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OLEFIN METATHESIS IN POLYCYCLIC FRAMES 1. A NEW WAY TO cis, syn, cis - TRICYCLOPENTANOIDS (acs-C_{11}-TRIQUINANES)

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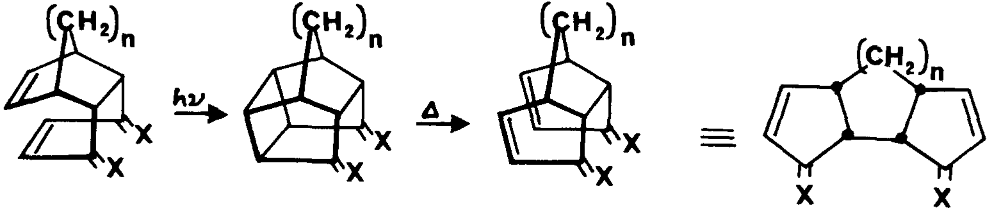
Summary: A novel olefin metathesis sequence permits ready access to functionalised cis, syn, cis-tricyclo $[6.3.0.0^{2,6}]$ undecane based bis-enones. These bis-enones have been shown to undergo cage cyclisation in sunlight with remarkable ease and efficiency.

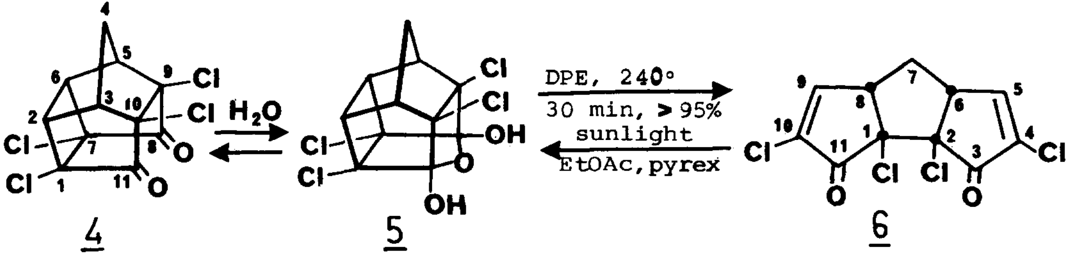
This communication is intended to stimulate interest in a new strategy for the creation of polycyclic cyclopentanoids with complete regio- and stereochemical control. The Scheme I depicts a general two step olefin metathesis sequence that involves a photochemical ${}_{\pi}2_{s} + {}_{\pi}2_{s}$ cycloaddition ($1 \rightarrow 2$) and a regiospecific thermal fragmentation of the saturated four membered ring ($2 \rightarrow 3$) to a variety of cis, syn, cis-tricyclic systems 3. At this time, however, we only wish to disclose the efficient formation of cis, syn, cis-tricyclo $[6.3.0.0^{2,6}]$ undecane (C_{11}-triquinane)[1,2] derivatives 6, 8 & 14 via the thermolysis of readily available pentacyclo $[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$ undecane based precursors 4[3], 7[4] & 13.

SCHEME I

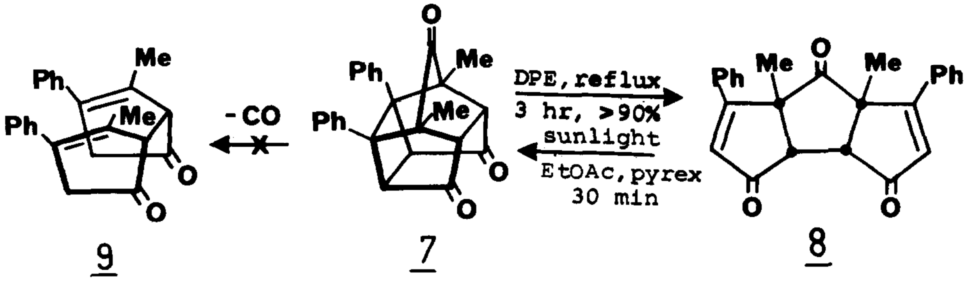


1.X =O etc. 2 3

Thermal activation of pentacyclic dione 4 or its hydrate 5 in diphenyl ether (DPE) at 240° (oil bath) for 30 min. led to near quantitative formation of 6, mp.149-50° (off-white needles from hexane-benzene). Stereostructure of 6 and its inherent symmetry was clearly revealed by its spectral characteristics: uv (MeOH): λ_{max} 244nm; ir (KBr): 1750 (carbonyl), 1603 and 1585 cm^{-1} (olefinic); ^{1}H nmr (100 MHz, $CDCl_3$): δ7.3(2H,d,J=2.5Hz,β-protons of α,β-unsaturated enone at C_5 & C_9), 3.7(2H,dd,$J_{6,7}$=$J_{7,8}$=10Hz,$J_{5,6}$=$J_{8,9}$=2.5Hz, allylic protons at C_6 and C_8), 2.85(1H,dd,J_{gem}=14Hz,$J_{6,7}$=$J_{7,8}$=10Hz,*endo*-proton at C_7), 2.05(1H,1/2 AB,d,J_{gem}=14Hz,exo-proton at C_7); ^{13}C nmr(25.0 MHz,$CDCl_3$)[5]:δ190.2 (s,C_3 and C_{11}), 154.2(d,C_5 and C_9), 133.6(s,C_4 and C_{10}), 76.7(s,C_1 and C_2), 56.6(d,C_6 and C_8), 30.4(t,C_7). More compelling evidence in support of formulation 6 flows from its extremely facile and quantitative photocyclisation to 4 in ethyl acetate (pyrex vessel) on exposure to sunlight for a few minutes[6].

