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# Peri-, Regio- and Stereoselectivities in Thermal Addition of Tropone to Allenic Esters

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**Abstract:** Thermal addition of tropone to allenic esters ($RR_1C=C=CHCO_2Et$, **Ia**, $R=R_1=H$; **Ib**, $R=H$, $R_1=CH_3$; **Ic**, $R=H$, $R_1=CH_3CH_2$; **Id**, $R=CH_3$, $R_1=CH_3CH_2$) furnishes 4+2 cycloadducts as major products, unlike the reported additions of tropone involving a few other allenic systems. The additions display $\pi$-facial selectivity resulting in preference for E geometry at the exocyclic double bond in the obtained adducts.

Of the many allowed modes of cycloadditions involving polyolefines, only a few are observed and this phenomenon of peri-selectivity is particularly interesting in case of additions involving troponoid systems. Tropones (and heptafulvenes) are anticipated, according to Woodward-Hoffmann rules[1] and their recent advancements[2], to react as $6\pi$ systems with dienes (6+4 cycloadditions), as $8\pi$ systems with electron deficient dienes (8+2 cycloadditions) and in 4+2 manner with electron rich dienophiles. However, the observed modes of additions have often defied the above predictions[3]. In the reported addition of tropone to phenyl- sulphonylallene[4a], tetraethyl-allenetetracarboxylate[4b] and heterocumulenes[5], only 8+2 cycloadducts have been obtained. We have now observed that thermal addition of tropone to allenic esters $\mathbf{1}_{\mathbf{a-d}}$ affords mainly 4+2 cycloadducts (total yield $\geq$ 30%)[6a]. However, the reactions of **1a, b** yield also 8+2 cycloadducts as minor products. In this paper, we report on the complete peri-,regio-and stereoselectivities in these reactions. The observed cycloadditions implicate mainly the electron deficient $C_2$-$C_3\pi$ bond of the allenic esters **1a-d**, albeit, in case of **1a-c** (4+2 mode), minor products result through addition involving the $C_3$-$C_4\pi$ bond as well. The 4+2 cycloadditions display $\pi$-facial selectivity leading to preference for E-geometry at the exocyclic double bond in the products. A rationalisation of the obtained results is proffered.

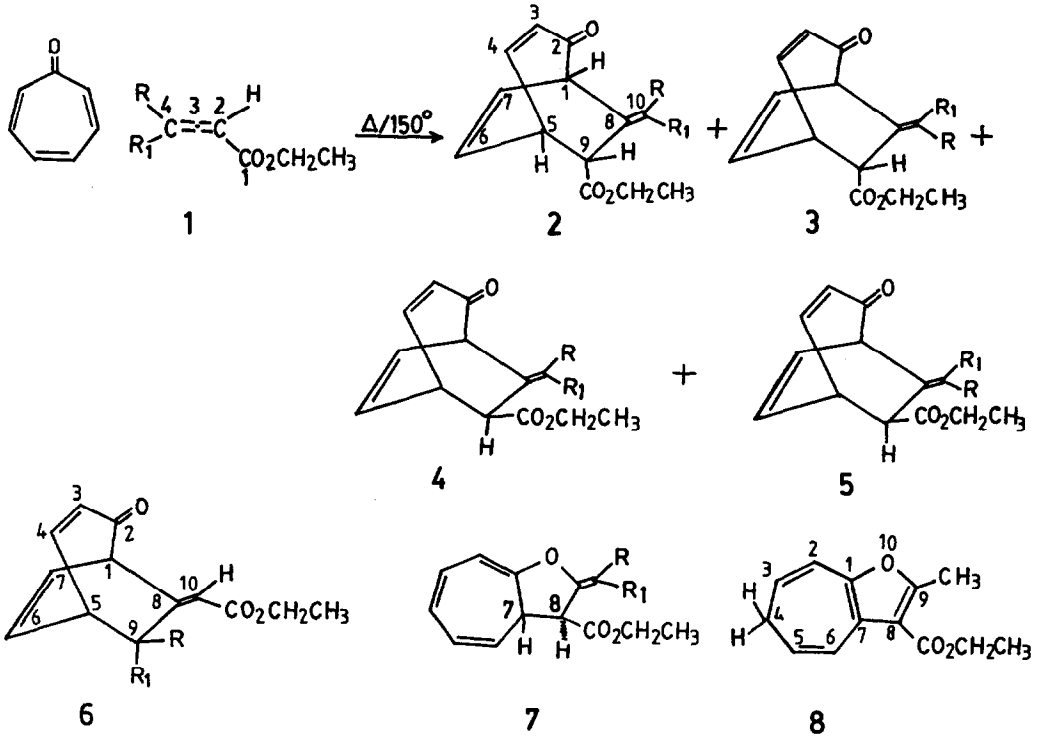
The various additions have been carried out by heating an equimolar mixture of tropone and allenic ester (neat) at bath temperature of 150°C

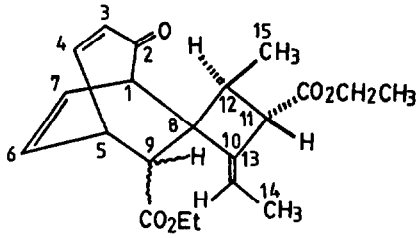
(under $N_2$) and the products resolved using chromatotron-2 and column chromatograhy. The assigned structures are based, interalia, on UV, IR, $^1$HNMR, $^{13}$C NMR and mass spectral analyses.

