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Cycloaddition Reactions of 2-Oxo-2H-cyclohepta[b]furan derivatives with Dienes and Dienophiles#

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Abstract

Cycloaddition reactions of 2-oxo-2H-cyclohepta[b]furan derivatives participating as 8π and 4π components respectively towards different dienes and dienophiles are described. The observed reactivity and periselectivity have been rationalized by AM1 calculations.

Key words: Fulvenes, Furans, Cycloadditions, Decarboxylation.

2-Oxo-2H-cyclohepta[b]furan derivatives **1a, b**, readily obtained from chlorotropone and the corresponding active methylene compound, can be viewed as electron deficient heptafulvenes [1-2]. In view of our current interest in the cycloaddition reactions of novel fulvenoids [3-8], we undertook a systematic investigation to unravel the cycloaddition profile of this conjugated 8π system with different alkenes, dienes and pentafulvenes. Yasunami and coworkers have earlier shown that **1a** undergoes facile [8+2] addition with electron rich alkenes such as enamines [9-13] and enol ethers [14-16]. We have recently observed that reactions of **1a**, with acyclic 1,3-dienes proceed in an [8+2] fashion yielding novel bicyclo [5.3.0] system [17]. In the case of aryl alkenes, the addition proceeded exclusively in a [4+2] mode [18], whereas in the case of pentafulvenes both [8+2] and [4+2] adducts were formed [19].

This paper is dedicated with respectful regards to Professor M. V. George on the occasion of his 70th Birthday

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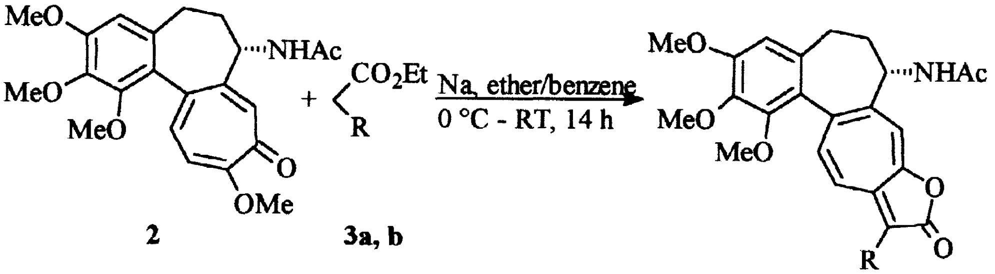
We have expanded these investigations to include the furanone derived from colchicine, with a view to modifying the C-ring of this important alkaloid. It is anticipated that products derived from these studies will possess interesting biological activity.

Results and Discussion

1. *Synthesis of 2-oxo-2H-cyclohepta[b]furan derivatives*

3-Substituted 2-oxo-2H-cyclohepta[b]furans **1a, b** were synthesized from chlorotropone by a procedure reported by Nozoe [20]. Similarly reaction of colchicine **2** with active methylene compounds in the presence of sodium in dry ether/benzene as the solvent system yielded the novel furan derivatives **4a, b** in good yields (Scheme 1).



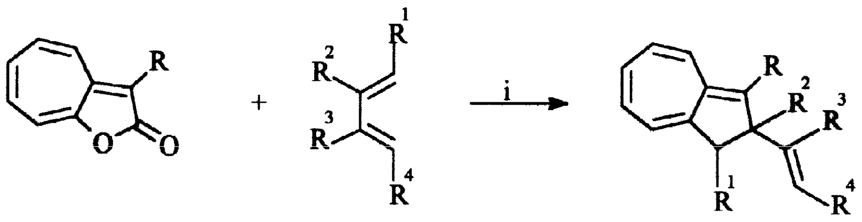
4a, R = CO_2Et, 60 %
4b, R = COMe, 55 %

Scheme 1

The products **4a, b** were isolated as yellow solids after column chromatography. Their structures were established by spectral analysis, including a doublet ^1H NMR signal at low field typical of H-5 of the 2-oxo-2H-cyclohepta[b]furan moiety and three resonances for carbonyl carbons in the ^{13}C NMR spectra. The formulae were confirmed by high resolution mass spectra.

2. *Cycloaddition reactions of 3-substituted 2-oxo-2H-cyclohepta[b]furan with acyclic 1,3-dienes.*

The reactions of **1a, b** with different acyclic 1,3-dienes at 130-150 °C in a Schlenk glass tube (S.T) sealed under argon afforded dihydroazulene derivatives in fairly good yields. The results are summarized in Scheme 2.



1a, b **5a-e** **6a-f**

i) Toluene, S.T, Ar, 130 °C-150 °C, 14 h.

Entry	Substituents	[8+2] adduct	Yield (%)*
1	R = CO_2Et, $R^1 = R^4 = H$ $R^2 = R^3 = CH_3$	**6a**	97
2	R = CO_2Et, $R^1 = R^3 = H$ $R^2 = CH_3$, R^4 = Ph	**6b**	71
3	R = CO_2Et, $R^1 = R^3 = H$ $R^2 = CH_3$, R^4 = 4-$OMeC_6H_4$	**6c**	51
4	R = CO_2Et, $R^1 = R^3 = H$ $R^2 = R^4 = CH_3$	**6d**	35**
5	R = CO_2Et, $R^1 = R^2 = CH_3$, $R^3 = R^4 = H$	**6e**	20**
6	R = $COCH_3$, $R^1 = R^4 = H$ $R^2 = R^3 = CH_3$	**6f**	68

