Tetrahedron Letters,Vol.26,No.20,pp 2475-2476,1985 0040-4039/85 $3.00 + .00
Printed in Great Britain

DIRECT ENTRY TO THE ALL-CIS TRICYCLO[5.2.1.0^{4,10}]DECANE (PERHYDROTRIQUINACENE) SKELETON BY A COBALT MEDIATED INTRAMOLECULAR CYCLIZATION

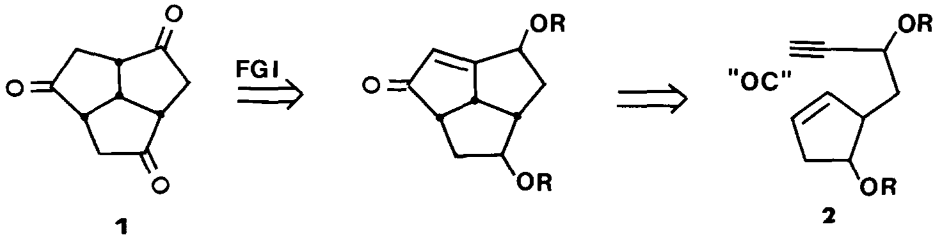
Elena Carceller, Víctor Centellas, Albert Moyano, Miquel A. Pericàs and Fèlix Serratosa

Departament de Química Orgànica, Facultat de Química, Universitat de Barcelona. c/ Martí i Franqués, 1. E-08028 Barcelona, Spain.

Summary.- The perhydrotriquinacene skeleton has been synthesized by a Pauson-Khand bis-annulation process.

Although several entries to the perhydrotriquinacene skeleton have been described over the last two decades[1], neither the problem of the regioselective functionalization, nor the question of the availability of substantial amounts of these derivatives have found a general satisfactory solution.

In the course of a research program devoted to the synthesis of polyquinanes[2], substantial amounts of triketone **1** were required, but the only access to this compound described so far in the literature, involving the hydroboration/oxidation of triquinacene, allows the preparation of 1 in only minute amounts through a costly and tedious separation of the intermediate regioisomeric triols[2a,3]. Among the several converging strategies[2] investigated by our group, we decided to explore the possibility of using the Pauson-Khand annulation[4], which has been successfully used in the synthesis of diquinanes[5] and, quite recently[6], of angularly fused triquinanes. Retrosynthetic analysis (Scheme I) of triketone **1** led us to consider the key synthon 2, which should afford the skeleton of **1** with the right functionality in a single intramolecular cyclization step.