The structure of 1:1 4+2 cycloadducts **2-6** is based on comparison of their spectral data (vide experimental) with that of the known 4+2 cycloadducts of tropone[3a,b,d,7]. However, the orientation of tropone moiety in the compounds **2-6** is based on the absence of coupling between $C_1$-H and $C_9$-Hs; $C_1$-H resonance, $\delta$ 3.92 **(2a)** and $\delta$ 4.27 **(3d)**, is easily identified (through homodecoupling experiments) from its LR coupling ($J_{1,3}$ ~ 2Hz) with $C_3$-H. The assigned expressions are also supported by $\delta$ $^{13}$C values for $C_1$ (60-64 ppm). The endo/exo orientation of the ethoxycarbonyl group at $C_9$ in adducts **2-5** is based [8,3 a,b,d], interalia, on $J_{5,9}$ which varied from 4-5 Hz in the exo-adducts (endo $C_9$-H, **4,5**) as compared with $J_{5,9}$ ~ 0-2 Hz in case of the endo adducts **2,3**. The assigned geometry at the exocyclic double bond in the adducts, **2b,c,d - 5b,c,d**, is based on comparison of allylic and homoallylic couplings within pairs of endo-adducts **2b,3b; 2c,3c; 2d,3d** and exo-adducts **4b,5b; 4c,5c; 4d,5d** and $^{13}$C chemical shifts for $C_1$ and $C_9$ within pairs of geometric isomers with reference to corresponding $\delta$ $^{13}$C values for $C_1$ and $C_9$ in **2a** and **4a** [cf.9]. The compounds **6a-c** were identified further by the presence of an 1H (olefinic H) signal in the $^1$H NMR spectrum [$\delta$ 5.99, t, J=2.17, **6a**; $\delta$ 6.00, m, **6b**; $\delta$ 5.94, bs, **6c**] and chemical shifts and multiplicity of $C_9$-Hs (vide experimental). The endo-orientation of alkyl groups at $C_9$ in **6b,c** followed from $^1$H NMR chemical shifts of $C_9$ alkyl hydrogens [$\delta$ 1.04, d, J=6.75, **6b**; $\delta$ 1.39, m, **6c**][10] and $J_{5,9}$[8,3a,b,d]. Although, **6b** and **6c** appeared each to be a single $C_{10}$ double bond isomer, the assigned geometry (E) is tenative here, and is based on the observed preferential formation of **6a**-E (in mixture with **6a**-Z, vide experimental)[6b].

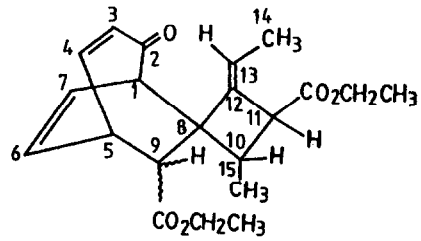
The compound **7b**, obtained as a minor product (4%) from the reaction of tropone with **1b**, gave spectral data in conformity with the known 8+2 cycloadducts of tropone[3,4]. The assigned trans-geometry at $C_7$- $C_8$ bond in **7b** is based on a low value of $J_{vic}$=3.5 Hz. However, the projected geometry at the exocyclic double bond in **7b** is tentative and follows essentially from mechanistic considerations and the presently-observed geometric preferences at the exocyclic double bond in the adducts **2,3,5** and **6**. The adduct **8**, derived from **1a** and tropone (10.2% yield), may have formed by 1,5 - and 1,3-H shifts of $C_7$ and $C_8$-H respectively in the initial 8+2 cycloadduct **7a**[6c]. Such a rearrangement of 8+2 adducts of tropone and allenic sulphones has been reported earlier[4a] and was shown to involve prototropic shifts

catalysed by the acidic surface of the reaction vessel. Again, from the reaction of tropone and **1b**, two 1:2 4+2 adducts (m/z 358, $M^+$) were isolated in low yield (~ 4% each), which have been tentatively assigned expressions, **9** (E and Z) and **10** (E and Z)[11]. Here, the regiochemistry of tropone addition has been ascertained from $C_1$-H coupling, revealed only with $C_{3-H}$ and $C_7$-H (homodecoupling), and downfield shift of C=O resonance ($\delta$ 202) with respect to $\delta$ C=O in other 4+2 adducts (~ $\delta$ 192) indicating loss of alkylidene group at $C_8$[cf.12]. The trans stereochemistry on the cyclobutane ring in **9** (E and Z) is based on low value of $J_{11,12}$ = 3.6 Hz, albeit, in **10** (E and Z), the value of $J_{11,12}$ = 5.62 Hz did not permit any stereochemical conclusions[13]. The endo orientation of ethoxycarbonylgroup at $C_9$ and the stereochemistry at the exocyclic double bond (cyclobutane ring) in **9** & **10** have been arrived at by considerations similar to those outlined above; the latter conclusions required use of allylic and homoallylic couplings.



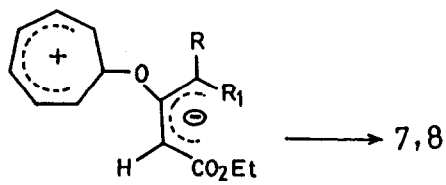


9(ExZ)



10(ExZ)

The preferred formation of 4+2 cycloadducts in the present work has been attributed, in our preliminary communication[6], to decreased electrophilicity of the central allenic carbon (**1b,c,d**) leading to suppression of the zwitterion **A**, believed to be an intermediate in the formation of 8+2 cycloadducts[cf.4]. This postulation is now further supported by the reaction of tropone with ester **1a** (which differs from esters **1b-d** in that this does not possess an electron releasing alkyl group at $C_4$) wherein an 8+2 cycloadduct **7a** is obtained in sizeable yield (> 10%).



A

The 4+2 addition of tropone to $C_2$-$C_3\pi$ bond of allenic esters can best be described as addition of an electron deficient diene to an electron deficient dienophile. For such additions, the difference in the energetics of a two-step and a concerted mechanism is not very high[2a], and a loss of selectivities is anticipated. However, the observed selectivities in this work i.e., endoselectivities, orientation of tropone moiety in the 4+2 cycloadducts and preference for E-geometry at the exocyclic double bond, a consequence of $\pi$-facial selectivity due to approach of the diene from the less hindered side, in **2-5**, are rationalised in terms of polar concerted cycloadditions where additional (polar) interactions lead to observed preferences [6a,9]. It may be mentioned here that a two-step mechanism involving polar intermediates has been proposed for 4+2 addition of tropone

to some electron deficient dienophiles[3a,5b].

