TABLE V

EQUILIBRATION CONSTANTS FOR 1-PHENYL-C^{14}-2,2-DIPHENYLETHYL ACETATE

Run	Assay of starting acetate, mc./mole	Time, hours	1.009 × $Ph_2{}^*CO$ assay (y), mc./mole	$k_{II} \times 10^2$, hours^{-1}
1	0.991	6	0.107	(2.950)
	(y_e 0.661)	22	.270	2.385
		30	.318	2.190
		46	.419	2.186
		71.5	.510	2.100
				2.215 ± 0.092
2	0.991	9	0.119	2.208
	(y_e 0.661)	21	.241	2.162
		44	.399	2.102
		48	.414	2.120
		52	.435	2.062
		57.5	.457	2.045
		70	.501	2.028
		76	.518	2.018
		95	.560	1.978
				2.080 ± 0.070

TABLE VI

ACETOXYL EXCHANGE CONSTANTS FOR 1,2,2-TRIPHENYLETHYL ACETATE-2-C^{14}

Run	Assay of starting acetate, mc./mole	Time, hours	Assay of recovered acetate ($a - x$) mc./mole	$k_{III} \times 10^2$, hours^{-1}
1	0.549	6.5	0.483	1.982
		23	.344	2.035
		30.75	.293	2.042
		47	.224	1.905
		54	.198	1.890
				1.971 ± 0.059
2	0.495	6	0.382	(4.318)
		22	.278	2.621
		30	.230	2.560
		46	.153	2.553
		71.5	.083	2.500
				2.558 ± 0.032
3	0.549	4.5	0.438	5.00
	(p-toluenesulfonic acid	23	.178	4.90
	concn. doubled)	27	.151	4.77
		30	.137	4.51
				4.79 ± 0.15
			(Divided by 2)	2.39 ± 0.07

phenone fraction was dissolved in 8 ml. of ethanol, treated with Norit and filtered through Celite, then 1.5 ml. of this solution was converted to the 2,4-dinitrophenylhydrazone (189 mg.) which was twice crystallized from dioxane and dried in an Abderhalden. The radioactivity assay was: 0.4495; 0.4473 average 0.4484 ± 0.0011 mc./mole. The remaining 6.5 ml. of ethanolic benzophenone was heated under reflux for 24 hours with 1 ml. of pyridine and 0.5 g. of hydroxylamine hydrochloride. The mixture was then poured into water and filtered, yielding 647 mg. of crude benzophenone oxime. This was not purified, since several model experiments had demonstrated that the crude oxime gave satisfactory yields in the Beckmann rearrangement. The oxime was dissolved in 12 ml. of concd. sulfuric acid and the solution was warmed on a steam-bath for one hour, after which time the cooled solution was poured over crushed ice. The resulting mixture was extracted three times with ether, the ether was clarified and concentrated, yielding 232 mg. of pure benzoic acid. This was twice crystallized from water, and identified by melting point and mixed melting point. The radioactivity assay was: 0.3238; 0.3217, average 0.3227 ± 0.0010 mc./mole of carbon-14. From these data it was calculated that $k_I = 2.03 \pm 0.12 \times 10^{-2}$ hours^{-1}, and $k_{II} = 2.11 \pm 0.08 \times 10^{-2}$ hours^{-1}, and that $k_{II}/k_I = 1.04 \pm 0.095$.

Radioactivity Determinations.—These were carried out in the normal fashion as described in the previous paper.[2] For the determination of the isomerization of doubly labeled acetate (I and II) described in the preceding section, the highest precision was necessary. This was obtained by weighing large samples (20–50 mg.) of analytical material on a micro-balance, and using the technique described for previous double-labeling experiments.[2]

OAK RIDGE, TENNESSEE

[CONTRIBUTION NO. 932 FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PITTSBURGH]

The Reaction of 1-Alkynes with Organometallic Compounds. I. 1-Hexyne with Some Alkyl and Alkenylmagnesium Halides

BY JOHN H. WOTIZ, C. A. HOLLINGSWORTH AND RAYMOND DESSY[1]

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In the reactions of some Grignard reagents with 1-alkynes the rate of the evolution of gas was measured. The following relative rates were found: MeMgI, 6; MeMgBr, 6; MeMgCl, 16; n-PrMgBr, 59; EtMgI, 71; EtMgBr, 100; EtMgCl, 155; i-PrMgBr, 210; AllylMgBr, 435. A possible explanation of these relative rates is proposed.