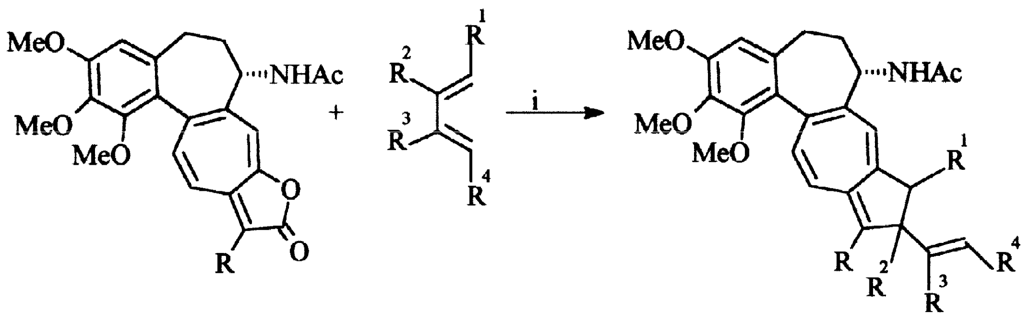
*Yield based on unreacted **1a, b**

** The yields can be improved by changing the reaction condition to xylene, S.T, Ar, 150 °C, with 10 equivalents of diene.

Scheme 2

Absence of the lactone absorption discernible from the IR spectra clearly indicated that the reaction proceeded in an [8+2] pathway followed by decarboxylation. The stereo and regio chemistry of the dihydroazulenes was ascertained from single crystal X-ray analysis of the [4+2] adduct of **6a** with maleic anhydride [17].

A similar reaction pattern was observed in cycloaddition reactions of furanones **4a, b** with acyclic 1,3-dienes (Scheme 3).



4a, b **5a-c** **7a-d**

i) Xylene, S.T, Ar, 190 °C, 36 h.

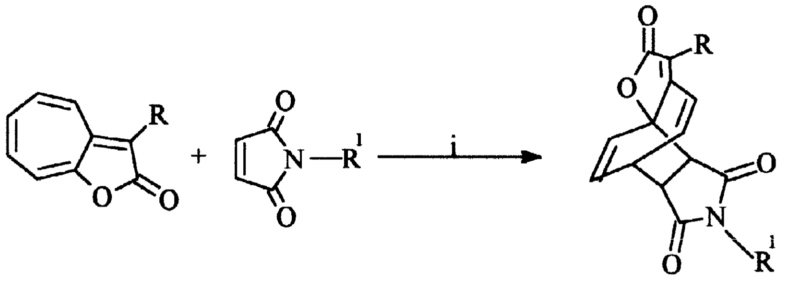
Entry	Substituents	[8+2] adduct	Yield (%)*
1	R = CO_2Et, $R^1 = R^4 = H$ $R^2 = R^3 = CH_3$	**7a**	74
2	R = CO_2Et, $R^1 = R^3 = H$ $R^2 = CH_3$, R^4 = Ph	**7b**	55
3	R = CO_2Et, $R^1 = R^3 = H$ $R^2 = R^4 = CH_3$	**7c**	48
4	R= $COCH_3$, $R^1 = R^4 = H$ $R^2 = R^3 = CH_3$	**7d**	90

*Yield based on unreacted **4a, b**

Scheme 3

3. *Cycloaddition reactions of 3-substituted 2-oxo-2H-cyclohepta[b]furan with dienophiles*

The reaction of 2-oxo-2H-cyclohepta[b]furan **1a, b** with maleimides in xylene in a Schlenk tube at 140 °C-150 °C afforded [4+2] adducts in very good yields (Scheme 4).



1a, b **8a, b** **9 a-d**

I) Xylene, S.T, Ar, 140 °C-150 °C, 48 h.

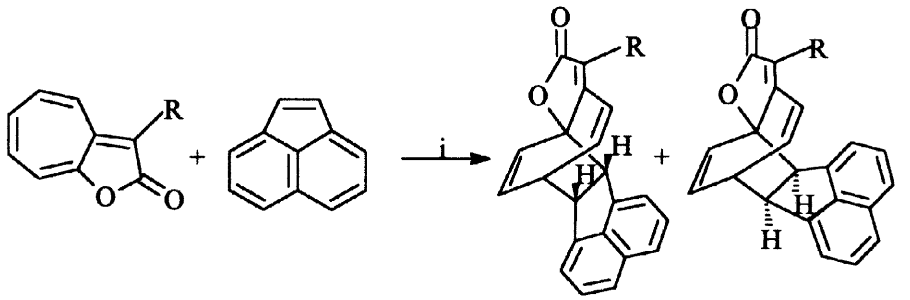
Entry	Substituents	Product (*endo:exo*)	Yield (%)*
1	R = CO_2Et, R^1 = Ph	**9a** (1:1)	81
2	R = CO_2Et, R^1 = H	**9b** (1.3:1)	61
3	R = $COCH_3$, R^1 = Ph	**9c** **	92
4	R = $COCH_3$, R^1 = H	**9d** **	69

*Yield based on unreacted **1a, b**. **Trace amount of *exo* isomer was also formed.

Scheme 4

The IR and ^{13}C NMR spectra of the adduct **9a** showed three carbonyl absorptions. The structure was further supported by the high resolution mass spectrum, which showed a molecular ion peak at *m/z* 391.10680.

