SYNTHESIS OF Z-ALLYLIC ACETATES VIA FRAGMENTATION

OF CYCLIC HOMOALLYLIC ALCOHOLS

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Summary: Z-Allylic acetates ($\underline{6a}$ — $\underline{6e}$) having an additional functional group as ketone or aldehyde were prepared via the fragmentation of the homoallylic alcohols ($\underline{5a}$ — $\underline{5e}$) in the presence of lead tetraacetate.

Allylic compounds such as acetates and alcohols have been of synthetic, mechanistic and biochemical importance for more than fifty years.¹ A novel method for the synthesis of acyclic Z-allylic acetates $\underline{6a} - \underline{e}$, having also an aldehyde or ketone group, by applying a fragmentation reaction on the homoallylic alcohols $\underline{5a} - \underline{e}$ is presented in this communication.

We have prepared² earlier the Z-allylic alcohol $\underline{2}$ and transformed it to the ketone $\underline{3}$; the key step in the preparation of $\underline{2}$ is the hydrolytic cleavage of the heterocyclic ring of the coumarin $\underline{1}$; the geometry of the double bond in $\underline{1}$ has been utilized in preparing the required geometrical isomer $\underline{2}$.



This investigation suggested that it may be possible to prepare acyclic unsaturated compounds of established geometry by cleaving suitably functionalized cycloalkenes employing reagents which do not react at the unsaturation site of the cycloalkene. Homoallylic alcohols are known to undergo facile fragmentation on treatment with lead tetraacetate (LTA).³ Hence, the homoallylic alcohols $5a - e^{4-6}$ were heated with LTA in benzene to furnish the Z-allylic acetates $6a - e^7$ having an additional functional group as an aldehyde or ketone. The interestisng intermediate 6b has been prepared by a number of investigators employing other routes.⁸ The presence of the aldehyde or ketone group in the allylic acetates $6a - e^{9,10}$ makes them attractive intermediates in synthetic organic chemistry.

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- REFERENCES AND NOTES
- (a) R.M.Magid, <u>Tetrahedron</u>, <u>36</u>, 1901 (1980); (b)A.Carpita, <u>Synthesis</u>, <u>469</u> (1982);
 (c)A.Pfenninger, <u>Synthesis</u>, <u>89</u> (1986); (d)J.K.Crandall, <u>Org.React.</u>, <u>29</u>, <u>345</u> (1983);
 (e)K.B.Sharpless and R.F.Lauer, J.Am.Chem.Soc., <u>95</u>, <u>2697</u> (1973); (f)G.Consiglio, F.Morandini and O.Piccolo, J.Am.Chem.Soc., <u>103</u>, 1846 (1981).
- 2. P.P.Sane, K.J.Divakar and A.S.Rao, Ind.J.Chem., 15B, 325 (1977).
- (a)K.Shankaran and A.S.Rao, <u>Ind.J.Chem.</u>, <u>18B</u>, 507 (1979); (b)K.Hensler and J.Kalvoda Angew.Chem.Int.Ed.Engl., 3, 525 (1964).
- 4. Compounds <u>5a</u>-<u>e</u>: Compounds <u>5a</u> and <u>5b</u> were prepared in 80% yields by reducing the corresponding ketones <u>4a</u> and <u>4b</u> with NaBH₄ in methanol at 25°C. Compounds <u>5c</u>, <u>5d</u> and <u>5e</u> were prepared in 70%, 60% and 65% yields by reacting ketone <u>4a</u> with phenyl-magnesium bromide, 4-methoxy phenylmagnesium bromide and methylmagnesium iodide respectively. They were purified by column chromatography over Al₂O₃.
- 5. (a)D.S.Noyce and M.Evett, J.Org. Chem., 37, 394(1972); (b)A.J.Birch, J.Chem. Soc., 593(1946)
- (a)E.A.Braude, A.A.Webb and M.U.S.Sultanbawa, J.Chem.Soc., 3328(1958); (b)E.J.Corey and D.V.Watt, <u>J.Am.Chem.Soc.</u>, <u>95</u>, 2303(1973); (c)G.M.Rubottom and J.M.Gruber, J.Org.Chem., 42, 1051(1977).
- 7. We have observed that when cis-1,4-diacetoxy-2-butene is heated with LTA in benzene for 8 hrs, it is recovered unchanged as shown by H-NMR and ¹³C-NMR. This suggests that under the experimental conditions employed, the Z-allylic acetates <u>6a-e</u> will not isomerise to the corresponding E isomers.
- (a)K.Mori, Tetrahedron, <u>33</u>, 289(1977); (b)G.Stork, M.Gregson and P.A.Grieco, <u>Tetrahedron Letters</u>, 1931 (1969).
- 9. Compound <u>6b</u> showed b.p. 120°C/5 mm; reported ^{8a} b.p. 105°C/2mm.The ¹H-NMR spectrum of the compound <u>6b</u> is in agreement with the reported ⁸ values. Compounds <u>6a, 6c, 6d</u> and <u>6e</u> were purified through preparative thin layer chromatography using a 1:4 mixture of pet.ether-chloroform followed by vacuum distillation. All of them showed a characteristic doublet (J=7Hz) at around 4, 5 6 (-CH₂-OAc). The structures assigned to <u>6a-e</u> are consistent with their IR and H-NMR data. All new compounds gave satisfactory elemental analysis.
- 10 The following typical experimental procedure is illustrative; A mixture of 18g of dry LTA (40 mmole) and 200 ml of dry benzene, was stirred at 50°C under N₂ for 15 minutes; then 3g of <u>5c</u>(17 mmole) in 20 ml of benzene was added dropwise during 10 min. The reaction mixture was heated under reflux for 6 hrs., and cooled to room temp. The excess of LTA was destroyed with ethylene glycol (5 ml). The reaction mix. was poured into 50 ml of water and extracted with 2x30 ml portions of ether. The combined extracts were washed with water (2x30 ml) and dried with Na₂SO₄. Removal of solvent in vacuo, furnished crude product which was purified by preparative TLC using 1:4 mixture of pet. ether-chloroform followed by vacuum dist. to give 2.1g (52%) of <u>6c</u>, b.p.145°C(Bath)/0.5 mm. H-NMR (90 MHz, CDCl₃) § ppm:2.0 (s, 3H, OAc); 2.5 (m, 2H, -CH₂-); 3.0 (t, 2H, -CO-CH₂, J=7 Hz); 4.48 (d, 2H, CH₂-OAc, J=7 Hz); 5.5-5.8 (m, 2H, CH=CH); 7.35 (m, 3H, ArH); 7.90 (m, 2H, ArH); IR(Neat)cm 1690, 1740; Anal.Calcd. for C₁₄H₁₆O₃: C, 72.39; H, 6.94. Found : C, 72.05; H, 7.09.

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