15 ml DMF in a sealed ampul was stirred at 50° C for 24 h, cooled to ~ 20° C, and poured into 100 ml water. The products were extracted with pentane and dried over MgSO₄. Pentane was evaporated off and the product was distilled in vacuum.

CONCLUSIONS

The regioselective arylation of unsaturated compounds was carried out under metal complex and phase transfer conditions by the action of aryl iodides.

LITERATURE CITED

- 1. W. P. Weber, Silicon Reagents for Organic Synthesis, Springer Verlag, Berlin (1983).
- 2. H. Sakurai, Pure Appl. Chem., 54, 1 (1982).
- 3. A. Hallberg and C. Westerlund, Chem. Lett., 1993 (1982).
- 4. N. M. Chistovalova, I. S. Akhrem, E. V. Reshetova, and M. E. Vol'pin, Izv. Akad. Nauk SSSR, Ser. Khim., 2342 (1984).
- 5. K. Karabelas and A. Hallberg, J. Org. Chem., 51, 5286 (1986) (and references therein).
- 6. A. Arcadi, S. Cacchi, and F. Marinelli, Tetrahedron Lett., 27, 6397 (1986).
- S. A. Shchepinov, M. L. Khidekel', and G. V. Lagozinskaya, Izv. Akad. Nauk SSSR, Ser. Khim., 2165 (1968).
- 8. R. F. Heck, Acc. Chem. Res., <u>12</u>, 146 (1979).
- 9. K. Karabelas, C. Westerlund, and A. Hallberg, J. Org. Chem., 50, 3896 (1985).
- 10. T. Jeffery, J. Chem. Soc., Chem. Commun., 1287 (1984).
- 11. I. L. Knunyants et al. (eds.), Syntheses of Organofluorine Compounds (Monomers and Intermediates [in Russian], Izd. Khimiya, Moscow (1973), pp. 141-142.

SYNTHESIS OF γ -LACTONES BY THE HYDROBORYLATION AND OXIDATION OF HOMOALLYLIG ALCOHOLS

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In previous work [1], we showed that the hydroborylation of terminal olefins in situ and the decomposition of the organoboranes formed with H_2CrO_4 in a single operation gives carboxylic acids with the starting carbon skeleton. In a study of the range of this reaction, we stablished that tertiary homoallylic alcohols (Ia) and (Ib) are convered to lactones (IIa) and (IIb) directly upon the oxidation of the organoboranes obtained in situ using the Jones reagent in ~60% yields.



n = 1(a), 2(b).

The products of the hydroborylation of secondary homoallylic alcohols under these conditions give low yields of lactones due to the competing oxidation of the OH group. Thus, in order to prepare γ -lactones from these alcohols, the hydroxyl group is protected by acetylation and then the terminal double bond is hydroborylated. The organoborane is oxidized to a carboxylic acid. Subsequent alkaline saponification of the acetate gives the γ -lactone. This method, starting from propionaldehyde, gave 4-hexanolide (III) which is a component of the aggregational pheromone for skin beetles [2].

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Ester (VII) is formed as a side-product upon the hydroborylation-oxidation of olefin (V) in addition to acid (VI). The total yield of pheromone (III) is ~30% in four steps.

These examples show that the $CH_2CH=CH_2$ group may be used in conjunction with the combined hydroborylation-oxidation operation as a synthetic equivalent of the $CH_2CH_2CO_2H$ group in the synthesis of lactones [3].

EXPERIMENTAL

All the boiling points were uncorrected. The reaction mixtures were analyzed by gasliquid chromatography on a Biokhrom-1 chromatograph using a 30 m \times 0.3 mm glass capillary column packed with 0.15% OV-101 with 2.4 kg/cm² helium pressure. The IR spectra were taken in CCl₄ on a UR-20 spectrometer. The PMR spectra were taken on a Bruker WM-250 spectrometer for solutions in CDCl₃.

<u>1-Oxaspiro[4.4]nonan-2-one (IIa)</u>. A sample of 0.16 g (5 mmoles) dry NaBH₄ was added with rapid stirring to a solution of 1.26 g (10 mmoles) 1-allylcyclopentanol (Ia) in 10 ml THF at 0-10°C and then 0.9 ml boron trifluoride etherate was added. The mixture was stirred for 1 h at 20°C and then cooled to 0°C. A sample of 4 ml of a solution of CrO_3 and H_2SO_4 in water (Jones reagent [4]) was added over 1 h. The mixture was stirred for 1 h at 0°C and 3 h at ~20°C. THF was distilled off in vacuum. The residue was extracted with three 10-ml portions of ether. The extract was washed with water, dried over MgSO₄, and evaporated. Distillation of the residue in vacuum gave pure lactone (IIa) bp 94-96°C (4 mm), $n_D^{21.5}$ 1.4920. The product yield was 0.85 g (61.5%). IR spectrum (ν , cm⁻¹): 1775, 1460, 1440, 1420, 1290, 1240, 1170, 1120, 1010. PMR spectrum (δ , ppm, J, Hz): 1.4-2.1 m (8H, CH₂ units), 2.29 t (2H, 2-H₂, J = 7), 2.56 t (2H, 1-H₂, J = 7). Gas-liquid chromatography at 120°C: R_{τ} = 8.5 min.