The reaction of substituted furanones with acenaphthylene in dry xylene in a Schlenk tube at 160 °C yielded [4+2] adducts in very good yields (Scheme 5). The *endo* and *exo* isomers were separated by silica gel column using ethylacetate-hexane mixture as eluent.



1a, b **10**

R = CO_2Et, **11(a:b**, 1.2:1), 86 %
R = COMe, **12(a:b**, 2.4:1), 74 %

i) Toluene, S.T, Ar, 160 °C, 20 h.

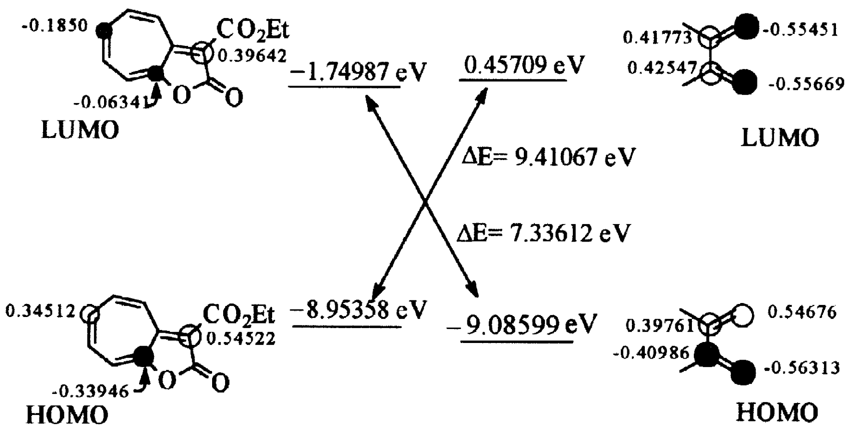
Scheme 5

The structures of the products were assigned on the basis of spectral analysis. The IR spectrum of **11a** showed two carbonyl absorptions at 1767 cm^{-1} and 1706 cm^{-1} characteristic of lactone and ester carbonyl groups respectively. In the ^1H NMR spectrum of **11a**, the bridgehead proton resonated at δ 3.93 as a multiplet. In the ^{13}C NMR spectrum, the characteristic signal corresponding to the bridgehead carbon adjacent to oxygen was visible at δ 87.31 and the other bridgehead carbon resonated at δ 52.86. The stereochemistry of the isomers was confirmed on the basis of X-ray analysis of **11b** [18].

4. Theoretical Considerations

In order to explain the observed reactivity and periselectivity in the above reactions, we have carried out AM1 calculations using PC SPARTAN Graphical Interface Package for

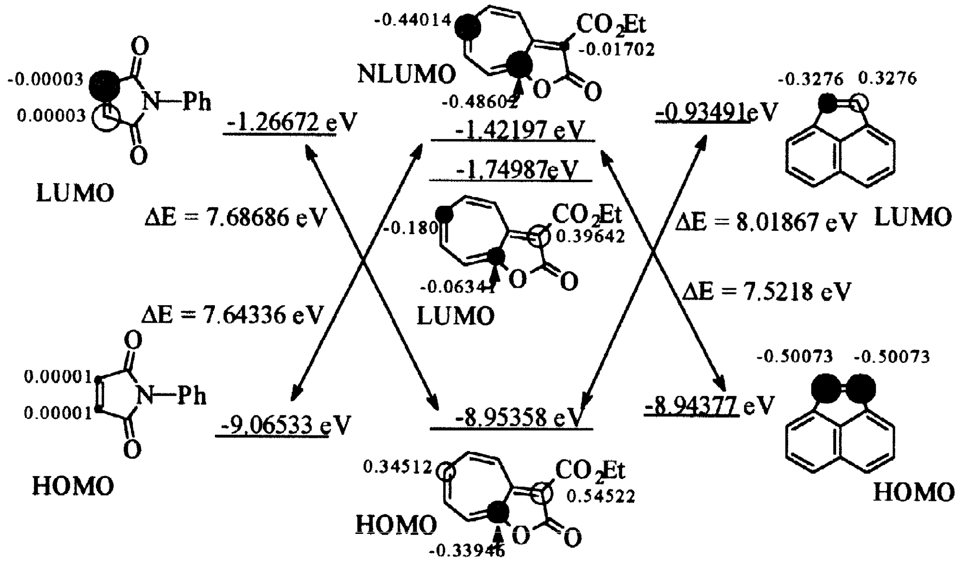
Molecular Mechanics and Molecular Orbital Models. The correlation diagrams for the reaction of ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate with 2,3-dimethyl- butadiene (Fig. 1), and dienophiles(Fig. 2) are illustrated below.



1a

Figure 1. Molecular orbital correlation diagrams of **1a** and 2,3-dimethylbutadiene

From the orbital coefficients of the reactants (Fig 1), it is clear that in the case of [8+2] addition only the interaction between the HOMO of ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate and the LUMO of 2,3-dimethylbutadiene is symmetry allowed. It is also noteworthy that the size and sign of the interacting orbitals are perfectly in match for the [8+2] addition mode rather than the competing [4+2] mode. Therefore, even though energetically slightly disfavored, the [8+2], cycloaddition is controlled by the HOMO of the ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate.



