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A Novel Periselective Cycloaddition of Cycloheptatriene with Cyclohexa-2,4-Dienones

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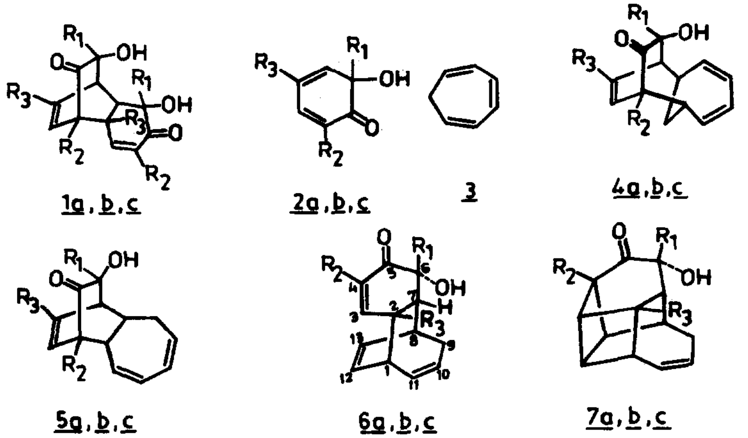
A highly periselective cycloaddition of cycloheptatriene and cyclohexa-2,4-dienones(**2a-c**) to *endo* tricyclic systems (**6a-c**) and their photo conversion to cage compunds (**7a-c**) has been reported. It has been shown that the adduct **6c** arise *via* Cope rearrangement of the initially formed π^{4s}(dienone) + π^{2s} (CHT) adduct **5c**.

There has been a resurgence of interest in the pericyclic reactions between complex conjugated polyenes such as tropone, fulvenes, cycloheptatriene, oxapines, and azapines, in order to explore higher order cycloadditions and their potential for rapid creation of complex carbocyclic systems. [1,2] Most of the studies in this area, however, have been restricted to molecular systems selected for examining mechanistic and theoretical aspects. Synthetic applications of pericyclic reactions between polyene addends have been limited due to multiple modes of cycloadditions and lack of periselectivity.[3]

In context with a synthetic endeavour, we required the tricyclic system 5 which we thought to assemble *via* cycloaddition between cycloheptatriene (CHT) and cyclohexa-2,4-dienone 2 (dienone). This thought was based on the observation that cyclohexa-2,4-dienones of type 2 react as 4π addend during their cycloaddition with dienes and as well as trienes.[4] At the outset, however, it was clear that cycloheptatriene (CHT) may undergo π^{6s}(CHT) + π^{4s}(dienone) , π^{4s}(CHT) + π^{2s}(dienone) and π^{2s}(CHT) + π^{4s}(dienone) type of cycloadditions, leading to a variety of products (**4-6**) (Scheme-1).

We wish to report herein a novel, highly periselective and synthetically useful cycloaddition of cycloheptatriene **3** with cyclohexa-2,4-dienones **2a,b** and **c** leading to adducts **6a,b** and **5c**, **6c** respectively. We also report that the adduct **6c** is formed *via* Cope rearrangement of the initially formed π^{4s}(dienone) + π^{2s}(CHT) adduct **5c** (Scheme 1). A facile photochemical π^{2s} + π^{2s} cycloaddition of **6a-c** to the corresponding cage compunds **7a-c** is also reported. To the best of our knowledge, this is the first report on the cycloaddition of cycloheptatriene and cyclohexadienones.

Generation of cyclohexadienone **2a** by pyrolysis[4] (160°C) of the diol-dimer **1a** and subsequent trapping with cycloheptatriene gave an adduct **6a** as exclusive product in excellent yield (82.5%). The structure of the adduct was revealed from the following data, m.p. 111°C, IR ν_{max} : 1690 cm^{-1}, ^{1}H NMR (300MHz, CDCl$_3$) δ : 6.53 (dd, J_1=10Hz, J_2=3Hz, 1H, H$_3$, proton at β-carbon of α,β -enone), 6.15 (dd with long range couplings, J_1=10Hz, J_2=3Hz, 1H,H_4, proton at α-carbon of α,β -enone), 6.02 (dd, J_1= J_2=8Hz, 1H, H_{12}/H_{13}), 5.92(dd, J_1=J_2=8Hz, 1H, H_{13}/H_{12}), 5.85(m of dd, J_1= 12Hz, J_2=9Hz, J_3=3Hz, 1H, H_{11}) and 5.48(t of d, J_1=12Hz, J_2=4Hz, 1H, H_{10}), 4.2(s, 1H, OH), 3.7(ABq, J=12Hz, 2H, CH_2Cl), 3.44(d of dd, J_1=8Hz, J_2=3Hz, 1H, H_2), 2.92 (d,J=8Hz, 1H, H_7), 2.78 (m, 2H) and 2.2 (m, 2H). These assignments were made with the help of



