{25} 1.5440. *p-Bromophenylacetylene* (8), m.p. 63–64°. *p-Chlorophenylacetylene* (8), m.p. 45–46°. *Triethylamine*, b.p. 89°, n_D^{20} 1.4020, was dried over sodium wire and distilled from methylmagnesium bromide to eliminate possible contaminants such as diethylamine. *Tetrahydrofuran*, b.p. 65°, n_D^{23} 1.4063, distilled once from ferrous sulfate and once from methylmagnesium bromide.

Ethylmagnesium bromide was prepared from Baker's magnesium turnings and purified, redistilled ethyl bromide in ether (Mallinkrodt anhydrous, analytical reagent). It was stored in an amber bottle fitted with a serum cap, under nitrogen. The concentration was determined by the gas-evolution method used in the rate determinations. The proper amounts were withdrawn using a hypodermic syringe.

The apparatus used in the present study consisted of a 100-ml. round-bottomed reaction vessel, equipped with a rubber serum cap for the introduction of all reactants. For agita-

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⁴ Courtesy of the General Aniline and Film Corp., Easton, Pa.

TABLE I
 RELATIVE REACTIVITIES OF ACETYLENES TOWARDS C_2H_5MgBr

Experiment	Terminal Acetylene	Relative Reactivity
1	$C_4H_9C\equiv CH$	100
2	$C_4H_9C\equiv CH + 1 M Et_3N$	> 500
3	$C_4H_9C\equiv CH + 1 M THF$	100
4	$C_5H_{11}C\equiv CH$	106
5	$HC\equiv C-(CH_2)_4-C\equiv CH$	100
6	$Cl-(CH_2)_3-C\equiv CH$	96
7	$C_4H_9-O-C\equiv CH$	> 500
8	$CH_3O-CH_2-C\equiv CH$	165
9	$\begin{array}{c} CH_3 \\ \\ C_2H_5O-C-C\equiv CH \\ \\ CH_3 \end{array}$	45
10	$\begin{array}{c} CH_3 \\ \\ CH_3-C-C\equiv CH \\ \\ CH_3 \end{array}$	23
11	$\begin{array}{c} CH_2=C-C\equiv CH \\ \\ CH_3 \end{array}$	40
12	$BrCH_2-C\equiv CH$	unknown but > 150
13	$C_6H_5-C\equiv CH$	77
14	$p-CH_3-C_6H_4-C\equiv CH$	77
15	$p-BrC_6H_4-C\equiv CH$	92
16	$p-ClC_6H_4-C\equiv CH$	167

tion a magnetically operated stirrer was used. The evolved gas was collected in 50-ml. burettes. Otherwise the experiments were conducted as previously described (1).

DISCUSSION

The relative reactivities toward ethylmagnesium bromide of the acetylenic compounds studied thus far differ at most by a power of ten. Some interpretations of the observed differences in reactivities (Table I) are as follows:

1. The marked increase in the reaction of ethylmagnesium bromide with hexyne-1 in the presence of triethylamine (Exp. 2) is noteworthy. It is probably due to the increase in the basicity of the solvent medium which enhances the reactivity of the Grignard reagent (1) and/or the 1-alkyne, possibly by an increase in the ease of dissociation. Tetrahydrofuran as a cosolvent (Exp. 3) apparently did not change the basicity of the medium. Any differences in the steric arrangement of the ether of solvation are therefore less important than are changes in basicity. However, a more detailed study of such problems will be the subject of a separate investigation.

2. In the alkylsubstituted acetylenes any change in structure occurring on a carbon atom more than two atoms removed from triple bond has little, if any, influence on the reactivity (Expts. 4, 5 and 6). The small observed differences in the reaction rates are within the limits of our experimental error and can also be explained on the basis of the observed differences of the boiling points of the reaction mixtures. In Expt. 5, 0.02 mole of the Grignard reagent was allowed to react with 0.01 mole of the octadiyne, and the reactivity of 100 shows the complete independence of reactivity of the two triple bonds.

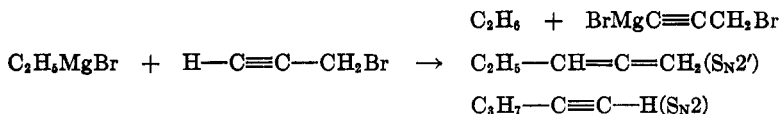
3. The electron-attracting property of oxygen is probably the reason for the increase in reactivities in Experiments 7 and 8. The availability of the acetylenic hydrogen⁵ apparently is greater in the case of the α -acetylenic ether (Exp. 7) than in the case of the β -acetylenic ether (Exp. 8). An alternate explanation of the increase in the reactivity in Exp. 7 would consider the possible increase in electron density at the triple bond because of a resonance influence of the oxygen. Such an increase in the "basicity" of the triple bond should enhance its coordination with the Grignard reagent and possibly decrease the rate of loss of the acetylenic hydrogen. Such explanations to be consistent with our findings would assume the greater influence of coordination. We reject an explanation involving coordination also on the grounds that the reactivity in Exp. 8 was still greater than 100 and in this case no reasonable resonance structure, which would increase the "basicity" of the triple bond, can be proposed. A further reason for our rejection of such an explanation can be found in the previously reported (1) experiment where the reactivity of hexyne-1 was not changed by the addition of the co-solvent hexyne-2 which could compete for the coordination of the Grignard reagent. So far, such a possible coordination was not experimentally established. However, this does not mean that the possible complexing of the acetylene with the Grignard reagent has no effect on the reactivity, but rather that the rate determining step is not appreciably affected by the electron density of the triple bond in the cases cited.

