Periselective [4π+2π] Cycloaddition Reactions of 3-Ethoxy Carbonyl-2H-cyclohepta[b]furan-2-one with Aralkenes

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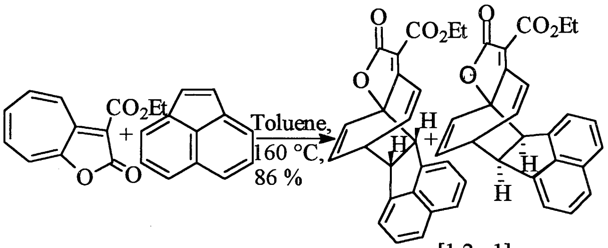
The periselective [4π+2π] cycloaddition reactions of 3-ethoxy carbonyl-2H-cyclohepta[b]furan-2-one with different aralkenes is described. The exclusive formation of [4π+2π] adducts in these reactions has been rationalised by MNDO and AM1 calculations.

The cycloaddition reactions of tropone and some of its derivatives have invoked considerable interest;1 cycloheptafuranones such as **1** also have been investigated. The latter can participate either as 8π or 4π system in cycloadditions. The [8π+2π] cycloadditions of cycloheptafuranones with enamines2 and enol ethers3 have been exploited in the synthesis of azulene derivatives. Isolated examples of the formation of [4π+2π] products along with [8π+2π] adducts have been reported.4,5

Our general interest in cycloadditions6 and the perception that **1** can be viewed as an encumbered electron deficient heptafulvene,7 along with the fact that no cycloaddition of **1** with aralkenes has been reported, prompted us to investigate its reaction with acenaphthylene, styrenes and indene and our preliminary results are presented here.

The reaction of acenaphthylene **2** with 3-ethoxy carbonyl [2H] cyclohepta[b]furan-2-one **1** presented in Scheme 1 is illustrative.8



1 **2** **3** [1.2 : 1] **4**

Scheme 1.

The products **3** and **4** were separated by chromatography on silica gel column followed by recrystallisation from dichloromethane/hexane. The IR spectra of the products showed two carbonyl group absorptions at 1770 cm^{-1} and 1702 cm^{-1} corresponding to the α,β–unsaturated lactone carbonyl group and ester carbonyl group respectively.9 ^{13}C NMR of the products showed a peak at 87 ppm, characteristic of the tertiary carbon adjacent to the lactone oxygen atom. Finally the structure of the adducts were confirmed by single crystal X-ray analysis of **4**.10

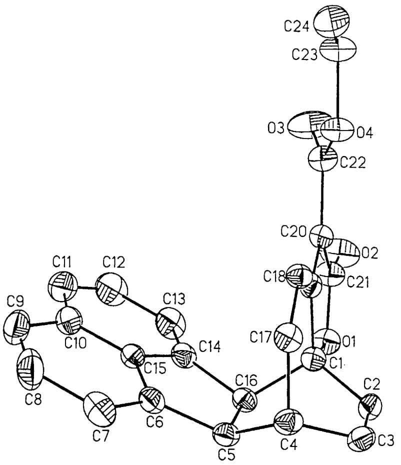
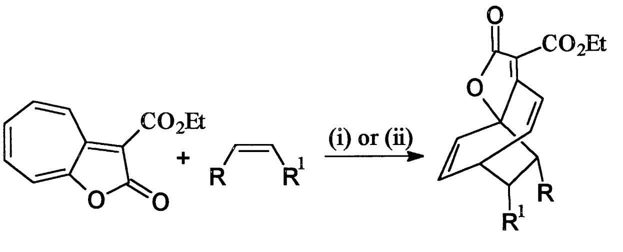


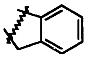
Figure 1. X-ray structure of **4.**

Similar reactions were observed with styrenes and indene; the results are summarised in Table **1**.



