Studies with Acetylenes. Part I. Some Reactions of Grignard Reagents with Alk-1-ynyl and Alk-1-enyl Halides.

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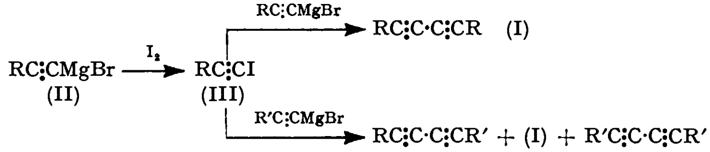
In the presence of small amounts of cuprous or cobaltous chloride, alk-1-ynyl halides condense with alkyl, aryl, and alkynyl Grignard reagents to give disubstituted acetylenes or diacetylenes. In the absence of the metal chlorides, alk-1-ynyl halides and alkyl (or aryl) Grignard reagents undergo metathesis.

With a cobaltous chloride catalyst, alkynyl Grignard reagents will also react with alk-1-enyl and alkyl halides giving vinylacetylenes and alkyl-substituted acetylenes, respectively.

This communication describes some reactions of alkynyl Grignard reagents with alk-1-ynyl and alk-1-enyl halides, and of alkyl and aryl Grignard reagents with alk-1-ynyl halides. These reactions, if carried out in the presence of cuprous or cobaltous chloride, afford diacetylenes, vinylacetylenes, and disubstituted acetylenes.

Alkynyl Grignard Reagents.—Grignard and his collaborators (Grignard and Perrichon, *Ann. Chim,*, 1926, **5**, 13; Grignard and Tchéoufaki, *Compt. rend.*, 1929, **188**, 357) reported that diacetylenes (I) were formed in good yield on treatment of an alkynylmagnesium halide (II) with half the amount of iodine required to give the alkynyl iodide (III). Although it was also stated that unsymmetrically substituted diacetylenes (IV) could be obtained by reaction of the alkynyl iodide (III) with the bromomagnesio-derivative (V) of the appropriate acetylene, the only example quoted was the preparation of "phenyltriacetylene" from phenylethynylmagnesium bromide and "iododiacetylene." However, this result must now be discounted since Schlubach and Franzen (*Annalen*, 1951, **573**, 115) have shown that iododiacetylene has properties very different from those reported by Grignard and Tchéoufaki for their starting material.



$$\mathrm{RC{\vdots}CMgBr}\ \text{(II)} \xrightarrow{\mathrm{I_2}} \mathrm{RC{\vdots}CI}\ \text{(III)} \xrightarrow{\mathrm{RC{\vdots}CMgBr}} \mathrm{RC{\vdots}C{\cdot}C{\vdots}CR}\ \text{(I)}$$

$$\text{(III)} \xrightarrow[\text{(V)}]{\mathrm{R'C{\vdots}CMgBr}} \underset{\text{(IV)}}{\mathrm{RC{\vdots}C{\cdot}C{\vdots}CR'}} + \text{(I)} + \underset{\text{(VI)}}{\mathrm{R'C{\vdots}C{\cdot}C{\vdots}CR'}}$$

In connection with a study of methods for the synthesis of erythrogenic acid and related compounds (cf. Black and Weedon, *J.*, 1953, 1785), Grignard's route to diacetylenes has been re-examined. Treatment of hexynylmagnesium bromide with 0·5 mol. of iodine, following Grignard's procedure, gave mainly iodohexyne (III; R = Bu), and only very small amounts of dodecadiyne (I; R = Bu). This failure of the iodohexyne to react further with the excess of Grignard reagent was reminiscent of the difficulty encountered by Danehy, Killian, and Nieuwland (*J. Amer. Chem. Soc.*, 1936, **58**, 611) in repeating Grignard and Lapayre's (*Bull. Soc. chim.*, 1928, **43**, 141) condensation of alkynylmagnesium halides with allyl bromide. The American authors found small amounts of cuprous chloride very effective in promoting the desired condensation. When this catalyst was used in the reaction of hexynylmagnesium bromide with iodine, dodecadiyne was formed in the same yield (70%) as that obtained by Grignard and Tchéoufaki without addition of catalyst.