4. In expt. 9 a β -acetylenic ether was found to have a reactivity of less than 100. This can be explained on steric grounds, as two methyl groups are present on the α -carbon atom. This more than compensates for the electron attraction of the oxygen. A stereoequivalent compound which did not have the oxygen (Expt. 10) reacted at a still lower rate. The presence of only one methyl group on the α -carbon atom (Expt. 11) also decreases the reactivity. The effect of the double bond in this compound cannot be ascertained from the available data.⁶

⁵ The term "availability of the acetylenic hydrogen" is used in this paper to offer correlations for most of the observations recorded here. However, it should not be indiscriminately replaced by the term "acidity of the acetylenic hydrogen" as such an expression may have different meanings because of differences in reference standards. The term "availability" is thus a composite of several factors which influence the rate of reactions, such as "acidity," electronegativity, resonance, steric, solvation, coordination, etc. of the alkyne as well as of the "Grignard reagent."

⁶ A less likely explanation of the rate retardation in compounds having methyl groups on the α -carbon atom would recognize the electron releasing property of the methyl group which would increase the "basicity" of the triple bond. The consequences and the rejection of an increase in basicity have been discussed in Part 3. The decreased reactivity of *tert*-

5. The reaction of propargyl bromide with ethylmagnesium bromide produced less than 15% of the theoretical amount of ethane. However, the rate of evolution was rapid and a reactivity of greater than 150 was estimated, showing again the effect of the presence of an electron-attracting atom on the rate of reaction. Since only 15% of the gas was evolved, two additional reactions were performed to investigate such behavior. The addition of alcohol after the cessation of gas evolution failed to liberate any additional ethane, showing that all of the ethylmagnesium bromide was consumed. When, on the other hand, an additional amount of the Grignard reagent was added, there was only a small (less than 5%) gas evolution, showing the absence of a major source of an acidic hydrogen. The presence of an absorption band near 1950 cm^{-1} in the infrared spectrum of the reaction mixture indicated the presence of an allenic product. At least three reactions took place in Expt. 11.



The fact that the major reaction product was formed by the $\text{S}_{\text{N}}2'$ reaction is noteworthy. Although the realization that allenic compounds are formed in such a reaction (9) has been reported, it was assumed *a priori* that the Grignard reagent reacts faster with acidic hydrogen than in a "coupling reaction."

6. The rather surprising observation that ethylmagnesium bromide reacts with phenylacetylene (Expt. 13) at a lower rate than with hexyne-1 may be explained on steric grounds. The "Fisher-Taylor-Hirschfelder" molecular model of phenylacetylene shows the great resemblance to the model of isopropenylacetylene which also showed low reactivity (Expt. 11). However, most differences in reactivities of *para*-substituted phenylacetylenes can be well-explained on the basis of an inductive influence of the substituent in the *para* position. Although the methyl group (Expt. 14) does not change the reactivity, the bromine increases the reactivity somewhat (Exp. 15) and the more electronegative chlorine brings about a considerable increase in reactivity (Expt. 16). Thus, Experiment 14 seems to indicate that the presence of a methyl group will not change greatly the reactivity of the acetylene because of electronic effects (+I or +M effects). However, the methyl group is responsible for differences in reactivity when it also produces steric factors (Expts. 9, 10, 11).

On the basis of the data presented a generalization could be advanced that the reaction of acetylenes with Grignard reagents is a function of the size of the acetylene substituent and that in a given series of acetylenic compounds with the same steric requirements, the observed relative reactivities are essentially measures of the inherent activity of the terminal hydrogen. Furthermore, it seems that the availability of the hydrogen is not greatly affected by the nature of substituent which is electron releasing because of resonance or hyperconju-

butylacetylene is therefore due to steric factors. Additional points will be considered in Part 6.

gation (Expt. 14). A number of observations in which the triple bond lacked "conjugative" ability are already recorded (10-12).

SUMMARY

The relative reactivities of some substituted terminal acetylenes, $R-C\equiv CH$, with ethylmagnesium bromide have been measured and are listed in Table I. Such reactions seem to be affected by the size of the substituent. However, in compounds with the same steric requirements the reactivities are a measure of the availability of the terminal hydrogen, which is especially dependent upon the inductive effect exerted by the substituent.

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