mospheric pressure for 72 h. Removal of the catalyst by filtration and the solvent by distillation gave an oil which was dissolved in methylene chloride and washed with sodium carbonate solution. Removal of the methylene chloride gave an oil which was purified by chromatography on silica gel using chloroform as an eluant. The acetyl derivative (**1a**, 0.69 g) is a liquid: n^{20}_D 1.5454; IR (film) 3.44, 6.06, 14.24 μm; NMR (CCl_4, 29 °C) δ 0.65–3.32 (m, 8 H, 4-, 5-, 6-, 7-CH_2), 1.88, 2.07 (2 s, 3 H, CH_3CO), 2.32, 2.38, 2.57 (3 s, 3 H, NCH_3), 2.57–3.10 (m, 2 H, CH_2N), 3.32–5.73 (m, 1 H, CH), 7.00–7.67 (m, 5 H, C_6H_5); at 87 °C the two singlets for the CH_3CO became one singlet at δ 2.02 and the three singlets for the NCH_3 became a singlet at δ 2.50.

Anal. Calcd for $C_{15}H_{22}N_2O$: C, 73.13; H, 9.00; N, 11.37; mol wt 246. Found: C, 73.48; H, 9.05; N, 11.40; mol wt 246 (mass spectrum).

1,1-Dimethyl-2-(*p*-nitrobenzyl)-2-acetylhydrazine:[6] NMR ($CDCl_3$, 30 °C) δ 2.27 (s, 3 H, CH_3CO), 2.50 (s, 6 H, 2 CH_3), 4.67 (s, 2 H, CH_2), 7.45 (d, 2 H, *o*-H's, J = 9 Hz), 8.15 (d, 2 H, *m*-H's, J = 9 Hz); NMR (−40 °C) δ 2.25 (s, 3 H, CH_3CO), 2.50 (s, 6 H, 2 CH_3), 4.65 (s, 2 H, CH_2), 7.45 (d, 2 H, *o*-H's, J = 9 Hz), 8.13 (d, 2 H, *m*-H's, J = 9 Hz); NMR ($CDCl_3$–CS_2, −83 °C), broadening of all three singlets.

Registry No. 1a, 75299-33-1; **1b**, 79868-87-3; **1b** picrate, 75299-34-2; **2**, 75311-36-3.

(6) S. Wawzonek and E. Yeakey, *J. Am. Chem. Soc.*, **82**, 5718 (1960).

Preparation and Some Properties of 4-Chloro-2-(and -4-) methyl-2-pentenes

Elliot N. Marvell* and Jeffrey W. Nelson[1]

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

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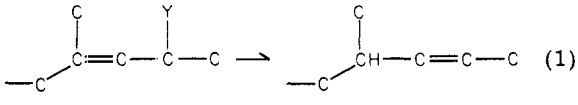
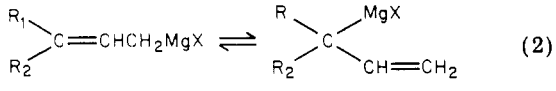
One sequence in a synthesis required the overall reductive process illustrated in eq 1. While a direct S_N2'



(1)

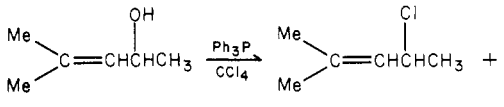
reduction might prove feasible, we considered the known protonation of an allylic Grignard, which generally leads to a less substituted olefin as the major product,[2] as a viable alternative. However, the mechanism of this protonation is not known and might reasonably bear a relation to the structure of the allylic Grignard reagent. These reagents are known to be equilibrating mixtures of the two covalent isomers (eq 2)[3] and when R_1 = Me, R_2 = H, or



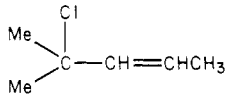
(2)

R_1 = R_2 = Me, the primary reagent is the dominant form.[4] However, no example of a secondary vs. tertiary system has been studied, and we decided to examine the protonation process in such a system, i.e., the simplest case possible—the Grignard from 4-chloro-2-methyl-2-pentene. When we initiated this project, the chloride had been reported as the main product (80%—along with 20% of its allylic isomer) from addition of hydrogen chloride to trimethylallene.[5] The mixture was described as being heat labile but capable of distillation under reduced pressure. While our studies were in progress a further report appeared which indicated that attempts to prepare the chloride gave 4-methyl-1,3-pentadiene from spontaneous loss of hydrogen chloride.[6] Since we have successfully prepared the chloride and have studied some of its properties, we report our results at this time.

