3,12-Cycloiceane (Pentacyclo[6.3.1.$0^{2,4}$.$0^{5,10}$.$0^{7,8}$]dodecane)

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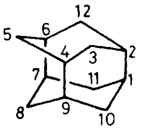
The first cyclo-derivative of iceane has been synthesized by taking advantage of the homo-Diels–Alder reaction of tricyclo[5.3.1.$0^{4,9}$]undeca-2,5-diene which results in a highly efficient one-step framework construction.

Iceane (**1**), named after its geometrical similarity to one of the crystalline forms of water,[1] is a rigid $C_{12}H_{18}$ hydrocarbon of high symmetry (point group D_{3h}) that consists of two chair and three boat cyclohexane rings. This unique and elegant system has been a stimulating target molecule for synthesis.[2] While several reports on the synthesis of iceane itself,[3] its heterocyclic analogues,[4] and functionalized derivatives[5] have appeared, no cyclo-derivative of iceane has been synthesized so far.

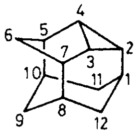
In the course of our continuing interest in synthesis and reactions of strained cage molecules related to iceane,[6—8] we recently reported that tricyclo[5.3.1.$0^{4,9}$]undeca-2,5-diene (**3**) possesses unusually high homo-Diels–Alder reactivity and that a cyclohomoiceane skeleton (**4**) can be constructed in one step through this reaction.[8] We report here the first, unambiguous synthesis of 3,12-cycloiceane (**2**) and its derivatives by taking advantage of the above highly efficient one-step framework construction (Scheme 1).

Hydroboration of the pentacyclotridecene (**5**), which was readily prepared *via* the homo-Diels–Alder reaction of (**3**) with maleic anhydride,[8] followed by Jones oxidation of the resulting alcohol gave the ketone (**6**)† in 80% yield. Standard conversion of (**6**) into the diazoketone (**7**) in 59% yield, followed by Wolff rearrangement of (**7**) *via* irradiation in MeOH through Pyrex brought about ring contraction to afford the methyl ester (**8**)‡ containing the 3,12-cycloiceane skeleton in 52% yield.

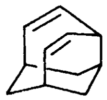
Decarboxylation of the ester (**8**) to the parent hydrocarbon (**2**) was carried out as follows.§ The methoxycarbonyl group was first oxidatively removed by a three-step sequence[9] to give the ketone (**10**). Thus, lithiation and sulphenylation of (**8**) gave the α-methylthiocarboxylic ester (**9**) in 79% yield.



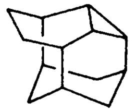
(**1**)



(**2**)



(**3**)



(**4**)

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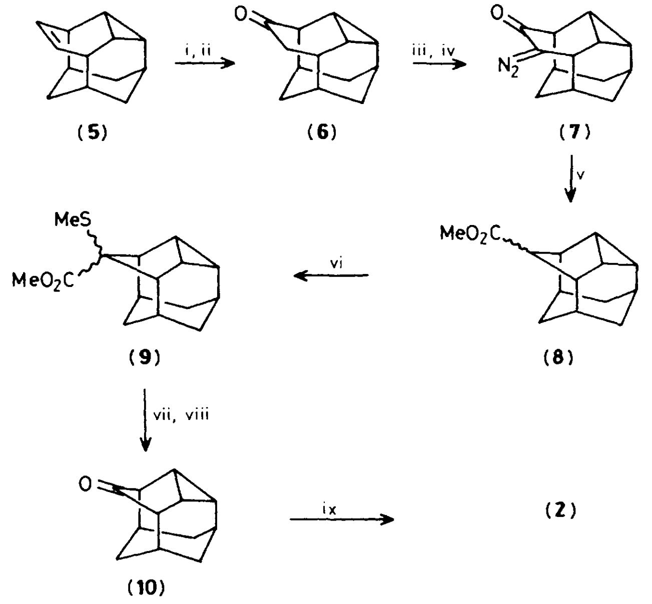
† All new compounds gave spectral data (mass, i.r., ^1H and ^{13}C n.m.r.) consistent with the proposed structures.

‡ The spectroscopic data of (**8**) suggested the formation of a single isomer, but the stereochemistry was not confirmed.

§ The usual Hunsdiecker decarboxylation was unsuccessful because of destruction of the cyclopropane ring.



Scheme 1. *Reagents:* i, B_2H_6, tetrahydrofuran (THF), then H_2O_2–NaOH; ii, CrO_3, H_3O^+; iii, HCO_2Me, NaH–Et_2O; iv, *p*-MeC_6H_4-SO_2N_3, Et_3N–CH_2Cl_2; v, *hv*, MeOH; vi, LiN(Pr^i)(cyclo-C_6H_{11}), MeSSMe–THF; vii, KOH–$(HOCH_2)_2$; viii, NCS, $NaHCO_3$–MeOH; ix, $NH_2NH_2{\cdot}H_2O$, KOH–$(HOCH_2)_2$.

Saponification of (**9**) followed by oxidative decarboxylation of the sodium salt with *N*-chlorosuccinimide furnished 3,12-cycloicean-5-one (**10**) in 53% yield. The structure of (**10**) was confirmed by spectroscopic analyses; *inter alia* its ^{13}C n.m.r. spectrum [δ 209.2(s), 39.6(d), 30.4(t), 30.2(t), 26.2(d), 19.9(d), 17.3(d), and 3.8(d)] clearly indicated C_s symmetry as well as the presence of a cyclopropane ring. The final step was Wolff–Kishner reduction of (**10**) to the parent hydrocarbon (**2**), the ^{13}C n.m.r. spectrum of which [δ 45.2(t), 32.7(t), 32.0(t), 30.2(d), 29.8(t), 25.6(d), 19.0(d), and 18.3(d)] again indicated C_s symmetry.

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