The addition of tropone to $C_3$-$C_4\pi$ bond of allenic esters **1a-c** leading to adducts **6a-c** may be viewed as a concerted addition in order to explain the preference for E geometry at the exocyclic double bond (in **6a-c**) and endo orientation of the alkyl groups, in **6b,c**. The endoselectivity of alkyl groups in concerted 4+2 additions has been the subject of discussion in the recent literature[14].

**EXPERIMENTAL**

General: Tropone and allenic esters[6a,9] **1a-d** were prepared according to literature methods. Infrared spectra were recorded on the Unicam SP-1200 and Nicolet-5DX fourier transform spectrometers. $^1H$ and $^{13}C$ NMR spectra were recorded on a Jeol-JNM FX-100 NMR spectrometer (99.55 MHz for $^1H$ and 24.99 MHz for $^{13}C$ nuclei) using TMS as internal standard and $CDCl_3$ as solvent; J values are reported in Hz. Mass and GCMS spectra were obtained on a Jeol-JMS-D 300 spectrometer. Silica gel used for column chromatrography was 60-120 mesh (E.Merck). Petroleum ether refers to 60-80° fraction.

**Thermal addition of tropone to ethyl buta-2, 3-dienoate (1a)**

Freshly distilled 1a (500 mg) and tropone (570 mg) were mixed in a 25 ml Rb flask, provided with a reflux condenser. The system was evacuated and filled with $N_2$ and was linked to a $N_2$ line through top of the condenser. The contents were heated at oil bath temperature of 150-155°C for 4h. when near total consumption of **1a** was observed (TLC). On cooling, a dark brown gummy material resulted. It was loaded onto Chromatotron-2(Harrison research, silica gel PF-254, Merck, 2mm). Elution with hexane-ethyl acetate gradient (5ml/min.) yielded : **8**, light yellow viscous material, 120 mg (10.2%), IR($CCI_4$): 1710 (ester C=0), 1620, 1600, 1540, 1500, 1460, 1380 $cm^{-1}$, $^1H$ NMR: $\delta$ 6.91 (bd, 1H, J 9.77), 6.55 (bd, 1H, J 8.45), 5.40 (m, 2H, $C_3$-H and $C_5$-H), 4.30 (q, 2H, J 7.10, -$OCH_2$-), 2.62 (t, 2H, J 6.5, $C_4$-Hs), 1.62 (s,3H, $C_9$-$CH_3$), 1.26 (t,3H), $^{13}C$ NMR: $\delta$ 166.6 (C-0), 154.3, 149.0 ($C_9$, $C_1$), 129.7, 128.5, 126.7, 124.3, 111.8, 108.2, 61.6, 31.9, 18.6, 14.0, mass: m/z 218 (5, $M^+$), 190, 172, 154, 112, 97, 95, 94, 85, 83, 77, 71, 69, 65, 57, 55, 43 (100); a colourless viscous oil (mixture of tetramers of **1a**), 80 mg, IR ($CCl_4$) : 1742, 1714, 1609 $cm^{-1}$, $^1H$ NMR : $\delta$ 7.24-6.84(m), 4.14 (q, J 7.10), 3.72 (q,J 7.60), 3.15 (d, J 7.60), 2.71 (dd, J 5.98, J 3.16), 2.24(d,J 7.60), 1.25 and 1.20 (overlapping triplets), $^{13}C$ NMR: $\delta$ 169.8, 166.5, 141.6, 133.1, 129.8, 128.1, 122.0, 118.0, 113.8, 111.7, 61.8, 61.5, 31.9, 30.5, 28.6, 26.4, 22.6, 14.3, 14.1, 14.1, mass: m/z 449 (5, $M^+$+1), 448 (25, $M^+$), 284, 283, 261, 236, 235, 219, 194, 193, 179, 165, 164, 149, 148, 147, 145, 121(100); **2a**, light yellow gummy material, 200 mg (17%), IR ($CCl_4$): 1735

