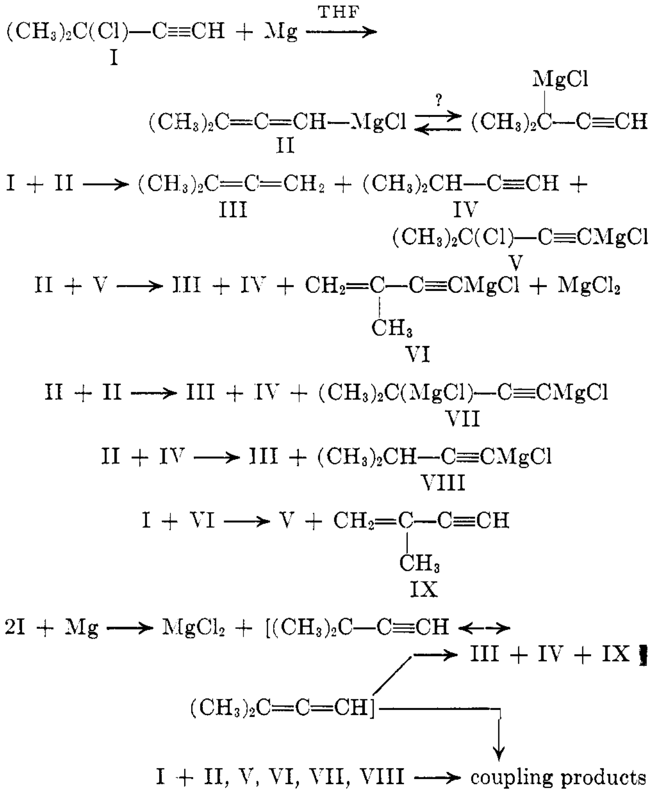
by reaction with acetone prior to hydrolysis produced mixtures of acetylenic and allenic alcohols and unidentified carbonyl compounds as well as the monomeric and dimeric hydrocarbons obtained by hydrolysis only. No pure, single alcohol could be distilled from any of these experiments.

The experimental evidence indicates that the reaction of *t*-propargylic chlorides with magnesium in THF produces a variety of Grignard reagents (probably four or five) and various monomeric and dimeric hydrocarbons as illustrated in the following equations.



$$\underset{\text{I}}{(CH_3)_2C(Cl){-}C{\equiv}CH} + Mg \xrightarrow{\text{THF}}$$

$$\underset{\text{II}}{(CH_3)_2C{=}C{=}CH{-}MgCl} \overset{?}{\rightleftarrows} (CH_3)_2\overset{MgCl}{\overset{|}{C}}{-}C{\equiv}CH$$

$$\text{I} + \text{II} \longrightarrow \underset{\text{III}}{(CH_3)_2C{=}C{=}CH_2} + \underset{\text{IV}}{(CH_3)_2CH{-}C{\equiv}CH} + \underset{\text{V}}{(CH_3)_2C(Cl){-}C{\equiv}CMgCl}$$

$$\text{II} + \text{V} \longrightarrow \text{III} + \text{IV} + \underset{\text{VI}}{CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}C{\equiv}CMgCl} + MgCl_2$$

$$\text{II} + \text{II} \longrightarrow \text{III} + \text{IV} + \underset{\text{VII}}{(CH_3)_2C(MgCl){-}C{\equiv}CMgCl}$$

$$\text{II} + \text{IV} \longrightarrow \text{III} + \underset{\text{VIII}}{(CH_3)_2CH{-}C{\equiv}CMgCl}$$

$$\text{I} + \text{VI} \longrightarrow \text{V} + \underset{\text{IX}}{CH_2{=}\underset{CH_3}{\underset{|}{C}}{-}C{\equiv}CH}$$

$$2\text{I} + Mg \longrightarrow MgCl_2 + [(CH_3)_2C{-}C{\equiv}CH \longleftrightarrow (CH_3)_2C{=}C{=}CH] \longrightarrow \text{III} + \text{IV} + \text{IX}$$

$$\text{I} + \text{II, V, VI, VII, VIII} \longrightarrow \text{coupling products}$$

Of the various Grignard reagents formed (II, V, VI, VII and VIII), II is the major product as with propargyl chloride itself. III, IV and IX illustrate monomeric hydrocarbons (III predominating) formed in small amount prior to hydrolysis and in larger amounts after. Major coupling products may be explained *via* coupling of propargylic–allenic radicals as shown, while radical disproportionation would yield III, IV, and IX.

