ice bath. After warming to room temperature, the two layers were separated, the aqueous layer extracted with chloroform, and the combined extracts dried over sodium sulfate. Evaporation of the chloroform yielded 2.1 g. (87%) of the hydrazide which after recrystallization from dilute ethanol and sublimation at 130° (0.1 mm.) gave colorless product, m.p. 157–159°.

trans-**3-Benzhydrylcyclopentene-4-carboxylic Acid (III).**—This acid was prepared by the hydrolytic fission of 7,7-diphenylbicyclo-[3.2.0]hept-2-en-6-one.[13] In the majority of experiments the melting points of the product indicated that almost pure *trans* acid was isolated rather than the mixture as reported by Farmer and Farooq.[13] Reducing the amount of base and reaction time did not alter the product melting point significantly. The pure *trans* acid was obtained by recrystallization once from petroleum ether then from methanol, m.p. 148–149°.

Elimination Studies of *trans*-**3-Benzhydrylcyclopentene-4-carboxylic Acid.**—The general procedure is exemplified by the following experiment. To a solution of 2.72 g. (0.0413 mole) of potassium hydroxide pellets in 50 ml. of diethylene glycol was added 4.5 g. (0.0162 mole) of *trans*-3-benzhydrylcyclopentene-4-carboxylic acid and the mixture heated at 180° for 2 days. After cooling and diluting with water the mixture was extracted with ether and the extracts dried over magnesium sulfate. Evaporation yielded the diphenylmethane.

The basic solution remaining after ether extraction was acidified with dilute hydrochloric acid, extracted with ether, and the combined extracts dried. Removal of the solvent yielded the residual starting *trans* acid.

The results of the elimination studies are given in Table I.

TABLE I

ELIMINATION STUDIES WITH *trans*-3-BENZHYDRYLCYCLOPENTENE-4-CARBOXYLATE SALTS

Weight of acid, g.	Solvent	Reaction time, hr.	Temp.	Ph_2CH_2, g. (yield)	recovery acid, g.
4.5[a]	Ethylene glycol	48	180°	0.1 (4%)	4.2
4.2[a]	Diethylene glycol	29	200–250°	.1 (4%)	4.1
2.2[a]	Diethylene glycol	8	250°	.05 (4%)	2.0
5.4[a]	Diethylene glycol	8	280–300°	.2 (6%)	5.2
4.7[b]	Diethylene glycol	9.5	200–250°	.2 (7%)	4.3

[a] Reaction mixture contains an excess of potassium hydroxide (see Experimental). [b] Preprepared sodium salt.

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Reaction of 1-Alkynes with Organometallic Compounds. XI. The Reactivity of Dialkylmagnesiums toward 1-Hexyne

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It was reported in the first paper[3] of this series that the relative reactivities toward 1-hexyne of diethyl ether solutions of alkylmagnesium halides (as determined from reaction half-lives) were in the order isopropyl > ethyl > *n*-propyl > methyl. This order was correlated with the number of β-hydrogens on the alkyl group, and it was suggested that this might be evidence for anionic hyperconjugation.[3,4]

The purpose of the present paper is to report results which show that the reactivities of diethyl ether solutions of some dialkylmagnesiums follow the same order as that observed for the Grignard reagents, and, therefore, the same correlation with the number of β-hydrogens applies. These dialkylmagnesium reactivities are in terms of rate constants corresponding to a two-step, competitive, consecutive, second-order mechanism. The agreement between this mechanism and the experimental data does not rule out the possibility that the mechanism is actually more complicated (for example, that dimers of the dialkylmagnesium may be present).

