930. *Researches on Acetylenic Compounds. Part LIV.* The Preparation and Synthetical Applications of Ethynylmagnesium Bromide.*

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Ethynylmagnesium bromide can be prepared in tetrahydrofuran solution by a reverse-addition technique. It converts many carbonyl compounds into the corresponding ethynylcarbinols in high yields.

In the condensation of metallic derivatives of monosubstituted acetylenes, $R\cdot C\equiv C\cdot M$, with carbonyl compounds, the bromomagnesium derivatives have important advantages over the sodium and lithium derivatives, and are generally chosen when possible.[1] In particular, they can readily be prepared in an organic solvent, and react smoothly with carbonyl compounds which are unstable under basic conditions. The bisbromomagnesium derivative of acetylene itself has frequently been used in this way, but although early workers probably did obtain reagents containing a certain amount of the monobromomagnesium derivative, the bisbromomagnesium compound always was clearly the major component.[1] A definite claim to have prepared the mono-compound was made by Grignard, Lapayre, and Tchéoufaki,[2] whose method involved saturation of an ethereal solution of ethylmagnesium bromide containing benzene with acetylene at 1·5 atmospheres. We must point out in this connection (*a*) that this increase in pressure could not be expected to change the course of the reaction significantly, and it has been repeatedly observed [1] that at atmospheric pressure even prolonged passage of acetylene does not alter the insoluble bis-derivative; (*b*) that we have been unable to reproduce the results described; and (*c*) that of the alleged reaction products obtained in this way, although all the known compounds, $R\cdot C\equiv CH$, described agreed well with literature reports, that which at the time was not known (pent-1-en-4-yne) has been proved subsequently [3] to possess properties (density and refractive index) widely different from those listed. In our hands ethynylmagnesium bromide disproportionated to acetylene and the bis-derivative under conditions much milder than those specified for the condensation reactions with benzyl and alkyl bromides, etc. The reaction with benzyl bromide was said [2] to give as one product a hydrocarbon, m. p. 80°, described as dibenzylacetylene, and subsequently said to be obtained [4] by catalytic reduction of diphenyldiacetylene. Dupont, Dulou, and Lefebvre [5] have prepared dibenzylacetylene by two unambiguous routes, and find it to be a liquid at room temperature. Repeating the work of Grignard, Lapayre, and Tchéoufaki [2] they obtained 1 : 4-dibenzylbenzene, m. p. 81—83°, and suggested that it was this substance that the latter authors had isolated. It would, of course, be impossible to obtain this compound by the second method described by Grignard and Tchéoufaki.[4]

In view of recent unfavourable comments [6] on the syntheses reported by Grignard and Tchéoufaki [7] of iodotriacetylene and phenyltriacetylene, which we endorse, it appears that the claims made in these papers should be treated with great caution.

It is clear that acetylene must give ethynylmagnesium bromide as the first product of its reaction with ethylmagnesium bromide—indeed this has been proved kinetically.[8] When the gas is passed into an ether or benzene solution, however, the sparingly soluble bisbromomagnesium derivative soon separates, and does not redissolve; presumably reaction (2) proceeds with a rate comparable with that of reaction (1), and, because the ethylmagnesium bromide is in excess, the bismagnesium bromide is formed almost quantitatively. Since the reactions of acetylenes with Grignard reagents in non-polar solvents are not

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* Part LIII, preceding paper.

[1] For a general review see Raphael, " Acetylenic Compounds in Organic Synthesis," Butterworth London, 1955, pp. 13 and 16, and references cited there.

[2] Grignard, Lapayre, and Tchéoufaki, *Compt. rend.*, 1928, **187**, 517.

[3] Paul and Tchelitsheff, *ibid.*, 1951, **233**, 1116.

[4] Grignard and Tchéoufaki, *ibid.*, 1929, **188**, 1531.

[5] Dupont, Dulou, and Lefebvre, *Bull. Soc. chim. France*, 1954, 653.