Experimental Section

The *t*-propargylic chlorides were prepared as described.[7]

General Procedure.—To 6.1 g (0.25 g-atom) of magnesium turnings and *ca.* 0.1 g of mercuric chloride in 50 ml of THF under nitrogen, in the usual apparatus, was added about 0.1 of a solution of 0.25 mole of *t*-propargylic chloride in 50 ml of THF. Warming to 60° often initiated reaction, although in some cases it was necessary to add a few small pieces of magnesium externally activated with ethylene dibromide in THF. Once reaction was initiated, the temperature was lowered to 40–45° and the remaining chloride added dropwise with stirring. Additional THF was added as needed to maintain fluidity. Approximately 75% of the magnesium was consumed under these conditions.

Distillation.—The crude product obtained from 3-chloro-3-methyl-1-butyne as described above was diluted with 100 ml of THF and 110 g was distilled. Fractional redistillation gave 2 g, bp 42–45°, shown by infrared and glpc to contain 3-methyl-1,2-butadiene (III), isopropylacetylene (IV), and isopropenylacetylene (IX) in the ratio 91:8:1.

Hydrolysis.—The Grignard residue from the distillation described above was hydrolyzed with 200 g of saturated ammonium chloride solution and 100 ml of water. The layers were separated and the aqueous layer was extracted with 100 ml of hexane. The organic layers were combined, dried over calcium chloride, and fractionally distilled. Two grams, bp 42–45°, had III, IV, and IX in the ratio 69:12:19. Another fraction, 3 g, bp 55–57° (40 mm), was shown by infrared and pmr to be a mixture of 3,3,4,4-tetramethyl-1,5-hexadiyne and 3,3,6-trimethylhepta-4,5-dien-1-yne in the ratio 78:21.

Vinylidenecyclohexane.—The general procedure described above was used with 1-ethynylcyclohexyl chloride. The mixture was stirred for 1 hr after addition of the chloride, then hydrolyzed. Distillation gave 14 g (50% yield), bp 50–80° (90 mm). On redistillation most of this material boiled at 138–141° [lit.[8] bp 56.5–58.5° (45 mm) and 138–141° (atm)], and infrared and glpc examination of this fraction showed it to be about 97% vinylidenecyclohexane containing 3% cyclohexylacetylene.

3-Ethyl-1,2-pentadiene was obtained in 62% yield and purity about 70% from 3-chloro-3-ethyl-1-pentyne as described above: 15 g, bp 40–51° (150 mm). The major contaminant was 3-ethyl-1-pentyne. A 3-g fraction of coupling products, bp 65–75° (5 mm), was isolated also; the infrared spectrum had strong acetylenic and allenic bands.

Acknowledgments.—The authors express their sincere thanks to Air Reduction Company, New York, New York, for generous samples of *t*-acetylenic carbinols and to Eli Lilly and Company, Indianapolis, Indiana, for financial support.

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[7] G. F. Hennion and A. P. Boiselle, *J. Org. Chem.*, **26**, 725 (1961).

[8] W. J. Bailey and C. R. Pfeifer, *ibid.*, **20**, 95 (1955).