1a

Figure 2. Molecular orbital correlation diagrams of **1a** with acenaphthylene and *N*-phenyl maleimide

In the case of [4+2] addition with acenaphthylene (Fig 2), it is clear that HOMO(**1a**)-LUMO(acenaphthylene), HOMO(acenaphthylene)-LUMO(**1a**), HOMO(acenaphthylene)-

NLUMO(**1a**) interactions are symmetry allowed. Among these the LUMO(**1a**)-HOMO(acenaphthylene) interaction is negligible due to the small coefficients at the reacting carbon centers of LUMO(**1a**). Between the other two possible interactions, the NLUMO(**1a**)-HOMO(acenaphthylene) interaction is favored because of the smaller gap between the interacting energy levels and good match of the size of the orbital coefficients. Therefore the [4+2] addition here is an inverse electron demand Diels-Alder reaction. It is also worthy of note that the size of orbital coefficients at the reacting carbons favors a [4+2] addition in preference to the [8+2] addition mode. Interestingly the addition of maleimides with ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate is controlled by HOMO(**1a**)-LUMO(*N*-phenylmaleimide) interaction, which is favored both energetically and by matching of the size of the orbital coefficients.

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Experimental details

All reactions were carried out in oven dried glassware under argon atmosphere. Analytical thin layer chromatography was performed on silica gel plates. Purification by gravity column chromatography was carried out using silica gel (100-200). Mixtures of ethylacetate-hexane and chloroform-methanol were used as eluents. Melting points are uncorrected. The IR spectra were recorded on a Nicolet impact 400D infrared spectrophotometer. NMR spectra were recorded on Jeol Ex-90 and Bruker 300 spectrophotometer using chloroform-d as solvent. The chemical shifts are given in the δ scale with tetramethylsilane as internal standard.

Data for compound **4a**

Diethyl malonate (0.24 g, 1.5 mmol) was added to powdered sodium (0.034 g, 1.5 mmol) in dry ether and stirred for 1 h in an ice-water bath. To the resulting solution, colchicine (0.3 g, 0.75 mmol) in dry benzene (20 mL) was added dropwise. The reaction mixture was stirred at room temperature overnight. Work up and silica gel column chromatography ($CHCl_3$) afforded furanone derivative of colchicine **4a** (0.216 g, 60%) as bright yellow crystals. (m.p. 178-181 °C).

IR (KBr): 3345, 2944, 1777, 1681, 1600, 1539, 1462, 1362, 1319, 1262, 1192, 1148, 1097, 1037, 920, 850, 798 cm^{-1}. ^1H NMR: δ 8.64 (d, J = 11.7 Hz, 1H), 8.44 (s, 1H), 8.14 (s, 1H), 7.82 (d, J = 11.19 Hz, 1H), 6.53 (s, 1H), 4.38 (q, J = 7.86 Hz, 2H), 3.86 (s, 6H), 3.61 (s, 3H), 2.45-2.36 (brs, 5H), 1.97 (s, 3H), 1.37 (t, J = 7.78 Hz, 3H). ^{13}C NMR: δ 169.53, 166.16, 162.27, 156.04, 153.51, 151.30, 150.20, 149.88, 143.41, 141.56, 134.03, 126.78, 124.82, 117.13, 116.94, 106.64, 60.72, 60.27, 59.41, 55.05, 51.99, 36.84, 28.84, 21.69, 13.18. HRMS: $C_{26}H_{27}O_8N$ 481.1736; Found: 481.17287.

Data for compound **4b**

Ethyl acetoacetate (0.19 g, 1.5 mmol) was added to powdered sodium (0.034 g, 1.5 mmol) in dry ether and stirred for 1 h in an ice-water bath. To the resulting solution, colchicine (0.3 g, 0.75 mmol) in dry benzene (20 mL) was added dropwise. The reaction mixture was stirred at room temperature overnight. Work up and purification afforded furanone derivative of colchicine **4b** (0.185 g, 55%) as bright yellow crystals (m.p. 135-138 °C).
IR (KBr): 3312, 2935, 2861, 1742, 1654, 1593, 1539, 1458, 1324, 1092, 798, 663, 616 cm^{-1}.
^1H NMR: δ 9.14 (d, J = 11.76 Hz, 1H), 8.09 (s, 1H), 7.94 (d, J = 11.82 Hz, 1H), 7.60 (s, 1H), 6.60 (s, 1H), 3.93 (s, 6H), 3.66 (s, 3H), 2.65 (s, 3H), 2.57-2.23 (br s, 5H), 2.07 (s, 3H).
^{13}C NMR: 194.74, 170.65, 169.03, 157.72, 154.63, 151.64, 150.89, 145.71, 143.86, 141.69, 134.94, 128.88, 125.69, 118.34, 107.61, 101.88, 61.70, 61.39, 60.87, 56.16, 52.98, 37.98, 30.50, 22.76. HRMS: $C_{25}H_{25}O_7N$ 451.1631; Found: 451.16477.

Data for compound **6a**

A solution of ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate **1a** (0.218 g, 1 mmol) and 2,3-dimethylbutadiene (0.410 g, 5 mmol) in dry toluene (0.5 mL) were sealed under argon in a Schlenk tube and heated at 150 °C for 14 h. The reaction mixture was chromatographed on a silica gel column (1% ethylacetate-hexane) to afford **6a** (0.175 g, 97%) as a blood-red viscous liquid. The unreacted furanone (0.064 g) was recovered using 30% ethylacetate-hexane as the eluent.
IR (film): 2972, 1686, 1540, 1449, 1400, 1260, 1156, 1053, 882, 784 cm^{-1}. ^1H NMR: δ 7.47 (d, J = 12.24 Hz, 1H), 6.00 (m, 4H), 4.72 (d, J = 8.97 Hz, 2H), 4.12, (q, J = 7.08 Hz, 2H), 2.53 (dd, 2H), 1.71 (s, 3H), 1.38 (s, 3H), 1.22 (t, J = 7.07 Hz, 3H). ^{13}C NMR: δ 166.54, 156.32, 153.20, 151.12, 133.05, 132.97, 130.92, 129.92, 129.91, 124.55, 108.70, 59.47, 51.14, 48.27, 25.66, 20.63, 14.39. HRMS: $C_{17}H_{20}O_2$: 256.14633; Found: 256.14628.

