

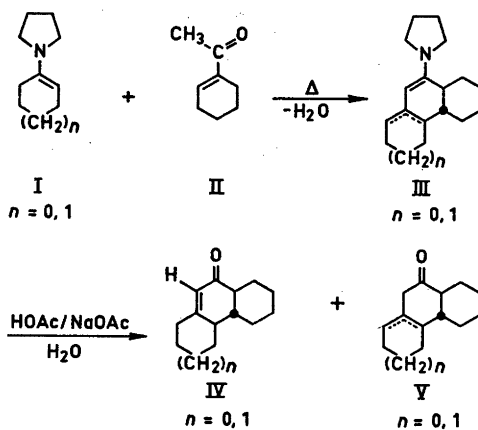


I ( $n = 1$ ) and methyl vinyl ketone: 1628 and 1600  $\text{cm}^{-1}$ ; its NMR (in  $\text{CDCl}_3$ ) singlet at  $\tau$  4.25 (vinyl H  $\alpha$  to carbonyl of IV,  $n = 1$ , impurity), singlet at  $\tau$  5.21 (vinyl  $\alpha$ -H of III,  $n = 1$ ) and a broad peak at  $\tau$  4.86 (vinyl  $\gamma$ -H of III,  $n = 1$ ) (see Ref. 2 for basis of assignments); and its UV spectrum:  $\lambda_{\text{cyclohexane max}}$  283  $\text{m}\mu$  ( $\epsilon$  27 400), lit.<sup>8</sup>  $\lambda_{\text{max}}^{\text{ether}}$  280–282  $\text{m}\mu$  ( $\epsilon$  22 700–24 100) for some pyrrolidine dienamines of  $\Delta^4$ -3-keto steroids.

The usefulness of enamines in synthesis was again demonstrated in the successful preparation of the previously unknown IV ( $n = 0$ ); earlier synthesis of IV ( $n = 0$ ) by reaction of cyclopentanone (VI) and II in the presence of various bases had failed, VI undergoing self-condensation instead.<sup>9</sup> This difference in reactivity in the Michael reaction between VI and its enamine had been noted earlier.<sup>1</sup> After refluxing 0.104 mole each of I ( $n = 0$ ) and II in 35 ml of xylene for 24 h under a water trap (1.9 ml water) and then vacuum-evaporating the xylene, distillation gave three lower-boiling fractions (total 1.5 g) followed by 3.8 g of impure III ( $n = 0$ ), b.p. 170–180°C (2.0 mm):  $\lambda_{\text{max}}^{\text{neat}}$  1710 m (presumably V,  $n = 0$ ), 1665 vs (presumably IV,  $n = 0$ ), 1623 s, 1595 s and

1575  $\text{vs cm}^{-1}$  (III,  $n = 0$ ,  $\text{>C=C-C=C-N<}$  absorptions). Presumably IV ( $n = 0$ ) and V ( $n = 0$ ) were formed because the pyrrolidine evolved was removed from the flask due to the high reaction temperature before being able to reform III ( $n = 0$ ) (see Ref. 1 for a mechanism that suggests this possibility).

Hydrolysis of the enamine III ( $n = 0$ ) in aqueous acetic acid-sodium acetate<sup>1</sup> gave 3.0 g of a mixture of ketones. Rapid chromatography (as above) of 0.90 g of this mixture gave two fractions. The first, 0.58 g of an oil, was largely (80% as a minimum from NMR) V ( $n = 0$ ):  $\nu_{\text{max}}^{\text{neat}}$  1710 vs and 1665  $\text{vs cm}^{-1}$  (IV,  $n = 0$ , impurity), and NMR (in  $\text{CDCl}_3$ ) small peak at  $\tau$  4.22 (vinyl H  $\alpha$  to carbonyl of IV,  $n = 0$ , present), small, poorly resolved triplet ( $J \sim 2.2$  c/s) at  $\tau$  4.52 (assigned to vinyl H of that isomer of V,  $n = 0$ , having such an H) and strong, complex absorption at  $\tau$  6.9–9.2 (analysis indicated that apart from the IV,  $n = 0$ , present, approximately 80% of the V,  $n = 0$ , was that isomer having a tetra-substituted olefinic bond). The second fraction was 0.09 g of an oil:  $\nu_{\text{max}}^{\text{neat}}$  1710 w (trace of V,  $n = 0$ ) and 1660  $\text{vs cm}^{-1}$ , which, when recrystallized from aqueous methanol at 0°C, gave 0.01 g IV ( $n = 0$ ): m.p. 61–63°C,  $\nu_{\text{max}}^{\text{KBr}}$  1710 vw and 1660  $\text{vs cm}^{-1}$ .



Earlier, in another enamine III ( $n = 0$ ) preparation, pure IV ( $n = 0$ ) crystallized from a distillation fraction: m.p. 65–66°C,  $\nu_{\text{max}}^{\text{KBr}}$  1660 vs and 1610 vw, sh  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}^{\text{ethanol}}$  238  $\text{m}\mu$  ( $\epsilon$  12 700); NMR (in  $\text{CCl}_4$ ) doublet ( $J = \pm 1.9$  c/s) at  $\tau$  4.28 (vinyl H  $\alpha$  to carbonyl) and strong, complex absorption at  $\tau$  7.2–9.2. From IV ( $n = 0$ ) was prepared a 2,4-dinitrophenylhydrazone, m.p. 209–210°C.

Spectral data were obtained on Perkin-Elmer No. 621 (IR), Perkin-Elmer No. 337 (IR of enamines and of liquid ketone mixtures), Cary No. 14 (UV) and Varian A-60 (NMR) spectrophotometers. Satisfactory carbon-hydrogen analyses were obtained on IV ( $n = 0$ ), IV ( $n = 1$ ), and their 2,4-dinitrophenylhydrazones (C. F. Geiger, Ontario, California).

Refinements of these procedures and extensions to other systems are under way. We are grateful to the San Diego State College Research Foundation for financial support of MFS and to Professor Arne Fredga for discussion and facilities made available to LHH. We thank the American-Scandinavian Foundation for a grant-in-aid to LHH.

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### Influence of Magnesium Purity on the Addition of Grignard Reagents to $\alpha,\beta$ -Unsaturated Esters

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In earlier papers we have treated the conjugate addition of butylmagnesium bromide to a variety of  $\alpha,\beta$ -unsaturated esters.<sup>1-13</sup> 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  $\alpha$ -(1-methylpentyl)- $\beta$ -methylglutarate.<sup>12</sup>

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 <sup>a</sup>	10	<10	20	5	10	<5	<5	<5	<40	80
II <sup>b</sup>	245	130	170	15	35	100	110	25	<40	65
III <sup>b</sup>	295	695	75	20	50	<5	45	20	<40	57
IV <sup>b</sup>	340	60	30	5	20	30	20	10	<40	68
V <sup>b</sup>	160	160	200	20	—	—	120	10	10	65
VI <sup>b</sup>	380	350	130	30	—	—	100	10	10	56

<sup>a</sup> Triply sublimed. <sup>b</sup> Commercial grade "Grignard magnesium".