[6] Schlubach and Franzen, *Annalen*, 1951, **573**, 115.

[7] Grignard and Tchéoufaki, *Compt. rend.*, 1929, **188**, 351.

[8] Kleinfeller and Lohmann, *Ber.*, 1938, **71**, 2608.

instantaneous and do not involve free ions—unlike analogous reactions with sodamide in liquid ammonia, for example [9]—one cannot assume either that equilibrium (3) would favour ethynylmagnesium bromide, or that it would be attained at a practicable rate. In fact, no clear-cut exchange reaction such as (3), between one acetylene and the bromomagnesium derivative of another, has yet been demonstrated; and even the reactions with alkylmagnesium halides are quite slow.[10] The best hope of obtaining ethynylmagnesium bromide therefore lay in avoiding reaction (2) by maintaining a local excess of acetylene through an inverse-addition technique, while at the same time further attempting to minimise the disproportionation reaction (3) by employing a good solvent for acetylene and for the bis-bromomagnesium derivative, such as tetrahydrofuran.

$$(1)\quad \mathrm{HC{\equiv}CH + EtMgBr \longrightarrow HC{\equiv}C{\cdot}MgBr + EtH}$$

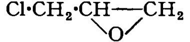
$$(2)\quad \mathrm{HC{\equiv}C{\cdot}MgBr + EtMgBr \longrightarrow BrMg{\cdot}C{\equiv}C{\cdot}MgBr + EtH}$$

$$(3)\quad \mathrm{HC{\equiv}CH + BrMg{\cdot}C{-}C{\cdot}MgBr \rightleftharpoons 2HC{\equiv}C{\cdot}MgBr}$$

When these conditions were employed a reagent was obtained which converted carbonyl compounds into their ethynylcarbinols in yields of up to 85%, no detectable quantities of the glycols being isolated. When the solution of the reagent was cooled a solid separated which was analysed by decomposition with an excess of dilute sulphuric acid, measurement of the volume of acetylene produced, and back-titration to estimate magnesium (as BrMg·OH). Values of 0·96 and 0·90 were obtained in replicate experiments for the ratio [C_2H_2 liberated] : [acid consumed]. When the solution was evaporated below 20° at 0·1 mm., partial disproportionation (—3) occurred, and decomposition of the residue gave an acetylene : magnesium ratio of 0·79, 0·74, and 0·74; warming to 50° *in vacuo* reduced the ratio to 0·37. With the normal procedure, when the acetylene was passed into the ethylmagnesium bromide, and even though the gas-stream was continued for some time beyond apparent saturation, the sparingly soluble derivative which separated gave ratios of acetylene : magnesium of 0·37 and 0·40 on decomposition. Thus the inverse-addition technique is essential for success. More surprisingly, the use of pure tetrahydrofuran as solvent is also an important factor; one experiment in which a 1 : 1 mixture of ether and tetrahydrofuran was used resulted in the formation of a 17% yield of the acetylenic glycol, at the expense of the desired alcohol. Attempts to employ ether or benzene as solvents gave virtually no acetylenic alcohol.

The reactions of ethynylmagnesium bromide so far investigated are indicated in the

Reactions of ethynylmagnesium bromide.