Less satisfactory results were achieved in the preparation of unsymmetrical diacetylenes, owing to the intrusion of side reactions not mentioned by Grignard and his co-workers. Treatment of iodohexyne (III; R = Bu) with phenyl- or *cyclo*hex-1-enyl-ethynylmagnesium bromide in the presence of cuprous chloride gave mixtures containing three diacetylenes (I, IV, and VI; R = Bu, R′ = Ph or *cyclo*hexenyl), from which the required unsymmetrical products were separated in only *ca.* 35% yield. A similar condensation of 1-bromohex-1-

yne with phenylethynylmagnesium bromide yielded a mixture from which phenyloctadiyne (IV; R = Bu, R′ = Ph) was isolated (15%), but a single attempt to prepare the latter from 1-bromo-2-phenylacetylene and hexynylmagnesium bromide was, surprisingly, unsuccessful.

Since Kharasch and his collaborators have shown that small amounts of cobaltous chloride exert a strong influence on the course of many reactions with alkyl and aryl Grignard reagents (cf. Hey, *Ann. Reports*, 1944, **41**, 195; 1948, **45**, 160), the use of this catalyst was considered. Condensation of hexynylmagnesium bromide with 1-bromohex-1-yne and with 1-bromo-2-phenylacetylene in presence of cobaltous chloride gave (30%) dodecadiyne and phenyloctadiyne, respectively. Similarly, reaction of phenylethynylmagnesium bromide with 1-bromo-2-phenylacetylene gave (30%) diphenylbutadiyne (I; R = Ph), but an attempt to prepare phenyloctadiyne from hexynylmagnesium bromide and 1-iodo-2-phenylacetylene failed, diphenylbutadiyne being the only diacetylene isolated (28%). Recently Schlubach and Franzen (*Annalen*, 1951, **572**, 116), using the same catalyst, prepared diphenylbutadiyne (I = Ph) in 75% yield from iodophenylacetylene and phenylethynylmagnesium bromide, but were unable to effect an analogous reaction between the same Grignard reagent and di-iodoacetylene.

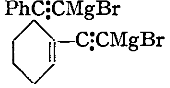
The simultaneous formation of symmetrical diacetylenes as by-products during the preparation of unsymmetrical compounds is probably due to the initial establishment of an equilibrium of the following type:

$$\mathrm{RC{\vdots}CI + R'C{\vdots}CMgBr \rightleftharpoons RC{\vdots}CMgBr + R'C{\vdots}CI}$$

[Analogous interchange reactions have been observed with alkyl and aryl Grignard reagents in the absence of catalyst (see below); also in the reaction of alkyl and aryl Grignard reagents with organic halides in the presence of cobaltous chloride (Kharasch and Fuchs, *J. Org. Chem.*, 1945, **10**, 292).] Subsequent condensation would then lead to a mixture of three diacetylenes, as is observed.

The majority of the results described above are summarised in Table 1. Clearly the alkynyl iodides are much superior to the bromides for the preparation of the symmetrical diacetylenes. The low yields (⯒35%) of unsymmetrical diacetylenes from the alkynyl iodides may be attributed mainly to interchange reactions of the type discussed above leading to symmetrical products, but there is some evidence that the alkynyl bromides are less reactive in these reactions as well as in the condensations with alkynyl Grignard reagents.

TABLE 1. *Yield* (%) *of diacetylene* (RC⋮C·C⋮CR′). [The use of a cuprous or cobaltous chloride catalyst is indicated by (Cu) or (Co), respectively.]