Mesityl oxide was reduced to 4-methyl-3-penten-2-ol by LAH according to the established procedure.[7] Initially we attempted to prepare the chloride using triphenylphosphine and carbon tetrachloride.[8] The reaction mixture, freed from triphenylphosphine oxide, gave an NMR spectrum indicating the presence of 4-chloro-2-methyl-2-pentene (**1**) and 4-chloro-4-methyl-2-pentene (**2**). How-



1



2

ever, attempted separation of the chlorides from the carbon tetrachloride either by distillation, column chromatography, or TLC led to either codistillation or decomposition. Treatment of the alcohol with concentrated hydrochloric acid gave a good yield of 2,4-dichloro-2-methylpentane. Hoping that the allylic chloride was generated initially in this reaction and the addition of hydrogen chloride was a subsequent reaction, we followed the course of the reaction with GLC. This showed that the postulated course was indeed correct and we were able to develop a satisfactory procedure, albeit of low isolated yield, for preparation of this rather unexpectedly difficult compound.

The chlorides **1** and **2** were always obtained as a mixture containing about 84% **1** and 16% **2** (by NMR). They can be isolated as a clear liquid by reduced-pressure distillation or by GLC. Structural assignments are based purely on the NMR and infrared data. The infrared spectrum shows the complete absence of hydroxyl, and the NMR spectrum closely resembles that of 4-methyl-3-penten-2-ol. The two spectra differ slightly in chemical shifts and the CHCl proton shows a clean pair of overlapping quartets instead of the broadened near quintet of the CHOH proton. The NMR spectrum of the allylic chloride also contains two new peaks, a very tight AB pattern with further splitting which is centered at ca. 5.70 and a singlet at 1.65. For the AB pattern J_{AB} is 15 Hz, reasonable for a *trans*-CH=CH system. We attribute these new bands to the presence of some 16% **2** in the mixture. The position of the doublet for the CH_3CH methyl group is apparently hidden under the peaks for **1**. However, the total integration accords well with the expectations of the 84:16 mixture.

The mass spectrum of the mixture proved surprising and quite interesting. For $C_6H_{11}Cl$ the molecular ions should be at m/z 118 and 120, but the major peaks in that area

(1) Taken from the senior thesis of J.W.N., Oregon State University, June 1977.

(2) Wilson, K. W.; Roberts, J. D.; Young, W. G. *J. Am. Chem. Soc.* **1950**, *72*, 215–217, and earlier papers in the series.

(3) Nordlander, J. E.; Roberts, J. D. *J. Am. Chem. Soc.* **1959**, *81*, 1769–1770. Whitesides, G. M.; Nordlander, J. E.; Roberts, J. D. *Discuss. Faraday Soc.* **1962**, *34*, 185–190.

(4) Nordlander, J. E.; Young, W. G.; Roberts, J. D. *J. Am. Chem. Soc.* **1961**, *83*, 494–495. Whitesides, G. M.; Nordlander, J. E.; Roberts, J. D. *Ibid.* **1962**, *84*, 2010–2011. Hutchinson, D. A.; Beck, K. R.; Benkeser, R. A.; Grutzner, J. B. *Ibid.* **1973**, *95*, 7075–7082.

(5) Bianchini, J. P.; Guillemonat, A. *Bull. Soc. Chim. Fr.* **1968**, 2120–2123.

(6) Stanberry, T. E.; Darmon, M. J.; Fry, H. A.; Lenox, R. S. *J. Org. Chem.* **1976**, *41*, 2052–2054.

(7) Cain, M. E. *J. Chem. Soc.* **1964**, 3532–3535.

(8) Snyder, E. *J. Org. Chem.* **1972**, *37*, 1466.