In our laboratory we had many times the opportunity to prepare 1-hexynylmagnesium bromide in five mole quantities. The preparation consists of treating 1-hexyne (I) with a Grignard reagent such as methyl (II) or ethylmagnesium bromide (III) in boiling ether. The completeness of reaction was noted by the termination of evolved gas (methane or ethane).

$$C_4H_9C{\equiv}C{-}H + R{-}MgX \longrightarrow C_4H_9C{\equiv}C{-}MgX + R{-}H(gas)$$

$$R = CH_3\ (II),\ C_2H_5\ (III)$$

We have observed that the reaction with ethylmagnesium bromide was finished shortly after the completion of addition whereas with methylmagnesium bromide we needed more than 24 hours before we considered the reaction to be finished. It was the purpose of this investigation to establish the rate of reaction of some Grignard reagents with 1-alkynes.

The literature contains two studies of the relative reactivities of Grignard reagents with compounds containing an "active" (acidic) hydrogen. Thus, the reactions with chloromagnesium phenyl-

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(1) National Science Foundation Predoctoral Fellow.

acetate, $C_6H_5CH_2CO_2MgCl$, in boiling ether showed reactivity i-Pr > Et > n-Pr > s-Bu > i-Bu > Me.[2] These reactions were complicated by the fact that the Grignard reagents were also able to react with the carboxy group. This possibility was eliminated in the study of reactivities of some Grignard reagents with indene in boiling butyl ether.[3] The relative order of reactivities was i-Pr > Et > n-Pr > s-Bu > Me > i-Bu. There was no attempt in either study to determine the kinetic order of reaction. In a study of the reaction of ethylmagnesium bromide with acetylene where the concentration of acetylene was kept constant and the rate of evolved ethane measured, it was found that the reaction was first order with respect to ethylmagnesium bromide.[4] The authors therefore favored the following reaction path.

$$H—C\equiv C—H + C_2H_5MgBr \longrightarrow H—C\equiv C—MgBr + C_2H_6$$

$$2H—C\equiv C—MgBr \longrightarrow BrMgC\equiv C—MgBr + H—C\equiv C—H$$

Nowhere in the literature were we able to find a study of relative reactivities of Grignard reagents with acetylene or substituted acetylenes.

Experimental

Grignard reagents were prepared in the conventional manner in about 3.0 *M* concentration. (Mallinckrodt Chemical Works ether, anhydrous, analytical reagent; J. T. Baker magnesium turnings, purified; halides purchased from the Columbia Chemical Co., Columbia, S. C.) Allylmagnesium bromide was prepared in a high ether dilution using the cyclic reactor.[5] The approximate concentration of Grignard reagents was established by titration of a hydrolyzed aliquot with standard acid using methyl red indicator. The concentration was determined with greater accuracy using the gas-evolution method as in the rate determinations. Solutions not older than two weeks were used in the reaction with hexyne.

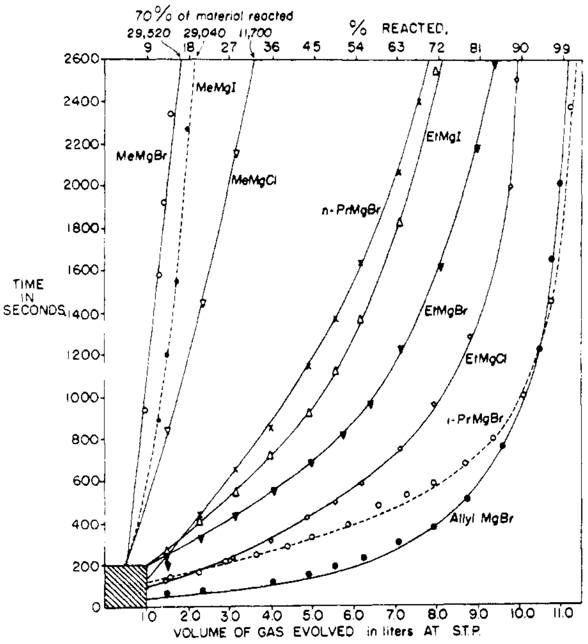

Fig. 1.—RMgX + hexyne-1.