A Method for the Preparation of Grignard Compounds in Hydrocarbon Solution

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Received September 1, 1965

The importance of Grignard reagents in synthetic organic chemistry is well known. Since the discovery of this reagent by Grignard in 1900, diethyl ether has been used almost exclusively as the solvent for the preparation of these compounds. More recently, another ether, tetrahydrofuran, has been employed to advantage for the preparation of certain Grignard compounds (*e.g.*, vinylmagnesium bromide and phenylmagnesium chloride) not readily prepared in diethyl ether.[2] Aliphatic[3] and aromatic[4] hydrocarbons have been used as diluents in the reaction of alkyl halides with magnesium; however, a mixture of insoluble products is produced, the composition of which appears to vary depending on the conditions of the reaction. Compounds of the composition R_3Mg_2X and MgX_2 have been isolated from the solid reaction products. The use of dimethylaniline as a catalyst for the reaction of RX and Mg in hydrocarbon diluent

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[1] Alfred P. Sloan Fellow.

[2] H. E. Ramsden, U. S. Patent 2,838,508 (1958).

[3] L. I. Zakharkin, O. Yu. Okhlobystein, and B. N. Strunin, *Tetrahedron Letters*, **No. 14**, 631 (1962).

[4] D. Bryce-Smith and G. F. Cox, *J. Chem. Soc.*, 1175 (1961).

TABLE I

GRIGNARD COMPOUNDS PREPARED IN BENZENE SOLVENT

Compd	Complexing agent	Yield, %	Calcd, % Mg	X	N	Found, % Mg	X	N	Ratio Mg:X:N
C_2H_5MgCl	$(C_2H_5)_3N$	97	12.8	18.7	7.4	13.0	18.6	7.1	1.05:1.03:1.00
C_2H_5MgBr	$(C_2H_5)_3N$	88	10.3	34.1	6.0	11.3	33.2	6.4	1.07:1.00:1.10
C_2H_5MgI	$(C_2H_5)_3N$	97	8.6	45.1	5.0	8.5	44.2	4.9	1.00:1.00:1.00
n-C_4H_9MgCl	$(C_2H_5)_3N$	93	11.2	16.3	6.4	11.0	16.0	5.9	1.09:1.08:1.00
C_6H_5MgBr	$(C_2H_5)_3N$	77	8.9	28.3	5.0	8.5	30.0	5.0	1.00:1.03:1.07

also has been reported;[5] however, once again the resulting magnesium product is insoluble.

We wish to report the preparation of typical Grignard compounds in hydrocarbon solvents such as benzene and toluene resulting in the production of true solutions. The method involves the reaction of an alkyl or aryl halide and magnesium turnings in benzene solvent in the presence of an equimolar amount of a tertiary amine. The preparation of true solutions by this method is somewhat unusual in that the same reaction using diethyl ether as the complexing agent results in the precipitation of solids of nonstoichiometric composition. The use of a tertiary amine as the complexing agent appears to be successful owing to the nondisproportionation tendency of the RMgX species when complexed to a tertiary amine.[6] This new method eliminates the use of the more expensive and hazardous diethyl ether and makes available Grignard compounds in hydrocarbon solution which should be of both academic and commercial value.

The results reported in Table I show that typical aliphatic and aromatic magnesium chlorides, bromides, and iodides are produced in good yield. The reactions are slightly more difficult to initiate than the corresponding reaction in diethyl ether. The reaction is normally started at room temperature to 50° and the reaction temperature is maintained no higher than 50° during reaction.

Triethylamine appears to be a good choice as the complexing agent, although other tertiary amines (such as tri-n-propylamine or tri-n-butylamine) should work as well. Trimethylamine has the disadvantage of low boiling point which makes the reaction difficult to start, and dimethylaniline has the disadvantage that not all Grignard compounds complexed with this amine are soluble in benzene. Our results using triethylamine in large excess as the solvent for the Grignard preparation indicates that quaternary salt formation ($R'X + R_3N \rightarrow R_3R'NX$) and dehydrohalogenation ($R'X + R_3N \rightarrow$ olefin $+ R_3NHX$) can be a problem. These results will be reported elsewhere. However, in benzene solvent, under the conditions employed, these side reactions were not detected.