Reagent	Product	Yield (%)	Yield (%) by other methods
$\mathrm{Me{\cdot}CO{\cdot}Et}$	$\mathrm{MeEtC(OH){\cdot}C{\equiv}CH}$	70	78 [a]
$\mathrm{Me{\cdot}CO{\cdot}CH_2Cl}$	$\mathrm{Me{\cdot}C(OH)(CH_2Cl){\cdot}C{\equiv}CH}$	60	25 [b]
$\mathrm{Me{\cdot}COPh}$	$\mathrm{MePh(OH){\cdot}C{\equiv}CH}$	35	47 [c]
$\mathrm{Ph_2CH{\cdot}CHO}$	$\mathrm{Ph_2CH{\cdot}CH(OH){\cdot}C{\equiv}CH}$	75	—
$\mathrm{CH_2{=}CH{\cdot}CHO}$	$\mathrm{H_2C{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH}$	45	58 [d]
$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CHO}$	$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH}$	85	75 [e]
$\mathrm{Ph{\cdot}CH{=}CH{\cdot}CHO}$	$\mathrm{Ph{\cdot}CH{=}CH{\cdot}CH(OH){\cdot}C{\equiv}CH}$	60	2,[f] 13·5 [g]
$\mathrm{Bu{\cdot}C{\equiv}C{\cdot}CHO}$	$\mathrm{Bu{\cdot}C{\equiv}C{\cdot}CH(OH){\cdot}C{\equiv}CH}$	85	—
$\mathrm{H{\cdot}CO_2Et}$	$\mathrm{HC{\equiv}C{\cdot}CH(OH){\cdot}C{\equiv}CH}$	40	<1 [h]
$\mathrm{Cl{\cdot}CO_2Et}$	$\mathrm{EtO{\cdot}CO{\cdot}C{\equiv}CH}$	Trace	
	$\mathrm{Cl{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}C{\equiv}CH}$		—
$\mathrm{Ph{\cdot}CH_2Br}$ [i]	No low-boiling product	—	—
$\mathrm{Ph_2C{=}CHBr}$ [i]	Recovered unchanged	—	—

[a] Thompson, Burr, and Shaw, *J. Amer. Chem. Soc.*, 1941, **63**, 186. [b] Herstein, *Zhur. obshchei Khim.*, 1942, **12**, 132. [c] Oroshnik and Mebane, *J. Amer. Chem. Soc.*, 1949, **71**, 2062. [d] Bohlmann and Viehe, *Chem. Ber.*, 1954, **87**, 712. [e] Heilbron, Jones, and Weedon, *J.*, 1945, 81. [f] Jones and McCombie, *J.*, 1942, 733. [g] Cymerman and Wilks, *J.*, 1950, 1208. [h] Lespieau, *Bull. Soc. chim. France*, 1939, **6**, 947. [i] $CoCl_2$ added.

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[9] Armitage, Jones, and Whiting, *J.*, 1952, 1993.

[10] Wotiz, Hollingsworth, and Dessy, *J. Amer. Chem. Soc.*, 1955, **77**, 103.

Table. For condensations with many saturated carbonyl compounds, and some αβ-ethylenic carbonyl compounds, the Grignard reagent is little if at all superior to the more easily prepared sodium or lithium acetylides. When the substance to be condensed readily polymerises (*e.g.*, cinnamaldehyde) or reacts with ammonia (chloroacetone), however, the new reagent is distinctly advantageous. The αβ-acetylenic aldehydes, in particular, could not formerly be condensed with acetylene, whereas they now give high yields of the alcohols R·C≡C·CH(OH)·C≡CH; recently a glycol, Pr·CH(OH)·C≡C·CH(OH)·C≡CH, of this type has been prepared by condensation of propiolaldehyde with (effectively) an ethynylcarbinol,[11] and these alcohols could presumably be obtained by using acetylenic hydrocarbons instead, but the present route is much more convenient. Penta-1 : 4-diyn-3-ol, an interesting and surprisingly stable compound, now becomes readily available.

Substitution of diacetylene for acetylene gave a reagent which converted acetone in 45—50% yield into the expected diacetylenic alcohol. This reaction also may have synthetical value.

