Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2005

Supporting Information for the paper:

Two-photon induced photodecarbonylation reaction of cyclopropenones.

by Nurtay Urdabayev, Andrei Poloukhtine, Vladimir V. Popik.

Experimental

Bis-*p*-anisylcyclopropenone (**1a**),[1] bis-p-(p-anisyl)phenylcyclopropenone (**1b**), and bis-(2-methoxy-1-naphthyl)cyclopropenone (**1c**)[1] were prepared by Friedel-Crafts alkylation of the corresponding naphthalenes with trichlorocyclopropenium cation followed by hydrolysis of the resulting 1,1-dichlorocyclopropenes.[2]

Bis-*p*-anisylacetylene (**2a**),[1] bis-p-(p-anisyl)phenylacetylene (**2b**), and bis-(2-methoxy-1-naphthyl) acetylene (**2c**)[1] were prepared by 350 nm irradiation of 10 mg sample of corresponding cyclopropenone in methanol.

Single-Photon Photochemistry. The preparative and analytical photolyses of cyclopropenones **1a-c** were conducted in methanol solutions using Rayonet photoreactor. The quantum yields of the photodecarbonylation reactions were measured in methanol solutions using ferrioxalate actinometry.[3] The concentration of the substrate was maintained to achieve an optical density of ca. 2 at 350 nm.

Two-photon Induced Decarbonylation of 1a-c. Two-photon experiments were conducted using 800 nm pulses generated by an amplified Ti:Sapphire laser (Hurricane by Spectra Physics) operating at 1 kHz. The laser beam was attenuated by a diaphragm with a 6.15 mm opening. Since the loss of laser beam energy (ca 7%) after the sample at the concentration of the substrate used in these experiments is mostly due to the losses on the phase boundaries, the laser power was measured before and after the cell and the average of these two values was used for calculations. The shape of the laser pulse was determined to be close to Gaussian with the width at half-height of 94 fs. Using these parameters we have calculated the distribution of light intensity and squared light intensity within the pulse assuming ideal Gaussian shape of the pulse. For the integration of the squared light intensity we have selected the integration limits of ± 100 fs from the center of the pulse, as the value I^2 at these extremes drops to less than 0.2% of the maximum.

The degassed 1.35 mL of ca. 10^{-3} M methanolic solutions of **1a-c** were irradiated in 1x1 cm quartz cell. The progress of the reaction was followed by measuring the concentration of acetylenes **2a-c** by HPLC. We have not observed decomposition of diarylacetylenes **2a-c** under the 800 nm irradiation.The cross-section of the solution in the cell is 1.35 cm^2, while the cross-section of the beam is 0.297 cm^2. Thus, the irradiated volume was 22% of the total volume. Duration of irradiation experiments required to achieve certain conversion was therefore scaled down by the factor of 0.22.

Table S1. Formation of acetylenes in two-photon induced decarbonylation of cyclopropenones **1a-c**

1c[a]			**1a**[b]		**1b**[b]	
Time of Irradiation (s)	Concentration of **1c** (M)	Yield of **2c**	Time of Irradiation (s)	Yield of **2a**	Time of Irradiation (s)	Yield of **2b**
0	9.83E-04	0.000	0	0.000	0	0.000
69	7.57E-04	0.127	1188	0.009	792	0.036
140	7.25E-04	0.267	2403	0.020	1602	0.068
206	5.85E-04	0.336	3646	0.031	2430	0.099
281	5.38E-04	0.461	4917	0.043	3278	0.132
368	4.75E-04	0.547	6217	0.058	4145	0.165
431	3.25E-04	0.570	7549	0.075	5032	0.208
529	2.92E-04	0.649	8912	0.091	5941	0.234
620	2.49E-04	0.666	10308	0.107	6872	0.270
822	1.15E-04	0.830				

[a] Pulse energy 910 μJ/pulse; [b] Pulse energy 630 μJ/pulse

Table S2. Formation of acetylenes in two-photon induced decarbonylation of cyclopropenones **1a-c** (variable pulse energy).

Pulse Energy (μJ/pulse)	Consumption of **1c**[a]	Yield of **2c**[a]	Yield of **2b**[b]
125	0.019	0.0165	0.016
130	0.015	0.0167	0.015
260	0.065	0.0712	0.034
265	0.074	0.0696	0.035
380	0.141	0.154	0.059
390	0.154	0.16	0.06
535	0.302	0.314	0.103
545	0.307	0.318	0.103
710	0.556	0.558	0.147
715	0.547	0.55	0.147
825	0.721	0.693	0.218
835	0.737	0.702	0.212

[a] after 486 s of irradiation; [b] after 1500 s of irradiation

[1] Wadsworth,D.H.; Donatelli,B.A. *Synthesis* **1981**, 285.

[2] Poloukhtine, A.; Popik, V.V. *J.Org.Chem.*, **2003**, *68*, 7833.

[3] Murov, S.L.; Carmichael, I.; Hug, G.L. in: Handbook of Photochemistry, Marcel Dekker: New York, 1993, p.299.