Grignard reagent (R′C⋮CMgBr)	Halide			
	BuC⋮CI	BuC⋮CBr	PhC⋮CI	PhC⋮CBr
BuC⋮CMgBr	<10; 71 * (Cu)	28(Co)	0(Co)	0(Cu); 31(Co)
PhC⋮CMgBr	35(Cu)	15(Cu)	75(Co) †	39(Co)
	34(Cu)			

* Iodohexyne formed *in situ*. † Schlubach and Franzen, *Annalen*, 1951, **572**, 116.

Since aryl and alkyl Grignard reagents condense with alk-1-enyl halides in presence of cobaltous chloride (Kharasch and Fuchs, *J. Amer. Chem. Soc.*, 1943, **65**, 504), it seemed probable that in the above reactions the alk-1-ynyl halides might be replaced by alk-1-enyl halides, thus providing a new route to vinylacetylenes. The catalysed condensations of hexynylmagnesium bromide with *iso*butenyl bromide, and of phenylethynylmagnesium bromide with styryl bromide, gave the vinylacetylenes, $\mathrm{CMe_2{:}CH{\cdot}C{\vdots}CBu}$ and $\mathrm{PhCH{:}CH{\cdot}C{\vdots}CPh}$, respectively. The recent claim (Herbert, *Chem. Ber.*, 1952, **85**, 475) that vinyldiacetylene can be obtained by heating vinyl bromide and monosodiodiacetylene in an inert solvent is of interest in connection with these results.

Both aryl and alkynyl Grignard reagents undergo coupling reactions on treatment with 1 mol. of cupric halide, giving symmetrical diaryls (Krizewsky and Turner, *J.*, 1919, 559; Sakellarios and Kyrimis, *Ber.*, 1924, **57**, 322) and diacetylenes (Danehy and Nieuwland, *J. Amer. Chem. Soc.*, 1936, **58**, 1609), respectively. The production of diaryls in good yield from the Grignard reagent and 1 mol. of an alkyl halide in the presence of cobaltous chloride (Kharasch *et al.*, *ibid.*, 1941, **63**, 2316; 1943, **65**, 493; 1944, **66**, 365) suggested that an analogous coupling reaction might be achieved with alkynyl Grignard reagents. However, all attempts to prepare diacetylenes in this way have been unsuccessful. Thus from hexynylmagnesium bromide and butyl bromide, in the presence of cobaltous chloride, the only product isolated was dec-5-yne. Condensations of this type between an alkyl halide and an alkynyl Grignard reagent have been reported to occur even without catalyst, but are exceptional (cf. Jacobs, *Org. Reactions*, 1949, **5**, 1).

Alkyl and Aryl Grignard Reagents.—Having examined the behaviour of alk-1-ynyl halides towards ethynyl Grignard reagents, we studied some analogous reactions with typical alkyl and aryl Grignard reagents. Such organometallic compounds have been condensed with dichloroacetylene ($\mathrm{ClC{\vdots}CCl}$) to give chloroacetylenes ($\mathrm{R'C{\vdots}CCl}$) (Ott and Bossaller, *Ber.*, 1943, **76**, 88). However, di-iodoacetylene, iododiacetylene, and various bromoacetylenes have been reported to undergo metathetical reactions :

$$\mathrm{RC{\vdots}CBr + R'MgBr \longrightarrow RC{\vdots}CMgBr + R'Br}$$

(Jositsch, *Bull. Soc. chim.*, 1906, **36**, 177; Kharasch, Lambert, and Urry, *J. Org. Chem.*, 1945, **10**, 298; Moulin, *Helv. Chim. Acta*, 1951, **34**, 2416; Schlubach and Franzen, *Annalen*, 1951, **572**, 116; **573**, 115). The effect of catalyst is known only in the reaction of 1-bromo-2-phenylacetylene with methylmagnesium bromide: condensation, instead of the normal interchange, occurred in the presence of cobaltous chloride giving phenylpropyne in 62% yield (Kharasch, Lambert, and Urry, *loc. cit.*). The yield of phenylpropyne in our catalysed reaction was $\ngtr$40%, phenylacetylene (*ca.* 30%) being formed simultaneously by metathesis.