1a,b,c 2a,b,c 3 4a,b,c

5a,b,c 6a,b,c 7a,b,c

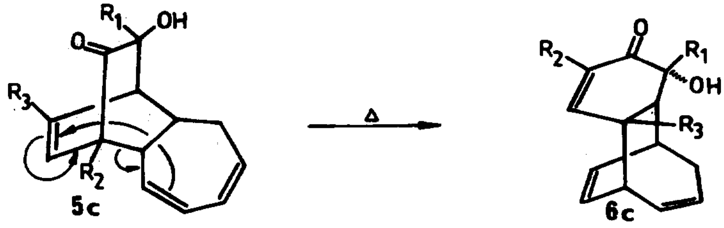
a, $R_1 = CH_2Cl$, $R_2 = R_3 = H$
b, $R_1 = R_2 = CH_3$, $R_3 = H$
c, $R_1 = R_2 = R_3 = CH_3$

Scheme-1

cosy experiment. The ^{13}C NMR of the adduct showed signals at δ 197.38(CO), 152.5, 134.1, 129.5, 127.2, 126.4 (olefinic carbons), 77.1(CH_2Cl), 52.8, 46.4, 45.3, 38.3, 35.5 and 28.6 for methine and methylene carbons. The *endo* stereochemistry of **6a** was confirmed through its facile photoconversion to the cage compound **7a** upon irradiation (200W, Hanovia, mercury vapour lamp) in acetone. Similarily the reaction of the diol-dimer **1b** with cycloheptatriene gave a single *endo* adduct **6b**[5] which also underwent $\pi^2s + \pi^2s$ photoreaction to the corresponding cage molecule **7b**[5] in excellent yield (84.5%).

It was surprising that the alternate modes of symmetry allowed[6,7] cycloadditions were not observed, especially since cyclohexadienones are well-known[4] to react exclusively as 4π addend during their cycloaddition with dienes/ trienes. In order to understand the observed periselectivity the coefficients of frontier molecular orbitals of 2 and 3 were examined, however it did not lead to any fruitful correlation.

Therefore it was considered[8] that the adducts **6a,b** may arise *via* Cope rearrangement of the initially formed π^4s(dienone) + π^2s(CHT) adducts **5a,b** whose formation is in agreement with FMO consideration. However, the attempts to isolate **5a,b** were unsuccessful. In this context, therefore we attempted the cycloaddition of **2c** with **3**. Indeed, the pyrolysis (150°C) of **1c** with **3** gave the $\pi^{4}s$(dienone) + $\pi^{2}s$(CHT) adduct **5c** (m.p. 123°C, IR ν_{max}: 1720 cm^{-1}) in addition to the enone **6c**,[9] the latter arising due to tandem $\pi^{4}s$(dienone) + $\pi^{2}s$(CHT) cycloaddition and a 3,3-shift, since the adduct **5c** was found to undergo a 3,3-shift to give **6c** (IR, NMR) upon further heating (150-160°C) (eq. 1). In view of this, it appears that the compounds **6a,b** might also be formed following a similar pathway.[10]



....Eq-1

In summary, we have explored the cycloaddition of cyclohexa-2,4-dienones with cycloheptatriene and demonstrated that the $\pi^{4}s$(CHT) + $\pi^{2}s$(dienone) adducts arise *via* atandem $\pi^{4}s$(dienone) + $\pi^{2}s$(CHT) addition and Cope rearrangement.

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5. Data for **7a**, m.p. 141°C. IR ν_{max}: 1720 cm^{-1}, ^{1}H NMR (300MHz,CDCl$_3$) δ : 5.8 (m of d J=12Hz,1H), 5.5 (m of dd, J_1=12Hz, J_2=18Hz, 1H), 3.6 (partof AB q, J= 12Hz, 1H,CH$_2$Cl), 3.42(part of ABq, J=12Hz,1H, CH$_2$Cl), 3.40(m,1H, CH), 3.13 (s,1H,OH), 3.05 (m,2H,CH), 2.85 (m,3H,CH), 2.65 (dt of part of ABq, J_1=18Hz, J_2=

6Hz, J_3=2Hz, 1H,CH_2), 2.5(q of part of ABq, J_1=18Hz, J_2=3Hz,1H,CH_2) and 2.30 (m,1H,CH); ^{13}C NMR(75MHz):δ 214.3, 132.4, 127.0, 78.85, 47.47, 46.7. 46.2, 44.6, 42.8, 42.37, 38.65, 37.8, 35.4 and 32.2. Analysis: Found, C, 67.3; H, 6.4%. Calcd. for $C_{14}H_{15}O_2Cl$, C, 67.06; H, 5.98%.

