of the sodium-ammonia reduction. A molecular-model construction of the allene suggests that *only* the *cis* isomer could be formed by catalytic hydrogenation.

## EXPERIMENTAL

*cis-Cyclooctene.* A solution of 21.6 g. of 1,5-cyclooctadiene[5] in 75 ml. of methanol was shaken with 0.5 g. of 5% palladium-calcium carbonate[3] under 2 atm. of hydrogen. The heat of reaction was conveniently dissipated by wrapping the bottle with a towel and periodically saturating it with acetone. Following the uptake of 1 mole-equivalent of hydrogen the suspension was filtered, diluted with 200 ml. of ether and washed repeatedly with water. The organic phase was dried (sodium sulfate) and fractionally distilled to give 19.1 g. (87%) of *cis*-cyclooctene, b.p. 144–145° (750 mm.). This sample was identical with material from the reduction of cyclooctatetraene; both contained about 4% of cyclooctane and no other impurity (vapor-liquid chromatography).

*9,9-Dibromobicyclo[6.1.0]nonane.* Cyclooctene (50 g., 0.45 mole) was added to a solution prepared by dissolving 20 g. (0.51 g.-atom) of potassium in 600 ml. of dry *t*-butyl alcohol. The flask was surrounded with ice and, while stirring, 127 g. (0.50 mole) of bromoform was added dropwise. After the addition was complete, stirring was continued for an hour and the contents were poured into 500 ml. of water. The mixture was extracted with several portions of pentane and the combined extracts were washed with water (2.5 l.), dried (sodium sulfate) and freed of solvent on a steam cone. Distillation of the residue gave 42 g. (33%) of 9,9-dibromobicyclo[6.1.0]nonane, b.p. 45° (0.15 mm.), $n_D^{27}$ 1.5105.

*Anal.* Calcd. for $C_9H_{14}Br_2$: C, 38.33; H, 5.00; Br, 56.67. Found: C, 38.63; H, 5.14; Br, 56.98.

The fore-run from the distillation (48 g.) consisted of unchanged cyclooctene and bromoform and was suitable for recycling. Vapor-liquid chromatography showed it to contain about 20 g. (40% recovery) of cyclooctene. A more efficient conversion was realized using the conventional large excess of olefin[2] but the procedure described is felt to be a satisfactory economic compromise.

*1,2-Cyclononadiene.* In a 500 ml., three-necked flask, equipped with a stirrer and over-size Dry Ice condenser, was placed 22 g. (0.92-g.-atom) of magnesium turnings and 200 ml. of anhydrous ether. While stirring and heating, 50 g. (0.18 mole) of 9,9-dibromobicyclo[6.1.0]nonane dissolved in 120 ml. of anhydrous ether was added in a dropwise manner. The need for the large surge-capacity of the condenser was due to the very rapid rate of reaction. Frequently, the reaction did not start until 20 min. to an hour after the addition was complete but after starting it was essentially complete in 3 or 4 min. Following this, stirring under reflux was continued for an additional 3 hr. and then ice and water were cautiously added. The mixture was processed as described for other cases[2] and the crude product distilled through an efficient column. There was obtained 13.0 g. (59%) of 1,2-cyclononadiene, b.p. 94° (44 mm.), $n_D^{27}$ 1.4953. Repeated attempts to obtain satisfactory analytical data suggested that the allene slowly absorbs oxygen.

*Anal.* Calcd. for $C_9H_{14}$: C, 88.45; H, 11.55. Found: C, 86.53; H, 11.55.

Vapor-liquid chromatography of a freshly distilled sample indicated it to be a single compound. The infrared spectrum possessed a medium-strong band at 5.10 $\mu$ (allene) but had no absorption in the 4.5–4.7 $\mu$ (acetylene) region.

