Supplementary Material (ESI) for Chemical Communications

Electronic Supporting Information:

Activation of oxygen by *S*-radicals: Experimental and comptational studies on a novel oxidation of alkynes to α-diketones

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Content:

A. General reaction procedures

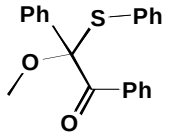
1) Generation of PhS• through autoxidation (method (ii)):

To a solution of **6** was added PhSH, and the reaction vessel (usually a test-tube) was fitted with a suba-seal and a needle outlet. The level of the reaction solution was marked. An O_2 balloon was attached to a long needle, which reached the base of the reaction vessel, ensuring that O_2 bubbled through the reaction solution. After the reaction, the solution was topped up to the mark to compensate for the solvent loss caused by the O_2 stream, and a known amount of standard solution (*n*-hexadecane in ethyl acetate) was added to the reaction solution, and the mixture was analysed by GC.

2) Generation of PhS• through anodic oxidation (method (iv)):

The electrochemical reactions were performed in an undivided cell equipped with a cylindrical platinum net anode and a centred corkscrew-shaped platinum counter electrode using a home-made potentiostat. The reaction cell was cooled with a water bath.
As an example, conditions for entry 16 in Table 1: **6** (0.4464 g, 2.50 mmol), tetraethylammonium toluene-4-sulfonate (Et_4NOTs) (2.2346 g, 7.41 mmol) and PhSH (2.55 ml, 25.0 mmol) were dissolved in acetonitrile (10 ml) and benzene (40 ml), and the mixture was electrolysed for 6 hours under a constant O_2 stream. The reaction solution was concentrated *in vacuo* and the residue partitioned between water and EtOAc. The aqueous layer was extracted with EtOAc (3x), and the combined organic extracts were washed with brine and dried ($MgSO_4$). *n*-Hexadecane (0.2503 g) was added and the mixture analysed by GC.

B. Spectroscopical data for compound 8b



2-Methoxy-1,2-diphenyl-2-(phenylthio)ethanone (**8b**):

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.92 (dd, ^{3}J = 1.25, 8.75 Hz, 2H), 7.43 (tt, ^{3}J = 1.25, 7.50 Hz, 1H), 7.29-7.19 (m, 5H), 7.15-7.12 (m, 3H), 7.09 (tt, ^{3}J = 1.75, 7.75 Hz, 2H), 6.97 (dd, ^{3}J = 1.25, 8.25 Hz, 2H), 3.58 (s, 3H) ppm.

^{13}C NMR ($CDCl_3$, 126 MHz): δ = 195.71, 139.57, 136.68, 133.62, 133.25, 130.56, 130.14, 128.37, 128.26, 128.01, 127.86, 127.69, 125.63, 102.62, 52.81 ppm.

Mp = 129.2 – 130.3 ^{o}C

HRMS for $C_{21}H_{18}O_2S\ Na^{+}$, calcd: 357.09197, found: 357.09205

Elemental analysis:
Calcd: C 75.43%, H 5.43%, O 9.57%, S 9.57%
Found: C 75.52%, H 5.47%, S 9.67% (N 0.00%)

IR:
$\tilde{\nu}$ (neat) = 3060 (w), 1683 (s), 1448 (s), 1235 (s), 1098 (s), 1076 (s), 734 (s), 692 (s), 668 (s), 641 (s) cm^{-1}.

C. Gaussian Archive Entries

All computations were performed at the BHandHLYP (or BHLYP)/cc-pVTZ level of theory.