Data for compound **6b**

Reaction of **1a** (0.20 g, 0.92 mmol) with **5b** (0.529 g, 3.68 mmol) at 130 °C, as described earlier for **6a** yielded **6b** (0.120 g, 71%) as a blood-red viscous liquid. The unreacted furanone (0.084 g) was recovered. IR (film): 2962, 1680, 1594, 1535, 1450, 1405, 1307, 1261, 1216, 1157,1053, 799, 695 cm^{-1}. ^1H NMR: δ 7.53 (d, J = 11 Hz, 1H), 7.15 (m, 6H), 6.17 (m, 5H), 4.17 (q, J = 7.14 Hz, 2H), 2.65 (dd, 2H), 1.45 (s, 3H), 1.26 (t, J = 7.12 Hz, 3H). ^{13}C NMR: δ 166.02, 163.55, 157.52, 155.10, 152.51, 137.89, 137.56, 132.82, 132.73, 130.58, 129.77, 128.28, 126.67, 126.10, 125.98, 124.52, 59.09, 48.68, 47.73, 25.35, 14.16. EIMS: *m/z* 319 (M^++1, 9.1), 318 (M^+, 33), 303 (100), 245 (50), 229, (87), 167 (88), 115 (82), 77 (68).

Data for compound **6c**

Reaction of **1a** (0.20 g, 0.92 mmol) with **5c** (0.478 g, 2.75 mmol), as described earlier for **6b** yielded **6c** (0.112 g, 51%) as a blood-red viscous liquid. The unreacted furanone (0.078 g) was recovered. IR (film): 2961, 1680, 1598, 1516, 1453, 1245, 1169, 1037, 968, 810, 740, 646 cm^{-1}. ^1H NMR: δ 7.55 (d, J = 12.29 Hz, 1H), 7.06 (m, 4H), 6.12 (m, 6H), 4.17 (q, J = 7.35 Hz, 2H), 3.80 (s, 3H), 2.66 (dd, 2H), 1.45 (s, 3H), 1.22 (t, J = 7.00 Hz, 3H). ^{13}C NMR: δ 166.11, 158.59, 155.25, 152.36, 135.50, 132.76, 130.61, 129.71, 128.55, 127.06, 125.51, 124.43, 113.78, 59.06, 55.10, 48.80, 47.67, 25.47, 14.19. MS: *m/z* 349 (M^++1), 348 (M^+), 333.

Data for compound **6d**

Reaction of **1a** (0.202 g, 0.93 mmol) with **5d** (0.304 g, 3.71 mmol), as described earlier for **6b** yielded **6d** (0.051 g, 35%) as a blood-red viscous liquid. The unreacted furanone (0.076 g) was recovered. IR (film): 2957, 2919, 1680, 1596, 1538, 1454, 1409, 1318, 1209, 1157, 1041, 970,789 cm^{-1}. ^1H NMR: δ 7.40 (d, J = 12.49 Hz, 1H), 5.63 (m, 6H), 4.12 (q, J = 7.20 Hz, 2H), 2.53 (dd, 2H), 1.61 (d, 3H), 1.30 (s, 3H), 1.22 (t, J = 7.38 Hz, 3H). ^{13}C NMR: δ 166.11, 155.43, 151.85, 138.13, 132.61, 132.40, 130.58, 129.48, 129.09, 124.05, 120.94, 58.95, 48.77, 47.40, 25.50, 17.80, 14.10. EIMS: *m/z* 257 (M^++1, 7), 256 (M^+, 35), 241 (100), 183 (40), 153 (36), 141 (75), 115 (42), 77 (15).

Data for compound **6e**

Reaction of **1a** (0.218 g, 1 mmol) with **5e** (0.328 g, 4 mmol), as described earlier for **6b** yielded **6e** (0.027 g, 20%) as a blood-red viscous liquid. The unreacted furanone (0.105 g) was recovered. IR (film): 2972, 2918, 1682, 1595, 1541, 1454, 1407, 1313, 1252, 1205, 1098, 1038, 796 cm^{-1}. ^1H NMR: δ 7.45 (d, J = 12 Hz, 1H), 5.95 (m, 4H), 5.20 (m, 1H), 4.18 (q, J = 7.45 Hz, 2H), 3.55 (dd, 1H), 2.85 (dd, 1H), 2.30 (dd, 1H), 1.55 (m, 6H), 1.20 (t, J = 7.73 Hz, 3H). ^{13}C NMR: δ 166.62, 158.33, 154.01, 137.92, 132.88, 132.55, 130.13, 129.96, 124.50, 123.84, 118.05, 59.09, 50.26, 39.02, 14.22, 13.21, 13.09. EIMS: *m/z* 257 (M^++1, 13), 256 (M^+, 75), 201 (65), 141 (35), 128 (100), 77 (12), 55 (30).

