Reaction of 1-Alkynes with Organometallic Compounds. VII.[1] Rate of Reaction of Hexyne-1 with Methyl- and Ethylmagnesium Halides in the Presence of Triethylamine

JOHN H. WOTIZ,[2] C. A. HOLLINGSWORTH, R. E. DESSY,[2a] AND LUNG CHING LIN[3]

The addition of triethylamine to ether solutions of Grignard reagents increases their reactivity toward hexyne-1. The increased reactivity is a function of the amount of the added amine, and the nature of the alkyl group and the halogen of the Grignard reagent. Triethylamine has no effect upon the rate of reaction of halogen-free diethylmagnesium with hexyne.

The rate of reaction of equivalent quantities of $RMgX$ ($R = CH_3$, C_2H_5; $X = Cl$, Br, I) with hexyne-1, $C_4H_9C \equiv C-H$, in the presence of various amounts of triethylamine cosolvent was determined. Fig. 1 represents the dependence of the relative reactivities[4] of such reactions as determined from their half lives, upon the triethylamine concentration.

EXPERIMENTAL

The Grignard reagents were prepared and purified as previously described.[4,5] *Diethylmagnesium* was the same as previously described.[6] *Ethylmagnesium bromide in triethylamine* was prepared by the addition of freshly distilled ethyl bromide in purified[5] triethylamine to a suspension of magnesium in triethylamine. After the exothermic reaction ceased, the solution was decanted into a nitrogen-filled bottle which was sealed with a serum cap. When the solution had remained at room temperature for a day, a precipitate formed. The clear supernatant liquid was forced into a smaller amber-colored storage bottle capped with a serum stopper. The concentration was determined by the Zerewitinoff method and found to be 0.38 molar. *The apparatus and the rate determinations* were the same as previously described.[5] In order to minimize the solubility of the evolved hydrocarbon, $R-H$, the reaction mixture was kept refluxing throughout the reaction. The reflux temperature increased proportionately with an increase in the concentration of amine. The increase was less than three degrees when the amine concentration was less than one molar. The increase was four and seven degrees when the amine concentration was two and three molar, respectively. The relative reactivities were not corrected for these differences in temperature of the refluxing mixture. The reaction in the absence of ether was kept at 36° ± 2 by thermostating the reaction flask. Duplicate measurements showed a precision of ±3.0% (average deviation from the mean) provided the relative

reactivity was not greater than 800. In faster reactions it was more difficult to maintain the pressure of 1 atm. during the reaction. In these cases the data are only good estimates of the rate of the reaction.

The observed rates are not a function of the time lapse[5] between the addition of the triethylamine to the Grignard reagent and the start of reaction brought about by the addition of hexyne. Thus in reactions where 30 sec., 5 min., or 4 hr. were permitted to elapse between the addition of triethylamine and the hexyne-1, the same values for the half lives were obtained.

DISCUSSION

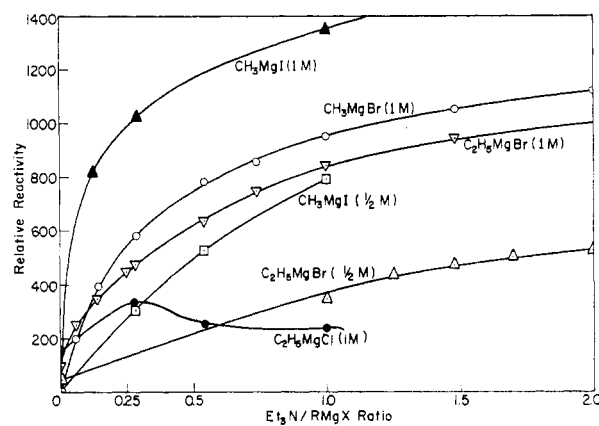Examination of the data in Table I and Fig. 1 reveals several important facts. The changing of

FIG. 1 RELATIVE REACTIVITIES AS A FUNCTION OF THE MOLE RATIO OF $(C_2H_5)_3N$ TO $RMgX$.

TABLE I

RELATIVE REACTIVITY OF EQUIVALENT QUANTITIES $RMgX$ AND $C_4H_9C \equiv C-H$ IN THE PRESENCE OF $(C_2H_5)_3N$

RMgX	Molar Conc. of Solution	Relative Reactivity $(C_2H_5)_3N$, Molar Conc.			
		0	0.25	0.5	1.0	19.0[a]
CH_3MgI	1.0	7	1000	1170	1350	...
CH_3MgI	0.5	3	500	790	...	...
CH_3MgBr	1.0	7	560	750	950	...
C_2H_5MgBr	1.0	100[b]	450	620	840	...
C_2H_5MgBr	0.5	48	210	340	520	...
C_2H_5MgBr	0.38	...	...	...	...	469[c]
C_2H_5MgCl	1.0	160[d]	...	...	240[d]	...
$(C_2H_5)_2Mg$	0.5	300	...	...	300	...

[a] No ether present. [b] Standard of reference.[4] [c] A saturated solution of C_2H_5MgBr in $(C_2H_5)_3N$ is 0.38 molar. [d] Reacting mixture was heterogeneous.