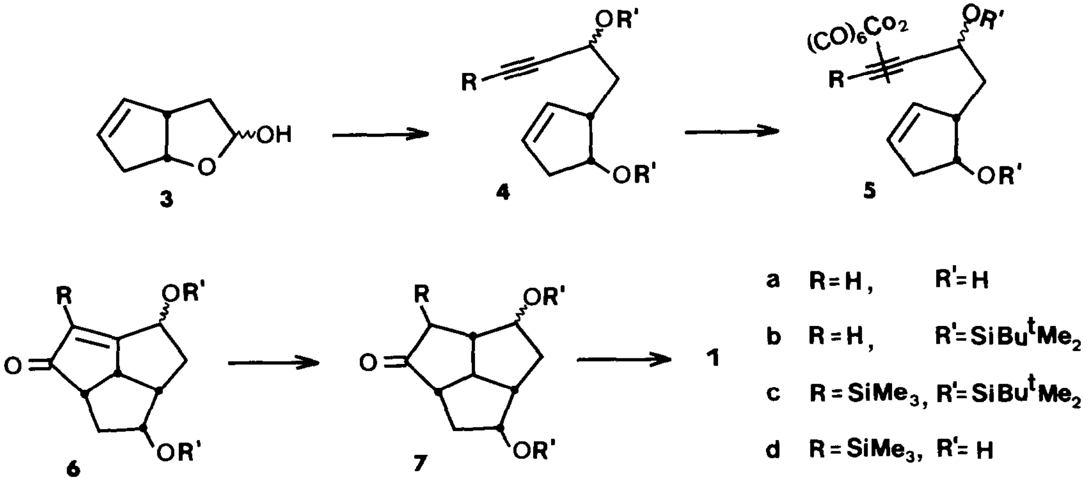
Scheme I

In the synthetic sense, the above ideas were actualized as follows (Scheme II): The known lactol 3[7] was added to a THF solution of ethynylmagnesium bromide affording in 95% yield a diastereomeric mixture of diols **4a**. After protection of the alcohols as tert-butyldimethylsilyl ethers (88%), the diastereomeric mixture of enynes **4b** was converted into the corresponding hexacarbonyldicobalt complex **5b**. When this compound was heated in a sealed tube, under CO atmosphere, for 5 days at 160° in isooctane solution, only low yields of the desired enone **6b** were obtained. However, when the terminal acetylenic carbon of 4b was silylated (87%) and the resulting protected enyne **4c** was converted into the corresponding cobalt complex 5c (85-100%), the silylenone **6c** could be obtained in 76% yield after cyclization for 3 days in the same conditions as above. It is worth noting that the addition of lithium trimethylsilylacetylide to lactol 3 transcurs in rather low yield (20%), so that the more direct route to **4c** through intermediate **4d** suffers the important drawback of a considerably lower overall yield.

The present sequence represents the first example of the perhydrotriquinacene skeleton construction via a cobalt mediated bis-annulation process and, due to the relatively small number of steps (9 steps starting from cyclopentadiene), compares very favorably with the previously described routes[1] to this system.

Finally, catalytic hydrogenation of **6c** (Pd/C) leads in almost quantitative yield to ketone **7b** which, in turn, can be converted to triketone 1[8] by cleavage of the *tert*-butyldimethylsilyl ethers (HF/H_2O/CH_3CN) followed by neutralization with pyridine and oxidation with pyridinium chlorochromate. Experimental details will be reported in a forthcoming paper.

The authors acknowledge a fruitful discussion with Dr. Andrew E. Greene as well as financial support from CAICYT (Proyecto n° 3218/83).



Scheme II

REFERENCES AND NOTES

1. a) R.B. Woodward, T. Fukunaga, and R.C. Kelly, J. Am. Chem. Soc., 1964, 84, 3162; b) For other leading references, see L.A. Paquette, "Topics in Current Chemistry", 1979, 79, pp. 114-122; ibid., 1984, 119, pp. 55 and 76-81.
2. a) F. Serratosa, "Dodecahedrane: A Synthetic Objective", Main Section lecture delivered at ESOC II, Stresa (Italy), June, 1981; b) E. Carceller, A. Moyano, and F. Serratosa, Tetrahedron Letters, 1984, 25, 2031; c) E. Carceller, A. Castello, M.Ll. García, A. Moyano, and F. Serratosa, Chemistry Lett., 1984, 775; d) E. Carceller, M.Ll. García, A. Moyano, and F. Serratosa, J. Chem. Soc., Chem. Commun., 1984, 825.
3. M.E. Osborn, S. Kuroda, J.L. Muthard, J.D. Kramer, P. Engel, and L.A. Paquette, J. Org. Chem., 1981, 46, 3379.
4. I.U. Khand, G.R. Knox, P.L. Pauson, W.E. Watts, and M.I. Foreman, J. Chem. Soc., Perkin Trans. 1, 1973, 977.
5. a) N.E. Schore and M.C. Croudace, J. Org. Chem., 1981, 46, 5436; b) C. Exon and P. Magnus, J. Am. Chem. Soc., 1983, 105, 2477.
6. M.J. Knudsen and N.E. Schore, J. Org. Chem., 1984, 49, 5025.
7. P.A. Grieco, J. Org. Chem., 1972, 37, 2363.
8. All new products were completely caracterized and gave the expected analytical and/or spectral data.

(Received in UK 1 March 1985)