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Supporting Information

Revealing Phenylium, Phenonium, Vinylenephenonium and Benzenium Ions in Solution

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Supporting Information

Experimental

General

NMR spectra were recorded on a 300 MHz spectrometer. The attributions were made on the basis of 1H and 13C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. The photochemical reactions were performed by using nitrogen-purged solutions in quartz tubes and a multilamp reactor fitted with six 15 W phosphor coated lamps (maximum of emission 310 nm) for the irradiation.

Nucleophiles **(**2,3-dimethyl-2-butene, 1-hexene, 1-hexyne, benzene and thiophene**)** and compounds **1**, **2** and **3b** are commercially available and freshly purified before use. Compounds **3c**, **4**, **5**, **6b**,**c** and **7c, 12, 13** have been previously isolated and characterized.[S1, 2] An authentic sample of compound **3a** was obtained by treating *p*-anisidine with acetic anhydride.

Irradiation of 4-chloro anisole in MeCN-H_2O in the presence of 1-hexene.

From 200 μl (1.5 mmol) of 4-chloroanisole and 1.88 mL (15 mmol) of 1-hexene in 30 mL of acetonitrile-water 5:1, irradiated for 36 hours. Purification by column chromatography (eluant: cyclohexane: ethyl acetate 9:1) gave 99 mg of **8a** (30% yield), 43 mg of (*E*)-1-(4-methoxyphenyl)-1-hexene (**9**, colourless oil, 15 % yield) and 4-methoxyphenyl-pentyl-ketone (**10**, 43 mg, 10% yield)

8a: ^{1}HNMR (δ, $CDCl_3$): 0.95 (t, 3H, *J* = 7 Hz), 1.35-1.80 (m, 6H), 2.95-3.05 (d, 2H, *J* = 7Hz), 3.80 (s, 3H), 4.05 (m, 1H), 6.8-7.15 (AA'BB', 4H). ^{13}CNMR (δ, $CDCl_3$): 13.9 (CH_3), 22.1 (CH_2), 28.5 (CH_2), 37.1 (CH_2), 39.9 (CH_2), 55.1 (CH_3), 64.3 (CH), 113.8 (2CH), 127.9, 130.2 (2CH), 158.3. IR (ν, neat): 2956, 1612, 1513, 1247, 1037, 820. Anal. Calcd. For $C_{13}H_{19}OCl$: C, 68.86; H, 13.45; found: C, 67.9; H, 13.1.

9: ^{1}HNMR (δ, $CDCl_3$): 0.90-0.95 (t, 3H, *J* = 7 Hz), 1.25-1.60 (m, 4H), 2.15-2.25 (t, 2H, J = 7Hz), 3.80 (s, 3H), 6.05-6.15 (m, 1H), 6.60-6,35 (d, 1H, *J* = 16 Hz) 6.85-7.30 (AA'BB', 4H). ^{13}CNMR (δ, $CDCl_3$): 14.0 (CH_3), 22.8 (CH_2), 32.6 (CH_2), 34.9 (CH_2), 55.2 (CH_3), 113.7, 113.8 (CH), 126.8 (CH), 130.3 (CH), 130.7 (CH), 158.5. IR (ν, neat): 2956, 1630, 1505, 1220, 1037, 819. Anal. Calcd. For $C_{13}H_{18}O$: C, 75.69; H, 8.80; found: C, 74.9; H, 8.6.

10: ^{1}HNMR (δ, $CDCl_3$): 0.90-0.95 (t, 3H, *J* = 7 Hz), 1.20-1.50 (m, 4H), 1.55-160 (m, 2H), 2.95-3.00 (t, 2H, *J* = 8 Hz), 3.80 (s, 3H), 6.95-7.90 (AA'BB', 4H).

^{13}**C**NMR (δ, $CDCl_3$): 13.9 (CH_3), 22.4 (CH_2), 24.2 (CH_2), 30.5 (CH_2), 38.2 (CH_2) 55.2 (CH_3), 113.5 (CH), 113.7, 130.1 (CH), 163.2, 199.2. IR (ν, neat): 2954, 1720, 1233, 1035, 842. Anal. Calcd. For $C_{13}H_{18}O_2$: C, 75.69; H, 8.80; found: C, 75.1; H, 8.9.