(ester C=0), 1672 (α,ß- unsaturated C=0) $cm^{-1}$, $^1H$ NMR: δ6.98 (dd, 1H, $C_4$-H, $J_{3,4}$ 11.23, $J_{4,5}$ 8.65), 6.55 (dd, 1H, $C_6$-H, $J_{6,7}$ 8.6, $J_{5,6}$ 7.85), 6.17 (dd, 1H, $C_7$-H, $J_{1,7}$ 6.84), 5.78 (split d, 1H, $C_3$-H, $J_{1,3}$ 2.0), 5.39 (bs, 2H, $C_{10}$-Hs), 4.13 (q, J 7.1, $-OCH_2-$,overlapping $C_1$-H resonances), 3.80-3.52(m, 2H, $C_5$-H and $C_9$-H, $J_{5,9}$0), 1.26 (t, 3H), $^{13}C$ NMR: 192.3 ($C_2$), 149.7 ($C_4$), 136.4 ($C_7$), 133.0, 130.3, 129.2, 125.2, 121.9, 118.2, 62.3($C_1$), 60.2($-OCH_2-$), 48.3($C_9$), 38.4($C_5$), 14.3, mass; m/z 219 (10, $M^+$ +1), 218 (30,$M^+$), 190, 189, 173, 172, 145(100), 144, 117, 116, 115, 105, 91, 77, 65, 63, 55; **4a**, light yellow semisolid, 90 mg (7.7%), IR ($CCl_4$): 1730 (ester C=0), 1670 (α,ß- unsaturated C=0) $cm^{-1}$, $^1H$ NMR : δ 7.01 (dd, 1H, $C_4$-H, $J_{4.5}$ 8.80, $J_{3,4}$ 11.11), 6.70 (dd, 1H, $C_6$-H, $J_{6,7}$ 8.34, $J_{5,6}$ 7.30), 6.10 (t, 1H, $C_7$-H, $J_{1.7}$ 6.95), 5.80 (split d, 1H, $C_3$-H, $J_{1,3}$ 2.05), 5.45 (bs, 2H, $C_{10}$-Hs), 4.20 (q, J 7.10, $-OCH_2-$, overlapping $C_1$-H resonance), 3.42 (m, 1H, $C_5$-H, $J_{5,9}$ 4.35), 2.86 (m, 1H, $C_9$-H), 1.26 (t, 3H), $^{13}C$ NMR: δ 193.6($C_2$), 170.4, 150.8 ($C_4$), 139.1, 131.2, 128.5, 125.4, 119.6, 61.6, 60.5, 49.4, 38.0, 14.2, mass: m/z 218 (15, $M^+$), 185, 173, 172, 155, 150, 149, 141, 138, 116, 115, 105, 91, 77, 28(100); **6a-E**, light yellow gummy material, 80 mg (7%), IR($CCl_4$): 1720 (ester C=0), 1680 (α,ß-unsaturated C=0), $^1H$ NMR: δ7.14 (dd, 1H, $C_4$-H, $J_{4,5}$ 8.78, $J_{3,4}$ 11.11), 6.65 (dd, 1H, $C_6$-H, $J_{6.7}$, 8.46, $J_{5,6}$ 7.75), 6.15 (t,1H, C7-H, $J_{1,7}$ 7.33), 5.99 (t,1H, $C_{10}$-H, J 2.17). 5.72 (split d, 1H, $C_3$-H, $J_{1,3}$ 1.85), 4.15 (q, J 7.1, overlapping $C_1$-H resonance at 4.2), 3.60 - 3.20 (m, 2H, $C_5$-H, $J_{5,9}$ 0), 2.83 (m,1H, $C_{9a}$-H, $J_{5.9}$ 4.91, $J_{9\alpha,10}$ 2.85), 1.26(t, 3H), $^{13}C$ NMR : δ 191.8 ($C_2$), 165.7 (ester C=0), 153.7 ($C_4$), 138.3 ($C_7$), 129.5, 129.1, 125.3, 118.8, 64.9 ($C_1$), 60.0 ($OCH_2$), 35.7, 34.6 ($C_5$, $C_9$), 14.2, mass: m/z 219 (10, $M^+$+1), 218(70,$M^+$), 163, 152, 149, 144, 125, 97, 77(100); **6a**, a mixture (2:1) of **6a-E** with **6a-Z** as light yellow gummy material, 40 mg, $^1H$ NMR (critical assignments): δ3.64-3.20(m, $C_5$-H and $C_{9ß}$-H), 2.64 (m,$C_{9\alpha}$ -H, $J_{9,5}$, 4.45, $J_{9a,10}$ 3.28); a light yellow semisolid, 35 mg (unidentified), IR($CCl_4$); 1710, 1590, 1480, 1460, 1380, 1260, 1120 $cm^{-1}$, $^1H$ NMR: δ7.29(m), 4.30 (t,J 6.60), 3.36 (m) (integral ratio 5:1:1), 1.52(m), 1.25(t), $^{13}C$ NMR: δ142.3, 134.1, 129.8, 127.6, 126.2, 121.9, 61.7, 33.7, 29.4, 28.9, 13.9, mass: m/z 218(25,$M^+$), 77(100).

**Thermal addition of tropone to ethyl penta-2,3-dienoate (1b)**

Freshly distilled tropone (440 mg) and **1b** (500 mg) were mixed and heated under conditions as described above, for 4h. The dark brown viscous material was loaded on a silica gel column (30g, column packed in hexane). Development of the column with hexane, hexane-benzene gradient, benzene followed by benzene-ethyl acetate gradient afforded: **7b**, light yellow viscous oil, 40 mg (4%), UV(EtOH): 310 (ε=4420), 215 (ε=16430) nm, IR (neat): 1730 ester C=O), 1620, 1600, 1560, 1440, 1380, 1270 and 1245 $cm^{-1}$,

