CHEMISTRY LETTERS, pp. 1077-1080, 1976. Published by the Chemical Society of Japan

THE REACTION OF 2-(1,3-BUTADIENYL)MAGNESIUM CHLORIDE

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The reaction of 2-(1,3-butadienyl)magnesium chloride (1) with aldehydes and ketones afforded a mixture of 1,3-dienyl alcohol (3) and 1,2-dienyl alcohol (4). The selective formation of another 1,3-dienyl alcohol (6) was observed when the Grignard reagent (1) was treated with epoxides. The latter reaction was applied to the synthesis of the sex attractant of a bark beetle.

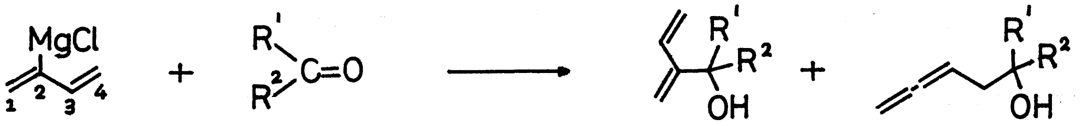
Although 2-(1,3-butadienyl)magnesium chloride (1) was originally prepared from 4-chloro-1,2-butadiene[1] and later one from easily accessible 2-chloro-1,3-butadiene (chloroprene),[2] only limited amount of information on its reactivity has been accumulated so far.[1,2,3] The unique structure of the compound 1, i. e., partially allylic and partially vinylic nature, stimulated us to investigate the reactivities of 1 toward aldehydes, ketones, and epoxides. As it is expected that the product derived from 1 will have diene function, the information thus obtained may provide a new and simple route to certain biologically active natural products.

The Grignard reagent 1 was prepared from chloroprene by Sultanov's method,[2] and was found to be stable at room temperature for a week or more under an argon atmosphere. Acetaldehyde (2a) was treated with an equimolar amount of 1 in tetrahydrofuran at ambient temperature for 1 hr. Usual work-up followed by distillation of the crude reaction products afforded a mixture of 2-(1-hydroxyethyl)-1,3-butadiene (3a) and 5-hydroxy-1,2-hexadiene (4a), bp 60°C/25mmHg, 3a/4a = 8/2, in 64% total yield. Similarly, formaldehyde (2b), 2-methylpropanal (2c), 4-methylpentanal (2d), and benzaldehyde (2e) were treated with 1 to give mixtures of the corresponding alcohols 3 and 4. The reaction of 1 with aliphatic aldehydes usually afforded the alcohol 3 as the major product, while that with aromatic aldehyde produced 4 predominantly. The results are summerized in Table I.

The similar product selectivity was observed in the reaction of ketones with 1

(Table I). Thus, alkyl ketones, such as acetone (2f) and cyclohexanone (2h), afforded the adducts 3 preferentially. On the other hand, aromatic ketones, especially benzophenone (2j), were converted selectively to the 1,2-dienyl alcohol 4 and only minor or undetectable amount of the corresponding 1,3-dienyl alcohol 3 was found in the product. An interesting result was observed when the reaction was applied to a sterically hindered ketone. Treatment of 1 with t-butyl metyl ketone (2g) now afforded the 1,2-dienyl alcohol 4g as the sole addition product, though the yield was not so satisfactory.

The following conclusions can be drawn from these results. 1) Although the IR and NMR spectra of 1 indicate[1] that magnisium atom is bound to the 2-carbon, the reagent 1 acts as both vinylic and allylic Grignard reagent in the reaction with carbonyl compounds. 2) In general, the reagent 1 adds preferentially at the



1 2 3 4

Table I. The reaction of 1 with aldehydes and ketones.

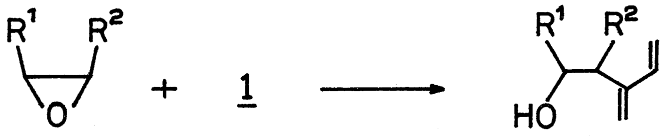
	Substrate R^1	Substrate R^2	Yield (%)	Product ratio* 3	Product ratio* 4	Bp of the mixture of 3 and 4 (°C/mmHg)
2a	Me	H	64	80	20	60/25
2b	H	H	42	57	43	54-55/24
2c	Pr^i	H	56	62	38	52/4
2d	Am^i	H	89	80	20	73-75/3
2e	Ph	H	73	39	61	72-74/2
2f	Me	Me	56	74	26	42-43/5
2g	Bu^t	Me	38	0	100	83-85/5
2h	$-(CH_2)_5-$		51	72	28	90-92/6
2i	Ph	Me	63	19	81	70-72/1.5
2j	Ph	Ph	92	0	100	161-163/0.6

* The product rations were calculated from NMR spectra of the mixture by comparing the integrals of peaks characteristic to 3 and 4.

C-2 carbon in the reaction with soft electrophiles,[4,5] while with relatively hard electrophiles, such as benzaldehyde and acetophenone, it adds at the harder terminus, i.e., C-4 position. 3) However, toward sterically encumbered ketones, it adds exclusively at the less crowded C-4 position.

When 1,2-epoxybutane (5a) was treated with 1, the normal adduct, 5-methylene-6-hepten-3-ol (6a) was obtained in 77% yield. Similarly, ethylene oxide (5b), cyclohexene oxide (5c), and epichlorohydrin (5d) gave selectively the corresponding normal adduct 6 in good yields. The results are summerized in Table II. In all these cases, there was observed no 1,2-dienyl alcohol in the product. The reaction of styrene oxide with 1 produced an adduct (6e) (60%) which was contaminated with a small amount of a 1,2-dienyl alcohol. The addition of organometallic compound to styrene oxide usually occurs on benzylic position[6] and the formation of 6e is in good accord with this phenomenon.

The product derived by the reaction of reagent 1 at C-2 position has 3-substituted 1,3-diene structure, which coincides with the partial structure of certain isoprenoids. The selective formation of 1,3-dienyl alcohol of type 6 can now conveniently be applied to the synthesis of monoterpene alcohol 6f, which is known as one of the principal components of the sex attractant produced in the frass of the male bark beetle, Ips confusus.[7] Thus the reaction of 1 with 4-methyl-1,2-



5 6

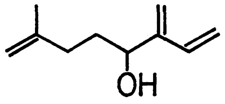
Table II. The reaction of 1 with epoxides 5.

Substrate	R^1	R^2	Yield (%)	Bp of 6 (°C/mmHg)
5a	Et	H	77	53/3
5b	H	H	50	68/23
5c	$-(CH_2)_4-$		51	63/1
5d	$ClCH_2$	H	58	76/4
5e	H	Ph	60	93/0.7

epoxypentane afforded the desired product 6f in 72% yield. The spectral data of 6f were identical with those of the published one.[7] The 1,3-dienyl alcohol 3d as well as the condensation product of 1 with 4-methyl-4-pentenal, i.e. 7 (85% yield), could be used as starting materials for the synthesis of naturally occuring furanoterpens.[8]

5-f

6-f



7

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(Received August 2, 1976)