Similarly *n*-butylmagnesium bromide and either 1-bromo- or 1-iodo-2-phenylacetylene with cobaltous chloride gave phenylhexyne in 32—34% yield; by use of cuprous chloride the yield of phenylhexyne from 1-bromo-2-phenylacetylene was raised to 46%. Reaction of butylmagnesium bromide with 1-bromo-2-phenylacetylene in absence of catalyst gave both phenylacetylene and butyl bromide, in *ca.* 60% yield, by the normal interchange reaction. The same bromo-acetylene and phenylmagnesium bromide in presence of cobaltous chloride gave tolane ($\mathrm{PhC{\vdots}CPh}$) in 39% yield. While the method of alkylating an acetylene *via* a halogen derivative will not, in general, afford any advantage over existing standard procedures [*e.g.*, treatment of the sodium derivative with an alkyl halide (cf. Jacobs, *loc. cit.*)], a method has not previously been available for the replacement of an acetylenic hydrogen atom by an aryl group.

The structures of the various products mentioned above were readily confirmed by comparing their light-absorption properties with those reported for authentic specimens, or for compounds with similar chromophores (see Table 2).

EXPERIMENTAL

Light-absorption measurements were determined in alcohol, unless otherwise stated.

Intermediates.—1-Bromo-2-phenylacetylene was prepared from phenylacetylene and potassium hypobromite (Straus, Kollek, and Heyn, *Ber.*, 1930, **63**, 1868); it had b. p. 58—61°/1 mm., 42°/0·3 mm., n_D^{18} 1·6100—1·6120. Light absorption: see Table 2. [The di-iodide had m. p. 64° (Nef, *loc. cit.*, gives m. p. 65—66°).] 1-Bromohex-1-yne was prepared similarly from hexyne in 80% yield, and from hexynylmagnesium bromide and bromine in 50% yield (cf. McCusker and Vogt, *J. Amer. Chem. Soc.*, 1937, **59**, 1307); it had b. p. 40—41°/10 mm., n_D^{19} 1·4666. 1-Iodohex-1-yne was obtained by the action of iodine on hexynylsodium in liquid ammonia (cf. Vaughn and Nieuwland, *ibid.*, 1933, **55**, 2150), and on hexynylmagnesium bromide in ether (cf. Grignard and Perrichon, *loc. cit.*) in 90 and 70% yield, respectively; it had b. p. 85°/40 mm., n_D^{19} 1·5173. The halogenoacetylenes all decomposed slowly at 0°.

Preparation of Grignard Reagents.—Throughout most of the investigations, the following procedures were adopted. Ethereal solutions (*ca.* 1M) of alkyl and aryl Grignard reagents were prepared at 0°. To ensure complete removal of any excess of alkyl or aryl halide (traces were found to have a deleterious effect on some of the subsequent condensations) the resulting solutions were boiled under reflux over magnesium (0·25 mol.) for 1·5 hr., and then cooled and decanted. Acetylenic Grignard reagents were prepared by heating an ethereal solution of ethylmagnesium bromide with the acetylene (1·1 mol.) under reflux for 1 hr. after the evolution of ethane ceased (total time *ca.* 3—4 hr.).

Condensations.—Unless otherwise stated the following general procedure was used.

Cobaltous chloride (dried at 150° *in vacuo*) or cuprous chloride was added to the stirred, well-cooled (ice–salt bath) ethereal solution of the Grignard reagent. The alkynyl or alkenyl halide was added during *ca.* 1·5 hr., and the mixture was stirred overnight at room temperature.

TABLE 2. *Light-absorption maxima, in* mμ (ε *in parentheses*).

