The Reaction of 1-Alkynes with Organometallic Compounds. XII.[1] The Rate of Reaction Ethyl Grignards with 1-Hexyne in Certain Ethers

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The rate of reaction of ethylmagnesium bromide with 1-hexyne has been extensively studied and was found to be a function of the structure of the acetylene[3] and the Grignard reagent.[4] The rate of reaction was also found to depend on the nature and structure of certain cosolvents. Thus, the addition of tertiary amines to ethyl ether solutions of ethylmagnesium bromide produced significant changes in the rates.[5,6] Similarly, the addition of a certain quantity of dioxane to the ether solutions of ethylmagnesium bromide also produced significant changes in rates which were dependent not only on the amount of added dioxane, but also on the time lapsed between the addition of dioxane and the reaction of the product with 1-hexyne.[7] On the other hand, the addition of tetrahydrofuran was found to be void of detectable changes in the rate of reaction.[3]

In order to ascertain the influence of the structure of an ether used as a solvent for ethyl Grignards in its reaction with 1-hexyne, the Grignard reagents were prepared directly in isopropyl and butyl ether, as well as in tetrahydrofuran and 2-methyltetrahydrofuran. In this way we avoided the chance of having traces of ethyl ether present, which is frequently the case in attempts to displace ethyl ether with some other solvent. The rates of reaction were established by measuring the evolution of ethane, using the experimental conditions previously described.[3]

In Table I we are listing the observed rates in terms of relative reactivities. The standard of comparison was again an equimolar solution of ethylmagnesium bromide and 1-hexyne in 1 N concentration with a bromine to magnesium ratio of 1.08. Such a reaction had an arbitrary assigned relative reactivity of 100. However, in the present study we have used a 10 to 1 molar ratio of hexyne to Grignard. This, in turn, was compared to a 10 to 1 molar ratio concentration in ethyl ether. The rate insensitivity of the presently used Grignard reagents to changes in reactant concentrations was recently reported.[1] In the present study attempts were also made to adjust the bromine to magnesium ratios in the Grignard close to 1.08 by the addition of appropriate quantities of magnesium bromide prepared in specified ethers.

TABLE I

THE REACTION OF ETHYL GRIGNARD WITH 1-HEXYNE IN CERTAIN ETHERS

$$C_4H_9C \equiv CH + C_2H_5MgBr \longrightarrow C_2H_6 + C_4H_9C \equiv CMgBr$$
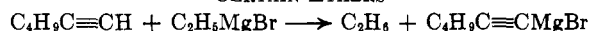
Molar ratio[a]	Solvent	Br : Mg	Relative reactivity
1:1	Et₂O	1.08	100[b]
10:1	*i*-Pr₂O	1.04	155
10:1	Bu₂O	1.06	130
10:1	Et₂O	1.05	110
10:1	THF	1.05	105
10:1	2-MeTHF	1.07	37

[a] Hexyne to Grignard.   [b] Standard of comparison. See ref. 3.

From the relative reactivities listed in Table I we see that the structure of the ether produced changes in the rate. The fastest reaction was in isopropyl ether. The difference in the reactivity between tetrahydrofuran and ethyl ether is probably within the limit of experimental error. The slowest reaction was observed in 2-methyltetrahydrofuran. The observed relative reactivities are generally in line with the determined basicities of ethers toward magnesium and other Lewis acids of comparable size.[8]

Thus our relative reactivities were a measure of relative base strength of studied ethers toward magnesium, which was a combination of electronic and steric effects. The found order of basicity was *i*-Pr₂O < Bu₂O < Et₂O < THF < 2-MeTHF.

Since we have previously demonstrated[9] that halogen-free diethylmagnesium in ether reacts about three times as fast with hexyne as a Grignard with a bromine to magnesium ratio of 1.08, it became of interest to ascertain the effect of the bromine to magnesium ratio on the rate of reaction in tetrahydrofuran. In Table II we are listing our findings.

A comparison of previous data in ethyl ether[9] shows that there are only small differences between the rates in ether and tetrahydrofuran in spite of the fact that the rates in ether were ascertained at equimolar concentration, whereas the rates in tetrahydrofuran were at 10 to 1 molar concentration, hexyne to diethylmagnesium. We have thus demonstrated again[1] that with the *presently* used magnesium and/or Grignard solutions there

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TABLE II

THE REACTION OF ETHYLMAGNESIUM BROMIDE AND
DIETHYLMAGNESIUM WITH 1-HEXYNE IN TETRAHYDROFURAN

$C_4H_9C\equiv CH$: organometal,

molar ratio	Br : Mg	Relative reactivity
1:1	0	350
10:1	0	330
10:1	1.00	134
10:1	1.05	105
10:1	1.17	80

is little dependence of the rate of reaction on the molar concentration of reactants.