Experimental Section

Although most of the Grignard compounds were prepared to produce a 1 M solution in benzene, ethylmagnesium bromide and n-butylmagnesium chloride have been prepared in concentrations approaching 2 and 3 M, respectively.

The general procedure for preparing Grignard compounds in benzene solvent is as follows. An alkyl halide (0.5 mole) dissolved in 400 ml of dry benzene was added to magnesium turnings (0.6 g-atom) diluted with 30 ml of benzene and 0.5 mole of triethylamine. Approximately 30 ml of the alkyl halide–benzene solution was added and the reaction was started by gentle warming. The remainder of the alkyl halide–benzene solution was added slowly over a 2-hr period keeping the reaction temperature at 40–50°. The resulting solution was clear and often colorless. It was separated from the excess magnesium turnings by filtration through a medium sintered-glass funnel. Yields were determined by isolation of the reaction product as a solid by removal of the solvent under vacuum followed by elemental analysis. Magnesium and halogen content were determined by EDTA analysis and nitrogen by titration of the tertiary amine.

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(5) R. Barré and J. De Repentigny, *Can. J. Res.*, **B27**, 716 (1949).

(6) E. C. Ashby, *J. Am. Chem. Soc.*, **87**, 2509 (1965).

Spectral Solvent Shifts. Substituent Effects. II[1]

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Received August 19, 1965

It has been known for many years that polar solvents cause displacements of the ultraviolet absorption maxima of aromatic compounds as compared to nonpolar solvents. There have been many attempts to explain these effects. Ungnada,[3] Nagakura and Baba,[4] Baba and Suzuki,[5] Utley,[6] Lees and Burawoy,[7] and Dearden and Forbes[8] have emphasized hydrogen bonding of the types solvent H→solute and solute H→solvent. Ungnade[3] and Schubert, *et al.*,[9] have shown the importance of ground-state solvation and excited-state solvation, red shifts being caused by greater solvation of excited states than ground states and blue shifts being due to highly solvated ground states that hinder excitation.

Bayliss and McRae[10] have considered the importance of the dipole moment transitions of the solute molecule in going from ground to excited state with the resultant greater solvation of the polar excited state. McRae,[11] Sembe,[12] and others believe that solvent shifts are related to the dielectric constant and refractive index of the solvent. West and Geddes[13] have recently con-

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(1) Part I: E. W. Crandall and J. Olguin, *J. Org. Chem.*, **29**, 2088 (1964).

(2) In part from the M.S. Thesis of J. Olguin.

(3) H. E. Ungnade, *J. Am. Chem. Soc.*, **75**, 432 (1953).

(4) S. Nagakura and H. Baba, *ibid.*, **74**, 5693 (1952).

(5) H. Baba and S. Suzuki, *J. Chem. Phys.*, **35**, 1118 (1961).

(6) J. H. P. Utley, *J. Chem. Soc.*, 3252 (1963).

(7) W. A. Lees and A. Burawoy, *Tetrahedron*, **19**, 419 (1963).

(8) J. C. Dearden and W. F. Forbes, *Can. J. Chem.*, **38**, 896 (1960).

(9) (a) W. M. Schubert, J. Robins, and J. L. Haun, *J. Am. Chem. Soc.*, **79**, 910 (1957); (b) W. M. Schubert, H. Steadley, and J. M. Craven, *ibid.*, **82**, 1353 (1960); (c) W. M. Schubert and J. M. Craven, *ibid.*, **82**, 1357 (1960).

(10) N. Bayliss and E. G. McRae, *J. Phys. Chem.*, **58**, 1002 (1954).

(11) E. G. McRae, *ibid.*, **61**, 562 (1957).

(12) K. Sembe, *Bull. Chem. Soc. Japan*, **34**, 722 (1961).

(13) W. West and A. L. Geddes, *J. Phys. Chem.*, **68**, 837 (1964).