Data for compound **6b**, liquid, IR ν_{max}: 1690 cm^{-1}, ^{1}H NMR(300MHz,$CDCl_3$):δ 6.15(m,1H), 5.95(d of dd, J_1=J_2=8Hz, J_3=1.5Hz,1H), 5.88(dd,J_1=J_2=8Hz, 1H), 5.82 (m,1H), 5.45(t of d, J_1=10Hz, J_2=3.5Hz,1H), 4.0(br s,1H),3.38(complex m,1H),2.81 (d,J=8Hz,1H), 2.7(m,2H), 2.17(m,2H), 1.8(dd, J_1=2.5Hz,J_2=1.25Hz,3H,CH_3), 1.2(s, 3H,CH_3),. ^{13}C NMR(75MHz): δ 202.5, 147.3, 134.2, 132.9, 130.7, 129.4, 127.5, 74.5, 49.6, 44.6, 38.9, 35.8. 29.7, 28.49, 15.45. Analysis: Found, C, 78.4; H,8.0% Calcd. for $C_{15}H_{18}O_2$, C, 78.26; H, 7.82%.

Data for compound **7b**, m.p. 110°C,IR ν_{max}: 1720 cm^{-1},^{1}H NMR(90MHz,$CDCl_3$) δ 5.5(m,2H,olefinic H), 3.45(m,1H,CH), 3.2-2.7(br 4H,CH), 2.6-2.3(m,5H,CH and OH), 1.22(s,3H,CH_3),and 1.20(s,3H,CH_3). ^{13}C NMR(75MHz): δ 218.8,132.3,127.2, 76.5,51.98,47.27,46.1,45.6,43.3,37.8,36.2,35.6,22.2, and 15.1. Analysis: Found, C, 78.4; H, 8.0%. Calcd. for $C_{15}H_{18}O_2$, C, 78.26; H, 7.82%.

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8. We are highly grateful to the referee for this suggestion.
9. Data for compound **5c**, m.p. 123°C. IRν_{max}: 3450, 1720 cm^{-1},^{1}H NMR(500MHz, $CDCl_3$):δ 6.0(m,1H), 5.9-5.8(m,3H), 3.45(d,J=10Hz,1H), 2.68(t,J=2Hz,1H), 2.6(d of t, J_1=10Hz,J_2=3Hz,1H), 2.18-2.05(complex m,3H), 1.92(d,J=1.5Hz,3H,CH_3), 1.25(s, 3H,CH_3),and 1.15(s,3H,CH_3). Analysis: Found, C, 78.43; H, 8.22%. Calcd. for $C_{16}H_{20}O_2$, C, 78.68; H, 8.19%.

   Data for compound **6c**, liquid, IRν_{max}:3480,1690 cm^{-1},^{1}H NMR(500MHz,$CDCl_3$) δ 6.05(dd, J_1=J_2=8Hz, 1H), 5.9(br s, 1H), 5.8(dd, J_1=J_2=8Hz, 1H), 5.75(t of dd, J_1=J_2=8.5Hz, J_3=3Hz, 1H), 5.46(t of d, J_1=11Hz, J_2=3.5Hz, 1H), 2.92(m,1H), 2.33 (s,1H), 2.31(d, J=8Hz, 1H), 2.18(m,2H),1.75(s,3H,CH_3), 1.45(s,6H, 2 x CH_3). This compound was irradiated to give **7c**, m.p. 120°C, IRν_{max}: 3480, 1710 cm^{-1} ^{1}H NMR(300MHz, $CDCl_3$): δ 5.6(complex m, 2H), 3.5(dd,J_1=15Hz,J_2=10Hz, 1H) 2.82(s,1H,OH), 2.6(m,1H), 2.45(complex, m,2H), 2.3(complex, m, 4H), 1.2(s,3H, CH_3), and 1.0(s, 6H, 2x CH_3). ^{13}C NMR(75MHz):δ 219.22(CO),132.21,125.97, 50.9, 48.7, 47.41, 44.81, 44.0, 36.23, 35.71, 27.25, 25.43, and 15.29.
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