

4. Leonard, N. J. and Musliner, W. J. *J. Org. Chem.* **31** (1966) 639.
5. Royals, E. E. and Hendry, C. M. *J. Org. Chem.* **15** (1950) 1147.
6. Rapson, W. S. and Robinson, R. *J. Chem. Soc.* **1935** 1285.
7. Linstead, R. P. and Walpole, A. L. *J. Chem. Soc.* **1939** 842.
8. Johnson, J. L., Herr, M. E., Babcock, J. C., Fonken, A. E., Stafford, J. E. and Heyl, F. W. *J. Am. Chem. Soc.* **78** (1956) 430.
9. Burekhalter, J. H. and Kurath, P. *J. Org. Chem.* **24** (1959) 990.

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Influence of Magnesium Purity on the Addition of Grignard Reagents to α,β -Unsaturated Esters

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In earlier papers we have treated the conjugate addition of butylmagnesium bromide to a variety of α,β -unsaturated esters.¹⁻¹³ During the years we have occa-

sionally repeated the addition of butylmagnesium bromide to *sec*-butyl crotonate and have found some unexpected variations in the yield of *sec*-butyl 3-methylheptanoate, although we at any given time, with the particular samples of reagents (Mg, ester *etc.*) used at that time, were able to reproduce our results with a good accuracy (1–2 % deviations).

In checking a variety of factors, which could cause these deviations, we have finally settled on the purity of the magnesium employed in the preparation of the Grignard reagent. Table I shows an analysis of six magnesium samples; I is a high purity magnesium (triply sublimed) yielding clear, colorless Grignard reagents, while II–VI are samples of commercial grade "Grignard magnesium" yielding the well known dark colored Grignard reagents containing colloid impurities. The last column shows the yield of *sec*-butyl 3-methylheptanoate obtained after preparation of butylmagnesium bromide from the sample and subsequent addition of *sec*-butyl crotonate.* The yield of *sec*-butyl 3-methylheptanoate shows a decrease with an increase in the combined iron and manganese contents in the magne-

* The yields are based on *sec*-butyl crotonate. The *sec*-butyl crotonate not accounted for in *sec*-butyl 3-methylheptanoate gives rise to a byproduct, di-*sec*-butyl α -(1-methylpentyl)- β -methylglutarate.¹²

Table I. Yields of *sec*-butyl 3-methylheptanoate obtained by reaction of *sec*-butyl crotonate with butylmagnesium bromide prepared from magnesium of varying purity.

Magnesium sample	Impurities (ppm)									Yield %
	Fe	Mn	Si	Cu	Zn	Pb	Al	Ni	Ca	
I ^a	10	<10	20	5	10	<5	<5	<5	<40	80
II ^b	245	130	170	15	35	100	110	25	<40	65
III ^b	295	695	75	20	50	<5	45	20	<40	57
IV ^b	340	60	30	5	20	30	20	10	<40	68
V ^b	160	160	200	20	—	—	120	10	10	65
VI ^b	380	350	130	30	—	—	100	10	10	56

^a Triply sublimed. ^b Commercial grade "Grignard magnesium".

Table 2. Yields of *sec*-butyl 3-methylheptanoate obtained by reaction of *sec*-butyl crotonate with butylmagnesium bromide, to which has been added iron or manganese.

Magnesium sample	Added impurity (ppm)		Yield %
	Fe ^c	Mn ^d	
I ^a	none	none	80
I ^a	400 ^b	none	70
I ^a	4000 ^b	none	62
I ^a	none	400 ^b	66
I ^a	none	4000 ^b	63

^a Triply sublimed magnesium. Analysis given in Table 1.

^b based on moles of butylmagnesium bromide.

^c Added as FeCl₃.

^d Added as MnCl₂.

sium, while there is no clear-cut dependence on the amount of other impurities.

To demonstrate that iron and manganese could be responsible for the variations in yield of *sec*-butyl 3-methylheptanoate, butylmagnesium bromide was prepared from the triply sublimed magnesium (I), and small amounts of anhydrous iron(III) chloride or manganese(II) chloride were added to the Grignard reagent prior to the addition of *sec*-butyl crotonate. In this manner one obtains dark colored Grignard solutions containing finely suspended iron or manganese (resulting from reduction of the halides by the Grignard reagent¹⁵) with an appearance similar to those obtained from impure magnesium. The results (shown in Table 2) clearly demonstrate that impurities of iron and manganese do have an undesirable effect on the reaction.

An even more pronounced effect of iron and manganese is found on the addition of butylmagnesium bromide to *sec*-butyl cinnamate. The yields of the corresponding 1,4-adduct, *sec*-butyl 3-phenylheptanoate *

* The amount of *sec*-butyl cinnamate not accounted for in the yield of *sec*-butyl 3-phenylheptanoate undergoes dimerisation to di-*sec*-butyl 2,3-diphenyladipate and the corresponding selfcondensation product *sec*-butyl 2-oxo-4,5-diphenylcyclopentanecarboxylate.¹⁴

Table 3. Yields of *sec*-butyl 3-phenylheptanoate obtained by reaction of *sec*-butyl cinnamate with butylmagnesium bromide.