The apparatus for the determination of individual reactivities consisted of a 1000-ml. three-neck flask with ground glass connections, fitted with an addition funnel, Hershberg type of stirrer made of nichrome wire, and a cold-finger type of condenser filled with a Dry Ice–acetone slurry or a mixture of ice and alcohol, depending on the boiling point of the gaseous product. A thermometer graduated in tenths of a degree reached into the liquid. The flask was heated in a Glas-Col heating mantle. The rate of heating and stirring was kept constant in all experiments by controlling the voltage.

A solution of the Grignard reagent corresponding to 0.55 mole (concentration by acid titration) was introduced into the flask and diluted to 500 ml. with dry ether and heated to reflux. The heater was removed while half a mole of hexyne was introduced over a period of about 60 seconds. The evolved gas was passed through two traps cooled in ice, and collected in a graduated cylinder over water. The time of 200-ml. increments of evolved gas was noted. We were unable to maintain a constant temperature of the reaction mixture as fast reactions evolved the gas at a rate which resulted in a cooling effect of the mixture. A decrease of up to four degrees in the temperature of the reaction mixture was thus noted. The reaction of methylmagnesium chloride, bromide and iodide showed a slight increase in the temperature over the initial and final temperatures.

In experiments 1, 2 and 3 (Table I) which proceeded at a very slow rate, the reaction was permitted to proceed to about 70% of completion after which time alcohol was added. In this manner we found the total volume of gas which could be obtained from the methylmagnesium halide present in a reasonable period of time.

Table I

The Reaction of RMgX (0.5 Mole) with Hexyne-1 (0.5 Mole) at the Reflux Temperature of the Mixture

Expt.		Half-life, sec.	Temp., °C. Init.	Min.-max.	Final	Relative reactivity
1	MeMgI	12,660	35.0	37.2	35.3	6
2	MeMgBr	13,000	35.0	37.0	35.5	6
3	MeMgCl[a]	5,025	35.0	36.4	34.8	16
4	n-PrMgBr	1,360	35.5	36.0	35.2	59
5	EtMgI	1,120	35.1	33.1	33.7	71
6	EtMgBr	792	35.3	33.2	34.2	100
7	EtMgCl[a]	516	35.0	32.0	33.4	155
8	i-PrMgBr	380	35.8	32.0	34.8	210
9	Allyl MgBr	185	35.2	31.0	34.7	435

[a] Heterogeneous.

The solubility of the evolved gas in the boiling reaction mixture was neglected. We feel that such an error was not great especially in the case of the lower boiling products. In some reactions (especially in experiments 1, 2 and 3) after the addition of the Grignard reagent there was a period of time when no gas was evolved. We are attributing such an "induction" period to the solubility of the produced gas in the ether. It is only after the solvent becomes saturated, that evolution gas can be measured. In some cases we have observed an initial fast evolution of gas which we believe to be due to the presence of small quantities of moisture in the hexyne. For these reasons we do not consider the data in the first 10% of the reaction to be very reliable.

Discussion of Results

A part of a plot of the amount of evolved gas against time in the reaction of Grignard reagents and hexyne-1 is in Fig. 1. The half-lives of these reactions (the time at which one-half of the theoretically possible amount of gas was evolved) are listed in Table I. The relative reactivities were determined by selecting the reaction of equimolar quantities of ethylmagnesium bromide with hexyne as 100. With the exception of the reaction of the two alkylmagnesium chlorides (expt. 3 and 7) with hexyne, the reaction mixture remained homo-

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[2] D. Ivanoff and A. Spassoff, *Bull. soc. chim.*, **51**, 619 (1932).

[3] D. Ivanoff and I. Abdouloff, *Compt. rend.*, **196**, 491 (1933).

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

[5] D. C. Rowlands, K. W. Greenlee and C. E. Boord, Abstracts of the 117th A.C.S. Meeting, Philadelphia, April, 1950.

geneous. The precipitates which appeared in expt. 3 and 7 were shown to be $MgCl_2$ by titration of total basic Mg and halide.

To test the precision and reproducibility of our experiments, we have repeated the reaction of I with III (expt. 6, half-life 792) using different lots of I and III. Thus we obtained (Table II) a half-life of eight hundred (expt. 10) and 784 (expt. 11). There was no change in the initial, minimum and final temperatures of the reaction mixture in these two experiments.