EXPERIMENTAL

Ethynylmagnesium Bromide.—A solution of ethylmagnesium bromide was prepared under nitrogen from magnesium (4·8 g.) in dry tetrahydrofuran (140 c.c.). While still warm, this was decanted under nitrogen into a dropping funnel attached to a flask equipped with a gas inlet and a mechanical stirrer, and containing tetrahydrofuran (80 c.c.). Acetylene, freed from acetone by passage through a trap at −80°, was introduced until the liquid was saturated, and throughout the addition of the ethylmagnesium bromide solution. The latter was added in 3—5 c.c. portions, each addition being followed by a brisk frothing of the liquid which was readily distinguished from the large bubbles of acetylene, and was allowed to subside before the next addition. If the temperature of the solution fell below about 20°, crystallisation of the ethylmagnesium bromide occurred to some extent, but the resultant suspension was easily added from a dropping-funnel; at the end of the reaction the resulting solution of ethynylmagnesium bromide also was saturated at about 25°, and yielded an easily stirred suspension on cooling.

Addition of a carbonyl compound (0·14 mole) in an equal volume of tetrahydrofuran with ice-cooling, followed by stirring overnight at room temperature, decomposition of the complex with saturated ammonium chloride solution, and isolation by distillation gave the yields quoted in the cases of ethyl methyl ketone, chloroacetone, acraldehyde (experiment by MR. IAN BELL), crotonaldehyde, and hept-2-ynal. B. p.s and refractive indices agreed with literature values, and the latter were constant to, at most, a range of 0·001. Acetophenone gave a mixture of the ethynylcarbinol and unchanged ketone, separated by chromatography on alumina, distillation of the ether–methanol eluates, and recrystallisation of the alcohol from light petroleum, giving needles, m. p. 49° (Zalkind and Ivanov [12] give m. p. 48·5—49°). Cinnamaldehyde gave a product, b. p. 90°/1 mm., which at once solidified and was crystallised from light petroleum (b. p. 40—60°), then having m. p. 67—68° (Jones and McCombie [13] give m. p. 66—67°).

1 : 1-*Diphenylbut*-3-*yn*-2-*ol*.—Diphenylacetaldehyde (8·5 g.) was treated with ethynylmagnesium bromide, as above. Isolation of the product gave a syrup which solidified and was crystallised from light petroleum (b. p. 40—60°), giving the *alcohol* as needles, m. p. 73—74° (Found: C, 86·45; H, 6·4. $C_{16}H_{14}O$ requires C, 86·45; H, 6·35%).

Penta-1 : 4-*diyn*-3-*ol*.—Ethyl formate (6 g.) in tetrahydrofuran (10 c.c.) was added at 0° to a solution of ethynylmagnesium bromide, prepared as above from magnesium (6 g.). Isolation as above and distillation gave a fraction, b. p. 80° (bath-temp.)/0·05 mm., which after crystallisation from light petroleum had m. p. 51—52° (Lespieau [14] gives m. p. 51·5—52°).

2-*Methylhexa*-3 : 5-*diyn*-2-*ol*.—A solution of ethylmagnesium bromide, prepared from magnesium (4·8 g.) in tetrahydrofuran (125 c.c.), was added during 1·5 hr. to a solution of diacetylene (12·5 g.) in tetrahydrofuran (100 c.c.) with ice-cooling under reflux (carbon dioxide–acetone). After 30 minutes' stirring acetone (8 g.) in tetrahydrofuran (10 c.c.) was added during 30 min. and the mixture was stirred overnight. Isolation of the product and distillation gave the

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[11] Petrov, *Zhur. obshchei Khim.*, 1955, **25**, 1101.
[12] Zalkind and Ivanov, *Zhur. obshchei Khim.*, 1941, **11**, 803.
[13] Jones and McCombie, *J.*, 1942, 733.
[14] Lespieau, *Bull. Soc. chim. France*, 1939, **6**, 947.

diacetylenic alcohol (6·6 g., 45%), b. p. 36°/0·5 mm., n_D^{20} 1·4935 (Armitage, Jones, and Whiting [9] give b. p. 39·5°/0·5 mm., n_D^{19} 1·4938). Crystallisation of the distillation residue gave a small yield of 2 : 7-dimethylocta-3 : 5-diyne-2 : 7-diol, m. p. and mixed m. p. 130—131°.

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