Irradiation of 4-chloroanisole in MeOH in the presence of 1-hexene

From 200 μl (1.5 mmol) of 4-chloroanisole and 1.88 mL (15 mmol) of 1-hexene in 30 mL of methanol, irradiated for 14 hours. Purification by column chromatography (eluant: cyclohexane) affording 68 mg of 1-(4-methoxyphenyl)-2-methoxy-hexane (**8b**, colourless oil 42 % yield) and a mixture of 71 mg of **8b** and 24 mg of 1-(4-methoxyphenyl)-1-methoxy-hexane (**11a**, 24 mg, 8 % yield)

8b: ^{1}HNMR (δ, $CDCl_3$): 0.90-0.95 (t, 3H, *J* = 7Hz); 1.30-1.35 (m, 4H), 1.45-1.50 (m, 2H), 2.70-2.80 (AB part of an ABX sistem, 2H), 3.25 (s, 3H), 3.75-3.80 (X part of an ABX sistem, 1H), 3.80 (s, 3H); 6.85-7.15 (AA'BB', 4H). ^{13}CNMR (δ, $CDCl_3$): 13.9 (CH_3), 22.7 (CH_2), 27.4 (CH_2), 33.0 (CH_2), 39.1 (CH_2), 55.1 (CH_3), 56.8 (CH_3), 82.4 (CH), 113.5 (CH), 127.8, 130.5 (CH), 158.9. Anal. Calcd. For $C_{14}H_{22}O_2$: C, 75.63; H, 9.97; found: C, 75.2; H, 9.1. IR (ν,neat): 2948, 1620, 1518, 1240, 1025, 832.

11b: ^{1}HNMR (δ, $CDCl_3$ from the mixture): 0.90-0.95 (t, 3H, *J* = 7Hz), 1.30-1.35 (m, 4H), 1.50-1.60 (m, 4H), 3.25 (s, 3H), 3.80 (s, 3H), 3.90-3.95 (t, 1H, *J* = 6Hz), 6.85-7.15 (AA'BB', 4H). ^{13}CNMR (δ, $CDCl_3$

from the mixture): 13.9 (CH_3), 22.4 (CH_2), 25.4 (CH_2), 31.7 (CH_2), 37.9 (CH_2), 55.1 (CH_3), 56.2 (CH_3), 83.6 (CH), 113.7 (CH), 127.8 (CH), 129.2, 157.8. IR of the mixture (ν,neat): 2956, 1612, 1513, 1247, 1037, 820.

Irradiation of 4-chloroanisole in TFE in the presence of 1-hexene

From 200 µl (1.5 mmol) of 4-chloroanisole and 1.88 mL (15 mmol) of 1-hexene in 30 mL of 2,2,2 trifluoroethanol (TFE), irradiated for 14 hours. Purification by column chromatography (eluant: cyclohexane) afford 46 mg of 1-(4-methoxyphenyl)-2-chlorohexane (**8a**, colourless oil, 36% yield) and 294 mg of a mixture of **8a** (76 mg), 1-(4-methoxyphenyl-1-trifluoroethoxyhexane (**8c**, 174 mg, 40 % yield) and 1-(4-methoxyphenyl)-2-trifluoroethoxyhexane (**11c**, 44 mg, 10% yield)

8c: ^{1}HNMR (δ, $CDCl_3$ from the mixture): 0.95 (t, 3H, *J* = 7 Hz), 1.20-1.40 (m, 4H), 1.45-1.70 (m, 4H), 3-70-3.80 (m, 2H), 3.80 (s, 3H); 4.30-4.40 (t, 1H, J = 7Hz), 6.80-7.05 (AA'BB', 4H). ^{13}CNMR (δ, $CDCl_3$): 13.8 (CH_3), 22.5 (CH_2), 27.6 (CH_2), 33.6 (CH_2), 39.8 (CH_2), 55.1 (CH_3), 65.6 (q, CF_3 *J* = 35 Hz), 83.4 (CH), 113.9 (CH), 130.2 (CH), 130.4, 135.0 (q, CF_3 *J* = 275 Hz), 158.3. IR of the mixture (ν, neat): 2934, 1612, 1513, 1278, 1160, 831.