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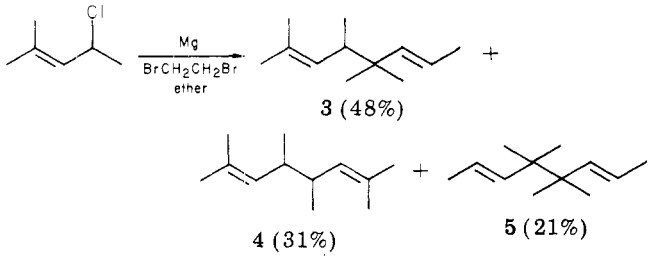
were at m/z 121 and 123! The peak at m/z 121 and a second at m/z 107 cannot correspond to any species containing one chlorine and both necessarily indicate the presence of more than six carbons. Furthermore, significant peaks appear at 149, 164, and 246. The small peak at 118 was found by high-resolution studies to have m/z 118.055 which corresponds only to $C_6H_{11}Cl$. The major group of low molecular weight ions can be accounted for as fragment peaks from the m/z 83 (82%) ion formed by loss of a chlorine atom. The presence of a significant radical cation at m/z 82 along with those at m/z 164 and 246 suggests strongly that **1** readily loses hydrogen chloride during introduction into the mass spectrometer and the diene forms dimers and trimers. Under different entry conditions, the intensities of these radical cation peaks varied considerably, and m/z 246 was often absent or of very low intensity.

With the chloride mixture in hand, we set out to prepare a Grignard reagent, but the chlorides were relatively unreactive unless the magnesium was preactivated with dibromoethane. Then reaction did occur, leading, however, only to a mixture of coupling products. The mixture was separated readily by GLC into a major (79%) and a minor (21%) fraction. The minor fraction was readily identified as 4,4,5,5-tetramethyl-2,6-octadiene (**5**), while the major



fraction contains a mixture of ca. 60% 2,4,5,5-tetramethyl-2,6-octadiene (**3**) and ca. 40% 2,4,5,7-tetramethyl-2,6-octadiene (**4**). In an attempt to limit the dimer formation we used Rieke magnesium.[9] The reaction mixture was treated with acetone but the expected tertiary alcohol constituted at best a trace constituent of the complex mixture. No pure compounds could be isolated. It is clear therefore that while **1** can be prepared, the great ease with which it loses hydrogen chloride has a strong influence on its chemistry.

Experimental Section[10]

4-Methyl-3-penten-2-ol. The alcohol was prepared by the procedure of Cain,[7] using a half-molar scale. The alcohol, bp 71 °C (44 mm), was obtained in 70% yield: IR (neat) 3430 (br), 1680; NMR (CCl_4) δ 1.12 (d, 3 H, J = 6 Hz), 1.55, 1.57 (2 d's, 6 H, $J \simeq 2$ Hz), 3.62 (OH), 4.43 (quintet, 1 H, J = 7 Hz), 5.15 (d of quintet, 1 H, J = 7.5, 1.5 Hz).

2,4-Dichloro-2-methylpentane. A sample, 2.0 g (0.02 mol), of the above alcohol was allowed to stand overnight in 25 mL of concentrated hydrochloric acid. The organic products were taken up in pentane, and the solution was washed with sodium bicarbonate and dried ($MgSO_4$). The main product was collected from GLC (2% SE-30 column at 77 °C); NMR (CCl_4) δ 1.57 (d, 3 H, J = 7 Hz), 1.66 (s, 6 H), 2.20 (d, 2 H, J = 5 Hz), 4.43 (near sextet, 1 H, $J \simeq 6$ Hz).

4-Chloro-2- (and -4-) methyl-2-pentene. The two isomeric chlorides were prepared by two procedures, but in all cases a mixture of the two in the ratio **1**/**2** of 84:16 was always obtained, and the two could not be separated.

Method A. A solution containing 8.45 g (84.5 mmol) of 4-methyl-3-penten-2-ol in 30 mL of pentane was shaken with 80 mL of 12 N hydrochloric acid for 20 min. The pentane layer was separated, washed with sodium bicarbonate solution, and dried ($MgSO_4$). The pentane was removed under reduced pressure and the residue was distilled, bp 37.5 °C (51 mm) [lit.[5] bp 45–46 (40 mm)], giving 2.4 g (29%) of clear liquid: IR (neat) 3040, 1670, 1380, 970 (w), 840; NMR (CCl_4) δ 1.53 (d, 3 H, J = 7 Hz), 1.72, 1.74 (overlapping d's, 6 H, $J \simeq 1.5$ Hz), 4.72 (overlapping q's, 1 H, J = 10, 7 Hz), 5.29 (2 septets, 1 H, J = 10, ~1.5 Hz). The NMR spectrum contains, along with the above two additional patterns which were attributed to 4-chloro-4-methyl-2-pentene, δ 1.65 (s), 5.70 (apparent AB, $J \simeq 15$ Hz). The integration of the δ 5.70 vs. the δ 4.72 + 5.29 multiplets is 5.5 to 28.5 which corresponds to about 16% of the lesser isomer. A GLC analysis (4% SE-30 column at 68 °C) of the mixture shows two peaks with the ratio 80:20, but collection of the major peak indicates that reequilibration had occurred during passage through the detector and collection system; mass spectrum, m/z (relative intensity) 164 (2.4), 149 (3.7), 121 (14.5), 118 (2.4), 107 (10.3), 83 (81.9), 82 (36.1), 67 (50.3), 55 (54.8), 53 (16.4), 43 (24.6), 41 (66.4), 39 (47.5). Under different entry conditions the peak ratios shift notably with m/z 118 being half as intense as m/z 121 and either m/z 67 or 83 being the base peak.