$^1$H NMR: δ6.64-6.07 (m, 3H, $C_3$-H, $C_4$-H and $C_5$-H), 5.82 (m, 1H, $C_6$-H), 5.24-4.90 (m, 2H, $C_2$-H and $C_{11}$-H), 4.20 (q,2H, J 7.08,-O-$CH_2$-), 3.89 (m, 1H, $C_8$-H, $J_{7,8}$ 3.50, $J_{8,11}$ 1.49), 2.88(m, 1H, $C_7$-H), 1.64 (split d, 3H, $C_{11}$-$CH_3$, J 6.86, $J_{8,12}$ 0.95), 1.24(t,3H), $^{13}$C NMR: δ170.8 (ester C=0), 148.0 and 140.0 ($C_1$, $C_9$), 129.2, 127.3, 124.4, 120.1, 98.8 and 95.9 ($C_{11}$, $C_2$), 61.5, 49.7 ($C_8$), 44.2 ($C_7$), 15.2, 14.2, mass: m/z 232 (20, $M^+$), 203, 186, 161, 159, 158, 146, 117, 105, 91, 85, 55, 28(100); **2b**, light yellow semisolid, 90 mg, UV (EtOH): 239 (ε =7120)nm, IR ($CCl_4$): 1726 (ester C=0), 1670 (α,ß-unsaturated C=0)$cm^{-1}$, $^1$H NMR: δ 6.95 (dd, 1H, $C_4$-H, $J_{4,5}$ 8.78, $J_{3,4}$ 10.98), 6.42 (b dd,1H, $C_6$-H $J_{6,7}$ 6.36, $J_{5,6}$ 7.17), 6.17 (split dd, 1H, $C_7$-H, $J_{1,7}$ 7.50, $J_{5,7}$ 1.60),5.95-5.48 [m,2H (5.82, q, $C_{10}$-H, $J_{10,11}$ 6.86), (5.73, split d, $C_3$-H, $J_{1,3}$ 1.65)], 4.28-3.96 [m,3H (4.12, q,-O-$CH_2$-, J 7.08), overlapping $C_7$-H around δ 4.14 (m)], 3.88-3.62 (m,2H,$C_5$-H and $C_9$- H, $J_{5,9}$ ≈ 0), 1.62 (bd, 3H, $C_{10}$-$CH_3$), 1.25 (t, 3H), $^{13}$C NMR: δ 194.6($C_2$), 171.2, 149.1 ($C_4$), 138.6, 135.4, 130.3, 128.7 and 126.8 ($C_8$, $C_6$, $C_7$, $C_{10}$ and $C_3$), 62.1 ($C_1$), 61.2 (-$OCH_2$-), 46.9 ($C_9$), 39.5($C_5$), 15.5 and 14.1, mass: m/z 232 (35,$M^+$), 203, 186, 160, 149, 148, 141, 131, 130, 129, 116, 91, 77, 55, 28(100); a mixture (2:1) of **2b** and **3b** (100 mg), total: **2b** 16.6%, **3b** 4%, IR ($CCl_4$): 1725(b), 1670 $cm^{-1}$, $^1$H NMR (signals due to **3b** and those overlapping with **2b**: δ 7.12 (dd, $C_4$-H, $J_{4,5}$ 8.79, $J_{3,4}$ 10.86), 6.62 (spilt t, $C_6$-H, $J_{6,7}$ 8.36, $J_{5,6}$ 7.06, $J_{1,6}$ , 1.49), 6.06 (split t, $C_7$-H, $J_{1,7}$ 7.89, $J_{5,7}$ 0.92), 5.88 - 5.38 [m, $C_3$-H and $C_{10}$-H (δ 5.52, split q, $C_{10}$-H in **3b**, $J_{10,11}$ 7.0, $J_{9,10}$ - 2.40)], 4.15(bq, J 7.08, overlapping $C_1$-H resonances), 3.90-3.98 (m, $C_5$-H and $C_9$-H), 1.55 (split d, $C_{10}$-Me, $J_{9,11}$ 1.30, $J_{10,11}$ 7.0), 1.25 (t), $^{13}$C NMR (resonances assigned to **3b** from paired signals): δ 193.5 ($C_2$), 171.7, 149.6, ($C_4$), 137.4, 135.2, 129.1, 127.9 and 126.5 (olefinic Cs), 61.8, 60.0 ($C_1$), 47.6 ($C_9$), 39.8 ($C_5$), 15.2 and 14.3; **4b**, light yellow semisolid (50 mg), UV (EtOH): 237 (ε=7120)nm, IR ($CCI_4$): 1728, 1665$cm^{-1}$, $^1$H NMR : δ 6.89 (dd,1H,$C_4$-H, $J_{3,4}$ 10.90, $J_{4,5}$ 8.30), 6.62 (split t, 1H, $C_6$-H, $J_{6,7}$ 8.09, $J_{5,6}$ 7.08, $J_{1,6}$ 1.0), 6.25 (split t, IH, $C_7$-H, $J_{1,7}$ 7.10, $J_{5,7}$ 1.22), 5.90 (split d, 1H $C_3$-H, $J_{1,3}$ 2.0), 5.52 (split q, 1H, $C_{10}$- H, $J_{10,11}$, 7.02, $J_{9,10}$ 1.85), 4.16 (q, J 7.08, -O-$CH_2$-, overlapped $C_1$-H resonance at δ 3.98-3.87), 3.75 (m,1H,$C_5$-H), 3.56 (m, 1H, $C_9$- H, $J_{5,9}$ 5.53), 1.52 (split d, 3H, $C_{11}$-Hs, $J_{9,11}$ 1.34), 1.25 (t, 3H), $^{13}$C NMR: δ 193.2 ($C_2$), 170.9, 149.5 ($C_4$), 137.0, 135.6, 130.7, 129.4, 126.8, 63.6 ($C_1$), 60.8, 47.9 ($C_9$), 39.5 (Cs), 15.4, 14.1; mass: m/z 232 (15, $M^+$), 208, 186, 159, 148, 131, 130, 126, 105, 91, 85, 77, 57, 55, 28(100; a mixtue (2:1) of **4b** with **5b** (40 mg), total: 4b 7.5%, 5b, 2.1%), $^1$H NMR (resonances assigned to **5b** and those overlapping with **4b**: δ 7.10 (dd, $C_4$-H), 6.52 (split t, $C_6$-H), 6.04 (split t, $C_7$-H, $J_{5,7}$ 2.3), 5.98-5.44 (m, $C_3$ and $C_{10}$-Hs), 4.16 (q, overlapping $C_1$-H resonances at δ 3.98-3.87), 3.82-3.65 (m, $C_5$-Hs), 3.60-3.46 (m, $C_9$-Hs), 1.60 (spit d, $C_{10}$-Me, $J_{10,11}$ 7.0, $J_{9,11}$ 2.10), 1.25 (bt), $^{13}$C NMR: δ 193.4