BuC⋮C·C⋮CBu	227(560)	239(490)	249—255(360)			
,, [1]	228(440)	239(390)	254(240)			
PhC⋮C·C⋮CBu	245(7500)	257(19,000)	271(26,000)	288(23,000)		
PhC⋮C·C⋮CH [2]	243(6000)	255(13,500)	269(21,500)	284(18,500)		
C_6H_9·C⋮C·C⋮CBu [3]	—	239(6000)	245(4500)	251(12,500)	265(18,000)	282(14,500)
CHMe:CH·C⋮C·C⋮CH [1] ...	230(2250)	238(5000)	—	251(10,000)	264(14,000)	280(11,000)
PhC⋮C·C⋮CPh	227(29,000)	247(29,000)	257(25,000)	287(22,000)	306(30,500)	327(30,500)
,, [4]	—	—	—	287	304	326
C_6H_9·C⋮C·C⋮C·C_6H_9 ...	229(37,500)	236(37,500)	246(27,500)	261(9000)	277(16,000)	292(22,000)
,, [5] ...	—	237(34,000)	246(29,000)	260(8000)	275(16,000)	291(23,000)
C_6H_9·C⋮C·C⋮C·C_6H_9 ...	—	—	—	—	—	308(17,000)
,, [5] ...	—	—	—	—	—	310(19,000)
CMe_2:CH·C⋮CBu	229(16,500)	235(13,500)				
CHMe:CH·C⋮CH [6]	222(11,000)	229 * (8000)				
PhCH:CH·C⋮CPh	308(35,000)	318(35,000)				
PhCH:CH·CH:CHPh [7]	—	328(41,000)				
PhC⋮CPh	281(26,500)	288(22,000)	297(26,500)			
,, [4]	278	288	296			
PhC⋮CH [8]	236(17,000)					
PhC⋮CMe	238(16,500)	249(16,500)				
PhC⋮CBu	240(18,000)	251(18,000)				
PhC⋮CBr	246(17,500)	251(17,500)				

[1] Armitage, Cook, Entwistle, Jones, and Whiting, *J.*, 1952, 1998. [2] Personal communication from Professor E. R. H. Jones and Dr. M. C. Whiting. [3] C_6H_9 = *cyclo*hex-1-enyl. [4] Schlubach and Franzen, *Annalen*, 1951, **573**, 110; determined in MeOH. [5] Bohlmann, *Chem. Ber.*, 1951, **84**, 545; determined in *cyclo*hexane; C_6H_9 = *cyclo*hex-1-enyl. [6] Armitage and Whiting, *J.*, 1952, 2005. [7] Hausser, Kuhn, and Smakula, *Z. physikal. Chem.*, 1935, *B*, **29**, 384. [8] Morton, Hassan, and Calloway, *J.*, 1934, 883; determined in hexane.

* Inflexion.

Excess of dilute acetic acid (10%) was added, and the ethereal layer was separated, washed with water, dried, and evaporated. The residue was then heated at 0·1 mm., and the low-boiling products were collected in a trap (alcohol–solid carbon dioxide) and subsequently distilled. High-boiling products were isolated by distillation of the tarry residue at 10^{-4} mm.

The specimens of unsymmetrical diacetylenes prepared from alkynyl iodides were frequently contaminated with traces of an iodine-containing impurity, which could be removed by treatment with alcoholic potassium hydroxide.

Yields of condensation products are based on the amount of organic halide used, allowance being made for the weight of recovered material where this is quoted.

Dodeca-5 : 7-*diyne.*—(*a*) Cuprous chloride was added to a stirred ethereal solution of hexynylmagnesium bromide (from 4·8 g. of magnesium and 16·5 g. of hexyne), and the mixture was boiled. A solution of iodine (25·5 g.) in ether (250 c.c.) was added rapidly, and heating under reflux was continued for 3 hr. The mixture was cooled and 2N-sulphuric acid was added. The ethereal layer was separated, washed with aqueous sodium thiosulphate (10% w/v), dried, and evaporated. Distillation of the residue gave dodeca-5 : 7-diyne (11·5 g.), b. p. 120°/13 mm., 85°/0·4 mm., n_D^{19} 1·4890 (Grignard and Tchéoufaki, *Compt. rend.*, 1929, **188**, 357, give b. p. 118—119°/4 mm.). Light absorption : see Table 2.