Method B. The pentenol, 1.00 g (9.98 mmol), was allowed to stand for several days with 2.68 g (10.2 mmol) of triphenylphosphine in 3.6 mL of carbon tetrachloride. The precipitated triphenylphosphine oxide was removed and the product was distilled. The carbon tetrachloride codistilled with the mixture of chlorides. The product showed the same spectra as the chloride mixture obtained by method A.

Dimer Formation. Grignard magnesium, 1.24 g (51 mmol), in 30 mL of ether, was activated with 1,2-dibromoethane, and 360 mg (3.04 mmol) of the chloride mixture in 25 mL of ether was added dropwise. The mixture was stirred at room temperature for 2.5 h and 4 mL of water was added slowly. Enough 2 N sulfuric acid was added to dissolve the precipitate and the ether layer was separated and dried ($MgSO_4$). Ether was removed with a spinning-band column and the residue was separated by GLC (2% SE-30 column, 65 °C). Two products were collected, a major (79%) and a minor (21%) fraction. The main fraction was identified spectrally as 2,4,5,5-tetramethyl-2,6-octadiene apparently contaminated with some 2,4,5,7-tetramethyl-2,6-octadiene: NMR (CCl_4) δ 0.81, 0.82 (2 d, J = 6 Hz), 0.89, 0.91 (2 s), 1.60, 1.70 (2 d), 1.68 (d), 4.90 (m), 5.33 (m) (decoupling showed multiplets at δ 4.90 and 5.33 were coupled to the methyls at δ 1.60 and 1.70); IR (CCl_4) 3040, 1660, 1380, 1360, 968, 850; mass spectrum, m/z (relative intensity) 166 (2.6), 83 (100), 82 (6.4), 55 (30.8), 43 (14.8), 41 (18.0). Assuming the mixture contains solely the two isomeric dimers, the integration indicates 60% 2,4,5,5- and 40% 2,4,5,7-tetramethyl-2,6-octadienes.

The minor fraction was pure *trans,trans*-4,4,5,5-tetramethyl-2,6-octadiene: NMR (CCl_4) δ 0.90 (s, 12 H), 1.68 (d, 6 H, J = 5.5 Hz), 5.29, 5.51 (AB of ABX_3, J_{AB} = 15, $J_{AX} \rightarrow 0$, J_{BX} = 5.5 Hz); IR (CCl_4) 3035, 1380, 1365, 975 cm^{-1}; mass spectrum, m/z (relative intensity) 166 (0.8), 83 (100), 55 (33.2), 43 (11.9), 41 (19.5).

Registry No. 1, 21971-94-8; 2, 68318-00-3; 3, 75232-90-5; 4, 65164-65-0; 5, 75232-91-6; 2,4-dichloro-2-methylpentane, 33484-86-5; 4-methyl-3-penten-2-ol, 4325-82-0.

(9) Rieke, R. D.; Bales, S. E. *J. Am. Chem. Soc.* **1974**, *96*, 1775–1781.
(10) The HA 100 NMR spectrometer used in this work was purchased with the aid of an instrument grant from the NSF.

Microbiological Preparation of (*S*)-(+)-2,3-Dihydroxy-3-methylbutanoic Acid by Syn Dihydroxylation of 3-Methylcrotonic Acid[1]

D. John Aberhart

Worcester Foundation for Experimental Biology, Shrewsbury, Massachusetts 01545

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I report the preparation of (2*S*)-2,3-dihydroxy-3-methylbutanoic acid (**1a**) by microbiological di-

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