 $\frac{1-0 \text{xaspiro}[4.5] \text{decan-2-one (IIb)}}{(10 \text{ mmoles}) 1-allylcyclohexanol (Ib)}, \text{ The product yield was 0.94 g (63%), bp 103-105°C} (2 \text{ mm}), np²⁰ 1.4895. IR spectrum (v, cm⁻¹): 1775, 1460, 1290, 1275, 1170, 1130. PMR spectrum (<math>\delta$, ppm, J, Hz): 1.2-2.0 m (10H, CH₂ units), 2.02 t (2H, 2-H₂, J = 7), 2.60 t (2H, 1-H₂, J = 7). Gas-liquid chromatography at 120°C: $R_{\tau} = 11.3 \text{ min}.$

<u>3-Hydroxy-5-hexene (IV)</u>. A solution of 4.06 g (0.070 mole) freshly distilled C_2H_5 CHO in 20 ml ether was added dropwise under argon with vigorous stirring to a solution of CH_2 = CHCH_2MgCl prepared from 7.7 g (0.1 mole) CH_2 =CHCH_2Cl and 2.8 g (0.115 mole) Mg in 100 ml abs. ether. This addition was carried out at -10°C. The mixture was stirred for 1 h at -10°C and for an additional 5 h at 20-25°C. The reaction mixture was decomposed with saturated aqueous NH_4Cl. The upper layer was separated. The aqueous phase was extracted with two 30-ml portions of ether and the combined ethereal solution was washed with water and saturated aqueous NaCl and dried over MgSO₄. The solvent was distilled off. Vacuum distillation of the residue gave alcohol (IV), bp 39-40°c (22 mm), nD¹⁹ 1.4327. The product yield was 5.2 g (74%). IR spectrum (ν , cm⁻¹): 3370, 3082, 1640, 1465, 1380, 1120, 1000, 918. PMR spectrum (δ , ppm, J, Hz): 0.89 t (3H, 1-H₃, J = 7), 1.44 m (2H, 2-H₂), 2.15 m (2H, 4-H₂), 2.28 br s (1H, OH), 3.51 m (1H, 3-H), 5.0-5.78 m (3H, CH₂=CH group). Gasliquid chromatography at 60°C: R_T = 5.3 min. Found, %: C 72.02; H 12.14. C₆H₁₂O. Calculated, %: C 71.95; H 12.08.

<u>3-Acetoxy-5-hexene (V)</u>. A sample of 0.1 g 4-dimethylaminopyridine (DMAP) was added to a mixture of 5 g (50 mmoles) alcohol (IV), 10 ml acetic anhydride, and 18 ml NEt₃ in 100

ml dry CH_2Cl_2 and maintained for 48 h at 20-25°C. Then, 100 ml water was added and the aqueous phase was extracted with three 100-ml ether portions. The organic solution was washed with saturated aqueous CuSO_4 and NaCl, dried over MgSO₄, and evaporated. The residue was dissolved in 50 ml pentane and filtered through 1.5-2 g neutral alumina. The filtrate was evaporated and the residue was distilled in vacuum to give 6.5 g (91%) acetate (V), bp 60-61°C (25 mm), np¹⁸ 1.4174. IR spectrum (ν , cm⁻¹): 3050, 1730, 1640, 1470, 1440, 1380, 1250, 1120, 1090, 1030, 920. PMR spectrum (δ , ppm, J, Hz): 0.87 t (3H, 1-H₃, J = 7), 1.56 m (2H, 2-H₂), 2.01 s (3H, CH₃CO), 2.28 m (2H, 5-H₂), 4.82 m (1H, 3-H), 5.04-5.70 m (3H, CH₂=CH group). Gas-liquid chromatography at 70°C: R_T = 5.2 min. Found, %: C 67.68; H 10.12. C₈H₁₄O₂. Calculated, %: C 67.57; H 9.93.