Kinetic Theory.—One would expect that the reaction of a dialkylmagnesium with 1-hexyne would involve at least two competitive, consecutive steps, and, if the dialkylmagnesium is dimerized in ether a four-step reaction would be involved. The nonlinear differential equations for any number of competitive, consecutive, second-order steps can be made linear and solved in terms of a time variable θ used by French.[5] For the reaction here under consideration, θ can be defined by

$$\theta = \int_0^t (b - P)dt \tag{1}$$

where b is the initial concentration of 1-hexyne, and P is the moles of hydrocarbon gas produced per liter of solution. θ can be calculated easily by graphical integration of the experimental curve for P *vs.* t. For a single reaction of any number of competitive, consecutive, second-order steps the integrated rate law takes the form

$$P/a = f(\theta) \tag{2}$$

where, for the case here under consideration, a is the initial concentration of alkyl groups (*i.e.*, twice the initial molarity of R_2Mg). According to equation 2, P/a does not depend upon a or b explicitly. For the two-step reaction with rate constants k_1 and k_2, equation 2 is

$$\frac{P}{a} = \frac{1}{2(k_1 - k_2)}\left[(2k_2 - k_1)e^{-k_1\theta} - k_1e^{-k_2\theta}\right] + 1 \tag{3}$$

Becker, *et al.*,[6] concluded, from vapor pressure data and from the kinetics of the reaction with benzonitrile, that diethylmagnesium dimerizes in tetrahydrofuran. If there are present in ethyl ether both monomers, R_2Mg, and dimers, $R_2Mg \cdot R_2Mg$, then the reaction with 1-hexyne would no longer be a single reaction. Equation 2, in general, would not hold, and P/a could depend explicitly upon both a and b.

Results

The experimental results for the reactions of three dialkylmagnesiums with 1-hexyne in ethyl ether are shown as plots of P/a *vs.* θ in Fig. 1 and 2. The values of a and b are given in Table I. Theoretical

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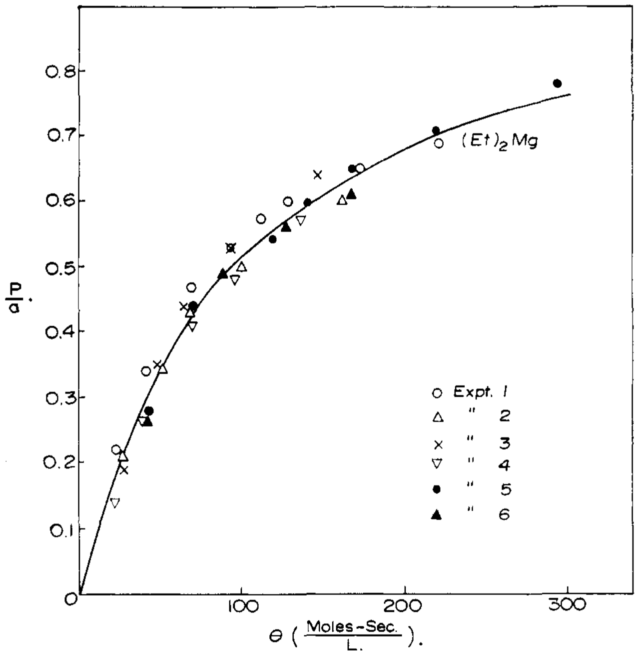

Fig. 1.—P/a vs. θ for diethylmagnesium. Points, experimental. Curve, theoretical. Experiment numbers are those given in Table I.

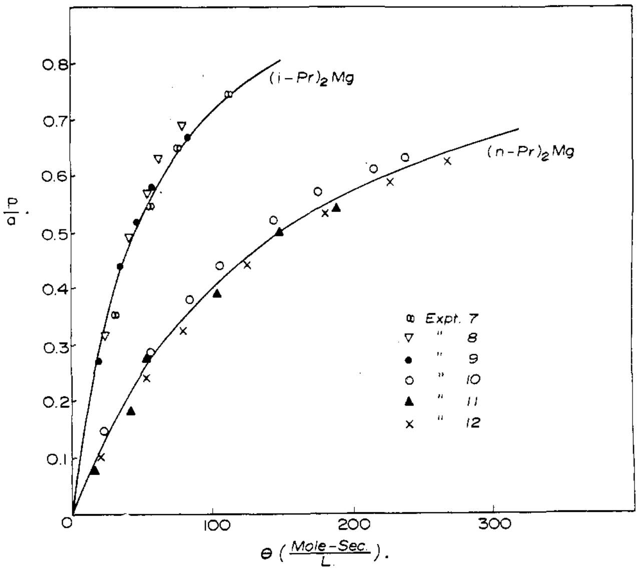

Fig. 2.—P/a vs. θ for di-n-propylmagnesium and diisopropylmagnesium. Points, experimental. Curves, theoretical. Experiment numbers are those given in Table I.