****Alternative procedure**

The yields of **6d** and **6e** can be improved by changing the reaction conditions to xylene, S.T. at 150 °C for 5 h. Yield of **6d** = 86%, yield of **6e** = 90%.

Data for compound **6f**

Reaction of **1b** (0.20 g, 1.06 mmol) with **5a** (0.434 g, 5.3 mmol), as described earlier for **6a** yielded **6f** (0.141 g, 68%) as a blood-red viscous liquid. The unreacted furanone (0.028 g) was recovered. IR (film): 2921, 2861, 1647, 1512, 1458, 1371, 1256, 1148, 899, 771 cm^{-1}. ^{1}H NMR: δ 7.8 (d, J = 12.04 Hz, 1H), 6.1 (m, 4H), 4.9 (d, J = 7.84 Hz, 2H), 2.8 (dd, 2H), 2.2 (s, 3H), 1.9 (s, 3H), 1.5 (s, 3H). ^{13}C NMR: δ 197.17, 155.73, 151.73, 150.30, 136.73, 133.72, 132.91, 131.06, 130.52, 125.24, 109.93, 50.68, 48.56, 29.32, 25.26, 20.25. MS: *m/z* $C_{16}H_{18}O$, 226 (M^+).

Data for compound **7a**

A solution of **4a** (0.05 g, 0.10 mmol) and 2,3-dimethylbutadiene (0.042 g, 0.52 mmol) in dry xylene (0.5 mL) were sealed under argon in a Schlenk tube and heated at 190 °C for 36 h. The reaction mixture was chromatographed on a silica gel column (1% methanol-chloroform) to afford **7a** (0.028g, 74%) as a blood-red viscous liquid. The unreacted furanone (0.015 g) was recovered.

IR (film): 3063, 2992, 2946, 1680, 1604, 1534, 1494, 1444, 1326, 1270, 1237, 1141, 1096, 1055, 737, 705 cm^{-1}. ^{1}H NMR: δ 7.38 (d, J = 12.69 Hz, 1H), 6.48 (s, 1H), 6.23 (m, 3H), 4.76 (d, J = 8.37 Hz, 2H), 4.11 (m, 2H), 3.90 (s, 3H), 3.88 (s, 3H), 3.82 (s, 3H), 2.78-2.41 (brs, 7H), 2.01 (s, 3H), 1.73 (s, 3H), 1.43 (s, 3H), 1.23 (t, J = 7.05 Hz, 3H). ^{13}C NMR: δ 169.41, 166.21, 155.11, 152.94, 151.63, 151.37, 151.13, 141.85, 141.75, 141.42, 137.11, 134.83, 128.01, 127.31, 126.80, 120.72, 108.45, 107.22, 61.41, 61.26, 59.11, 56.01, 51.50, 50.80, 38.09, 30.06, 25.57, 22.94, 20.47, 14.19.

Data for compound **7b**

Reaction of **4a** (0.10 g, 0.21 mmol) with **5b** (0.158 g, 1.1 mmol), as described earlier for **7a** yielded **7b** (0.033 g, 55%) as a blood-red viscous liquid. The unreacted furanone (0.05 g) was recovered. IR (film): 3299, 2935, 2362, 1667, 1606, 1526, 1445, 1222, 1135, 1094 cm^{-1}. ^{1}H NMR: δ 7.29 (m, 8H), 6.46-6.14 (m, 4H), 4.14 (q, J = 7.08 Hz, 2H), 3.89 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 2.88-2.16 (brs, 7H), 2.06 (s, 3H), 1.50 (s, 3H), 1.24 (t, J = 7.05 Hz, 3H). ^{13}C NMR: δ 169.27, 166.04, 154.38, 152.95, 151.40, 141.51, 138.12, 137.86, 137.35, 134.35, 134.13, 128.37, 127.33, 126.73, 126.06, 120.76, 107.15, 61.42, 61.23, 59.11, 55.94, 51.49, 47.74, 38.16, 30.00, 25.81, 22.98, 20.58, 14.32.

Data for compound **7c**

Reaction of **4a** (0.204 g, 0.42 mmol) with **5c** (0.174 g, 2.12 mmol), as described earlier for **7a** yielded **7c** (0.095 g, 48%) as a blood-red viscous liquid. The unreacted furanone (0.022 g) was recovered. IR (film): 3299, 2942, 2854, 1694, 1600, 1533, 1492, 1445, 1404, 1351, 1330, 1243, 1142, 1094, 1040. ^{1}H NMR: δ 7.28 (m, 2H), 6.49 (s, 1H), 6.22 (m, 3H), 5.69 (d, J = 6.42 Hz, 1H), 4.15 (q, J = 7.58 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H), 3.82 (s, 3H), 2.74-2.45 (brs., 7H), 1.97 (s,3H), 1.68 (s, 3H), 1.35 (s,3H), 1.27 (t, J = 6.96 Hz, 3H). ^{13}C NMR: δ 169.28, 167.78, 166.51, 166.10, 154.52, 152.65, 151.08, 141.12, 138.13, 136.85, 134.61, 134.43, 127.67, 127.02, 126.57, 120.95, 120.50, 106.94, 61.16, 61.02, 55.76, 51.22, 50.13, 49.47, 47.12, 37.80, 29.78, 25.72, 22.70, 17.73, 14.02

