Supplementary Information

Transient Absorption Studies of the Photo-Claisen and Photo-Fries Rearrangements

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Kinetic Modelling Equations

$$[\text{ExcitedState}]\,(t) = X_1 e^{-k_1 t} \tag{1}$$

$$[\text{PhO}^{\bullet} + \text{R}^{\bullet}](t) = \frac{k_1 X_1}{k_2 - k_1 + k_3}\left(e^{-k_1 t} - e^{-(k_2+k_3)t}\right) \tag{2}$$

$$[\text{Recombination Products}](t) = \frac{k_2 X_1}{k_2 + k_3} - \frac{k_2 X_1 e^{-k_1 t}}{(k_2 - k_1 + k_3)} + \frac{k_1 k_2 X_1 e^{-(k_2+k_3)t}}{(k_2 + k_3)(k_2 - k_1 + k_3)} \tag{3}$$

$$[\text{PhO}_e + \text{R}_e](t) = \frac{k_3 X_1}{k_2 + k_3} - \frac{k_3 X_1 e^{-k_1 t}}{(k_2 - k_1 + k_3)} + \frac{k_1 k_3 X_1 e^{-(k_2+k_3)t}}{(k_2 + k_3)(k_2 - k_1 + k_3)} \tag{4}$$

$$\text{Observed radical signal} = [PhO^{\bullet} + R^{\bullet}](t) + [PhO_e + R_e](t) \tag{5}$$

UV/Visible Spectra

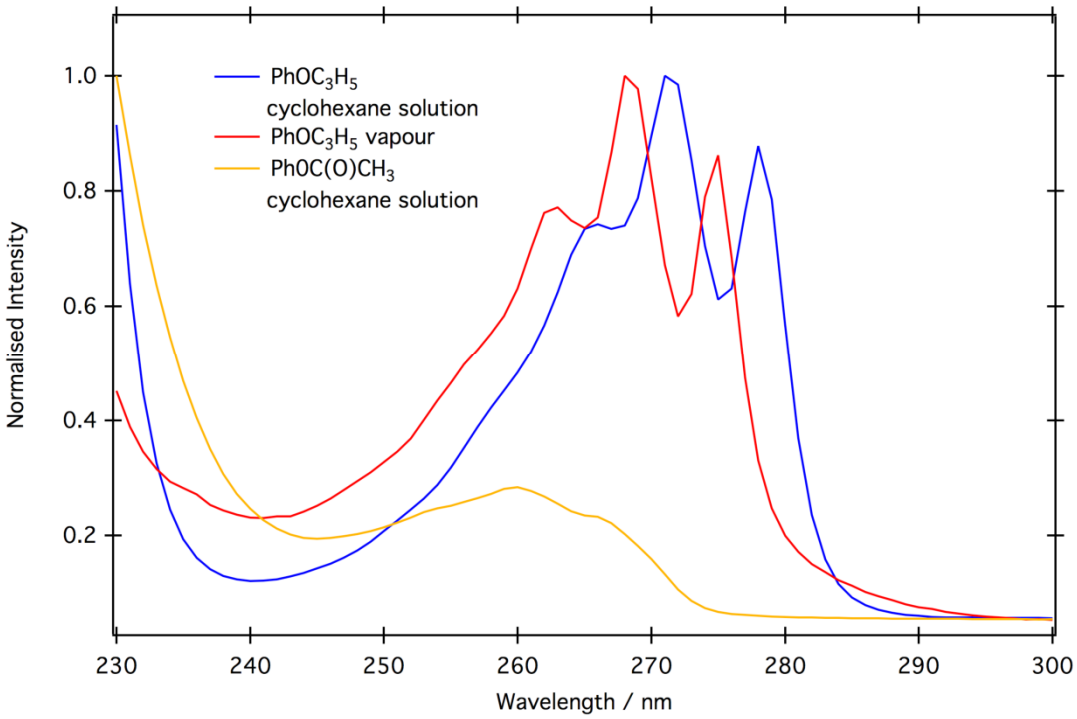

Figure S1 – Normalised UV-visible spectra of $PhOC_3H_5$ in cyclohexane solution and in the vapour phase and $PhOC(O)CH_3$ in cyclohexane solution.

Table S1 – Calculated harmonic wavenumber and IR transition strengths of the fundamental vibrations of $PhOC_3H_5$ and associated substituted cyclohexadienones. All calculations were carried out using the Gaussian 09 computer package, structures were optimised and fundamentals calculated at the B3LYP/6-311+g(d,p) level of theory.