Experimental

The gas-collecting system and the determination of rates was the same as previously described.[3] Ethers were purified by distilling from ethylmagnesium bromides prepared in them. 1-Hexyne was purchased from Farchan Research Laboratories, redistilled, and sealed in vials until ready for use. Magnesium turnings were from an unknown lot purchased from Eastman Organic Chemicals. Analysis of the metal was not known.

Diethylmagnesium was prepared by the dioxane precipitation method.[10] The solvents were removed in vacuo. The light green solid remaining was redissolved in dry tetrahydrofuran forming a light yellow solution. It contained less than 0.3 mole % of bromine.

A tetrahydrofuran solution of magnesium bromide was prepared by treating bromine with magnesium in dry tetrahydrofuran. The solution was analyzed for total magnesium and bromine content. The preparation of magnesium bromide in ether was previously described.[11]

The Grignard reagents were prepared from ethyl bromide in the appropriate ethers. With the exception of ether and tetrahydrofuran, the bromine to magnesium ratios of the formed solution were sufficiently close to 1.08 so that they did not require adjustments with solutions of magnesium bromide in the appropriate ethers.

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Perhalo Ketones. IV.[1] The Reaction of Perhaloacetones with Phosphorus Pentachloride

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The perhalofluorochloroacetones are not readily susceptible to attack by reagents that normally lead to replacement of the carbonyl oxygen.[3] This inertness is in marked contrast with their considerable reactivity toward nucleophiles[4] and other polar functions.[5]

This study has indicated that these perhaloacetones are resistant to the action of phosphorus pentachloride under conditions which lead to replacement of the

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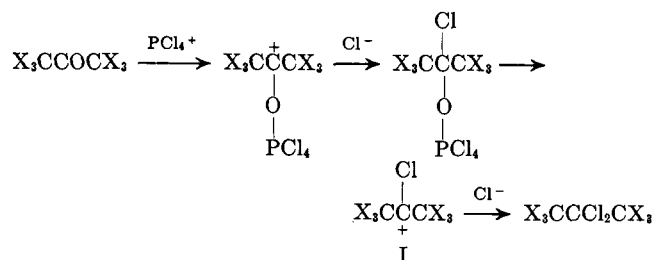
carbonyl oxygen even in highly substituted ketones. They were recovered unchanged after refluxing with phosphorus pentachloride, either in the presence or absence of inert solvents. Although pentachloroacetone is converted to heptachloropropane with PCl_5 at 180° in 6–8 hr.,[6] the perhaloacetones gave extremely low yields at 200° for 24 hr. with excess reagent in a rocking autoclave. Not until temperatures of 250° or higher were employed did substantial reaction occur, except in the case of hexachloroacetone which reacted at 230°. At 275–300° fair yields of the corresponding perhalopropanes were obtained (Table I) in 5 hr. Since the unreacted ketones are either readily soluble in aqueous base,[7] or react with it, the perhalopropanes were obtained in high purity. These compounds have previously been prepared only by multistep syntheses.

TABLE I

PREPARATION OF PERHALOPROPANES

Perhalopropane formed	B.p., °C.	% yield[a]	—% fluorine— Calcd.	Found
$F_3CCCl_2CF_3$	33–34[b]	31	51.7	51.6
$F_3CCCl_2CF_2Cl$	72[c]	50	40.2	40.0
$ClF_2CCCl_2CF_2Cl$	112–113[d]	61	29.8	29.9
$ClF_2CCCl_2CFCl_2$	152[d]	48	21.2	21.1
$Cl_2FCCCl_2CFCl_2$	194[e]	62	12.9	13.2
$Cl_3CCCl_2CCl_3$[f]	270–271[g]	85		

[a] Based on the amount of ketone used. [b] J. T. Maynard, J. Org. Chem., 28, 113 (1963). [c] A. L. Henne, A. M. Whaley, and J. K. Stevenson, J. Am. Chem. Soc., 63, 3478 (1941). [d] A. L. Henne and M. W. Renoll, ibid., 61, 2489 (1939). [e] A. L. Henne and E. C. Ladd, ibid., 60, 2491 (1938). [f] Run at 230°. [g] F. Kraft and V. Merz, Ber., 8, 1296 (1875). Product gives an infrared spectrum identical with that of sample purchased from Aldrich Chemical Co.

This resistance of the perhaloacetones to phosphorus pentachloride is attributed to the negative inductive effect of the halogen clusters surrounding the carbonyl group,[8] which reduces electron availability at the carbonyl oxygen and inhibits attack by the chlorophosphonium ion, PCl_4^+.[9] It would also make the formation of the carbonium ion I difficult, since departure of the oxygen atom with its pair of bonding electrons would be electronically unfavorable.

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