C.1 PhS• and *O*-centred radical species

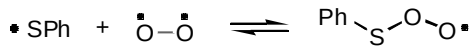
1. PhS•

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET22\FOpt\UBHandHLYP\CC-pVTZ\C6H5S1(2)\KJWTAN\11-Jan-2007\0\\#BHANDHLYP/CC-PVTZ SCF=(QC,DIRECT) OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Geometry optimization of PhS radical\\0,2\S,-1.5586695957,-2.3906381217,-0.0000000129\C,-0.7023325411,-0.906756946,-0.0000000017\C,0.7004746526,-0.8889884765,0.0000000056\C,1.3839921574,0.3032503104,0.0000000021\C,0.6885880407,1.50222813,0.0000000015\C,-0.6974889742,1.5049912926,0.000000002\C,-1.3884096833,0.3169904968,0.0000000036\H,-2.4616546307,0.3049001942,0.0000000057\H,-1.2326440659,2.4364524203,-0.0000000012\H,1.225824853,2.4326842533,-0.000000008\H,2.4582346018,0.3053553377,-0.0000000035\H,1.2265851854,-1.8244688912,0.0000000068\\Version=x86-Linux-G03RevB.04\HF=-629.7603902\S2=0.804801\S2-1=0.\S2A=0.752117\RMSD=0.000e+00\RMSF=9.411e-05\Dipole=0.5725265,0.991914,0.\PG=C01 [X(C6H5S1)]\\@

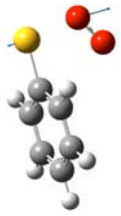
2. O_2 (triplet)

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET4\FOpt\UBHandHLYP\CC-pVTZ\O2(3)\KJWTAN\12-Feb-2007\0\\#BHANDHLYP/CC-PVTZ SCF=(QC,DIRECT) OPT=(READFC) NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Geometry optimization of oxygen\\0,3\O,-3.0933452079,0.17857143,0.\O,-4.2736119521,0.17857143,0.\\Version=x86-Linux-G03RevB.04\HF=-150.3058351\S2=2.016138\S2-1=0.\S2A=2.000133\RMSD=0.000e+00\RMSF=7.171e-05\Dipole=0.,0.,0.\PG=D*H [C*(O1.O1)]\\@

3. Transition state for:



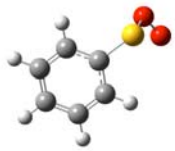
14



1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET9\FTS\UBHandHLYP\CC-pVTZ\C6H5O2S1(2)\KJWTAN\14-Feb-2007\0\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(TS,NOEIGENTEST,READFC) OPTCYC=500 NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Finding TS from PhSOOrad: O2 addn to PhSrad\\0,2\C,-2.0856238184,-0.0153057532,0.061826247\C,-1.8706882536,-1.3242964999,-0.3282427505\C,-0.6081296187,-1.8815888663,-0.2414779833\C,0.4422649741,-1.1315102816,0.2380928789\C,0.2346521191,0.1846508402,0.6418105725\C,-1.0384341086,0.7391970222,0.5417156772\S,1.5540398503,1.1320732461,1.2391747284\O,2.158978625 3,1.893771665,-0.540270303\O,1.5010717879,1.5432494797,-1.5053021119\H,-1.1904168704,1.7568089257,0.8459088387\H,-3.0668767153,0.4145046414,-0.0111066239\H,-2.6888472845,-1.9112397314,-0.702438655\H,-0.4450953941,-2.8972865051,-0.5492068381\H,1.4274047067,-1.5505311829,0.309518323\\Version=x86-Linux-G03RevB.04\HF=-780.0473664\S2=1.034729\S2-1=0.\S2A=0.763502\RMSD=4.596e-09\RMSF=2.719e-06\Dipole=-0.8860297,-0.7134102,0.0694686\PG=C01 [X(C6H5O2S1)]\\@

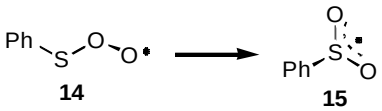
ν_{im} = -506.192 cm^{-1}

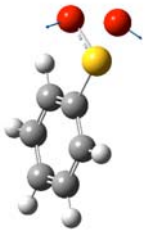
4. PhSOO• (**14**)