($C_2$), 149.7, 137.4 (b), 135.4, 129.5, 128.6, 127.1 ($C_4$, $C_7$, $C_6$, $C_{10}$ and $C_3$), 61.5 ($C_1$), 60.5, 48.8 ($C_9$), 39.5 (b), 15.6, 14.1; **6b**, light yellow thick oil, 36 mg, IR ($CCl_4$): 1720 (ester C=0), 1675 (α,ß-unsaturated C=0)$cm^{-1}$, $^1H$ NMR ($CDCl_3$): δ 7.09 (dd, 1H, $C_4$-H, $J_{3,4}$ 10.5, $J_{4.5}$ 8.20), 6.58 (bt, 1H, $C_6$-H, J 8.3Hz), 6.20 (bt, 1H, $C_7$-H), 6.00 (bs, 1H, $C_{10}$-H), 5.78 (split d, 1H, $C_3$-H, $J_{1,3}$ 2.2), 4.18 (bq, 3H, J 7.08,-$OCH_2$-, overlapping $C_1$-H resonance), 3.78-3.28 (m, 2H,$C_5$-H and $C_9$-H, $J_{5,9}$ ≈ 4), 1.26 (t,3H, J 7.08), 1.02 (bd, 3H, J 6.5, $C_9$-$CH_3$), mass: m/z 232 (10,$M^+$), 204, 298, 297, 296, 172, 126, 105, 92(100) ; light yellow semi-solid, **9** (E&Z), 40 mg (4.2%), UV (EtOH): 232 (ε=5733), 282 (ε=630) nm, IR ($CCl_4$): 1720 (b), 1670 $cm^{-1}$, $^1H$ NMR (mixture of isomers, 5:1): δ 7:11 (dd, $C_4$-H, $J_{3,4}$ 10.75, $J_{4,5}$ 8.20), 6.60 (split t, $C_6$-H, $J_{5,6}$ 7.17, $J_{6,7}$ 8.76), 6.28-5.47 [m, δ 6.12 (split t, $C_{7-H}$, $J_{1,7}$ 7.16), 5.77 (split d, $C_3$-H, $J_{1,3}$ - 2.17), 5.60 (split q, $C_{13}$-H in 9-Z, $J_{13,14}$ 6.86, $J_{11,14}$ 2.02)], 5.34 (q,$C_{13-H}$ in E isomer, $J_{13,14}$ 7.40), 4.52 (dq, $C_{12}$-H, $J_{12,15}$ 6.47, $J_{11,12}$ 3.68), 4.19 and 4.16 (overlapping qs, J 7.01), 3.93-3.80 (m, $C_1$-H), 3.52-3.28 (m, $C_5$-H & $C_9$-H), 3.20 (m, $C_{11}$-H), 1.70 (split d, $C_{14}$-Hs of Z isomer, $J_{11,14}$ 2.02), 1.57 (bd, $C_{14}$-Hs of E isomer, $J_{13-14}$ 7.0), 1.32-1.09 (m, ester methyls and $C_{15}$-Hs), $^{13}C$ NMR: δ 202 ($C_2$), 171.5; 169.8 (ester C=0), 154.5 ($C_4$), 138.3, 130.2, 129.9, 127.8, 125.6, 117.9, 111.4, 67.4 ($C_6$), 61.1(-0-$CH_2$-), 60.0 ($C_1$), 55.9 ($C_{11}$) 43.1, 40.2, 38.7 ($C_5$,$C_9$, $C_{12}$), 18.9 ($C_{14}$), 14.2 and 13.3, mass: m/z 359 (3, $M^+$+1), 358 (15,$M^+$), 312, 285, 284, 259, 253, 252, 239, 238, 55(100); colourless gummy material (mixture of **10**-E/Z isomers, 1:1), 30mg (3.2%),UV (EtOH): 233 (ε = 6516)nm, IR ($CCl_4$): 1720 (b), 1680 $cm^{-1}$, $^1H$ NMR : δ 7.12 (dd, $C_4$-H, $J_{4,5}$ 8.76, $J_{3,4}$ 11.15), 6.60 (t, $C_6$-H, $J_{5,6}$, $J_{6,7}$ 7.09), 6.16 (bt, $C_7$-H, $J_{1,7}$ ≈ 7.0), 5.88 (m, $J_{1,3}$ ≈ 2.28), 5.68-5.24 (m, overlapping qs, $C_{13}$-H, $J_{13,14}$ 7.27 and 7.07), 4.36-3.96 [m (qs at δ 4.14 and 4.17), J 7.1, overlapping $C_1$-H], 3.64-3.08 (m, $C_5$-H, $C_9$-H and $C_{11}$H), 2.42 (m, $C_{12}$-H, $J_{12,15}$ 6.58, $J_{11,12}$ 5.62), 1.68 (bd, $C_{14}$-Hs of E isomer), 1.54 (split d, $C_{14}$-Hs of Z isomer, $J_{11,14}$ ≈ 2.88), 1.36-1.08 (m, ester methyls and $C_{15}$-Hs), mass: m/z 358(5, $M^+$), 329, 312, 285, 284, 256, 252, 105, 91, 28 (100), GCMS analysis: A 1% solution of the crude reaction product was subjected to GCMS analysis (SE30, 3mm x 3M, 120-250°C, 10°/min, He, 1.4 Kg/$cm^2$) when four peaks corresponding to 1:1 adducts of tropone with **1b** (m/z 232) appeared at retention times of 7.4, 7.7, 8.0 and 9.0 min. Other recognisable peaks were at retention times of 13.0 min. (m/z 378, dimer of **1b**), 14.7 min. and 15.0 min. (m/z 358, 1:2 adducts of tropone with **1b**). Other peaks appearing at retention times of 1.4 (m/z 162), 3.0 (m/z 155), 6.0 (m/z 207), 14.0 (m/z 259) and 16.0 (m/z 207) min. were not probed further.

