Journal of Organometallic Chemistry, 179 (1979) C1—C4
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Preliminary communication

THE STRUCTURES OF ALKENYL- AND ALLYL-MAGNESIUM INTERMEDIATES IN THE SELF-HYDROGENATION OF PROPYNE AND ALLENE ON MAGNESIUM FILMS

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(Received July 12th, 1979)

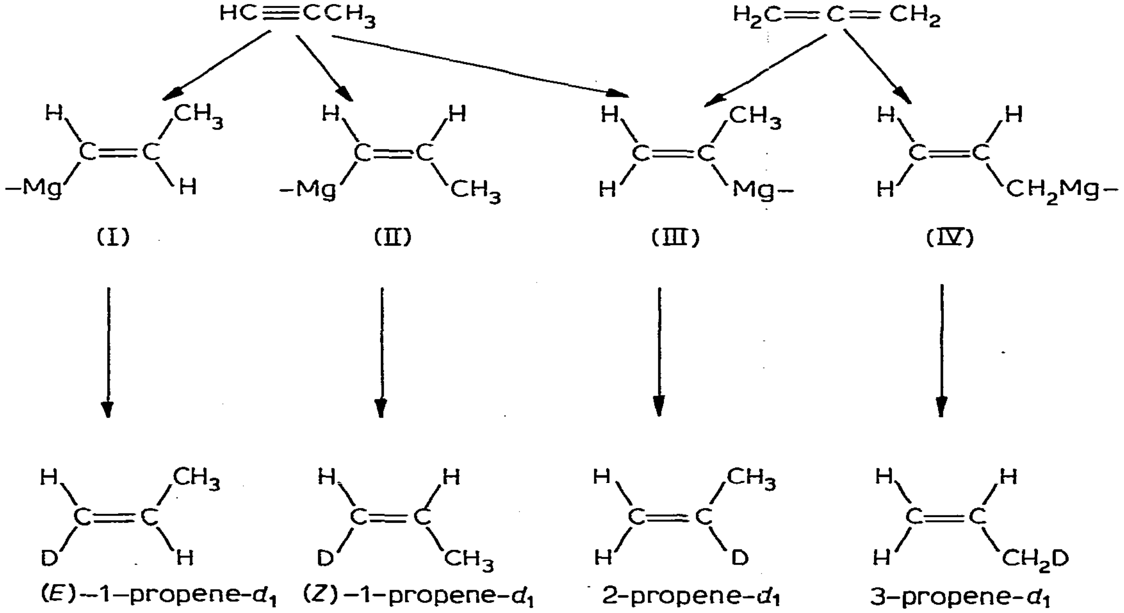
Summary

The structures of the C_3H_5Mg intermediates formed in the reactions of propyne and allene on magnesium films were determined by converting them into propene-d_1 compounds, which were analyzed by microwave spectrometry. Propyne gives mainly the (E)-n-propenyl intermediate. Allene, although largely isomerized to propyne before reaction, gives both allyl and 2-propenyl intermediates, with the first slightly predominant. The formation of these intermediates is assumed to involve hydrometalation of propyne and allene by magnesium hydride.

The hydrometalation of alkynes, and to a smaller extent of 1,2-dienes, has been studied for a number of transition and non-transition metal hydrides. Among those, magnesium hydride until recently appeared to be rather inert in this type of reactions, but in 1978 there were two independent reports of hydrometalation of alkynes by magnesium hydride, in homogeneous and heterogeneous media, respectively [1,2]. In the latter work [2], involving reactions of propyne and allene on magnesium films, superficial magnesium hydride, produced from the dehydrogenation of a part of the reagent, promoted the hydrogenation of another part to propene. The hydrogenation was shown to occur stepwise, as in catalytic hydrogenation, via half-hydrogenated intermediates, assumed to result from multiple C—C bond insertion into Mg—H bonds, and characterized as propene-d_1 after D_2O treatment.

The determination of the structures of these intermediates appeared worthwhile in several respects, and particularly for attempting to correlate heterogeneous half-hydrogenated states and homogeneous hydrometalation adducts. With this in mind, the mixtures of deuteropropenes (mainly d_1) resulting from D_2O treatment of magnesium films after contact reactions of propyne and allene for one hour at 100°C were analyzed by microwave spectrometry [3]. The locations of the D atoms in the propene-d_1 revealed the previous points of attachment of the C(3) molecules to the metal.

The possible structures of these intermediates and of the resulting propenes are depicted in Scheme 1, and the structural distributions of the propene-d_1 compounds are shown in Table 1. The corresponding alkenyl- and allylmagnesium compound I—IV are assumed to be initial reaction products.



SCHEME 1. Possible structures of the C_3H_5Mg intermediates and of the corresponding propenes.