Without the copper chloride catalyst the yield of dodecadiyne did not exceed 10%, even after the reaction mixture had been heated for 9 hr.

(*b*) Reaction of hexynylmagnesium bromide (from 3·9 g. of magnesium and 13·2 g. of hexyne) with 1-bromohex-1-yne (16·1 g.) in presence of cobaltous chloride (1·0 g.) gave dodeca-5 : 7-diyne (4·6 g.), b. p. 122°/10 mm., n_D^{19} 1·4890.

1-*Phenylocta*-1 : 3-*diyne*.—(*a*) Reaction of hexynylmagnesium bromide (from 3·9 g. of magnesium and 13·2 g. of hex-1-yne) with 1-bromo-2-phenylacetylene (18·2 g.) in presence of cobaltous chloride (1·0 g.) gave: (i) Recovered bromophenylacetylene (6·3 g., 35%). (ii) 1-*Phenylocta*-1 : 3-*diyne* (3·7 g.), b. p. 107°/1 mm., n_D^{23} 1·5922 (Found: C, 92·0; H, 7·65. $C_{14}H_{14}$ requires C, 92·25; H, 7·75%). Light absorption : see Table 2.

Repetition of the preceding experiment with cuprous chloride (0·6 g.) instead of cobaltous chloride led to the recovery of bromophenylacetylene (60%) and the formation of a tar; no diacetylenes were detected.

Reaction of hexynylmagnesium bromide with 1-iodo-2-phenylacetylene in presence of cobaltous chloride gave diphenylbutadiyne (28%), m. p. 85—86°, and iodohexyne (23%), but no phenyloctadiyne.

(*b*) To a boiling ethereal solution of phenylethynylmagnesium bromide (from 2·4 g. of magnesium and 11·0 g. of phenylacetylene) were added cuprous chloride (0·4 g.) and then, during 1 hr., 1-iodohex-1-yne (18·0 g.). The mixture was stirred and heated under reflux for 6 hr. and then cooled. 2N-Sulphuric acid was added, and the ethereal layer was separated, washed with aqueous sodium thiosulphate solution (10% w/v), dried, and evaporated. Distillation of the residue gave: (i) Crude dodeca-5 : 7-diyne (*ca.* 2 g.), b. p. 70—80°/0·4 mm. (ii) 1-Phenylocta-1 : 3-diyne (4—5 g.), b. p. 91—93°/0·01 mm., n_D^{19} 1·5942 (Found: C, 91·9; H, 8·05%). Light absorption : maxima, 2450, 2580, 2730, and 2900 Å; ε = 7500, 17,500, 29,000, and 24,500, respectively. (iii) Diphenylbutadiyne (3·2 g.), b. p. 100° (bath temp.)/10^{-5} mm., which crystallised from methanol in needles, m. p. 87°.

A similar condensation of phenylethynylmagnesium bromide with 1-bromohex-1-yne gave phenyloctadiyne in 15% yield.

1-cyclo*Hex*-1′-*enylocta*-1 : 3-*diyne*.—1-Iodohex-1-yne (20·0 g.) was added to a suspension of *cyclo*hex-1′-enylethynylmagnesium bromide (from 2·4 g. of magnesium and 10·6 g. of ethynyl*cyclo*hexene) and cuprous chloride (0·4 g.) in ether (150 c.c.). The mixture was heated under reflux for 2 hr. and then cooled. 2N-Sulphuric acid was added and the products were isolated in the usual manner giving : (i) Dodeca-5 : 7-diyne (3·5 g.), b. p. 70—75° (mainly 72°)/0·3 mm., n_D^{22} 1·4891. (ii) 1-cyclo*Hex*-1′-*enylocta*-1 : 3-*diyne* (6·0 g.), b. p. 112°/0·2 mm., n_D^{22} 1·5537 (Found : C, 90·1; H, 9·8. $C_{14}H_{18}$ requires C, 90·25; H, 9·75%). Light absorption : see Table 2. (iii) A solid residue (4·0 g.) which, after sublimation at 80—90° (bath temp.)/10^{-5} mm. and crystallisation from methanol, gave 1 : 4-di*cyclo*hex-1′-enylbutadiyne as needles, m. p. and mixed m. p. 63° (Bohlmann, *Chem. Ber.*, 1951, **84**, 545, gives m. p. 60°). Light absorption : see Table 2.