**Thermal addition of tropone to ethyl hexa-2,3-dienoate (1c)**

Freshly distilled **1c** (500 mg) and tropone (380 mg) were mixed and heated at 150°C for 4h. under the conditions as described above. The dark brown gummy material was chromatographed on a silica gel column (30 gm, packed in hexane). Elution with hexane, hexane-benzene gradient, benzene, followed by benzene-ethyl acetate gradient afforded: **2c**, light yellow semisolid, 140 mg, UV (EtOH): 238 ($\epsilon$=3500)nm, IR ($CCl_4$): 1730 (ester C=0), 1680 ($\alpha$,ß-unsaturated C=0)$cm^{-1}$, $^1H$ NMR: $\delta$ 6.95 (dd, 1H, $C_4$-H, $J_{3,4}$ 11.54, $J_{4,5}$ 8.76), 6.46 (split dd, 1H,$C_6$-H, $J_{5,6}$ 7.16, $J_{6,7}$ 8.56, $J_{1,6}$ 1.06), 6.21 (split dd, 1H, $C_7$-H, $J_{1,7}$ 8.20, $J_{5,7}$ 1.46), 5.90-5.60 [m, $\delta$ 5.78 (split d, $C_3$-H, $J_{1,3}$ 2.27), $\delta$ 5.74 (bt, $C_{10}$-H, $J_{10,11}$ 7.36)], 4.15 q, -O-$CH_2$-, J 7.10, overlapping $C_1$-H resonance), 3.86-3.60 [m, $\delta$ 3.76 (m, $C_5$-H, $J_{5,9} \approx 0$), 2.70 (bs, $C_9$-H)], 2.07 (quintet, 2H, $C_{11}$-H, $J_{11,12}$ 7.36), 1.26 (t, 3H, J 7.10), 0.96 (t, 3H, $C_{12}$-Hs), $^{13}C$ NMR: $\delta$ 194.3, 171.2, 149.1 ($C_4$), 137.2, 134.0, 130.5, 127.9, 126.9, 62.1 ($C_1$), 61.2, 46.6 ($C_9$), 39.5, 23.4, 14.1, 13.3, mass: m/z 246 (20, $M^+$) 218, 201, 173, 172, 146, 145, 139, 92, 77, 55 (100); a mixture (1:1) of **2c** and **3c** (35 mg), total: **2c** 17.8%, **3c** 2%, IR ($CCl_4$): 1730(b), 1685(b) $cm^{-1}$, $^1H$ NMR (peaks assigned to **3c** and those overlapping with **2c**) : $\delta$ 7.14 (dd, $C_4$-H), 6.64 (dd, $C_6$-H), 6.06 (split dd, $C_7$-H), 5.94-5.60 (m, $C_3$-Hs in **2c** and **3c** and $C_{10}$-H in **2c**), 5.45 (split t, $C_{10}$-H, in **3c**, $J_{10,11}$ 7.0, $J_{9,10}$ 1.60), 4.30-3.94 (m, -$OCH_2$-and $C_1$-Hs in **2c** and **3c**), 3.88-3.52 (m, $C_5$-H and $C_9$-H), 1.64 (m, $C_{11}$-Hs, $J_{9,11} \approx 2.30$), 1.24 and 1.25 (overlapping ts), 0.96 (bt), mass: m/z 246 (15, $M^+$); **4c**, light yellow semisolid, 50 mg, UV (EtOH): 237 ($\epsilon$=5130)nm, IR($CCl_4$): 1725, 1670 $cm^{-1}$, $^1H$ NMR: $\delta$ 6.86 (dd, 1H, $C_4$-H, $J_{3,4}$ 10.90, $J_{4,5}$ 8.26), 6.50 (split dd, 1H, $C_6$-H, $C_{6,7}$ 8.65, $J_{5,6}$ 7.45, $J_{1,6}$ 0.99), 6.25 (split t, 1H, $C_7$-H, $J_{7,1}$ 8.06, $J_{5,7}$ 1.49), 5.81 (split d, 1H, $C_3$-H, $J_{1,3}$ 1.95), 5.62 (split t, 1H, $C_{10}$-H, $J_{10,11}$ 7.32, $J_{9,10}$ 2.19), 4.12 (q,-$OCH_2$-, J 7.06, overlapping $C_1$-H resonance at $\delta$ 3.98), 3.74 (m, 1H, $C_5$-H), 3.61 (m, 1H, $C_9$-H $J_{5,9}$ 4.50), 1.86 (b quintet, 2H, $C_{11}$-Hs), 1.25 (t, 3H),6.95 (t, 3H, J 7.32), $^{13}C$ NMR: $\delta$ 193.4 ($C_2$), 170.8, 144.8, 136.6, 135.5, 130.7, 129.8, 128.4, 64.8 ($C_1$), 60.9, 48.1 ($C_9$), 39.5 ($C_5$), 23.4, 14.1 and 13.2, mass: m/z 246 (5,$M^+$), 200, 173, 172, 149 (100); a mixture (1:1) of **4c** with **5c**, 24 mg, total: **4c** 7%, **5c** 1.4%, IR ($CCl_4$): 1725(b), 1670(b) $cm^{-1}$, $^1H$ NMR (peaks assigned to **5c** and those overlapping with **4c**): $\delta$ 6.96-6.76 (overlapping dds, $C_4$-H) 6.86-6.38 (overlapping ts, $C_6$-H), 6.38-6.08 (overlapping dds, $C_7$-H), 5.92 (split d, $C_3$-H, 5.38 (split t, $C_{10}$-H, $J_{9,10}$ 2.60, $J_{10,11}$ 7.16), 4.35-3.92 (m,-$OCH_2$- and $C_1$-H), 3.86-3.62 (m, $C_5$-H), 3.38 (m, $C_9$-H, $J_{9,11} \approx 2$), 1.25 (bt), 0.96 (bt), mass: m/z 246 (5, $M^+$); **6c**, gummy material, 30 mg (3.4%), IR ($CCl_4$): 1708 (conjugated ester C=0), 1680 $cm^{-1}$, $^1H$ NMR: $\delta$ 7.11 (dd, 1H, $C_4$-H, $J_{3,4}$ 11.15, $J_{4,5}$ 8.24), 6.60 (dd, 1H, $C_6$-H, $J_{6,7}$ 8.45, $J_{5,6}$ 7.13), 6.20 (dd, $C_7$-H, $J_{7,1}$ 7.85), 5.92 [bs, $C_{10}$-H, partially overlapping $C_3$-H at $\delta$ 5.88

(split d, $J_{1,3}$ 2.12)], 4.14 (q, $-OCH_2-$, J 7.1, overlapping $C_1$-H resonance), 3.80-3.12 (m, 2H, $C_5$-H and $C_9$-H, $J_{5,9} \approx 3.85$), 1.40 (m, $C_9-CH_2-$, overlapping triplet at $\delta$ 1.28), 0.92 (t,3H), mass: m/z 246 (15, $M^+$), 227, 192, 173 (100), 163. Later elutions gave dimers and trimers (mass) of **Ic**.