$PhOC_3H_5$		**2,4-(Allyl)cyclohexadienone**		**2,5-(Allyl)cyclohexadienone**	
Wavenumber (cm^{-1})	Intensity (km/mol)	Wavenumber (cm^{-1})	Intensity (km/mol)	Wavenumber (cm^{-1})	Intensity (km/mol)
42.4	0.7	32.9	1.9	44.9	1.9
72.6	0.1	57.4	0.8	81.7	1
102.5	0.3	93.6	0.5	86.3	0.2
207.6	0.4	185.8	3	170.7	2
260.6	1	196.9	0.7	260.7	1.3
324.6	7.3	296.3	3.9	287.8	1.9
365.9	0.9	364.1	2.3	386.1	0.7
421	0	433.9	1.5	401	1.3
511.4	2.4	469.4	3.7	460.9	10.5
518.5	7.9	489.6	8.1	475.4	2.7
558.9	6.8	520.1	8.4	522.3	12.9
626	0.4	571.6	3.1	590	1.3
669.4	7.9	629.2	2.5	624.9	10.4
698.3	23.6	716.2	38.2	750.8	4.7
761.7	69.3	743.4	38.2	763.7	0.4
793.9	13.6	779.1	19.1	772.7	4.9
830	0.4	842.9	1.9	812.9	1.8
896.1	7.1	848.6	6.6	878	50.5
929.1	4	947.2	1.7	897.7	5.6
961.4	50.3	954.9	47.8	930.7	24.9
972.3	0.1	967.3	6.1	952.4	39.5
982.6	2.7	974.8	1.2	955.6	7.6
989.3	0.1	999.6	1.4	1009.3	4.3
1008.9	3.1	1009.1	2.4	1020.8	0.5
1027.9	43.9	1020.9	0.6	1025.6	9.2
1034.8	24.8	1030.1	20.1	1038	17.3
1051.9	57.5	1045.4	11.1	1052.3	5.2
1105.2	9.7	1122.7	7.3	1125.9	8.6
1173.2	1.5	1160.6	19.7	1159.9	7.2
1178	5.8	1196.6	12.7	1190.9	12.1
1196.4	30.5	1207.8	4.7	1209.8	0.5
1245.1	235.1	1247.9	20.7	1247.9	2.7
1294.3	53.7	1267.3	2.8	1272.8	26.2
1321	0.6	1310.9	4.8	1324.2	1.1
1338.3	52.7	1329.6	2.1	1349.5	2.4
1357.1	14.2	1356.9	11.3	1372.8	0.7
1386.7	2	1402	6.1	1414.6	19.2
1459.4	15.7	1445.9	6.3	1416.2	0.9
1484.4	0.9	1451.3	6	1454.5	2.8

1502	10.1	1492.2	7.9	1482.8	9.4
1522.4	117.8	1602.3	38.3	1650.8	2.6
1622.8	25	1684.2	29.3	1686	19.5
1640.1	87.7	1697.5	16.8	1702.3	8.5
1701.2	2.5	1719.2	255.5	1723.4	385.6
3016.3	30.3	3005.5	0.6	2953.7	7.3
3095.9	17.4	3022.2	16.1	3010.3	32.3
3127.4	13.2	3091.6	2.9	3060.5	16.9
3151.2	5.8	3123.2	14.8	3124	12.1
3164.2	2.1	3130.8	4.2	3132.7	3
3171.5	11.5	3154.1	2.5	3135.7	13.4
3188	21.4	3160.7	11.4	3142.3	10.5
3195.4	9.4	3181.8	19.3	3181.8	12.8
3205.5	6.3	3190.9	7.1	3183.5	0.9
3213.5	11.8	3211	14	3211.3	12

Table S2 – Calculated harmonic wavenumber and IR transition strengths of the fundamental vibrations of $PhOC(O)CH_3$ and associated substituted cyclohexadienones. All calculations were carried out using the Gaussian 09 computer package, structures were optimised and fundamentals calculated at the B3LYP/6-311+g(d,p) level of theory.

