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A NEW SYNTHESIS OF 1,7-DIOXASPIRO[5 5]UNDECANES APPLICATION TO A RECTAL GLAND SECRETION OF THE OLIVE FRUIT FLY (DACUS OLEAE)

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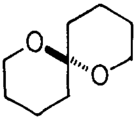
Abstract The oxirane ring of the tetrahydropyranyl ether of 3,4-epoxybutan-1-ol underwent nucleophilic scission by the organocuprate derived from 6-lithio-3,4-dihydro-2(H)-pyran to give an intermediate which was converted to 4-hydroxy-1,7-dioxaspiro[5 5]undecane on acid hydrolysis.

The olive fruit fly Dacus oleae (Gmelin) is a major pest in the Mediterranean basin From the rectal glands of sexually mature females Baker and co-workers[1] identified 1,7-dioxaspiro[5.5]undecane (1) as a major component of the sex pheromone. More recently[2] two minor components, 3- and 4-hydroxy-1,7-dioxaspiro[5 5]undecane (2 and 3 respectively) have been obtained from the same source. In this letter we report a new synthesis of (3) in which a cyclic vinyl ether carbanion serves as a masked bifunctional carbonyl anion [3]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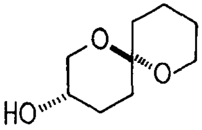

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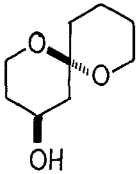

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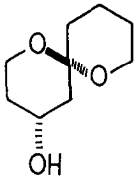

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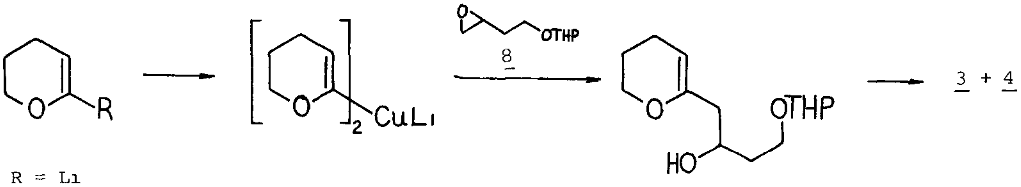
Heteroatom-facilitated metalation[4] of 3,4-dihydro-2(H)-pyran (5) with t-BuLi according to the procedure of Boeckman[5] gave the corresponding lithium derivative (6) which was converted to the homocuprate derivate (7) by treatment with CuI in THF. The cuprate (7) reacted with oxirane (8)[6] at 0-20° C to give a single major component (9) which, without further purification, was treated with aqueous acid to give (3) and its C-4 epimer[2] (4) (ca 20 1 respectively) in 64% yield after column chromatography. Pure racemic (3) was obtained by crystallisation.



6 R = Li
5 R = H

7

9

In general, the lithium carbanions derived from vinyl ethers are only moderately nucelophilic towards alkyl halides and react sluggishly, if at all, with oxiranes[5] The organocuprate derived from α-ethoxyvinyl-lithium couples with allylic halides and undergoes 1,4-addition to enones[7,8] but it does not react with oxiranes Little is known about the nucleophilicity of the organocuprates such as (7) derived from cyclic vinyl ether carbanions Therefore, the clean scission of oxirane (8) by (7) is noteworthy and its application to the synthesis of spiroketals[9] potentially useful

Experimental To a stirred solution of 2 5 g (30 mmols) of dihydropyran (5) in 6 cm^3 of THF was added dropwise 21 cm^3 of a 1.7M solution of t-BuLi in pentane at -78°C The mixture was then stirred at -5 to 0°C for 1 h and re-cooled to -78°C The resultant solution of (5) was transferred via a canula under N_2 pressure to a rapidly stirred suspension of 2 9 g (15 mmol) of CuI in 15 cm^3 THF at -78°C whereat it was stirred for 45 min A solution of oxirane (8) (1.70 g, 10 mmol) in 5 cm^3 THF was added and the mixture allowed to warm slowly to room temperature After 2 h at room temperature the mixture was quenched with 50 cm^3 of saturated NH_4Cl containing 10% NH_4OH and extracted with ether (2 x 60 cm^3). The crude oil obtained after ether drying over $MgSO_4$ and evaporation was dissolved in a mixture of conc HCl, water, and THF (1 5 20) and allowed to stand at room temperature overnight whereupon the mixture was neutralised with aqueous $NaHCO_3$ and extracted with ether (2 x 60 cm^3) After drying over Na_2SO_4, the combined extracts were evaporated to give 2.83 g of an oil which was chromatographed on 50 g of Kieselgel 60 (230-400 mesh) Elution with 1 1 ether light petroleum gave 1 09 g (64%) of (3) contaminated by ca 5% of its C4 epimer (4) Pure (3) was obtained as white prisms from cold light petroleum m.p 48-49°C, ν_{max} (film) 3400, 1062, 1048, and 985 cm^{-1}, ^1H n m.r (400 MHz, C_6D_6) δ 3 99 (1H, dt, J 11 5, J' 5.5 Hz), 3 65-3 40 (4H, m), 1 96 (1H, ddd, J 12 5, J' 5, J" 2 Hz), 1 92-1.80 (1H, m), 1 62-1.55 (2H, m), 1 46-1 27 (4H, m), 1 23-1 16 (2H, m), 1 19 (1H, dd, J 12, J' 11 Hz), ^{13}C n m r ($CDCl_3$) δ 92 3, 64 0, 60 3, 58 8, 45 1, 35 5, 35 0, 25 1, and 18.5, (Found C, 63 05, H, 9.4, $C_9H_{16}O_3$ requires C, 62 8, H, 9 4%)

Acknowledgement We thank the SERC and Pfizer Central Research for generous financial support

References

1 R. Baker, R Herbert, P E House, O T Jones, W Francke, and W Reith, J Chem. Soc Chem. Commun , 1980, 52

2 R Baker, R. Herbert, and A H Parton, J Chem Soc Chem Commun , 1982, 601.

3 U. Schöllkopf and P Hänssle, Justus Liebigs Ann 1972, 763, 208, J E Baldwin, G A Höfle, and O W Lever, J Am Chem Soc , 1974, 96, 7125

4. Review A Krief, Tetrahedron, 1980, 36, 2531

5. R.K Boeckman and K J Bruza, Tetrahedron, 1981, 37, 3997

6. The oxirane (8) [b p 74-75°/1 mm Hg, ν_{max} (film) 2940, 1200, 1125, 1080 and 1035 cm^{-1}, δ (90 MHz, $CDCl_3$), 4.55 (m, 1H), 3 8 (m, 2H), 3 4 (m, 2H), 2 9 (m, 1H), 2 4 (m, 1H), 2.2 (m, 1H), 1 1-1 9 (m, 8H)] was prepared by m-chloroperoxybenzoic acid epoxidation of the tetrahydropyranyl ether of 3-butenol H Kohn, M B Bean, C Von Rohrscheidt, M R Willcott, and E W Warnhoff, Tetrahedron, 1981, 37, 3195

7 R.K Boeckman, K.J. Bruza, J.E Baldwin, and O.W Lever Jr., J Chem Soc., Chem. Comm., 1975, 519.

8 C G Chavdarian and C H. Heathcock, J Am Chem Soc , 1975, 97, 3822

9 For a related approach to spiroketals, see R K Boeckman, K J Bruza, and G R Heinrich, J Am. Chem Soc , 1978, 100, 7101

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