ELIMINATIONS ON HALO-ORGANOMAGNESIUM HALIDES

SYNTHESIS OF ALLENES VIA ALLENYLCARBENE

Félix Serratosa

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Departamento de Química Orgánica de Barcelona, Patronato "Juan
de la Cierva" de Investigación Técnica (C.S.I.C.).
Universidad de Barcelona

HENNION and his co-workers in a series of papers (1) exa-
mined the products and kinetics of base-catalyzed reactions of tertiary
propargyl halides and postulated "allenylcarbenes" as intermediates.
Hartzler (2), as Doering did before with Hine's dihalocarbene inter-
mediates (3), succeeded in capturing the disubstituted allenylcarbenes
with olefins. However, the results were not so dramatic when propar-
gyl bromide itself was investigated (4).

In order to obtain evidence of the allenylcarbene intermediacy in
the base-catalyzed reactions of propargyl bromide, we became interes-
ted in the reaction of Grignard reagents with this primary acetylenic
bromide.

If propargyl bromide reacts with Grignard reagents as an ace-
tylene, 3-bromo-propynylmagnesium bromide (I) would be formed
which upon γ-elimination of magnesium bromide would give the allenyl-

carbene (II). Examples of eliminations on intermediate halo-organo-
metallic halides from the reaction of dihalocompounds with metals
(Mg or Zn) can be found in the chemical literature (5), though only
a few ones refer to the generation of carbene intermediates. Simmons
and Smith (6), for example, have reported the preparation of methyle-
ne, from diiodomethane and zinc-copper couple, by means of an α-eli-
mination on the intermediate iodomethylzinc iodide. Similarly, the reac-
tion of chloroform with Grignard reagents (7) probably takes place
through the formation of trichloromethylmagnesium halide followed by
sucesive α-eliminations of magnesium halide and further reaction of
the intermediate carbenes with the nucleophilic base. In this context,
the striking resemblance of $Cl_3C-MgCl$ or $Cl_3C-MgC_6H_5$ with the
"potential dichlorocarbenes" $Cl_3C-HgCl$ and $Cl_3C-HgC_6H_5$ (8) is
noticeable, and competitive reactions in the presence of olefins strongly
support the carbene mechanism (α -elimination) (9).

Actually, the reaction of Grignard reagents with propargyl bro-
mide has been already reported by Prevost and his collaborators (10),
but probably mistakenly interpreted in the light of more recent advan-
ces on the field of carbene chemistry.

Our experimental results as well as those previously reported
in the chemical literature have been summarized in Table I.

These experimental facts can be rationalized assuming that
Grignard reagents actually react with either one of the two reactive
sites of propargyl bromide molecule (Chart I) depending upon the
temperature, the solvent and the nature of radical R (in the order
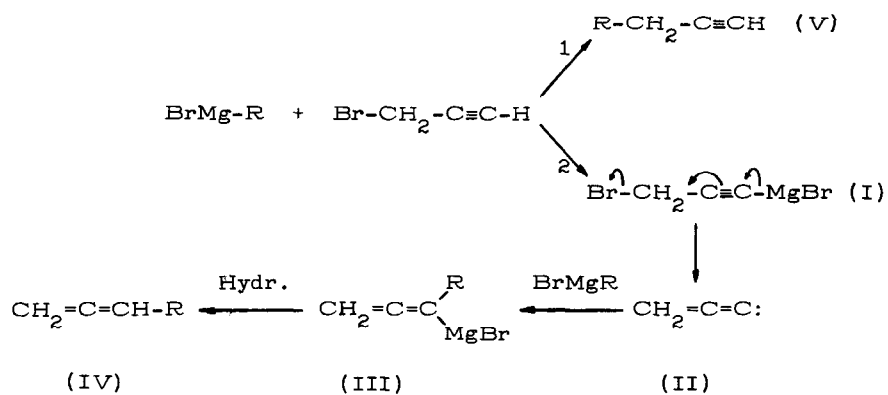of basicity: ethylnyl < aryl < alkyl).

TABLE   I

Reactivity of Grignard reagents (R-MgBr) _versus_ propargyl bromide

R	t	Solvent	Catalyst	Major reaction product[*]	Suggested mechanism[*]	Ref.
Ethynyl-	40º	ether	Cu_2Cl_2	V	1	(11)
Aryl-	<0º	ether	--	V + IV	1 + 2	(10,12)
Alkyl-	40º	ether	--	V + IV	1 + 2	(10)
Alkyl-	<0º	ether	--	IV	2	(10)
Alkyl-	<0º	THF	--	V	1	-

[*]
   See Chart I

CHART   I

Ethynylmagnesium bromides only react with propargyl bromide under drastic conditions (boiling ether and catalyst) (11), according to a metathetical process (path 1), to give the corresponding acetylene (V). The more basic alkylmagnesium bromides under similar conditions (boiling ether) lead to "complex results", as it was pointed out by the French workers, since two mechanisms are operating. However, the lower the temperature the slower the reaction rate of the metathetical process (path 1), and below 0ºC propargyl bromide reacts with alkylmagnesium bromides, in ether solution, almost exclusively as an acetylene (path 2) to give the acetylenic Grignard derivative (I) which undergoes spontaneous γ -elimination and affords the reactive intermediate allenylcarbene (II). The allenylcarbene reacts further on with a second mole of Grignard reagent to give a monosubstituted allenylmagnesium bromide (III) which upon hydrolysis affords the allene (IV) in almost quantitative yield. Minor quantities of monosubstituted acetylene (V), from the metathetical process, are formed even at -15ºC. However, v.p.c. shows ca. 100% purity for simply distilled allenes from the reaction at -40ºC, provided highly pure reagents are used.

On the other hand, since arylmagnesium bromides are more reactive but less basic than the alkyl analogs, a ∼1:1 mixture of acetylene (V) and allene (IV) is always formed (10,12).

According to the "two mechanisms hypothesis", substitution of tetrahydrofuran (THF) for ether should favor the metathetical process even at low temperature[†] , and this has been found to be the case, the monosubstituted acetylene (V) being the major product isolated from the reaction of alkylmagnesium bromides in THF at -15ºC.

The reported results rule out another apparent nucleophilic substitution involving propargylic rearrangement described yet in the chemical literature (13) and give further evidence that while this rearrangement is possible in electrophilic substitutions -involving the propargyl "anion"- it is questionable in nucleophilic substitutions that involve the formation of the "cation" $HC\equiv C-\overset{+}{C}H_2$ in which the strained allenyl limiting form, $H\overset{+}{C}=C=CH_2$, with a positive charge on a trigonal carbon atom, would be highly unfavored (1, 14, 15)[††] .

[†] While the Grignard derivative of propargyl bromide is successfully prepared in ether solution, THF leads exclusively to duplication (10).

[††] Note that quite a different situation is found in allylic rearrangements: $\overset{+}{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\overset{+}{C}H_2$

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