CIS-*Cyclononene* A. *Hydrogenation.* 1,2-Cyclononadiene (7.0 g.) was shaken in a suspension of 150 mg. of 10% palladium-charcoal and 200 ml. of methanol under a pressure of 2 atm. The theoretical quantity of hydrogen was absorbed in 1 hr. when the rate dropped abruptly. The usual isolation procedure and distillation of the product gave 5.4 g. (76%) of *cis*-cyclononene, b.p. 85–86° (45 mm.), $n_D^{27}$ 1.4748 [lit.[1] b.p. 167–169° (740 mm.), $n_D^{20}$ 1.4799]. The infrared spectrum was identical with that reported and had no absorption in the 10.25 $\mu$ region which is reported to be characteristic of the *trans* isomer.[1] Chromatography showed the sample to be a single substance.

*Anal.* Calcd. for $C_9H_{16}$: C, 87.01; H, 12.99. Found: C, 86.93; H, 12.87.

B. *Sodium-ammonia.* To a solution of 9.0 g of sodium dissolved in 250 ml. of liquid ammonia (used without purification) was added 11.0 g. of 1,2-cyclononadiene in 50 ml. of anhydrous ether. The solution was stirred at its boiling temperature for 1 hr. and then treated with excess ammonium chloride. Evaporation of ammonia and processing of the residue in the usual manner gave 9.5 g. (85%) of *cis*-cyclononene, b.p. 81–82° (38 mm.) which was identical in all respects with that obtained by hydrogenation.

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# The Rate of Reaction of Hexyne-1 with Substituted Phenylmagnesium Bromides

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Previous kinetic studies of the reactions of Grignard reagents with weak acids have been limited to the alkyl series because the gasometric method in common use required that a volatile hydrocarbon be evolved in the reaction[1]:

$$RMgX + RC{\equiv}CH \longrightarrow RH + RC{\equiv}CMgX \quad (1)$$

Several approaches to the problem of following the kinetics of reactions which do not yield volatile products have been made by groups at the University of Pittsburgh[2] and in our laboratory. The Pittsburgh group has recently completed a preliminary study of the reaction of phenylmagnesium bromide with hexyne-1 using VPC as a tool.[3] Their data will be published in the near future.

We have determined the rates of reaction of a series of substituted phenylmagnesium bromides with hexyne-1 in ether by following the rate of change of the dielectric constant of the reaction mixture with time. The reactions were run under pseudo-first order conditions in ether with a

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

(2) L. V. Guild, C. A. Hollingsworth, D. McDaniel, Sunil-kumar Podder, J. H. Wotiz, and M. Tirpak.

(3) L. V. Guild, Masters dissertation, University of Pittsburgh, 1960.

twenty-fold excess of hexyne-1 and obeyed the first order rate law for at least three half-lives. A determination of reaction rate of a solution $0.2M$ in both phenylmagnesium bromide and hexyne-1 obeyed the second order equation past 70% completion, indicating that this reaction is first order in Grignard reagent and in hexyne-1, and is second order overall. The rate constant for the second order reaction was 28% above that for the first-order determinations; this is probably due to solvent effects from the excess of hexyne-1 used.[4] The relative reactivities and rate constants of the compounds investigated are given in Table I.

TABLE I

$$Z\text{—}C_6H_4MgBr + C_4H_9C{\equiv}CH \xrightarrow{31.5^\circ} Z\text{—}C_6H_5 + C_4H_9C{\equiv}CMgBr$$

| Compounds | $k$, L./Mole-Sec. | Approximate Relative Reactivity[a] |
|---|---|---|
| $m$-$CF_3C_6H_4MgBr$ | $0.22 \times 10^{-4}$ | 2 |
| $m$-$ClC_6H_4MgBr$ | $0.33 \times 10^{-4}$ | 3 |
| $p$-$ClC_6H_4MgBr$ | $0.6 \times 10^{-4}$ | 6 |
| $C_6H_5MgBr$ | $2.80 \times 10^{-4}$ | 25 |
| $p$-$CH_3C_6H_4MgBr$ | $6.22 \times 10^{-4}$ | 60 |

[a] Relative reactivities are corrected to a basis of 35° and equimolar reactant concentrations ($0.2M$), with the value for $C_2H_5MgBr$ taken as 100 (*cf.* ref. 1).