4-Acetoxyhexanoic Acid (VI). A sample of 1.42 g (10 mmoles) acetate (V) was added to a suspension of 0.18 g (5 mmoles) NaBH4 in 10 ml THF and then, 0.8 ml freshly distilled boron trifluoride etherate was added with rapid stirring at 5-10°C. Stirring was continued for 1 h at 20°C. The mixture was then cooled to 0°C and 5 ml 6 N Jones reagent was added dropwise with care. Stirring was continued for 1 h at 0°C and for an additional 2 h at 18-20°C. THF was distilled off. The residue was dissolved in 15 ml water and extracted with three 30-ml ether portions. The ethereal layer was separated into acid and neutral fractions by the action of three 20-ml portions of saturated aqueous NaHCO3. The aqueous bicarbonate extract was acidified to pH 2 and extracted with three 20-ml ether portions. The extract was washed with saturated aqueous NaCl, dried over MgSO,, and evaporated. Pure acid (VI) was obtained as a colorless liquid with n_D^{18} 1.4407. The yield of this product was 0.87 g (51%). IR spectrum (v, cm⁻¹): 3400-2800, 1740, 1710, 1460, 1380, 1250, 1180, 1030. PMR spectrum (δ , ppm, J, Hz): 0.85 t (3H, 6-H₃, J = 7), 1.0-2.0 (4H, CH₂ units), 2.10 s (3H, CH₃CO), 2.33 m (2H, 2-H₂), 4.8 m (1H, 4-H), 11.5 br s (1H, CO₂H). The neutral ethereal layer was washed with water and saturated aqueous NaCl, dried over MgSO4, and evaporated to give the 4-acetoxyhexyl ester of 4-acetoxyhexanoic acid (VII) as a colorless, chromatographically uniform liquid (thin-layer chromatography). The product yield was 0.27 g (17%). IR spectrum (v, cm⁻¹): 1740, 1460, 1375, 1250, 1180, 1120, 1095, 1040. PMR spectrum (δ , ppm, J, Hz): 0.90 t (6H, two CH₃ groups, J = 7), 1.0-1.8 m (10H, CH₂ units), 1.95 s and 1.97 s (6H, two Ch₃CO groups), 2.15 m (2H, CH₂CO), 3.70 m (2H, CH₂OCOR), 4.70 m (2H, two HCOAc).

<u>4-Hexanolide (III)</u>. A sample of 1 g KOH powder was added in portions to a mixture of 0.7 g acid (VI), 4 ml methanol; and 4 ml water at 18-20°C. The mixture was stirred for 4 h at this temperature. Methanol was distilled off and 10 ml water was added. The alkaline aqueous solution was extracted with ether and then acidified with 2 N H₂SO₄ to pH 2 and further extracted with three 30-ml ether portions. The extract was washed with saturated aqueous NaCl, dried over MgSO₄, and evaporated. Distillation of the residue in vacuum gave pure lactone (III), bp 95-97°C (10 mm), nD¹⁸ 1.4370. The product yield was 0.40 g (86%). IR spectrum (v, cm⁻¹): 1775, 1460, 1420, 1380, 1280, 1220, 1185, 1170, 1130, 1100, 1025. PMR spectrum (δ , ppm, J, Hz): 0.94 t (3H, 6-H₂, J = 7), 1.45-2.0 m (4H, 5-H₂), 2.47 m (2H, 2-H₂), 4.38 m (1H, 4-H). Gas-liquid chromatography at 100°C: R_T = 4.0 min. Found, %: C 62.94; H 8.49. C₆H₁₀O₂. Calculated, %: C 63.13; H 7.83 (bp 103°C (14 mm), nD¹⁵ 1.4433 [5]).

CONCLUSIONS

1. The hydroborylation of tertiary homoallylic alcohols in situ and oxidation of the resultant organoboranes using chromic acid in one operation gives γ -lactones with the original carbon skeleton in ~60% yield.

2. The extension of this method to acetates of secondary homoallylic alcohols in the case of 3-acetoxy-5-hexene permitted the simple synthesis of 4-hexanolide, which is a component of the aggregational pheromone of skin beetles.

LITERATURE CITED

- Nguyen Cong Hao, M. V. Mavrov, and É. P. Serebryakov, Izv. Akad. Nauk SSSR, Ser. Khim., 251 (1986).
- K. V. Lebedeva, V. A. Minyailo, and Yu. B. Pyatnova, Insect Pheromones [in Russian], Izd. Nauka, Moscow (1984), p. 63.
- 3. D. Caine and A. S. Frobese, Tetrahedron Lett., 883 (1978).
- 4. K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, J. Chem. Soc., 39 (1946).
- 5. O. Riobe, C. R. Acad. Sci., <u>247</u>, 1016 (1958).