3-Methylindenylmagnesium Bromide, a Butenyl Grignard Reagent

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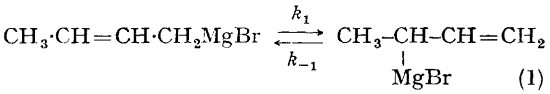
THE ability of allylic Grignard reagents to yield products derived from starting halide and the corresponding allylic isomer has stimulated extensive investigation into the reactions and properties of this class of organometallic compounds. Several general reviews give details of these investigations.[1,2]

Roberts and co-workers[3] have shown by a convenient n.m.r. technique that allylmagnesium bromide is either a rapidly equilibrating mixture of classical structures or a bridged structure with magnetically equivalent protons. These authors have further shown by n.m.r. that butenylmagnesium bromide exists wholly as crotylmagnesium bromide, *e.g.*, $k_{-1} \longrightarrow >> k_1$ in equation (1).

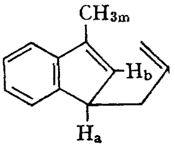
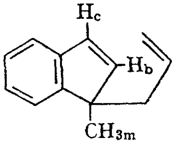


$$\mathrm{CH_3{\cdot}CH{=}CH{\cdot}CH_2MgBr} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{CH_3\text{-}\underset{\displaystyle MgBr}{\underset{|}{C}H}\text{-}CH{=}CH_2} \qquad (1)$$

In our studies[4] on 1-substituted allylindenes we have made an observation which prompts us to report chemical evidence for the possible existence

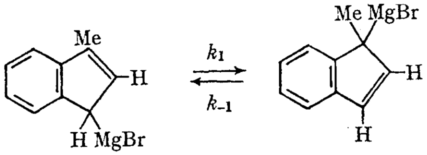
TABLE 1

N.m.r. data of 1-*allyl*-3-*methyl- and* 1-*allyl*-1-*methyl-indene**

	Chemical shifts				Coupling constants
	H_c	H_b	H_a	H_m	(c./sec.)
	—	6·06	3·25	2·07	$J_{a,b}$ = 1·65; $J_{b,m}$ = 2·30
	6·57	6·22	—	1·22	$J_{b,c}$ = 6·60

* Chemical shifts are in p.p.m. downfield from tetramethylsilane

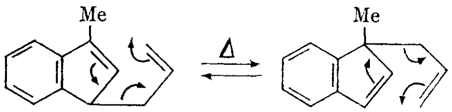
of an equilibrium between the secondary and tertiary allylic isomers in the 3-methylindenyl-magnesium bromide system (equation 2). Reaction



(2)

of the Grignard reagent, formed from the exchange reaction of 3-methylindene and ethylmagnesium bromide, with allyl bromide gives a 3 : 1 mixture of 1-allyl-3-methylindene and 1-allyl-1-methylindene as shown unequivocally by n.m.r. spectroscopy. In Table 1 is shown the abbreviated data of the n.m.r. spectra of the two isomers. The ratio of products was determined on the basis of the integrated areas of methyl signals in the n.m.r. spectrum of the mixture.

That the ratio of products is a measure of an allylic Grignard equilibrium process and not a Cope[5] type thermal rearrangement process as



shown above was borne out in the following series of experiments. A 3 : 1 mixture of 1-allyl-3-methylindene and 1-allyl-1-methylindene when heated to its normal distillation temperature retained its composition over the course of 8 hr. Accordingly, samples of each of the pure olefins (obtained by v.p.c.) retained their original composition under the same conditions.

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[1] M. S. Kharasch and O. Reinmuth, "Grignard Reactions of Non-metallic Substances", Prentice-Hall Inc., New York, 1954, Chapter XVII.

[2] R. H. Wolfe and W. G. Young, *Chem. Rev.*, 1956, **56**, 753.

[3] G. M. Whitesides, T. E. Nordlander, and J. D. Roberts, *Discuss. Faraday Soc.*, 1962, **34**, 185.

[4] P. T. Lansbury and E. J. Nienhouse, manuscript in preparation.

[5] A. C. Cope and H. Levy, *J. Amer. Chem. Soc.*, 1944, **66**, 1684.