A plot of log k versus Hammett sigma values for the various substituents yielded a value of $\rho = -2.5$. This indicates the reaction is facilitated by increased electron density at the $\alpha$-carbon atom of the Grignard reagent and that the attack is electrophilic in nature.

In addition to permitting the determination of the relative reactivities of arylmagnesium halides, this method should be of wide use in following the kinetics of many organometal reactions in solution, provided a change in dielectric constant accompanies the progress of the reaction and all products remain in solution. The use of dielectric constant in following organic reactions has been described previously.[5] This method is particularly well suited to the study of organometal reactions in solution since external electrodes on the reaction cell prevent contamination of the sample, and the cell holder can conveniently be mounted in a dry box to prevent atmospheric destruction of sensitive organometallic compounds.

## EXPERIMENTAL

*Arylmagnesium bromides* were prepared in the usual manner.[1] The concentration of the Grignards was determined by the method of Gilman.[6] Hexyne-1 was freshly distilled and stored in a nitrogen atmosphere; ethyl ether was distilled from lithium aluminum hydride.

*Determination of rates.* The dielectric apparatus consisted of a Sargent Model V Oscillometer, operating at 5 megacycles/sec. connected to an auxiliary cell compensator which provided a means of obtaining a linear relationship between dielectric constant and instrument scale divisions. The output of the oscillometer was piped into a dry-box to the cell holder. The cell was a vessel presenting an annular sample space between two concentric glass cylinders on whose external surfaces are fused metallic electrode surfaces.[7] Its total volume was 10 ml.

The dielectric constants of phenyl and 1-hexynyl Grignards in ether were found to be a linear function of concentration below $0.2M$. The dielectric constants of hexyne-1 and benzene solutions in ether varied only slightly with concentration in the range used; this variation was linear.

Rate determinations were made using $0.15M$ arylmagnesium bromide and $3.0M$ hexyne-1 in ethyl ether to provide pseudo-first order kinetics. The Grignard reagent and ether were placed in the dielectric constant cell.

When the sample reached thermal equilibrium, the hexyne-1 was added and the cell shaken to mix the reactants, and placed in the cell holder. The cell holder was mounted in an air bath maintained at 31.5° ± 0.1° by a surrounding thermostatted oil bath.

Readings were taken at regular intervals, and the first order rate constant calculated from a plot of log $[(D_t - D_\infty)/(D_0 - D_\infty)]$ versus time. $D_t$ represents the dielectric constant at $t$, $D_0$ at the start of the reaction, and $D_\infty$ at "infinite time" (at least ten half-lives). The runs made at equimolar concentrations were performed in a similar manner. Plots of $[(D_0 - D_\infty)/(D_t - D_\infty)]$ versus $t$ were used to evaluate the kinetic picture.[8] Duplicate measurements were made on all runs. The values reported are the averages. The precision is within ±3%.

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[4] The investigations of the Pittsburgh group of the reaction of hexyne-1 with phenylmagnesium bromide in ether and tetrahydrofuran consisted of VPC analysis of gas samples from above the surface of the boiling reaction media. All reactions were run at equimolar concentrations near $0.2M$. The reactions appeared to obey first order kinetics in ether, but appeared to exhibit second-order kinetics (with reduced rate) when tetrahydrofuran was added. No attempt to determine what was the controlling reagent in the ether solution reaction was made.

[5] D. G. Flom and P. J. Elving, *Anal. Chem.*, **25**, 541 (1953); P. J. Elving, *Faraday Soc. Discussions*, **17**, 156 (1954); P. J. Elving and J. Lakritz, *J. Am. Chem. Soc.*, **77**, 3217 (1955); S. F. Voltz and M. W. Rigg, *J. Phys. Chem.*, **58**, 537 (1954).

[6] H. Gilman, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

[7] Paul H. Sherrick *et al.*, *Manual of Chemical Oscillometry*, E. H. Sargent and Co., Chicago, 1954, p. 6.

[8] *Cf.* A. A. Frost and R. G. Pearson, *Kinetics and Mechanism*, Wiley, New York, 1953, p. 28; P. J. Elving, *Faraday Soc. Discussions*, **17**, 156 (1954).