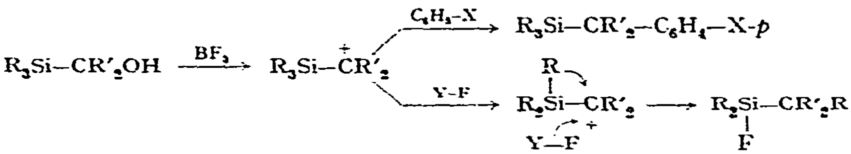

The reactions were carried out by bubbling BF_3 into stirred solutions of the carbinols in appropriate solvents. Structures assigned have been confirmed by analysis, infrared and NMR spectra, and in some cases mixed melting points with authentic samples prepared by different unambiguous routes. We are continuing our investigations on these reactions from both the mechanistic and synthetic point of view. To date it has provided an excellent route to certain substituted diphenyl- and triphenylmethylsilanes, obtainable only with difficulty by other routes.

This research was supported by a grant in the form of a Fellowship to G.E.L. by Dow Corning Silicones of Canada and by the National Research Council of Canada.

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1 C. EABORN, *Organosilicon Chemistry*, Butterworth, London, 1960, p. 434.
2 F. C. WHITMORE, L. H. SOMMER AND J. R. GOULD, *J. Am. Chem. Soc.*, 69 (1947) 1976.
3 C. EABORN AND J. C. JEFFREY, *J. Chem. Soc.*, (1957) 137.
4 N. F. ORLOV, B. N. DOGLOV AND M. G. VORONKOV, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, (1960) 1607; *Chem. Abstr.*, 55 (1961) 9316.
5 L. H. SOMMER, *U.S. Patent* 2,713,063; *Chem. Abstr.*, 50 (1956) 5742.

Received September 29th, 1964

J. Organometal. Chem., 2 (1964) 491–493

The effect of copper(I) chloride on the addition of Grignard reagents to ester carbonyl groups

As part of a study of the conjugate addition of Grignard reagents to α,β-unsaturated esters[1] (for leading references see ref. 1) we have recently investigated the reaction of butylmagnesium bromide with *sec*-butyl cyclopropanecarboxylate and di-*sec*-butyl cyclopropane-1,1-dicarboxylate[2]. We found that for both these esters the Grignard reagent attacks the ester molecule at the carbonyl group only, the sole reaction product being a tertiary alcohol. When the reactions were carried out in the presence of copper(I) chloride the direction of the attack was still the same, but the ratios produced of tertiary alcohol to unreacted ester were considerably smaller than when the reactions were uncatalyzed. This effect of copper(I) chloride was particularly pronounced in the case of the cyclopropanemonocarboxylic ester.

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J. Organometal. Chem., 2 (1964) 493–494

We then turned to ordinary saturated esters in order to see whether this effect of impeding the attack of the Grignard reagent on the ester carbonyl is a general one, and we now want to report that this indeed appears to be the case. The results are shown in Table 1.

TABLE I

YIELDS IN PERCENT OF TERTIARY ALCOHOLS FORMED BY UNCATALYZED OR COPPER(I) CHLORIDE CATALYZED REACTIONS OF ESTERS WITH BUTYLMAGNESIUM BROMIDE

sec-Butylester unless otherwise indicated	*Uncatalyzed*			*Catalyzed*		
	Yield	*Ester recov.*	*Yield based on consumed ester*	*Yield*	*Ester recov.*	*Yield based on consumed ester*
Cyclopropanecarboxylate	53	41	63	22	68	67
Cyclopropane-1,1-dicarboxylate	90	2	92	73	8	80
Propionate	47	not determined		31	not determined	
Butyrate	55	31	80	15	80	72
Caproate	52	28	71	29	63	78
Caproate, reaction with methylmagnesium bromide	64	28	90	67	14	78
Ethyl caproate	77	5	81	71	14	83
Isobutyl methyl ketone	79	10[a]	88[a]	81	10[a]	90[a]

[a] Read ketone instead of ester in the column head.

In the reactions with the *sec*-butyl esters of propionic, butyric and caproic acids with butylmagnesium bromide, the yields of tertiary alcohol were considerably reduced by the presence of copper(I) chloride. We are now pursuing further studies as to the nature of this effect and its relation to other effects, on the course of Grignard reactions previously reported[1]. At the present time there may be some evidence that a steric effect is involved, since the effect is not observed in the case of a methyl ketone, and only a feeble effect, if any, is found in the case either of an ethyl ester reacting with butylmagnesium bromide or of a *sec*-butyl ester reacting with methylmagnesium bromide.

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1 S. JACOBSEN, AA. JART, T. KINDT-LARSEN, I. G. KROGH ANDERSEN AND J. MUNCH-PETERSEN, *Acta Chem. Scand.*, 17 (1963) 2423.
2 B. HILMER NIELSEN AND J. MUNCH-PETERSEN, paper to be submitted to *Acta Chem. Scand.*

Received September 28th, 1964

J. Organometal. Chem., 2 (1964) 493–494

ERRATUM

In the article VINYL DERIVATIVES OF METALS. XVIII, *J. Organometal. Chem.*, 1 (1963) 141, the abscissa of Fig. 2. shoud read: 6.0 5.0 4.0 3.0 2.0

D. SEYFERTH