Data for compound **7d**

Reaction of **4b** (0.039 g, 0.086 mmol) with **5a** (0.036 g, 0.432 mmol), as described earlier for **7a** yielded **7d** (0.0235 g, 90%) as a blood-red viscous liquid. The unreacted furanone (0.015 g) was recovered. IR (film): 3272, 2942, 2854, 1661, 1600, 1492, 1431, 1404, 1324, 1243, 1121, 724 cm^{1}. ^{1}H NMR: 7.70-7.06 (m, 4H), 6.27 (s, 1H), 4.89 (d, J= 5.89 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.81 (s, 3H), 2.86-2.39 (brs, 7H), 2.30 (s, 3H), 2.03 (s, 3H), 1.77 (s, 3H), 1.64 (s, 3H). ^{13}C NMR: δ 197.66, 169.47, 155.44, 153.11, 151.15, 141.53, 139.27, 138.67, 136.24, 135.25, 134.76, 128.33, 128.08, 122.03, 118.21, 110.07, 107.75, 107.23, 61.46, 61.36, 56.08, 51.61, 49.73, 38.30, 34.00, 32.89, 29.69, 25.84, 18.16, 14.10.

Data for compound **9a**

Ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate **1a** (0.218 g, 1 mmol) and *N*-phenylmaleimide (0.26 g, 1.5 mmol) in dry xylene (0.5 mL) were sealed under argon in a Schlenk tube and heated at 140-150 °C for 48 h. The reaction mixture was chromatographed on silica gel column. Elution with 50% ethylacetate-hexane afforded **9a** (0.25 g, 81%) as a mixture of *endo* and *exo* isomers. The unreacted furanone (0.044 g) was recovered.

IR (KBr): 3063, 2969, 2348, 1782, 1715, 1634, 1492, 1398, 1200, 1050, 757 cm^{-1}. ^{1}H NMR: δ 7.49 (m, 6H), 7.27 (m, 5H), 7.15 (m, 2H), 6.97 (t, J = 8.41 Hz, 1H), 6.69 (t, J = 8.51 Hz, 1H), 6.59 (m, 1H), 6.35 (m, 2H), 4.33 (m, 4H), 4.11 (m, 3H), 3.7 (m, 3H), 1.33 (m, 6H). ^{13}C NMR: δ 176.15, 175.76, 173.64, 172.56, 167.83, 166.55, 163.16, 161.39, 148.40, 147.79, 133.03, 132.00, 131.12, 130.25, 129.77, 129.74, 127.69, 127.58, 122.85, 122.05, 116.41, 114.62, 85.66, 84.95, 61.90, 61.87, 48.80, 48.66, 45.54, 44.07, 39.01, 38.09, 14.43, 14.39. HRMS calcd for $C_{22}H_{17}O_6N$ (M^+): 391.10559, found 391.10680.

Data for compound **9b**

Reaction of **1a** (0.218 g, 0.21 mmol) with maleimide (0.15 g, 1.5 mmol), as described earlier for **9a** yielded **9b** (0.15 g, 61%) as a mixture of *endo* and *exo* isomers. The unreacted furanone (0.047 g) was recovered. IR (KBr): 3258, 3076, 2962, 2854, 2780, 1775, 1721, 1627, 1479, 1458, 1404, 1351, 1256, 1050, 811 cm^{-1}. ^{1}H NMR: δ 9.51 (s, 1H), 9.18 (s, 1H), 7.28 (m, 2H), 7.03 (t, J = 8.84 Hz, 1H), 6.81 (t, J = 8.55 Hz, 1H), 6.53 (m, 2H), 6.23 (m, 2H), 4.37 (m, 4H), 4.05 (m, 3H), 3.53 (m, 3H), 1.38 (m, 6H). ^{13}C NMR: δ 176.61, 176.17, 173.77, 173.66, 165.84, 165.05, 164.78, 162.80, 161.05, 160.84, 146.88, 145.74, 133.26, 132.49, 132.36, 130.06, 122.82, 122.08, 115.22, 113.85, 84.64, 84.05, 61.77, 61.72, 48.66, 48.21, 45.16, 44.46, 37.39, 36.84, 14.14. HRMS calcd for $C_{16}H_{13}O_6N$ (M^+): 315.07428, found 315.07436.

Data for compound **9c**

Reaction of **1b** (0.2 g, 1.1 mmol) with *N*-phenylmaleimide (0.25 g, 1.5 mmol), as described earlier for **9a** yielded **9c** (0.323 g, 92%) as an *endo* isomer (m.p. 110-113 °C) with a trace amount of *exo* isomer. The unreacted furanone (0.017 g) was recovered. IR (KBr): 3064, 2913, 1768, 1710, 1682, 1610, 1581, 1509, 1386, 1300, 1242 cm $^{-1}$. ^{1}H NMR: δ 7.48 (m, 4H), 7.12 (d, J = 6.84 Hz, 2H), 6.98 (m, 1H), 6.66 (m, 1H), 6.35 (m, 1H), 4.20 (m, 1H), 4.01 (d, J = 9.80 Hz, 1H), 3.79 (m, 1H), 2.48 (s, 3H). ^{13}C NMR: δ 193.95, 174.85, 172.87, 169.00, 161.85, 148.07, 133.93, 132.05, 128.94, 128.63, 126.71, 122.33, 112.14, 85.07, 47.97, 43.14, 37.62, 29.24. HRMS calcd for $C_{21}H_{15}O_5N$ (M^+): 361.09503, found 361.09420.