**Thermal addition of tropone to ethyl 4-methylhexa-2,3-dienoate (1d)**

Freshly distilled **1d** (600mg) and tropone (420 mg) were mixed and heated under the conditions as employed above. The crude dark brown product was chromatographed over silica gel (30 gm, column packed in pet ether). Elution with pet ether, pet ether - benzene gradient, benzene, followed by benzene-ethyl acetate gradient yielded: **2d**, light yellow gummy material, 135 mg, UV (EtOH): 235 ($\epsilon$=4972)nm, IR ($CCl_4$): 1730, 1680 $cm^{-1}$, $^1H$ NMR: $\delta$ 7.04 (dd, 1H,$C_4$-H, $J_{3,4}$ 11.45, $J_{4,5}$ 9.45), 6.60 (split t, 1H, $C_6$-H, $J_{6,7}$ 9.85, $J_{5,6}$ 7.17, $J_{1,6}$ 1.40), 6.30 (split t, 1H, $C_7$-H, $J_{1,7}$ 7.36, $J_{5,7}$ 1.19), 5.85 (split d, 1H, $C_3$-H, $J_{1,3}$ 2.0), 4.39 (split d, 1H, $C_1$-H), 4.12 (bq, 2H, J 7.10), 3.85-3.56 (m,2H, $C_5$-H and $C_9$-H), 2.25-1.52 (m, $C_{10}-CH_2-$ with $C_{10}-CH_3$ as a split singlet at $\delta$ 1.82, J $\approx$ 1.39), 1.24 (t, 3H), 0.96 (t, 3H, $C_{10}-CH_2-CH_3$): mass: m/z 261 (20, $M^+$+1), 260 (60,$M^+$), 232, 231, 215, 214, 187 (100); 1:1 mixture (75 mg), total: **2d** 17%, **3d** 4%, $^1H$ NMR (peaks assigned to **3d** and those overlapping with **2d**) : $\delta$ 7. 14-6.80 (m, 1H, $C_4$-H), 6.70-6.55 (two split ts, $C_6$-H), 6.34-5.96 (m, 1H, $C_7$-H), 5.85 and 5.79 (two split ds, $C_3$-H), 4.47 (split d, $C_1$-H), 4.12 (bq,$-OCH_2-$), 3.90-3.40 (m, $C_5$-H and $C_9$-H), 2.30-1.52 [m, $C_{10}-CH_2-$ with $C_{10}-CH_3$ as split singlets at $\delta$ 1.83 (**2d**) and 1.57 (**3d**), J $\approx$ 0.98], 1.24 (bt), 0.96 and 0.91 (ts, $C_{10}-CH_2-CH_3$); mixture ($\approx$ 5:1, 90 mg) of **4d** with **5d**, IR ($CCl_4$): 1730 (b), 1675 $cm^{-1}$, $^1H$ NNMR : $\delta$ 6.86 (overlapping dds, $C_4$-H, $J_{3,4}$ 11.0, $J_{4,5} \approx 8.5$), 6.64 (split t, $C_6$-H), 6.34 and 6.30 (overlapping dds ($C_7$-H), 5.89 and 5.84 (overlapping split ds, $C_3$-H), 4.38-4.24 (overlapping split dds, $C_1$-H), 4.12 (bq,$-OCH_2-$), 3.89-3.66 (m, $C_5$-H, $J_{4,5} \approx 4.0$), 3.42 (m, $C_9$-H), 2.35-1.54[m, $C_{10}-CH_2-$ with a split singlet at $\delta$ 1.80 (J 1.49, $C_{10}$-Me in **4d**)], 1.58 (bs, $C_{10}$-Me, **5d**), 1.26 (bt), 0.96 and 0.90 (overlapping ts), mass: m/z 260 (35, $M^+$); colourless viscous oil(?), 35 mg, UV (EtOH): 282 ($\epsilon$=8235), 233 ($\epsilon$=2700)nm, IR: 1718 (ester C=0), 1580, 1480, 1410 (C=C)$cm^{-1}$, $^1H$ NMR: $\delta$ 7.07 (d, 1H, $C_6$-H, J 6.97), 6.00 (d, 1H, $C_3$-H, J 2.13), 5.68 (d, 2H, $C_1$-Hs), 4.16 (q, J $\approx$7.07, $-OCH_2-$), 2.20-1.40 (m, $C_2-CH_2-$, $C_7$-H and $C_8$Hs), 1.40-1.0 (m), 0.91 (bt, $C_9$-Hs and $C_2-CH_2-CH_3$, $J_{8,9}$ 7.27), $^{13}C$ NMR: $\delta$ 166.3, 165.4, 128.8, 120, 119.0, 112.7, 111.4, 60.3, 37.4, 29.4, 27.8, 27.3, 19.4, 14.3, 12.5 and 10.3, mass: m/z 309 (2, $M^+$+1), 308 (15,$M^+$), 278, 263, 262, 235, 234, 233, 220, 173, 57 (100); a mixture of cyclobutane dimers of **1d**, 120mg, UV (EtOH): 280 ($\epsilon$ 8239), 230 ($\epsilon$ 3111)nm, IR($CCl_4$): 1725 (b), 1660 (w), 1590, 1460, 1440, 1380 $cm^{-1}$, $^1H$ NMR : $\delta$ 5.82 (bs), 4.14 (overlapping qs, J 7.08, $-OCH_2$), 3.79, 3.46, 3.32, 3.25 (singlets, cylobutane Hs), 2.50-1.40

(m at δ 1.82, 1.65, 1.49 and 1.42), 1.40-0.70 (m, overlapping triplets at δ 1.07, 0.99, 0.91, 0.84 and 0.78, J ≈ 7.48), $^{13}C$ NMR: δ 172.3, 172.0, 171.9, 166.3, 165.9, 165.8 and 165.6 (ester carbonyls), 146.9, 145.8, 145.5, 149.9, 131.5, 127.8, 127.4, 110.0, 109.5, 109.3 (olefinic Cs), 60.7, 60.4, 60.3, 59.7, 59.3 ($-OCH_2-$),54.1, 54.0, 51.6, 51.2, 50.8, 50.3, 47, 33.7, 30.0, 29.7, 29.1, 28.3, 27.8, 27.1, 26.1 ($-CH_2$), 25.2, 23.7, 19.4, 18.5, 17.8, 16.6 (methyls), 14.3, 14.2 ($O-CH_2-CH_3$), 12.7, 12.4, 11.5, 8.9, 8.7 ($-CH_2-CH_3$), mass: m/z 309 (3,$M^+$+1), 308 (60, $M^+$), 279, 264, 263, 262 (100).

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## References and Notes

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