1 **5**(a-e) **6**(a-e)

Table1. Cycloadditions of styrenes and indene with **1**

Reagent	Substituent	Yield(%)^{a,b}	Isomeric Ratio endo:exo
5a(i)	R= Ph-, R^1= H-	56[90]	2.7 : 1
5b(ii)	R= 4-MeO-Ph-, R^1=H-	35[52]	2.5 : 1
5c(ii)	R= 4-Me-Ph-, R^1=H-	37[80]	2.4 : 1
5d(ii)	R= 4-Cl-Ph-, R^1=H-	38[88]	2.5 : 1
5e(ii)	R, R^1 = 	64[99]	1.2 : 1

a. Isolated yield. b. Yield based on unreacted **1** in brackets.
Reaction conditions:(i) Neat, 150 °C, sealed tube, 12 h.
(ii) Toluene, 140 °C, sealed tube, 24 h.

MNDO and AM1 calculations11 were carried out using MOPAC version 5 and from the energy levels and orbital coefficients of **1** and aralkenes, it was found that in the case of [4π+2π] cycloaddition, the interaction of NLUMO(**1**) and HOMO(aralkene) is favoured. It is also worthy of note that the orbital coefficients of the reacting carbon centres favoured a [4π+2π] addition in preference to [8π+2π] addition. The observed regiochemistry in products **6**(a-e) is also in accordance

with the MNDO calculations.

In conclusion we observed a facile and exclusive $[4\pi+2\pi]$ cycloaddition of 1 with aralkenes and the products appear attractive from the point of view of further transfomations.

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8 Typical Experimental procedure. 3-Ethoxycarbonyl-2H-cyclohepta[b]-furan-2-one (109 mg, 0.5 mmol) and acenaphthylene (229 mg, 1.5 mmol) were dissolved in dry toluene (0.5 ml) in a Schlenk glass tube and it was sealed under nitrogen and heated at 160 °C for 20 h. When all the dienophile was reacted (as indicated by tlc), the reaction mixture was chromatographed on silica gel column. Elution with 5% ethyl acetate in hexane afforded **3** and **4** (57.3%) in 1.2 : 1 ratio. The unreacted cyclohepta[b]furan-2-one (33%) was recovered by elution with 30% ethyl acetate in hexane. The products were crystallised from dichloromethane/hexane mixture as colourless crystals.

9 Spectral data for illustrative example **4**: Colourless crystalline solid mp 188-190 °C; IR(KBr)- 2362, 1770, 1702, 1615, 1300, 1248, 1197, 1030, 714cm^{-1}. ^{1}H NMR in CDCl$_3$ δ: 7.62-7.19(m,6H), 6.70(d,1H), 6.58(m,1H), 6.36(m,2H), 4.62(d,1H), 4.39(m,1H), 4.20(m,3H), 1.24(t,3H); ^{13}C NMR in CDCl$_3$ δ: 168.47, 166.45, 160.86, 148.55, 143.57, 140.25, 140.00, 133.50, 132.84, 131.42, 128.17, 127.76,124.06, 123.54, 121.67, 120.37,118.30, 113.53, 87.89, 61.01, 52.68, 46.65, 41.27, 13.96. Analysis: Found C-77.85%, H-4.88% (calculated C 77.82%, H- 4.89%)

10 Single crystal X-ray analysis co-ordinates and parameters. Crystal data for **4**: $C_{24}H_{18}O_4$, colourless crystals, F*w*= 370.38, 0.35x 0.35x0.35 mm, monoclinic, space group$P2_1/C$;unit cell dimensions: a = 16.9700(3)Å, α = 90 deg, b = 19.68390(10) Å, β = 105.41deg, c = 11.3640(2) Å, γ = 90deg. R indices(all data) RI = 0.1011, WR2 = 0.2049. V = 3659.51(9) Å^3, Z = 8, D*calc* = 1.345 Mg/m^3, F(000) = 1552, Absorption coefficient = 0.091mm^{-1}. Reflections collected = 18592. Strucure solution and refinement were carried out using SHELXTL-PLUS (5.03) software package (Sheldrick, G. M, Siemens Analytical X-ray Division, Madison, WI 1995).

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