$PhOC(O)CH_3$		**2,4-(Acetyl)cyclohexadienone**		**2,5-(Acetyl)cyclohexadienone**	
Wavenumber (cm^{-1})	Intensity (km/mol)	Wavenumber (cm^{-1})	Intensity (km/mol)	Wavenumber (cm^{-1})	Intensity (km/mol)
24.7	1.3	35.3	6.8	34.6	8.7
63.4	1.4	52.3	1.5	55	6.7
91.2	1.9	154	2.3	120.7	0
116.2	3.9	170.8	1.3	171.8	2.2
263.5	2.1	192.8	7.4	183.5	0.9
327.4	1.6	310.7	1.4	326.2	5
394.1	1.6	339.8	2.3	362.3	1.7
419.3	0	453.9	1.7	384.9	1
505.9	11.9	464.6	0.9	454.9	11.1
539.7	10.3	490.8	9.2	508.8	0.9
597.3	3.8	536.2	11.9	563	20.8
629.6	0.1	568.8	13.3	579	2.2
671.3	5.1	592.8	9.4	593.4	2.5
698.4	34.8	651.5	23.7	643.8	37.8
758.4	29.8	747.7	64	769.1	6.6
820.9	21.2	789.1	7	777.6	0.3
837.7	1.2	810.4	10	810.9	2.4
904.3	20.7	868.4	3.7	879.4	75.7
938.7	31.8	948.3	6.8	908.5	32.1
977.5	0.3	977.7	1.1	969.3	6.2
997	0.1	991.8	6.1	986.1	19.7
1016.9	41.4	1003	4.5	1003.7	4.5
1021.9	31.7	1016.6	24.5	1022.6	0.1
1044.3	17.2	1022.4	0.1	1027.3	0.1
1063.8	6.4	1064.2	8	1067.9	2.7
1097	7.7	1155.7	123.4	1153.3	86.8
1180	8.4	1162.5	13.9	1163.5	45
1185	48.4	1192	5.2	1199.8	4.8
1211.3	554.7	1217.6	33.1	1244.1	19
1223.3	97.4	1238.2	26.3	1271.4	25
1329	1.6	1302.5	3.9	1341.5	1.7
1347.3	0.9	1383.7	41.6	1388	36
1400	53.9	1397	11.3	1408.4	13.9
1471.7	15.8	1441.5	5.7	1414.5	9.4
1476.6	10.9	1466.4	14.5	1460.2	15.6
1484.8	1.9	1470.4	22.1	1473.2	13.2
1520.5	53.4	1595.2	50.2	1645.7	2.1
1633.3	18.6	1677.9	47	1678.5	2.2
1637.9	10.4	1715.1	273.7	1721.5	519.8
1819.6	251.5	1790	279.8	1790.6	224.8

3051.4	1.7	3025.1	1.1	3020.7	1.3
3111.2	4.2	3033.3	1.8	3036.1	0.7
3157.6	6.8	3097.2	4	3096	3.6
3168.1	0.2	3145.6	8.5	3144.4	9.1
3177.3	8.7	3159.1	7.2	3145	6.6
3188.7	19.2	3171.3	1.8	3156	3
3196.9	6.9	3188.2	10.4	3184.6	8.5
3207.4	2	3193.5	5.7	3186.4	1.1

Table S3 – Comparison of the experimental wavenumbers of features observed in the TVA spectrum of $PhOC_3H_5$ in cyclohexane with the calculated harmonic wavenumber of the species to which they have been assigned (detailed in table S1). The numbers in brackets are the calculated values after application of a scaling factor of 0.98).

Experimental wavenumber / cm^{-1}	**Assigned species**	**Calculated wavenumber / cm^{-1}**
1415	S_1	-
1495	S_0	1522 (1492)
1516	S_1	-
1586	S_0	1622 (1590)
1598	S_0	1640 (1607)
1672	substituted cyclohexadienone (2,4/2,5)	1719 (1685)/1723 (1689)

Table S4 - Comparison of the experimental wavenumbers of features observed in the TVA of $PhOC_3H_5$ in cyclohexane with the calculated harmonic wavenumber of the species to which they have been assigned (detailed in table S2). The numbers in brackets are the calculated values after application of a scaling factor of 0.98).

Experimental wavenumber / cm^{-1}	**Assigned species**	**Calculated wavenumber / cm^{-1}**
1546	-	-
1557	S_1	-
1604	S_0	1633 (1600)
1697	substituted cyclohexadienone (2,4/2,5)	1715 (1681)/1722 (1688)
1765	substituted cyclohexadienone (2,4/2,5)	1790 (1754)/1791(1755)
1803	S_1	-
1820	S_0	1820 (1784)
1864	acetyl radical	1864[a]

[a] Literature experimental value; B. M. Giuliano, I. Reva, L. Lapinski, and R. Fausto, *J. Chem. Phys.*, 2012, **136**, 024505.