11b: ^{1}HNMR (δ, $CDCl_3$ from the mixture): 0.95 (t, 3H, *J* = 7 Hz); 1.35-1.80 (m, 4H), 1.50-1.60 (m, 2H), 2.70-2.85 (dq, 2H, *J* = 8 and 2 Hz),, 3.70-3.80 (m, 2H), 3.80 (s, 3H), 3.85-3.90 (d, 1H, *J* = 3Hz), 6.80-7.05 (AA'BB', 4H). ^{13}CNMR (δ, $CDCl_3$): 13.8 (CH_3), 22.1 (CH_2), 31.4 (CH_2), 37.2 (CH_2), 44.2 (CH_2), 55.1 (CH_3), 65.6 (q, CH_2 *J* = 35 Hz), 83.6 (CH), 113.9 (CH), 130.2 (CH), 132.7, 135.0 (q, CF_3, *J* = 275 Hz), 159.3.

Irradiation of 4-chloroanisole in presence of thiophene

From 200 µl (1.5 mmol) of 4-chloroanisole (**3**), 200 µl of triethylamine (TEA, 1.5 mmol) and 3,00 mL (30 mmol) of thiophene in 30 mL of 2,2,2 trifluoroethanol (TFE), irradiated for 24 hours. (consumption: 80%). Purification by column chromatography (eluant:

cyclohexane: ethyl acetate 9:1) afford a white solid containing of 2-(4-methoxyphenyl)-thiophene, (**14a**, 96 mg, 42 % yield) and 3-(4-methoxyphenyl)-thiophene (**14'**, 23 mg, 8% yield)
14 and **14'** showed ^{1}H-NMR spectra identical to those reported in the literature.[S3,4]

Nanosecond Laser Flash Photolysis. The setup for the nanosecond absorption measurements was described previously.[S5] The minimum response time of the detection system was of ca. 2 ns. The laser beam (a JK-Lasers Nd-YAG operated at λ = 266 nm, pulse FWHM 20 ns) was focused on a 3 mm high and 10 mm wide rectangular area of the cell and the first 2 mm in depth were analyzed at a right angle geometry. The incident pulse energies used were < 17 mJ/cm^2 (5 mJ/pulse). The bandwidth used in the spectrokinetic measurements was typically 2 nm. The spectra were reconstructed point by point from time profiles taken each 5-10 nm. The sample absorbance at 266 nm was typically 1-1.5 over 1 cm. Oxygen was removed by vigorously bubbling the solutions with a constant flux of Ar, previously passed through a suitable trap to prevent evaporation of the sample. The solution, in a flow cell of 1 cm path, was renewed after few laser shots. The temperature was 295 $\pm$ 2 K. The detector system was perturbed from 290 nm to 380 nm by the intense emission of **1**, generated by the laser excitation. These troubles were minimized by using neutral density filters at the entrance slit of the monochromator and pulsing the 150 W high pressure Xe-lamp at high currents (~200 mA for 1 ms) to increase the intensity of the analyzing light. In spite of this, transient spectra below 380 nm were not significant before 20-30 ns from pulse end. Acquisition and processing of absorption signals were performed by a home made program using Asyst 3.1 (Software Technologies, Inc.). Nonlinear fitting of absorbance change profiles using mono or biexponential functions was performed by the least square method. χ^2 and distribution of residuals were used to judge the goodness of the fit.

Calculations. The structure and energy of singlet and triplet 4-methoxyphenylium ions and the PES for the reactions with ethylene, acetylene and benzene were calculated at the UB3LYP/6-31G(d) level by using the Gaussian 03 package[S6] (see Table S1). UV spectra of intermediates were calculated by a TDDFF method.[S7] The resulting spectra were plotted by means of the GaussSum program, with a fixed FWHM of 3000 cm^{-1} (see Fig. 5).[S7]

Table S1. Cartesian coordinates and energies for the optimized geometries obtained with Ub3LYP 6-31G(d) level

1$^{+\cdot}$.