The yield of *cyclo*hexenyloctadiyne was lowered to 26% when 0·25 mol. % instead of 2 mol.% of catalyst was used. In a reaction at 20° for 24 hr. appreciable quantities of material were recovered.

Diphenylbutadiyne.—Reaction of phenylethynylmagnesium bromide (from 3·9 g. of magnesium and 16·5 g. of phenylacetylene) with 1-bromo-2-phenylacetylene in presence of cobaltous chloride (1·0 g.) gave diphenylbutadiyne (7·0 g.), b. p. 110° (bath temp.)/10^{-5} mm. One crystallisation from alcohol gave needles, m. p. 86—87° (Grignard and Tchéoufaki, *Compt. rend.*, 1929, **188**, 357, give m. p. 86·5—87°). Light absorption : see Table 2.

2-*Methylnon*-2-*en*-4-*yne*.—Reaction of hexynylmagnesium bromide (from 3·9 g. of magnesium and 13·2 g. of hexyne) with *iso*butenyl bromide (13·5 g.) (Braude and Coles, *J.*, 1950, 2012) in presence of cobaltous chloride (1·0 g.) gave 2-*methylnon*-2-*en*-4-*yne* (3·2 g.), b. p. 100°/85 mm., n_D^{21} 1·4610 (Found : C, 88·0; H, 11·5%; hydrogen number, 48, equivalent to 2·8 double bonds. $C_{10}H_{16}$ requires C, 88·15; H, 11·85%). Light absorption : see Table 2.

1 : 4-*Diphenylbutenyne*.—Reaction of phenylethynylmagnesium bromide (from 3·9 g. of magnesium and 16·3 g. of phenylacetylene) with β-bromostyrene (18·3 g.) in presence of cobaltous chloride (1·0 g.) gave 1 : 4-diphenylbutenyne (5·0 g.), which crystallised from alcohol in needles, m. p. 95·5—96° [Pinckard, Wille, and Zechmeister, *J. Amer. Chem. Soc.*, 1948, **70**, 1938, give m. p. 96° (corr.)]. Light absorption : see Table 2. The m. p. of the product was strongly depressed on admixture with diphenylbutadiyne. Bromostyrene (9·3 g.) and phenylacetylene (3·3 g.) were recovered.

Dec-5-*yne*.—Reaction of butyl bromide (13·7 g.) with hexynylmagnesium bromide (from 3·9 g. of magnesium and 13·2 g. of hexyne) in presence of cobaltous chloride (1·0 g.) gave dec-5-yne (3·3 g.), b. p. 100°/80 mm., n_D^{22} 1·4340 (Bried and Hennion, *J. Amer. Chem. Soc.*, 1937, **59**, 1310, give b. p. 106°/80 mm., n_D^{25} 1·4311).