Magnesium sample	Added Fe ppm ^b	Yield %
I ^a	—	90
III ^a	none	35
I ^a	1 000	20
I ^a	10 000	0

^a Analysis given in Table 1.

^b Added as FeCl₃.

(shown in Table 3) decrease markedly with an increase in the amount of iron and manganese present in the Grignard reagent.

These results conclusively show that attention should be paid to the purity of the magnesium used for preparation of Grignard reagents, first, because commercial "Grignard magnesium" contains amounts of iron and manganese sufficiently large to be detrimental to the desired reaction. Secondly, the amounts of impurities in commercial "Grignard magnesium" show variations large enough to make quantitative results on Grignard reactions of doubtful value.

Experimental. Additions were carried out non-catalyzed, on a 0.1 mole scale, as previously described.¹⁶ When iron(III) chloride was employed, it was added to the stirred Grignard reagent at room temperature 30 min prior to addition of *sec*-butyl crotonate. When manganese(II) chloride was employed, it was added to the Grignard reagent at room temperature and refluxed for 1 h prior to addition of the *sec*-butyl crotonate.

The *sec*-butyl 3-methylheptanoate was isolated by distillation of the reaction mixture through a simple 45 cm × 8 mm Podbielniak type column with a tantalum spiral, a heated jacket and a partial reflux head.¹⁷

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1. Munch-Petersen, J. *J. Org. Chem.* **22** (1957) 170.
2. Munch-Petersen, J. *Acta Chem. Scand.* **12** (1958) 967.
3. Bjerl Nielsen, E., Munch-Petersen, J., Møller Jørgensen, P. and Refn, S. *Acta Chem. Scand.* **13** (1959) 1943.
4. Bretting, C., Munch-Petersen, J., Møller Jørgensen, P. and Refn, S. *Acta Chem. Scand.* **14** (1960) 151.
5. Munch-Petersen, J. and Køgs Andersen, V. *Acta Chem. Scand.* **15** (1961) 271.
6. Munch-Petersen, J., Bretting, C., Møller Jørgensen, P., Refn, S., Køgs Andersen, V. and Jart, A. *Acta Chem. Scand.* **15** (1961) 277.
7. Munch-Petersen, J. and Køgs Andersen, V. *Acta Chem. Scand.* **15** (1961) 293.
8. Køgs Andersen, V. and Munch-Petersen, J. *Acta Chem. Scand.* **16** (1962) 947.
9. Jacobsen, S., Bitsch, V. and Munch-Petersen, J. *Acta Chem. Scand.* **17** (1963) 825.
10. Kindt-Larsen, T., Bitsch, V., Krogh Andersen, I., Jart, A. and Munch-Petersen, J. *Acta Chem. Scand.* **17** (1963) 1426.
11. Jacobsen, S., Jart, A., Kindt-Larsen, T., Krogh Andersen, I. and Munch-Petersen, J. *Acta Chem. Scand.* **17** (1963) 2423.
12. Bitsch, V., Jacobsen, S., Krogh Andersen, I. and Munch-Petersen, J. *Acta Chem. Scand.* **17** (1963) 1433.
13. Munch-Petersen, J. *Bull. Soc. Chim. France* **1966** 471.
14. Rosendal Jensen, S., Kristiansen, A. and Munch-Petersen, J. *To be published.*
15. Kharasch, M. and Reinmuth, O. *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, New York 1954, p. 121.
16. Munch-Petersen, J. *Org. Syn.* **41** (1961) 60.
17. Cason, J. and Rapoport, H. *Laboratory Text in Organic Chemistry*, 2nd. Ed., Prentice-Hall, Englewood Cliffs, N. J. 1962, p. 289 ff.

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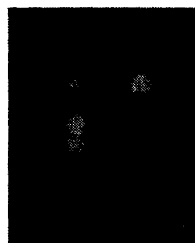
A Thin-layer Chromatographic Method for the Separation and Identification of Phorbic and Piscidic Acids

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Phorbic and piscidic acids were recently found to make up a major part of the nonvolatile organic acids in several plants¹⁻⁵ and it was presumed that, in a near future, there would be a need for appropriate analytical methods in connection with investigations of their metabolism. In the present investigations emphasis was placed on separation and identification of the pure acids. Preliminary applications of the methods to plant materials are reported. Detection of piscidic acid (*p*-hydroxybenzyl-tartaric acid) by means of thin-layer chromatography did not involve special difficulties. Being a phenolic acid, piscidic acid can easily be detected by means of spray reagents like Fast blue salt B. This reagent produces a yellow-brown color with piscidic acid.

Detection of phorbic acid, on the other hand, proved to be more difficult. The difficulties are mainly related to the tendency of the acid to form lactones, which give rise to several spots and heavy tailing during the chromatography. This problem was acute in one-dimensional chromatography of the acid and even more evident in two-dimensional chromatography.



a b

Fig. 1. a: Phorbic acid dilactone in water. b: Phorbic acid dilactone in acetone.

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