curves given by equation 3 and with the values of k_1 and k_2 given in Table I are also shown in Fig. 1 and 2. There may be a small dependence on a indicated, but in this respect the results are not conclusive. The results do show clearly that the order of reactivity is isopropyl > ethyl > n-propyl, in agreement with the order previously found for the corresponding Grignard reagents.[3] Also, it is clear that the reaction consists of at least two steps and that the first half of the alkyl groups are more reactive than the second half.

Experimental

Materials.—1-Hexyne (Farchan) was passed over alumina and distilled [b.p. 68°, (745 mm.)].

TABLE I

INITIAL CONCENTRATIONS AND RATE CONSTANTS (33 ± 1°)

Expt.	R_2Mg	a^a	b^a	k_1^b	k_2^b
1	Et_2Mg	1.01	0.89	2.2×10^{-2}	3.0×10^{-3}
2	Et_2Mg	.57	.52		
3	Et_2Mg	.55	.50		
4	Et_2Mg	.46	.41		
5	Et_2Mg	.47	.76		
6	Et_2Mg	.17	.76		
7	$(i\text{-Pr})_2Mg$	.44	.60	4.0×10^{-2}	8.0×10^{-3}
8	$(i\text{-Pr})_2Mg$	.55	.50		
9	$(i\text{-Pr})_2Mg$	.39	.39		
10	$(n\text{-Pr})_2Mg$	.88	.74	1.3×10^{-2}	2.0×10^{-3}
11	$(n\text{-Pr})_2Mg$	.54	.50		
12	$(n\text{-Pr})_2Mg$	.70	.65		

[a] The value of a is twice the initial molarity of R_2Mg and b is the initial molarity of 1-hexyne. [b] k_1 and k_2 are second-order constants expressed l × mole^{-1} × sec.$^{-1}$.

The dialkylmagnesiums were prepared from the Grignard reagents by the addition of dioxane as described previously.[7] In all cases analysis showed that the resulting ethyl ether solution of dialkylmagnesium contained excess basic magnesium. In three separate preparations of diethylmagnesium the ratios of active dialkyl to total basic magnesium was 0.72, 0.73, and 0.77. The ratios of active dialkyl to total basic magnesium for the diisopropyl and the di-n-propyl were 0.85 and 0.90, respectively. Care was taken to keep moisture and oxygen from the starting materials and reagents. The alkyl bromides were freshly fractionally distilled; dioxane was fractionally distilled from sodium; the ether (Mallinckrodt, anhydrous, analytical reagent) was freshly opened and stored over sodium for several hours before use; the products were transfered under cover of prepurified nitrogen and stored in serum rubber capped bottles. Samples were removed by means of hypodermic syringes. All of the dialkylmagnesiums gave a negative bromide test with silver nitrate.

Apparatus.—The apparatus and method used to determine the rates by gas evolution were the same as those described in previous papers.[8,9] Special care was taken to prevent an increase in pressure within the apparatus when gas was evolving rapidly. This was a problem for reactions with a half-life of less than 4 min. An increase in pressure of 1 or 2 cm. was found to cause enough "hold up" of gaseous product (probably mostly in the condenser, which was charged with ice and alcohol or Dry Ice and acetone) to cause a significant decrease in the value obtained for k_1.

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3-Mercaptopropionamidine and S-2-Amidinoethyl Thiosulfuric Acid[1]

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Recently reported[2,3] syntheses of S-substituted mercaptoamidine derivatives attest interest in aminoalkane-

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