Synthesis of all possible stereoisomers of 6,10,13-trimethyltetradecan-2-one, male-produced sex pheromone of *Pallantia macunaima*

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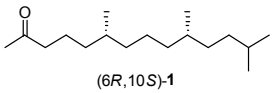
Sex pheromone; 6,10,13-trimethyltetradecan-2-one; chiral sulfone.

INTRODUCTION

Pallantia macunaima (Heteroptera, Pentatomidae) is one important heteropteran pest found in southern Bazil. Previously, we reported the structural elucidation, synthesis and absolute configuration of sex pheromone for this species. The male-specific compound was identified as (6*R*,10*S*)-6,10-13-trimethyltetradecan-2-one ((6*R*,10*S*)-**1**), the first ketone pheromone described in stink bugs.[1] Here in, we wish to describe an alternative methodology to prepare all isomers of 6,10,13-trimethyltetradecan-2-one.



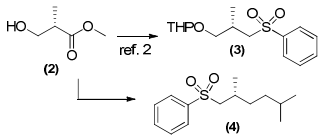
(6*R*,10*S*)-**1**

RESULTS AND DISCUSSION

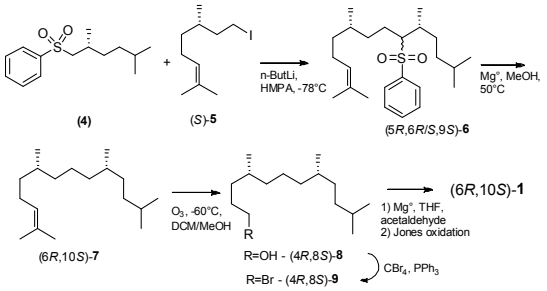
Initially the hydroxi-ester **2** was converted into different sulfones (Scheme 1).[2] The iodides (*R*)/(*S*)-**5**, were synthesized from commercial (*R*)-citronellol (98% *e.e.*) and (*S*)-citronellol (99% *e.e*).

The coupling between a buthyllithium-generated carbanion of sulfone **4** with iodide (*S*)-**5**, gave a new sulfone (5*R*,6*R/S*,9*S*)-**6** in 68% yield (Scheme 2).[3] The reductive removal of the sulfonyl moiety of (5*R*,6*R/S*,9*S*)-**6**, was achieved smoothly by using magnesium turnings in methanol.[4] Ozonolysis of (6*R*,10*S*)-**7** and reductive workup gave (4*R*,8*S*)-**8**. The Grignard reagent prepared from (4*R*,8*S*)-**9** was allowed to react with acetaldehyde, leading to the secondary alcohol, that was submitted to Jones oxidation affording the first isomer (6*R*,10*S*). The another stereoisomer (6*S*,10*S*)-**1** was synthesized following combination of sulfone **4** and iodide (*R*)-**5**.

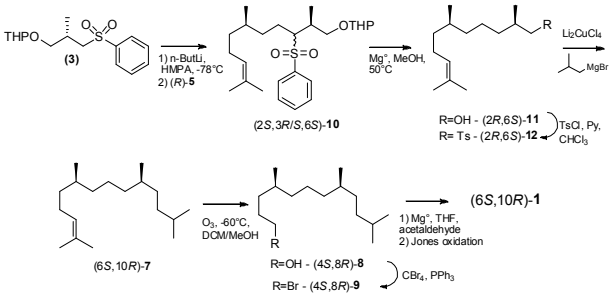
In a slightly different procedure (Scheme 3), the coupling of sulfone **3** with iodide (*R*)-**5** proceeded smoothly to afford (2*S*,3*R/S*,6*S*)-**10**,[3] with was further desulfonated to give the alcohol (2*R*,6*S*)-**11**.[4] This compound was then converted into the corresponding tosylate and coupled with isobutylmagnesium bromide in the presence of Li_2CuCl_4 to afford the alkene (6*R*,10*R*)-**7**. With this compound in hands, we have employed the same reaction sequence described above to prepare the desired isomer (6*S*,10*R*)-**1**.



Scheme 1



Scheme 2



Scheme 3

CONCLUSION

In conclusion, our synthetic approach using chiral iodides prepared from citronellol has allowed the synthesis of all possible isomers of 6,10,13-trimethyltetradecan-2-one. Further experiments employing enantiopure, as well as racemic compounds, are underway in the laboratory and the field.

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