TABLE 1

STRUCTURAL DISTRIBUTION OF $[^2H]_1$ PROPENES RESULTING FROM THE REACTION OF PROPYNE AND ALLENE ON MAGNESIUM FILMS FOR ONE HOUR AT 100°C FOLLOWED BY D_2O TREATMENT

Reagent	% propene-d_1 among total propene [a]	(*E*)-1-propene-d_1	(*Z*)-1-propene-d_1	2-propene-d_1	3-propene-d_1 [b]
$HC{\equiv}CCH_3$	70	80.9	15.3	3.8	—
$H_2C{=}C{=}CH_2$	61	67.5	11.8	9.7	10.9

[a] Mass spectral data. [b] Sum of two distinct subspecies, which are considered to be equivalent for the present research.

The possibility of magnesium hydride addition-elimination which might lead to some isomerization or rearrangement before deuterolysis, was considered. However, no clearcut evidence could be found for a magnesium hydride addition-elimination [4]: the addition of a second MgH unit upon C_3H_5Mg would produce, at least transiently, dimetalated propane, and hence propane-d_2, which was not detected [2]. Furthermore, the thermal decompositions of 1-propenylmagnesium bromide (80% (*E*), from pure (*E*)-1-bromo-1-propene [5]) and of allylmagnesium bromide, analogous to compounds I, II and IV, respectively, were briefly investigated. Both reagents, although having an H atom on the

β-carbon atom, decompose slowly at 100°C to afford mainly propene. Therefore their main decomposition route is not β-hydride elimination. That makes unlikely the participation of a magnesium hydride elimination-addition process. The non-occurrence of β-elimination in the case of the 1-propenyl-Grignard reagent (80% (*E*)), despite its seemingly favourable geometry, is significant, since other organometallics of similar structures decompose thermally by β-hydride elimination [4,6]. These results suggest that the alkenyl- and allyl-magnesium intermediates trapped as propene-d_1 are initial reaction products, and that the second step in the self-hydrogenation of propyne and allene to propene on magnesium films implies their thermal decomposition by hydrogenolysis of their C—Mg bonds and reductive elimination.

As seen in Table 1, propyne gives a mixture of (*E*)- and (*Z*)-1-propene-d_1 and 2-propene-d_1. The absence of 3-propene-d_1 shows that previous propyne-allene isomerization has no relevance for the subsequent reaction of propyne with magnesium hydride.

The large predominance of (*E*)-1-propene-d_1 indicates that propyne gives mainly the (*E*)-n-propenyl intermediate I, as in homogeneous hydrometalations and in catalytic heterogeneous hydrogenation [7—10]. This structure is consistent with the *cis*-addition of Mg—H bonds to the $C\equiv C$ bond, with the orientation dictated either by steric or by electronic control. Therefore both regio- and stereo-selectivities of the Mg—H addition to propyne can be rationalized by a classical four-center transition state:

(I)

The (*Z*)-1-propene-d_1 can be accounted for by the isomerization of the initially-formed (*E*)-intermediate I. Indeed, the addition of M—H bonds to $C\equiv C$ bonds is usually *cis*, and in several cases where *trans* adducts were obtained, it was shown that they resulted by isomerization of initially-formed *cis* adducts [4,11—14]. However, the absence of experimental support for an isomerization of the (*E*)-intermediate I before deuterolysis does not preclude the initial formation of the (*Z*)-n-propenyl intermediate II.

Lastly, propyne provides a small amount of 2-propene-d_1 arising from the isopropenyl intermediate III, indicating that the addition of the Mg atom to propyne does not occur exclusively at the terminal position; a similar result has been noted in hydrostannation [7].

Allene provides a mixture of the four isomeric d_1 propene compounds. The high yield of (*E*)- and (*Z*)-1-propene-d_1, which cannot be formed directly from allene, shows that the allene-propyne isomerization and the subsequent reaction of propyne with magnesium hydride are much faster than the hydrometalation of allene itself. The latter does occur, however, to give the allylic intermediate IV and the isopropenylic intermediate III.

The ratio 1-propene-d_1/2-propene-d_1 obtained from propyne allows an estimate to be made of contribution of allene to the intermediate III. It emerges that: (i) the ratio of propynic/allenic intermediates obtained from allene (ca. 82.5/17.5) is close to the propyne-allene equilibrium (87/13 at 100°C); (ii) allene affords both intermediates IV and III in the approximate ratio 62/38.

The predominance of the allylic intermediate IV suggests that the terminal allenic positions are the most favoured sites for magnesium atom attack, as in heterogeneous catalytic hydrogenation [10] and in homogeneous hydrometalation [15—19]*. However, the regiospecificity and the easy formation of diadducts in the homogeneous hydrometalations [15—18] are in contrast with the moderate regioselectivity and the exclusive formation of the monoadduct, seemingly without intermediacy of a diadduct, in the reaction of allene with magnesium hydride on magnesium films. Although the absence of ligands is expected to minimize the steric control of hydrometalation in the case of metallic films, more work is required for a full understanding of these discrepancies.

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*Insertion of allene into transition metal hydrides results in π-allylic complexes [19].