Data for compound **9d**

Reaction of **1b** (0.1 g, 0.53 mmol) with maleimide (0.077 g, 0.79 mmol), as described earlier for **9a** yielded **9d** (0.063 g, 69%) as an *endo* isomer (m.p. 180-183 °C) with a trace amount of *exo* isomer. The unreacted furanone (0.04 g) was recovered. IR (KBr): 3184, 2962, 1769, 1715, 1674, 1600, 1573, 1398, 1344, 1283, 1189, 1108, 825 cm^{-1}. ^{1}H NMR: δ 10.3 (s, 1H), 7.19 (m, 2H), 6.81 (m, 1H), 6.14 (m, 1H), 3.97 (m, 1H), 3.74 (d, J = 9.87 Hz, 1H), 3.55 (m, 1H), 2.36 (s, 3H). ^{13}C NMR: δ 194.06, 176.44, 174.54, 169.33, 165.31, 162.23, 148.02, 133.97, 131.86, 122.24, 84.98, 48.48, 44.41, 37.85, 29.26. Analysis calcd. for $C_{15}H_{11}O_5N$: C 63.16%, H 3.89%; N 4.91, found: C 63.22%, H 3.97%, N 4.93 %.

Data for compounds **11a** and **11b**

Ethyl 2-oxo-2H-cyclohepta[b]furan-3-carboxylate **1a** (0.109 g,0.5 mmol) and acenaphthylene (0.22 g, 1.5 mmol) in dry toluene (0.5 mL) were sealed under argon in a Schlenk tube and heated at 160 °C for 20 h. The reaction mixture was chromatographed on silica gel column. Elution with 5% ethylacetate-hexane afforded **11a** (0.058 g, 47%) and **11b** (0.046 g, 39%) as colourless solids. The products were crystallized from dichloromethane-hexane as colourless crystals, m.p. 144-147 °C and 188-190 °C, respectively. The unreacted furanone (0.036 g) was recovered.

Endo adduct **11a** IR (KBr): 2355, 1767, 1706, 1613, 1398, 1255, 1205, 1029, 782 cm^{-1}. ^{1}H NMR: δ 7.48 (m, 8H), 5.95 (m, 1H), 5.79 (d, J = 8.79 Hz, 1H), 4.42 (q, J = 7.08 Hz, 2H), 4.18 (d, J = 7.73 Hz, 1H), 4.07 (t, J = 7.90 Hz, 1H), 3.93 (m, 1H), 1.43 (t, J = 7.18 Hz, 3H). ^{13}C NMR: δ 168.11, 168.04, 161.52, 149.27, 144.81, 141.32, 140.67,131.28, 130.91, 129.74, 128.26, 127.51, 123.93, 123.57, 123.46, 121.34, 118.27, 112.67, 87.31, 61.40, 52.86, 47.84,42.72, 14.17. Analysis calcd. for $C_{24}H_{18}O_4$: C 77.82%, H 4.89%; found: C 77.83%, H 4.80%.

Exo **adduct 11b [18]**

Data for compounds **12a** and **12b**

Reaction of **1b** (0.1 g, 0.53 mmol) with acenaphthylene (0.12 g, 0.79 mmol), as described earlier for **11a & 11b** yielded **12a** (0.049 g, 52%) and **12b** (0.021 g, 22%) as colourless solids. The products were crystallized from dichloromethane-hexane as colourless crystals, m.p. 137-140 °C and 177-180 °C, respectively. The unreacted furanone (0.048 g) was recovered.

Endo adduct **12a** IR (KBr): 2341, 1753, 1683, 1608, 1517, 1489, 1404, 1360, 1250, 1020, 783 cm^{-1}. ^1H NMR: δ 7.51 (m, 8H), 5.78 (m, 1H), 5.62 (d, J = 8.73 Hz, 1H), 4.02 (d, J = 7.50 Hz, 1H), 3.92 (t, J = 7.56 Hz, 1H), 3.79 (m, 1H), 2.52 (s, 3H). ^{13}C NMR: δ 195.40, 170.34, 167.85, 150.75, 144.90, 141.45, 140.43, 131.39, 131.08, 129.34, 128.32, 127.78, 124.07, 123.67, 123.07, 121.85, 118.40, 118.02, 87.66, 53.08, 47.94, 43.22, 30.50. HRMS calcd for $C_{23}H_{16}O_3$ (M^+): 340.10995, found 340.10998.

Exo adduct **12b**

IR (KBr): 2371, 1756, 1685, 1605, 1564, 1397, 1361, 1294, 1249, 1200, 1009, 783 cm^{-1}. ^1H NMR: δ 7.53 (m, 6H), 7.25 (d, J = 6.51 Hz, 1H), 7.15 (m, 1H), 5.92 (m, 1H), 5.77 (d, J = 8.72 Hz, 1H), 4.16 (d, J = 7.63 Hz, 1H), 4.06 (m, 1H), 3.89 (m, 1H), 2.65 (s, 3H). ^{13}C NMR: δ 194.56, 170.38, 167.98, 150.68, 145.19, 141.72, 140.70, 133.75, 131.95, 128.70, 127.88, 127.72, 124.40, 124.06, 122.34, 120.50, 118.66, 118.58, 88.42, 53.48, 48.36, 43.62, 30.78. Analysis calcd. for $C_{23}H_{16}O_3$: C 81.16%, H 4.74%; found: C 80.68%, H 5.11%. HRMS calcd for $C_{23}H_{16}O_3$ (M^+): 340.10995, found 340.10998.

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