Pergamon

Tetrahedron Letters, Vol. 38, No. 6, pp. 1081-1082, 1997
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0040-4039/97 $17.00 + 0.00

PII: S0040-4039(96)02473-2

A New Synthesis of Truxenone

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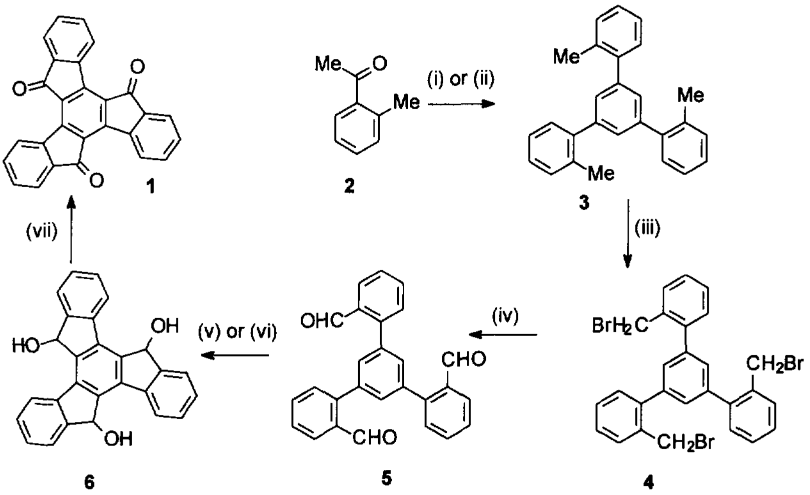
Abstract Truxenone was prepared from 1,3,5-(o-carboxyphenyl)benzene via the cyclotrimerisation of 2-methyl acetophenone.

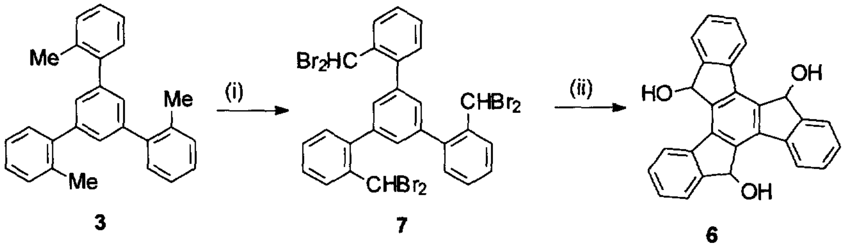
Fullerene fragments which can be derived retrosynthetically from the Buckminsterfullerene surface are providing a novel opportunity for the exploitation of Flash Vacuum Pyrolysis.[1] The synthesis of the strained polycyclic framework requires high temperatures to drive two, three or four endothermic cyclisation reactions which have been successful for the synthesis of Corannulene [2], Semibuckminsterfullerene[3] and its half bowl isomer[4] respectively. Truxenone **1** is a key intermediate for the synthesis of the chlorinated truxenene precursor[3] to Semibuckminsterfullerene and is of interest to us as a core building block for the preparation of further trisymmetric Buckybowl precursors. Although Truxenone **1** can be prepared by the cyclotrimerisation of indan-1,3-dione in cH_2SO_4[5], we required a milder method which would allow the regioselective synthesis of various substituted truxenones.

Cyclotrimerisation of 2-methyl acetophenone **2** by the Wirth method[6] or with silicon tetrachloride in ethanol[7] gives the trimer **3** which was brominated with N-bromosuccinimide to the tris-bromo derivative **4** in 52% yield using azobisisobutyronitrile as initiator.[8] Oxidation to the tris aldehyde **5**[9] was best accomplished with a traditional method by treatment with 2-nitropropane and sodium ethoxide in ethanol.[10] The bromomethyl groups are sterically hindered and the 2-nitropropane anion is an oxidant of low steric demand.



(i) $SiCl_4$, EtOH, Δ 24h, 32% (ii) $HC(OMe)_3$, EtOH, dry HCl, RT, 24hr, 43%
(iii) NBS (3eq), AIBN, CCl_4, Δ 3hr, 52% (iv) NaOEt, Me_2CHNO_2, EtOH, RT, 20hr, 32%
(v) Gaseous BF_3, benzene, RT, 3hr, 51% (vi) 5% cH_2SO_4/THF, RT, 12hr, 42%
(vii) PCC, DCM, RT, 4hr, 32%

Treatment of aldehyde **5** with either gaseous BF_3 in benzene or a catalytic amount of cH_2SO_4 in THF effected three consecutive cyclisations to give the tris alcohol **6** as a mixture of two diastereoisomers in 35% yield. Oxidation with PCC[11] in dichloromethane gave truxenone **1** which was of high purity and did not require purification by soxhlet extraction. The tris alcohol **6** can also be prepared in 20% yield directly from the hexabromo derivative **7** by treatment with cH_2SO_4 in THF which presumably generates the tris aldehyde **5** in situ. The hexabromo compound **7** was prepared by bromination of 1,3,5-(o-methylphenyl)benzene **3** with six equivalents of NBS. Although monobromination of aryl methyl groups can sometimes lead to over bromination, dibromination is clean and easily controlled because the dibromobenzyl group does not undergo further bromination under these reaction conditions.



(i) NBS (6eq), AIBN, CCl_4, Δ 3hr, 72%
(ii) 5% cH_2SO_4/THF, Δ 5hr, 20%

This methodology provides a convenient and alternative route to Truxenone.

Acknowledgements
This research was supported by the Engineering and Physical Sciences Research Council of the United Kingdom.

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(*Received in UK* 7 *November* 1996; *revised* 18 *December* 1996; *accepted* 20 *December* 1996)