Tetrahedron Letters,Vol.25,No.32,pp 3481-3482,1984 0040-4039/84 $3.00 + .00
Printed in Great Britain

A NOVEL SYNTHETIC APPROACH TO ANGULARLY FUSED TRICYCLOPENTANOIDS

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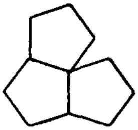
Summary: *Cationic transannular cyclisation of the type 8-5→5-5-5 provides a short, convenient access route to spiro-fused tricyclo (6.3.0.0^{1,5}) undecane system.*

Since early 1970, a variety of natural products bearing the spiro-fused tricyclopentanoid moiety 1 have been encountered in Nature.[1] Prominent among them are the sesquiterpene isocomene 2, diterpene laurenene 3[2] and sesterterpene retigeranic acid 4.[3] The unique nature of the carbocyclic framework, presence of plethora of quaternary carbon centres and interesting biosynthetic origin have made these compounds the focus of attention of synthetic chemists over the past few years. Barring some notable exceptions,[4] synthetic approaches to 1 and congeners hinges on the quaternisation and annulation of the third 5-membered ring on a preformed bicyclo (3.3.0) octane precursor.[1] Herein, we describe a new way to tricyclo (6.3.0.0^{1,5}) undecane system 1 which involves carbonium ion mediated transannular cyclisation of a suitably functionalised bicyclo (6.3.0) undecane derivative as the pivotal step (5→6).



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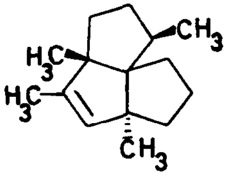

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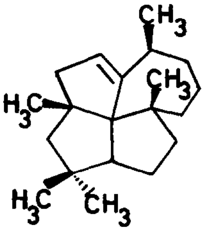

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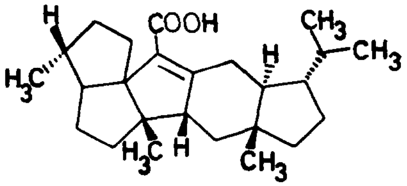

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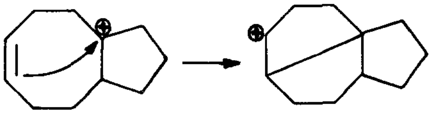
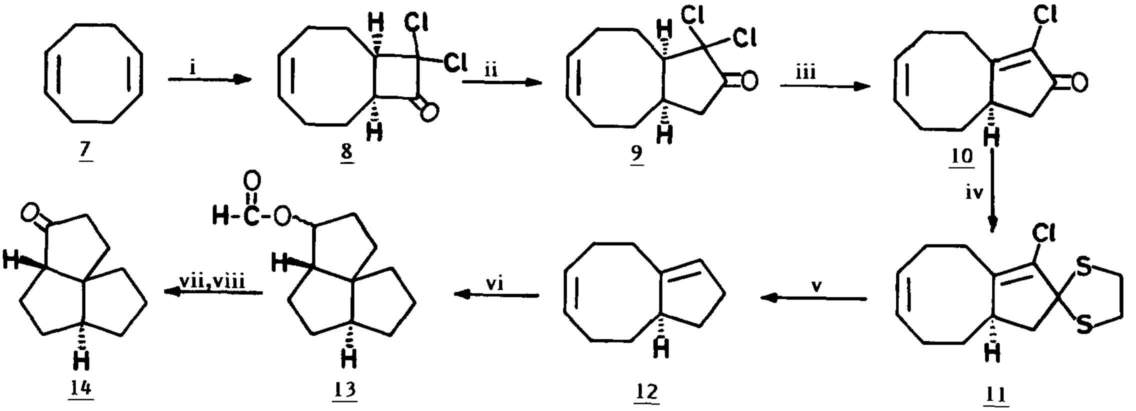


5 6

The key bicyclic diene 12 was realised from commercially available 1,5-COD 7 in a straightforward manner as delineated in the scheme. Dichloroketene addition to 8, followed by diazomethane ring expansion to 9 and mono-dehydrochlorination led to the α-chloro enone 10.[5,6] Thioketalisation to 11 and metal-ammonia reduction cleanly furnished the volatile 8-5 carbocyclic diene 12. Formolysis of 12 gave formate(s) 13 which on base hydrolysis and Jones oxidation yielded tricyclo (6.3.0.0^{1,5}) undecan-4-one 14. The structure of 14 was revealed by the presence of quarternary carbon at δ 59.2(s)

Scheme



Reagents & Yields: (i) $Cl_3C.\overset{O}{\overset{\|}{C}}.Cl$-Zn/Cu, Et_2O, 5h, 58%; (ii) CH_2N_2-Et_2O-MeOH, 5°, 1h, 80%; (iii) Li_2CO_3-DMF, 80°, 30 min, 83%; (iv) $(CH_2SH)_2$-C_6H_6-PTS, 9h, 82%; (v) Na-liq.NH_3-Et_2O, -35°, 2h, 55%; (vi) 90% HCOOH, 80°, 3h; (vii) 10% KOH-MeOH-H_2O, Δ, 1.5h; (viii) Jones reagent, 20°, 41% from 12.

in the ^{13}C nmr spectrum besides other complimentary spectral data.[5] The ready availability of 14 sets the stage for further tactical modification of scheme for elaboration to natural products based on this ring system. Efforts towards this end will be reported in due course.

Acknowledgement: This research was supported by U.G.C., India in the form of Special Assistance Programme in Organic Chemistry.

References and Notes:

1. L.A. Paquette and A. Leone-Bay, J. Am. Chem. Soc., 1983, 105, 7352 and comprehensive references cited therein.
2. R.E. Corbett, D.R. Lauren and R.T. Weavers, J. Chem. Soc., Perkin Trans. I, 1979, 1774.
3. M. Kaneda, R. Takahashi, Y. Iitaka and S. Shibata, Tetrahedron Letts., 1972, 4609.
4. M.C. Pirrung, J. Am. Chem. Soc., 1979, 101, 7130; P.A. Wender and G.B. Dreyer, Tetrahedron, 1981, 37, 4445; E. Wenkert and T.S. Arrhenius, J. Am. Chem. Soc., 1983, 105, 2030.
5. All the compounds reported here gave satisfactory spectral data and only for two key compounds is summarised here. 12: IR (thin film): 720, 1660, 3025 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz): δ 5.4-5.7 (2H,m), 5.36(1H,s), 1.3-2.8(13H,m); ^{13}C NMR ($CDCl_3$, 25MHz): δ 149.4(s), 130.2(d), 129.5(d), 127.5(d), 45.7(d), 35.2(t), 33.9(t), 32.5(t), 29.7(t), 25.9(t), 25.6(t). 14: IR(thin film): 1740 cm^{-1}; ^1H NMR ($CDCl_3$, 100 MHz): δ 1.24-2.4(16H,m); ^{13}C NMR ($CDCl_3$, 25 MHz): δ 223.5(s), 60.5(d), 59.2(s), 51.5(d), 41.0(t), 39.6(t), 35.0(t), 34.5(t), 34.3(t), 30.7(t), 26.9(t).
6. J.P. Depres and A.E. Greene, J. Org. Chem., 1980, 45, 2036.

(Received in UK 2 April 1984)