E = -806.0820551 Ha

C	-0.77488800	-1.04584200	0.00009600
C	0.59093800	-1.17829400	0.00009800
C	1.41915700	-0.01826100	0.00004100
C	0.85763100	1.28677200	0.00000500
C	-0.50470700	1.42755900	0.00003000
C	-1.34675000	0.26461000	0.00012000
H	-1.40677700	-1.92600800	0.00010100
H	1.05330400	-2.15956800	0.00007200
H	1.51070600	2.15252500	-0.00007300
H	-0.98122300	2.40225600	-0.00004500
O	-2.63223400	0.51702700	0.00006600
C	-3.63463400	-0.53599500	-0.00017200
H	-3.53171300	-1.14192300	0.90323900
H	-4.58679600	-0.00992500	-0.00099500
H	-3.53057400	-1.14271500	-0.90291200
Cl	3.11120400	-0.20671500	-0.00007200

Adduct **16**$^{+}$.

E = -424.4553125 Ha

C	-0.68251500	1.49418500	0.00043100
C	0.68510100	1.49590500	0.00021200
C	1.42059100	0.27139000	-0.00032000
C	0.70152200	-0.96161300	-0.00061700
C	-0.67141200	-0.99195900	-0.00043500
C	-1.38955600	0.24360200	0.00008100
H	-1.26628200	2.40876600	0.00084800
H	1.22636700	2.43772900	0.00044500
H	1.26723700	-1.88810500	-0.00100200
H	-1.20134100	-1.93725400	-0.00063400
C	2.93090900	0.31854800	-0.00094000
C	3.66235200	-0.98163400	0.00134900
H	3.22442200	0.93211000	0.86865300
H	3.97010400	-1.44694800	-0.92843300
H	3.96156900	-1.44827400	0.93329200
H	3.22365700	0.92840200	-0.87335100
O	-2.69678900	0.34809200	0.00031200
C	-3.56816400	-0.81441500	-0.00007000
H	-4.57595400	-0.40469900	-0.00033400
H	-3.39393700	-1.40518900	-0.90253400

Adduct **17**$^{+}$

E = -424.5193587 Ha

C	-0.41439800	1.42511200	-0.00008600
C	0.93934900	1.26781100	-0.00007800
C	1.53938500	-0.04668000	0.00002300
C	0.65386700	-1.18313600	-0.00002800
C	-0.70623000	-1.03529000	-0.00007100
C	-1.26228000	0.27718800	0.00001000
H	-0.88123300	2.40395800	-0.00011500

H	1.58739000	2.14027900	-0.00017300
H	1.08481700	-2.18113200	0.00002000
H	-1.34923500	-1.90667000	-0.00024500
C	2.94959100	-0.21613300	-0.72438500
C	2.94958400	-0.21607100	0.72449100
H	3.26732600	0.66883100	-1.26624400
H	3.05634600	-1.15043100	1.26597000
H	3.26734200	0.66893100	1.26627000
H	3.05639000	-1.15052500	-1.26580200
O	-2.54942400	0.53580700	0.00016300
C	-3.53669600	-0.52343000	-0.00001400
H	-4.49611600	-0.00983900	-0.00023300
H	-3.43509100	-1.13307000	-0.90154800
H	-3.43557700	-1.13301600	0.90162900

Adduct **19**$^{+}$.

E = -423.2194372 Ha

C	0.55462100	1.31898400	-0.00004200
C	-0.79476600	1.07382000	-0.00011500
C	-1.25152400	-0.27709600	-0.00005200
C	-0.31212400	-1.35816800	0.00000500
C	1.02799600	-1.09727000	0.00005700
C	1.51127400	0.25250200	0.00006100
H	0.91427200	2.34376000	-0.00007500
H	-1.50039000	1.89576600	-0.00026000
H	-0.70250300	-2.37020400	0.00004000
H	1.73485400	-1.92001000	0.00013300
C	2.90690200	0.57977500	0.00012900
H	3.15442100	1.64340400	0.00020400
C	3.93777500	-0.28919600	-0.00006100
H	4.14043100	-1.35227700	-0.00031200
O	-2.51392500	-0.63827200	-0.00011500

C	-3.58957500	0.33448000	0.00013300
H	-3.53608400	0.94918200	-0.90191400
H	-4.50119400	-0.25952300	0.00020000
H	-3.53588200	0.94909700	0.90222400

Adduct **19’**$^{+}$.