Table II

Ethylmagnesium Bromide and Hexyne

Expt.	Mole used C_2H_5MgBr	Hexyne	Temp., °C.			Half-life, sec.
			Init.	Min.	Final	
10	0.5	0.5	35.3	33.2	34.2	800
11	0.5	0 5	35.3	33.2	34.2	784
12	1.0	0.5	37.8	32.5	34.5	340[a]
13	0.5	1.0	35.2	33.0	36.8	487[a]
14	0.5 Plus 0.5 of $C_4H_9{\equiv}CMgBr$	0.5	36.8	33.0	34.6	815
15	0.5 Plus 0.5 of hexyne-2	0.5	38.1	35.0	36.5	845

[a] Half-life at 5.6 liters.

We also have treated II and III with heptyne-1. The found half-lives of 11,250 and 740 compare well with one of I with II (13,000 expt. 2) and I with III (792, expt. 6). There were small differences in the boiling points of the reaction mixture due to the difference in the boiling points of hexyne and heptyne.

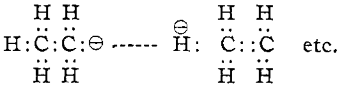
The influence of an excess of III on the half-life of the reaction of I with III was determined by expt. 12 (Table II) and the effect of an excess of I on the half-life of the same reaction determined by expt. 13. In order to determine whether the formed hexynylmagnesium bromide influences the rate of reaction, we have treated an equimolar quantity of I with III in its presence (expt. 14). The found half-life agrees well with the ones of experiments 10 and 11.

The effect of a non-terminal acetylenic linkage upon the half-life of the reaction of I with III was determined in expt. 15 using hexyne-2. The half-life of this reaction is in close agreement with those of expt. 10 and 11.

Several observations should be noted: (1) Changing the halogen in a given alkylmagnesium halide produced a change in the rate of reaction. The alkylmagnesium chloride reacts significantly faster than the bromide. There is little difference in the reaction of the bromide and iodide when the alkyl group is a methyl, whereas in the case of the ethylmagnesium bromide there is a marked increase in its reactivity over the ethylmagnesium iodide. (2) The reactions of methylmagnesium halides were found to be significantly slower than the other reactions. (3) The alkylmagnesium bromides showed an increase in the reactivity as the number of β-hydrogen atoms was increased. The product of the half-life and the number of β-hydrogen atoms is approximately a constant (2,500 ± 8%).

The commonly accepted formulation of many reactions of Grignard reagents involves preliminary formation of a coördination complex followed by an intramolecular migration of the alkyl group of the reagent with its pair of electrons. Such a mechanism is generally in agreement with the kinetics reported for the reaction of Grignard reagents with benzonitrile[6] and does not disagree with the results reported in this paper.

In such a mechanism it would not seem unreasonable that the relative reactivities of different Grignard reagents should parallel the stabilities as anions of the alkyl groups of the reagents. On this basis one would expect allylmagnesium bromide to be the most reactive of those tried as is observed. Among the alkylmagnesium halides examined, there appears to be a simple correlation between the number of β-hydrogens and the reactivity, *i.e.*, isopropyl > ethyl > *n*-propyl > methyl. Possibly this reflects a "hyperconjugation" effect of the sort suggested by Polanyi[7] which is illustrated below for ethyl.



$$\begin{matrix} & \mathrm{H} & & \mathrm{H} & & & \ominus & \mathrm{H} & & \mathrm{H} & \\ \mathrm{H}: & \ddot{\mathrm{C}} & : & \ddot{\mathrm{C}} & :\ominus & \text{------} & \mathrm{H}: & \ddot{\mathrm{C}} & :: & \ddot{\mathrm{C}} & \text{etc.} \\ & \ddot{\mathrm{H}} & & \ddot{\mathrm{H}} & & & & \ddot{\mathrm{H}} & & \ddot{\mathrm{H}} & \end{matrix}$$

However, this suggestion is not entirely in agreement with the order of reactivity found for the reactions of various Grignard reagents with indene[3] or chloromagnesium phenylacetate,[2] where the *sec*-butyl group is out of "order."[8]

A more detailed analysis of the rate data is being made, and will be reported in a later paper.

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[6] C. G. Swain, This Journal, **69**, 2306 (1947).

[7] E. C. Bongham, M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **37**, 377 (1947).

[8] Appreciation is extended by the authors to Referee 1 for his suggestions concerning the phraseology of this discussion.