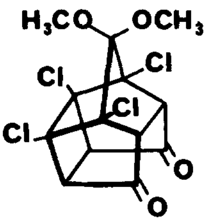


The hemicyclone derived pentacyclic trione 7[4] in refluxing DPE (3 Hr) was transformed to bis-enone 8, mp.203-05° [pale yellow microcrystals from benzene, uv (MeOH): λ_{max} 286nm; ir (KBr): 1740(cyclopentanone), 1710 (cyclopentenone with extended phenyl conjugation), 1590 cm^{-1}(olefinic); ^{1}H nmr(100 MHz,$CDCl_3$): δ7-7.5(m,10H,aromatic), 6.22(s,2H,olefinic protons at C_4 and C_{10}), 3.2(s,2H, methine protons at C_1 and C_2), 1.6(s,6H,quaternary methyls at C_6 and C_8); ^{13}C nmr(25.0 MHz,$CDCl_3$):δ212.6(C_7), 203.9(C_3 and C_{11}), 173.9(C_5 and C_9), overlapping cluster at 131.7, 130.7, 128.6, 128.3, 128.0(aromatic and C_4,C_{10}), 62.3(C_6 and C_8), 55.7(C_1 and C_2), 23.2(CH_3 at C_6 and C_8)] in over 90% yield. The assignment of stereostructure 8 follows reasonably from its parentage and, a fortiori, from its ^{1}H and ^{13}C nmr parameters detailed above. Quite signifi-



cantly and to our surprise, we observed no perceptible decarbonylation of trione 7 to 9 under our thermolysis conditions. On brief exposure to sunlight in ethyl acetate (pyrex vessel), the tricyclic bis-enone 8 reverted back to pentacyclic 7 in 100% yield.

Our initial observations indicate that the presence of halogens at C_1 and C_7 and/or of phenyl groups at C_2 and C_6 of the pentacyclo $[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]$ undecane frame were essential for the efficient metathesis reaction. For example, 10[3] and 11[7] remained essentially unchanged under the conditions (refluxing DPE) compounds 4 and 7 underwent facile cyclobutane rupture[8]. Similarly, the parent[3] dione 12 remained un-anhilated even at the forcing temperature of 400°[9]. However, the 1,7-dichloro-pentacyclic dione 13, in DPE at 220° (3hr) furnished the tricyclopentanoid 14, mp.186-7°, in good yield (60%) and it in turn reverted back to 13 on exposure to sunlight (ethyl acetate- pyrex vessel, 5 hr, 85%).



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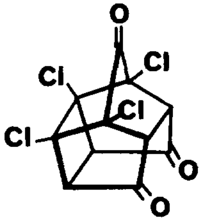

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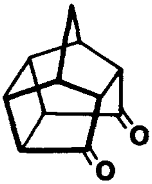

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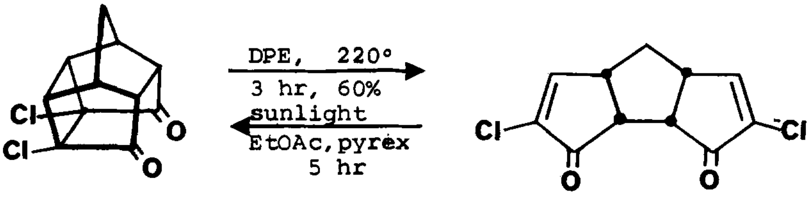

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Finally, the ready availability of cis, syn, cis- tricyclo $[6.3.0.0^{2,6}]$ undecane based bis-enones, with their folded topology and replete with symmetrically disposed functionality, provides alternate avenues for elaboration to interesting cyclopentanoid polyhedra, e.g. peristylane[1] and dodecahedrane. Progress towards these objectives will be revealed in due course.

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References and Notes:

1. P.E. Eaton, R.H. Mueller, G.R. Carlson, D.A. Cullison, G.F. Cooper, T-C. Chou and E-P. Krebs, J. Amer. Chem. Soc., 99, 2751 (1977), see foot note 2 in this paper.
2. To our knowledge, only two multistep synthetic entries to the cis, syn, cis- tricyclo [$6.3.0.0^{2,6}$] undecane ring system are known. P.E. Eaton, C. Giordano, G. Schloemer and U. Vogel, J. Org. Chem., 41, 2238 (1976); J.S.H. Kueh, M. Mellor and G. Pattenden, J. Chem. Soc. Chem. Comm., 5 (1978). See also, R.D. Little, A. Bukhari and M.G. Venegas, Tetrahedron Letts., 305 (1979).
3. R.C. Cookson, E. Crundwell, R.R. Hill and J. Hudec, J. Chem. Soc., 3062 (1964).
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5. ^{13}C nmr spectra were recorded on a JEOL FX-100 spectrometer operating at 25.0 MHz in the FT mode. All chemical shifts except for 8 are with respect to internal TMS. Off-resonance multiplicities are given in parenthesis.
6. This noteworthy sunlight photocyclisation has encouraged us to actively evaluate the system $4 \rightleftarrows 6$ and its congeners for the chemical storage of solar energy. Our findings, particularly the effect of catalysts on $4 \rightarrow 6$ conversion along with the kinetic data will be reported shortly.
7. A.P. Marchand and T.C. Chow, Tetrahedron, 31, 2655 (1975).
8. When 10 and 11 were subjected to more stringent conditions of thermolysis (upto 400°) in a static system, extensive charring was observed.
9. This observation has been previously recorded[3].

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