(1) Part VI, *J. Am. Chem. Soc.*, **79**, 358 (1957).

(2) Present address: Research Center, Diamond Alkali Co., Painesville, Ohio.

(2a) Present address: Department of Chemistry, University of Cincinnati, Cincinnati, Ohio.

(3) Abstracted from thesis of L. C. L. presented in partial fulfillment of the requirement for the degree of Master of Science, 1957. (Present address: Department of Chemistry, National Taiwan University, Taipei, Formosa, China).

(4) J. H. Wotiz, C. A. Hollingsworth and R. E. Dessy, *J. Am. Chem. Soc.* **77**, 103 (1955).

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

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

the halogen in a given alkylmagnesium halide produces a difference in the rate of reaction. The iodide is more affected by the presence of amine than the bromide and chloride. There is a reversal in the order of reactivity in case of CH_3MgBr and CH_3MgI brought about by triethylamine cosolvent. However, the addition of amine does not change the rate of reaction of a halogen-free solution of diethylmagnesium.

Triethylamine increases the rate of reaction of hexyne with methylmagnesium halides more than with ethylmagnesium halides. Thus the order of reactivity of methyl- and ethylmagnesium bromides (1 molar solution) is reversed if at least 0.1 mole-equivalent of triethylamine is present.

Because of the variation of the temperature during the reaction, it is not possible to determine accurately the rate laws from the individual gas evolution curves. However, casual inspection of the data indicates that the reactions are approximately second order. Thus, it can be seen from Table I

that the relative reactivities are approximately doubled when the concentrations of the alkylmagnesium halide and the hexyne are both doubled, the molarity of amine being constant.

The influence of triethylamine upon the rate of reaction of the Grignard reagent with hexyne cannot be the result of a shift in the Schlenk equilibrium[6,7] since the relative reaction of halogen-free diethylmagnesium

$$2\ RMgX \rightleftharpoons R_2Mg{\cdot}MgX_2 \rightleftharpoons R_2Mg + MgX_2$$
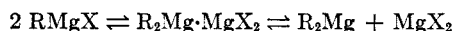
is independent of the amine concentration. This is likely due to the existence of a different mechanism of reaction. However the coordination of the amine with the magnesium atom of reacting species is not an important factor in determining the rate of reaction.

PITTSBURGH, PA.

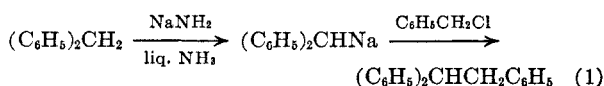(7) J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, J. Org. Chem., 21, 1063 (1956).

Conjugate Addition Condensations of Diphenylmethane Involving Methylene Hydrogen by Potassium Amide. Cyclizations of Products by Polyphosphoric Acid[1]

MARVIN T. TETENBAUM AND CHARLES R. HAUSER

Potassium diphenylmethide, prepared from diphenylmethane and potassium amide, was condensed through conjugate addition with ethyl cinnamate, and the resulting ester was cyclized by means of polyphosphoric acid to form a cyclic ketone. Potassium diphenylmethide also underwent conjugate addition with benzalacetophenone and α-phenylcinnamonitrile but these products failed to be cyclized by polyphosphoric acid. Potassium diphenylmethide underwent with ethoxymethylenemalonic ester conjugate addition accompanied by elimination to form an ester that yielded an aromatic product on cyclization.

Diphenylmethane has previously been shown to enter into several types of carbon-carbon condensations through the metalation of its α-hydrogen by means of sodium or potassium amide in liquid ammonia. Thus, this hydrocarbon has been alkylated,[2] acylated,[3] carbethoxylated,[3] carbonated,[3] and condensed with the carbonyl group of ketones or aldehydes.[4] An example of the alkylation that has been realized quantitatively is represented by Equation 1.[2]

$$(C_6H_5)_2CH_2 \xrightarrow[\text{liq. }NH_3]{NaNH_2} (C_6H_5)_2CHNa \xrightarrow{C_6H_5CH_2Cl} (C_6H_5)_2CHCH_2C_6H_5 \quad (1)$$

In the present investigation, diphenylmethane was found to undergo through its potassium or sodium derivative still another type of condensation, involving conjugate addition with α,β-unsaturated carbonyl compounds or nitriles. This type of condensation is of special interest since certain of the products obtained were cyclized by means of polyphosphoric acid. These reactions will be considered on the basis of the α,β-unsaturated compound empolyed.

Reaction with ethyl cinnamate. Potassium diphenylmethide, prepared from molecular equivalents of diphenylmethane and potassium amide in liquid ammonia containing some ether, underwent conjugate addition with an equivalent of ethyl cinnamate in this medium to form ester I, which was saponified to give acid II in 84% overall yield (Equation 2).

---

(1) Supported by the Office of Ordnance Research, U. S. Army.

(2) C. R. Hauser and P. J. Hamrick, Jr., J. Am. Chem. Soc., 79, 3142 (1957).

(3) R. S. Yost and C. R. Hauser, J. Am. Chem. Soc., 69, 2325 (1947).

(4) P. J. Hamrick, Jr., and C. R. Hauser, unpublished results.