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CARBOMAGNESIATION OF SEVERAL NORBORNENE

DERIVATIVES CATALYZED BY Cp₂ZrC1₂

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In our previous work [1], we carried out the carbomagnesiation of α -olefins by Et₂Mg and EtMgBr with Cp₂ZrCl₂ as catalyst. In contrast to the uncatalyzed reaction [2], the use of Cp₂ZrCl₂ leads to rigorous regioselectivity under mild conditions. Acyclic and monocyclic olefins which are disubstituted as the double bond do not undergo this reaction [3]. In order to expand the scope of this reaction, we studied the reaction of Et₂Mg and EtMgBr with bicyclo[2.2.1]heptene derivatives containing highly active double bonds.

Bicyclo[2.2.1]heptene (I) reacts in the presence of catalytic amounts of Cp_2ZrCl_2 with an equimolar amount of Et_2Mg to give 60-65% yields of organomagnesium compound (OMC) (II) which gives (2-exo-ethyl)bicyclo[2.2.1]heptane (III) upon hydrolysis. This result indicates that carbomagnesiation occurs by cis addition at the exo side of (I):



By analogy, endo-tricyclo $[5.2.1.0^2, {}^6]$ -3,8-decadiene (dicyclopentadiene) (IV) reacts with (IV) to give a mixture of OMC (V) and (VI) which differ in the position of the ethyl group relative to the double bond. Upon hydrolysis, this mixture gives exo-9-ethyl-endotricyclo $[5.2.1.0^2, {}^6]$ dec-3-ene (VII) and exo-9-ethyl-endo-tricyclo $[5.2.1.0^2, {}^6]$ dec-4-ene (VIII) in 2:3 ratio.

The carbomagnesiation of bicyclo[2.2.1]heptadiene (IX) proceeds differently. In this case an OMC product formed in not less than 70% yield hydrolyzes to 3-ethylnortricyclene (XI), indicating intramolecular rearrangement of the initially formed OMC (Xa):



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TABLE 1. ¹³ C NMR Spectra of Reaction Products (III), (XI), (VII), and (VIII)	C12			12,29 q	12,46 q
	C11			29,30 t	29,78 t
	G ¹⁰		•	38,40 t	38,40 t
	ů	12,40 t	12,72 t	30,30 t	40,07 d
	ບ	29,69 t ⁻	29,00 t	41,1 3 d	31,99 t
	C7	35,27 t	34,22 t	44,13 d	35,63 d
	C.	28,95 t	9 , 60 d	41, 89 d	42,56 d
	Ce	30,25 t	22,50 t	32,40 t	33,64 t
	Ct	36,62 d	32,60 d	132,57 d	132,57 d
	C3	38,10 t	47,18 đ	130,81 d	1 30,38 d
	C	40,87 d	14,63 d	53,75d	52,42 d
	ö	44,47 d	11,51 d	38,71 d	45,69 d
	Compound	5	The second	3 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	5 0 10 10 10 10 10 10 10 10 10 10 10 10 1

The reactivity of EtMgBr was found to be much lower than for diethylmagnesium as in the case of the catalyzed carbomagnesiation of α -olefins [3]. Thus, the yields of carbomagnesiation products (III), (VII), (VIII), and (XI) do not exceed 30-35% even when using a fourfold excess of EtMgBr. On the other hand, a twofold excess of Et₂Mg increases the conversion of the starting olefins (I), (IV), and (IX) to 90-95%. In this case, no effect of the nature of the carbomagnesiation reagent on the stereochemistry of the products formed was observed.

EXPERIMENTAL

The experiments were carried out in an argon atmosphere. The hydrocarbon samples used had at least 98% purity and were redistilled over LiAlH₄ immediately prior to use. A sample of Et₂Mg was obtained by the disproportionation of EtMgBr according to Strohmeier and Seifert [4] while Cp₂ZrCl₂ was obtained according to Freidlina et al. [5]. The gas-liquid chromatography was carried out on a Khrom-5 chromatograph with a flame-ionization detector on a 3.7 m × 3 mm column packed with 15% PEG-6000 on Chromaton N-AW. The PMR spectra were taken on a Tesla BS-487B spectrometer at 60 MHz relative to HMDS. The ¹³C NMR spectra were taken on a Jeol-90Q spectrometer for solutions in CDCl₃. The mass spectra were obtained on an MKh-1306 mass spectrometer with 70-eV electron ionization energy and 150°C ionization chamber temperature.

GENERAL METHOD FOR THE CARBOMAGNESIATION

A sample of 1 mmole Cp_2ZrCl_2 was added with stirring to a solution of 20 mmoles Et_2Mg or EtMgBr in ether (1.6-1.7 mmoles/ml) at about 20°C and then the required amount of (I), (IV), or (IX) was added. The mixture was stirred for 45 h at about 20°C. The cooled catalysate was hydrolyzed by saturated aq. NH₄Cl. The ethereal layer was separated, dried over MgSO₄, and analyzed by gas-liquid chromatography. The individual products were separated by vacuum distillation. The physical constants of (III), (VII), (VIII), and (XI) coincide with literature values [6, 7]. In addition, their structure was confirmed by NMR spectroscopy (Table 1).

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CONCLUSIONS

1. Cp_2ZrCl_2 catalyzes the stereoselective cis-carbomagnesiation of norbornene and dicyclopentadiene by diethylmagnesium and ethylmagnesium bromide.

2. In the case of norbornadiene, the carbomagnesiation is accompanied by an intramolecular rearrangement leading to a substituted nortricyclene.

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