of *p*-hydroxybenzaldehyde in 25 ml of absolute alcohol was refluxed for 16 hr. The solution was concentrated to 15 ml and chilled. The precipitate was filtered, dried, and recrystallized from absolute alcohol to give 1.60 g (73%) of IV, a pale yellow, crystalline solid, mp 145–146°.

Anal. Calcd for $C_{11}H_{14}N_2O_4$: C, 55.45; H, 5.92; N, 11.76. Found: C, 55.65; H, 6.17; N, 11.98.

3-Benzylamino-2-oxazolidinone (Ia). A. Cyclization of (2-Chloroethyl) 3-Benzylcarbazate (IIa).—The procedure of Delaby[2] was followed to prepare (2-hydroxyethyl) 3-benzylcarbazate (IIIa) from benzylhydrazine and ethylene carbonate and to convert IIIa to IIa. Cyclization of IIa to Ia, which was not explicitly described in Delaby's papers, was performed as follows. A solution of 2.29 g (0.01 mole) of IIa in 25 ml of absolute alcohol stirred under nitrogen was treated, over 10 min, with 0.23 g (0.01 g-atom) of sodium in 10 ml of absolute alcohol. The solution was stirred 0.5 hr and then refluxed 1 hr. After cooling, the precipitated sodium chloride was filtered and the alcohol was stripped *in vacuo*. Recrystallization of the residue from benzene gave 1.06 g (55%) of Ia as small colorless needles, mp 70–72° (lit.[2] mp 70°).

B. Reduction of 3-Benzylideneamino-2-oxazolidinone.—3-Benzylideneamino-2-oxazolidinone was prepared in 95% yield (mp 143–145°) from 3-amino-2-oxazolidinone and benzaldehyde by the procedure of Gever, *et al.*[5] To 5.0 g (0.026 mole) of the benzylidene compound in 100 ml of absolute alcohol stirred under nitrogen was added 2 g of 5% palladium on charcoal. Hydrogen gas was bubbled through the solution for 4 hr. The catalyst was filtered and the solution was concentrated to 25 ml. The precipitate obtained on chilling was filtered, dried, and recrystallized from benzene to yield 4.90 g (97%) of Ia, mp 71–72°.

Anal. Calcd for $C_{10}H_{12}N_2O_2$: C, 62.48; H, 6.29; N, 14.58. Found: C, 62.71; H, 6.38; N, 14.42.

The infrared spectrum of this material was identical with that of the material in preparation A above: mmp 70–72°.

(2-Chloroethyl) 3-phenylcarbazate (VI) was prepared, in 67% yield, from 2-chloroethyl chloroformate and phenylhydrazine by the method of Dox:[6] mp 90–91° (lit.[6] mp 89°); infrared (mineral oil mull), 3340, 3210, 1705, 1595, 1545, 1490, 1300, 1280, 1255, 1240, 1180, 1145, 1080, 1070, 1025, 940, 895, 755, and 700 cm^{-1}.

Cyclization of VI. 3-Anilino-2-oxazolidinone (VIII).—Compound VI was treated with sodium ethoxide by the method of Dox[6] to give a 50% yield of VIII: mp 118–120° (lit.[6] mp 120°); infrared (mineral oil mull), 3260, 1745, 1595, 1480, 1460, 1410, 1280, 1240, 1105, 1030, 970, 890, 840, 760, and 700 cm^{-1}.

(2-Chloroethyl) 3-Acetyl-3-phenylcarbazate (IX).—To a solution of 3.0 g (0.02 mole) of 1-acetyl-1-phenylhydrazine[8] in 50 ml of dioxane was added over 10 min a solution of 2.86 g (0.02 mole) of 2-chloroethyl chloroformate in 10 ml of dioxane and a solution of 2.02 g (0.02 mole) of triethylamine in 10 ml of dioxane. After stirring 1 hr at 25°, the solution was refluxed 1 hr and then chilled. Precipitated sodium chloride was filtered and the dioxane was stripped *in vacuo*. Recrystallization of the residue from absolute alcohol gave 2.75 g (54%) of IX, small, white crystals, mp 100–102°.

Anal. Calcd for $C_{11}H_{13}ClN_2O_3$: C, 51.46; H, 5.07; N, 10.92. Found: C, 51.26; H, 5.15; N, 11.17.

3-(N-Acetyl-N-phenylamino)-2-oxazolidinone (X). A. From VIII.—A solution of 1.0 g (0.0056 mole) of VIII in 2 ml of acetic anhydride was refluxed for 18 hr. Acetic acid and excess anhydride were stripped *in vacuo*. The oily residue on standing several days solidified. Recrystallization from benzene–petroleum ether (bp 30–60°) then gave 0.71 g (58%) of white cuboids, mp 67–69°.

Anal. Calcd for $C_{11}H_{12}N_2O_3$: C, 59.99; H, 5.49; N, 12.72. Found: C, 59.72; H, 5.28; N, 12.43.

B. From IX.—Sodium (0.115 g, 0.005 g-atom) in 20 ml of absolute alcohol was added over 10 min to 1.28 g (0.005 mole) of IX in 50 ml of absolute alcohol. A precipitate rapidly formed. The mixture was refluxed 2 hr, chilled, and the sodium chloride was filtered. Extraction of the residue with benzene, followed by stripping of the benzene, gave a white solid. Recrystallization from benzene–petroleum ether yielded 0.67 g (61%) of VIII, mp 67–68°.

The infrared spectrum of this compound was identical with that of the compound in preparation A above: mmp 67–68°.