1-*Phenylprop*-1-*yne* (*cf. Kharasch, Lambert, and Urry,* J. Org. Chem., **1945**, **10**, 298).—Reaction of methylmagnesium bromide (from 3·9 g. of magnesium) and 1-bromo-2-phenylacetylene (18·3 g.) in presence of cobaltous chloride (1·0 g.), and decomposition of the complex, gave: (i) Phenylacetylene (4·0 g., 34%), b. p. 96°/100 mm., n_D^{19} 1·5485—1·5500; the mercury salt had m. p. 124—125° (Johnson and McEwen, *J. Amer. Chem. Soc.*, 1926, **48**, 469, give m. p. 124·5—125°). (ii) 1-Phenylprop-1-yne (4·7 g., 41%), b. p. 66°/15 mm., n_D^{19} 1·5615; light absorption, see Table 2 (Truchet, *Ann. Chim.*, 1931, **16**, 395, gives b. p. 71—74°/15 mm., n_D^{18} 1·561). (iii) Diphenylbutadiyne (0·7 g.), b. p. 130° (bath temp.)/10^{-3} mm., which crystallised from alcohol in needles, m. p. and mixed m. p. with the specimen described above, 84—86°.

1-*Phenylhex*-1-*yne*.—(*a*) Reaction of butylmagnesium bromide (from 2·9 g. of magnesium) with 1-bromo-2-phenylacetylene (13·5 g.) in presence of cobaltous chloride (0·75 g.) gave 1-phenylhex-1-yne (4·9 g.), b. p. 105°/10 mm., n_D^{20} 1·5345 (Johnson, Schwartz, and Jacobs, *J. Amer. Chem. Soc.*, 1938, **60**, 1882, give b. p. 109—110°/12 mm., n_D^{20} 1·5347) (Found: C, 90·8; H, 9·05. Calc. for $C_{12}H_{14}$: C, 91·1; H, 8·9%). Light absorption: see Table 2. No diphenylbutadiyne was detected.

When the reaction was carried out at −50°, most of the materials were recovered, and a small amount of diphenylbutadiyne was isolated.

(*b*) Reaction of butylmagnesium bromide (from 3·0 g. of magnesium) with 1-iodo-2-phenylacetylene (21 g.) in presence of cobaltous chloride (0·75 g.) gave 1-phenylhex-1-yne (4·6 g.), b. p. 105°/10 mm., n_D^{23} 1·5310. No diphenylbutadiyne was detected.

(*c*) Reaction of butylmagnesium bromide (from 3·9 g. of magnesium) with 1-bromo-2-phenylacetylene (18·1 g.) in presence of cuprous chloride (0·6 g.) gave 1-phenylhex-1-yne (7·3 g.), b. p. 110°/10 mm., n_D^{21} 1·5310. No diphenylbutadiyne was detected.

Repetition of the preceding experiment without a catalyst, and decomposition of the complex, gave: (i) Phenylacetylene (6·5 g.), b. p. 130°, n_D^{26} 1·5430; the mercury salt had m. p. 124°. (ii) Butyl bromide (7·7 g.), b. p. 100°, which was converted into *S*-butylthiourea picrate, m. p. 175° undepressed on admixture with an authentic specimen.

Diphenylacetylene (*Tolane*).—Reaction of phenylmagnesium bromide (from 3·9 g. of magnesium) with 1-bromo-2-phenylacetylene (16·0 g.) in presence of cobaltous chloride (1·0 g.) gave: (i) Diphenylacetylene (5·5 g.), b. p. 90—97°/0·5 mm., which crystallised from alcohol in leaflets, m. p. 61—62° (Found: C, 94·0; H, 5·8. Calc. for $C_{14}H_{10}$: C, 94·35; H, 5·65%) (Paillard and Wieland, *Helv. Chim. Acta*, 1938, **21**, 1356, give m. p. 62°); light absorption, see Table 2. (ii) Diphenylbutadiyne (0·2 g.), m. p. 82—85° undepressed on admixture with the specimen described above.

Repetition of the preceding experiment without the catalyst led to an almost quantitative recovery of phenylacetylene; diphenylbutadiyne (0·2 g.) was also isolated.

Analyses and light-absorption measurements were carried out in the microanalytical (Mr. F. H. Oliver) and spectrographic (Mrs. A. I. Boston) laboratories of this Department.

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