A Kinetic Study of Additions of Dialkylmagnesium Compounds to a Cyclopropene

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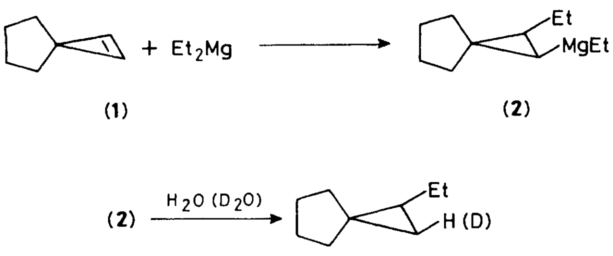
Addition of dialkylmagnesium compounds in tetrahydrofuran to spiro[2.4]hept-1-ene is kinetically first order in each component; at 35.5 °C, relative rates of addition of R_2Mg where R is methyl, ethyl, isopropyl, and t-butyl are 1, 10.3, 32, and 8, respectively.

Addition of organomagnesium compounds to isolated (non-conjugated) alkene functions generally has been observed only with particularly reactive organomagnesium compounds (*e.g.*, allyl or t-butyl) and with alkenes that have little substitution (*e.g.*, ethylene or monoalkylethylenes) or significant strain.[1,2] Only additions of allylic organomagnesium compounds have been studied kinetically,[3] and for several reasons, including the possibility of bond formation at the γ-carbon, mechanisms of their reactions may be atypical.

So that addition of a wider range of organomagnesium compounds could be studied, we chose as the alkene a cyclopropene (**1**). Additions of several organomagnesium compounds to cyclopropenes have already been reported.[4] Moreover, the configurational stability[5] of cyclopropyl-



(1) (2)

(2)

(3)

magnesium compounds permits determination of the stereochemistry of the addition of the components (R and MgX) of the organomagnesium compounds.† The products and kinetics of reactions of (1) with an excess of Et_2Mg in tetrahydrofuran (THF) were studied with particular care. Quenching with H_2O gave (3) in yields of up to 60—70% based on (1). N.m.r. spectral analysis of the product obtained after quenching with D_2O showed deuterium to be exclusively (>98%) *cis* to the ethyl group.‡ Two products accounting for up to 5—10 and 2—4% of (1), respectively, contained the elements of one ethane plus two (1) units, and one ethane plus three (1) units. Some (1) remained after long reaction times but was mainly the result of conversion of (1) into a metallated species that re-formed (1) upon hydrolysis.§

Formation of (3) was followed by g.c. analysis of hydrolysed aliquots of the reactions. THF was chosen as the solvent since Et_2Mg is monomeric in it over the concentration range that was used.[6] So that the assumption that $[(3)]_\infty = [(1)]_0$ would not introduce a significant error, data for formation of only the first 10% or so of (3) were used to determine pseudo-first-order rate constants for the appearance of (3). Rate constants determined in this fashion when either $[(1)]_0$ or $[Et_2Mg]_0$ was varied showed the reaction to be first order in each component.¶ Transition metal impurities, a significant problem in additions to ketones,[7] probably did not significantly affect the rates. Addition of iron [as pentane-2,4-dionatoiron(II)] at levels considerably higher than would be introduced by the magnesium samples that were used did accelerate the formation of (3), but also led to the formation of additional products that were not otherwise encountered. Moreover, essentially identical rates were obtained using Et_2Mg prepared with two different grades of magnesium (Cerac; Dow, triply sublimed).

Table 1. Second-order rate constants for addition of dialkylmagnesium compounds to (1) at 35.5 °C in THF.

R in R_2Mg	$10^5 k$, $dm^3 mol^{-1} s^{-1}$	(average deviation)	Relative rate
Me	0.116	(±0.017)	1
Et	1.20	(±0.12)	10.3
Pr^i	3.67	(±0.45)	32
Bu^t	0.91[a]	(±0.07)	8[a]

[a] Metallation is sufficiently fast relative to addition when di-t-butylmagnesium is used to make this value somewhat less accurate than the others.

Rate constants for the addition of other dialkylmagnesium compounds to (1) to form products similar to (3) are summarized in Table 1. Any mechanistic speculations must accommodate the observations that addition is exclusively *syn*, kinetically second order, and relatively insensitive in rate to the structure of the dialkylmagnesium compound. Interestingly, the relative insensitivity of the rates to α-alkyl substitution and even the primary < secondary > tertiary order resemble effects observed in intramolecular cyclizations of unsaturated Grignard reagents.[8] The primary < secondary > tertiary pattern suggests that α-alkyl groups exert competing effects, reasonably a rate-increasing electronic effect and a rate-decreasing steric effect. Assuming that a very large electronic effect is not fortuitously being masked, however, it is reasonable to propose that by the transition state of the rate-determining step, either little R–Mg bond cleavage and R–C bond formation have occurred or they have proceeded to a similar extent.

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† Products obtained from addition of various Grignard reagents to other cyclopropenes followed by carbonation or hydrolysis have resulted from *syn* addition.[4]

‡ We assume that hydrolysis of organomagnesium compounds proceeds with retention of configuration and that (2) therefore is *cis*.

§ Much of the reisolated (1) was monodeuteriated when quenching was with D_2O.

¶ Since no systematic changes in rate were noted over the portions of the reactions used to determine rate constants, any formation of (3) by reaction of (2) with (1) did not complicate the kinetics.

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8 For critical reviews, see E. A. Hill, *J. Organomet. Chem.*, 1975, **91**, 123; E. A. Hill, *Adv. Organomet. Chem.*, 1977, **16**, 131. These reactions are readier than intermolecular additions of organomagnesium compounds to alkenes, but the concentrations of the organomagnesium and alkene functions cannot be varied independently, an impediment to mechanistic study. Moreover, formation of rings in the additions poses steric restraints that complicate the interpretation of the rates.