E = -423.2466852 Ha

C	-0.72776700	-1.19394000	-0.00049300
C	0.63198700	-1.04050400	-0.00019800
C	1.18357000	0.27468300	-0.00004400
C	0.33374800	1.42198100	-0.00017000
C	-1.02057000	1.26337600	-0.00021400
C	-1.62053800	-0.05626200	-0.00037600
H	-1.16359200	-2.18911600	-0.00087200
H	1.27962900	-1.90869300	-0.00011300
H	0.80080900	2.40093000	-0.00020400
H	-1.67644900	2.12917700	-0.00009400
H	-3.46248100	-0.27653100	-1.63136200
C	-3.05541400	-0.23331600	-0.63334100
C	-3.05497800	-0.23364300	0.63422100
H	-3.46051800	-0.27701900	1.63283900
O	2.46969800	0.53614100	0.00028800
C	3.46067300	-0.51992200	0.00014400
H	3.36110000	-1.12998900	-0.90137300
H	4.41830000	-0.00296800	-0.00021000
H	3.36134200	-1.12963700	0.90190900

Adduct **20**$^{+}$.

E = -578.1366303 Ha

C	-0.19668700	-0.94993700	0.00950600
C	-1.52992800	-1.32409700	0.01835400
C	-2.54398800	-0.34681800	0.00524400
C	-2.19296600	1.01221800	-0.01718700
C	-0.84756500	1.38044800	-0.02637800
C	0.15520800	0.41033100	-0.01354700
H	0.57143800	-1.71945200	0.02031700
H	-1.81924600	-2.36959200	0.03566300
H	-2.95231000	1.78483000	-0.02779700
H	-0.59357500	2.43758500	-0.04397500
H	1.86951900	0.65186800	-2.20226200
C	2.34141700	0.39026100	-1.25891100
C	3.51842700	-0.31579500	-1.22900700
C	1.65261400	0.81479000	-0.02159500
C	4.09118300	-0.63614400	0.02114100
H	4.00667100	-0.63445400	-2.14399600
C	2.33494800	0.45291300	1.23897800
H	1.63756200	1.92516100	-0.04994500
C	3.51173500	-0.25430500	1.25058300
H	5.02069200	-1.20120000	0.03769100
H	1.85832400	0.76155500	2.16556600
H	3.99478100	-0.52738200	2.18290900
O	-3.80534900	-0.81708100	0.01581100
C	-4.89436100	0.10859400	0.00484000
H	-5.79680800	-0.50220400	0.01668900
H	-4.87465600	0.75118100	0.89271500
H	-4.87982000	0.72400300	-0.90218600

Table S2. Calculated electronic transitions for cationic intermediates by the TD-UB3LYP method at 6-31G(d) level.

Wavelength (nm)	Oscillator strength

$1^{+\cdot}$.

746.47	0.0006
469.71	0.0
448.44	0.1374
373.55	0.0
292.34	0.0265
283.56	0.0255
271.64	0.0
262.34	0.1879

$^{1}15^{+}$

886.799	0.0131
609.194	0.0
539.222	0.0001
343.149	0.0
334.124	0.0

$^{3}15^{+}$

784.159	0.0004
381.863	0.0
376.769	0.076
322.286	0.0
283.637	0.0001
281.231	0.0

17^{+}

402.465	0.0
374.176	0.0
277.747	0.0

271.881	0.15
260.853	0.37
237.684	0.0
237.039	0.0
236.010	0.0
225.068	0.0
217.977	0.0083
211.258	0.066
201.756	0.0

16^{+}

802.533	0.0005
414.134	0.118
386.000	0.0
378.275	0.0001
347.906	0.0
312.403	0.005
312.277	0.004
299.556	0.0003

19^{+}

655.754	0.002
512.137	0.114
349.259	0.000
330.024	0.001
312.293	0.266
299.520	0.113
294.847	0.001
275.231	0.000

19’$^{+}$

395.746	0.000

371.920	0.000
290.925	0.000
286.402	0.000
281.294	0.000
274.743	0.000
269.418	0.147
259.667	0.292

20^{+}

2492.127	0.000
2242.825	0.000
805.348	0.000
794.358	0.000
558.307	0.000
388.297	0.000
385.317	0.004
377.365	0.000

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