Grignard Reagents from *t*-Propargylic Chlorides[1]

G. F. HENNION AND C. V. DIGIOVANNA

Department of Chemistry, University of Notre Dame,
Notre Dame, Indiana 46556

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It is well known that Grignard reagents are rapidly decomposed by 1-alkynes (as with other active hydrogen compounds) and the mechanisms[2] of such reactions have received careful study. Thus, it may seem surprising that propargyl bromide reacts with magnesium under ether, if a little mercuric chloride is added, to form a Grignard reagent[3] which, in turn, reacts with carbonyl compounds[4] to yield propargylcarbinols, $RR'C(OH)CH_2C{\equiv}CH$. Jacobs and Moore[5] reported that propargyl bromide and chloride and the isomeric haloallenes form the *same* Grignard reagent which has the allenic structure, $CH_2{=}C{=}CHMgX$. Hydrolysis gave allene and methylacetylene (ratio 80:20), while treatment with ketones gave exclusively propargylic products as claimed earlier by Gaudemar.[4]

We describe now many efforts to form Grignard reagents from *t*-propargylic chlorides, $RR'C(Cl)C{\equiv}CH$, which indicated that the reaction with magnesium is considerably more complicated than with propargyl chloride itself. The important observations are as follows. (A) Three *t*-chlorides ($R = R' = CH_3$; $R = R' = C_2H_5$; and RR'C = cyclohexyl) failed to react with magnesium under ether under all conditions tried, including catalysis with mercuric chloride and Pearson's entrainment method,[6] generally useful with inert halides. (B) Reactions with magnesium proceeded smoothly in tetrahydrofuran (THF) at 40–60° provided the magnesium was activated with mercuric chloride and (in some instances) ethylene dibromide. In all cases the magnesium consumed was appreciably less than theoretical, suggesting that coupling reactions and/or Grignard alkylations were involved. (C) Experiments with 3-chloro-3-methyl-1-butyne ($R = R' = CH_3$) included, in one case, distillation prior to hydrolysis or other postreaction; the distillate contained considerable dimethylallene contaminated with isopropylacetylene and traces of isopropenylacetylene. (D) Hydrolysis of freshly prepared crude reaction products, followed by work-up in the usual manner, gave poor yields (not over 50%) of monomeric hydrocarbons found to be mixtures of allene, alkylacetylene, and alkenylacetylene. Higher boiling distillates showed acetylenic, allenic, and conjugate olefinic infrared bands; glpc examination of these fractions showed them to be complex mixtures of coupling products. (E) Attempts to identify specific Grignard reagents

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[1] Paper 82 on substituted acetylenes; previous paper, G. F. Hennion and C. V. DiGiovanna, *J. Org. Chem.*, **30**, 3696 (1965).

[2] (a) J. H. Wotiz and G. L. Proffitt, *ibid.*, **30**, 1240 (1965), and earlier papers; (b) H. Hashimoto, T. Nakano, and H. Okada, *ibid.*, **30**, 1234 (1965), and references cited.

[3] C. Prevost, M. Gaudemar, and J. Honigberg, *Compt. Rend.*, **230**, 1186 (1950); *Bull. Soc. Chim. France*, 679 (1959).

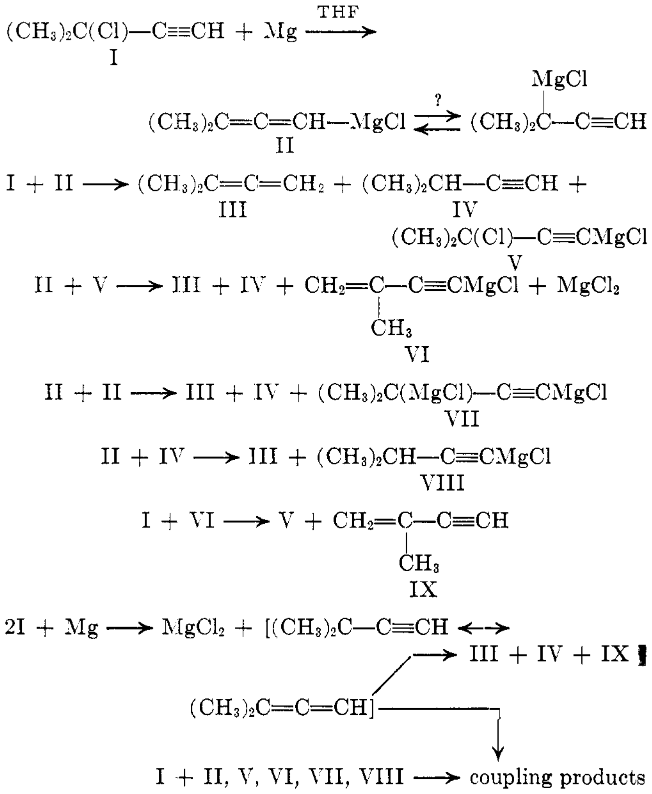
[4] M. Gaudemar, *Compt. Rend.*, **233**, 64 (1951); *Ann. Chim.* (Paris), [13] **1**, 161 (1956).

[5] T. L. Jacobs and T. L. Moore, Abstracts of Papers, 141st Meeting of the American Chemical Society, Washington, D. C., March, 1962, p. 19–O.

[6] D. E. Pearson, D. Cowan, and J. D. Beckler, *J. Org. Chem.*, **24**, 504 (1959).

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.



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

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

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

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

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

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

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

$$2\text{I} + Mg \longrightarrow MgCl_2 + [(CH_3)_2\dot{C}{-}C{\equiv}CH \longleftrightarrow (CH_3)_2C{=}C{=}\dot{C}H] \longrightarrow \text{III} + \text{IV} + \text{IX}$$

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

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.

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A Method for the Preparation of Grignard Compounds in Hydrocarbon Solution

E. C. ASHBY[1] AND R. REED

Department of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332

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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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