1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET5\FOpt\UBHandHLYP\CC-pVTZ\C6H5O2S1(2)\KJWTAN\11-Jan-2007\0\\#BHANDHLYP/CC-PVTZ SCF=(QC,DIRECT) OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Geometry optimization of PhS-O-O radical, input geom from PhSOOrad5.out\\0,2\C,-2.1884391941,-0.0671960142,0.1807030878\C,-1.9490332268,-1.3566741271,-0.2547851093\C,-0.6586463286,-1.8475106863,-0.3076960306\C,0.3983164035,-1.0494698481,0.0773050244\C,0.1611467882,0.2468414524,0.508765162\C,-1.1352748176,0.7365381289,0.5626426467\S,1.5065008059,1.2602500784,1.0181897966\O,1.9267952086,1.9953302822,-0.4812283316\O,2.6045899484,1.2323542727,-1.2720080689\H,-1.3070679072,1.740292185,0.900906281\H,-3.1926600238,0.3106522733,0.222014854\H,-2.7709113524,-1.9813686695,-0.5516278777\H,-0.4763962074,-2.8503599548,-0.6452855067\H,1.4053779034,-1.4171793727,0.0421070722\\Version=x86-Linux-G03RevB.04\HF=-780.0562032\S2=0.757515\S2-1=0.\S2A=0.75004\RMSD=0.000e+00\RMSF=5.746e-06\Dipole=-1.0879515,-0.732626,0.3064231\PG=C01 [X(C6H5O2S1)]\\@

5. Transition state for:

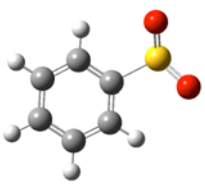




1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET9\FTS\UBHandHLYP\CC-pVTZ\C6H5O2S1(2)\KJWTAN\29-Aug-2007\0\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(TS,NOEIGENTEST,READFC) OPTCYC=500 NOSYMM FREQ=NORAMAN GEOM=CHECKPOINT GUESS=CHECK\\TS for rearrangement of PhSOOrad to PhS(O)Orad (geom fr PhSO2rearrTS6.chk)\\0,2\C,-2.088087439,0.0459958408,-0.0049453115\C,-1.9641764222,-1.317272213,-0.2108581377\C,-0.7162041846,-1.9097359646,-0.2145585563\C,0.4112287017,-1.1427546502,-0.0093496623\C,0.2745785581,0.2202234206,0.1945745532\C,-0.9707352544,0.8249005655,0.1961105456\S,1.737785115,1.1436406819,0.44526661\O,1.3139872737,2.45153376,1.1157662763\O,1.4031805278,2.6797559214,-0.5573226367\H,-1.0443407571,1.8839909036,0.3464413494\H,-3.0599408671,0.502577888,-0.0057858022\H,-2.8412280414,-1.916316511,-0.3685923608\H,-0.6202914471,-2.967144785,-0.3734156934\H,1.3851559866,-1.5979151079,-0.0051844637\\Version=x86-Linux-G03RevB.04\HF=-780.0037242\S2=0.80864\S2-1=0.\S2A=0.751836\RMSD=3.288e-09\RMSF=5.504e-06\Dipole=-0.6489991,-1.559754,-0.004561\PG=C01 [X(C6H5O2S1)]\\@

ν_{im} = -1451.769 cm^{-1}

6. PhS(O)O• (**15**)



1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET17\FOpt\UBHandHLYP\CC-pVTZ\C6H5O2S1(2)\KJWTAN\18-Mar-2004\0\\#BHANDHLYP/CC-PVTZ SCF=(QC,DIRECT) OPT=(READFC) NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Geometry optimization of oxygen\\0,2\C,-1.822086319,0.6831568987,0.0939814437\C,-1.9025457975,-0.6796655552,-0.1216711088\C,-0.763329034,-

1.4171157726,-0.3836618604\C,0.4666847869,-0.7951218302,-0.434938175\C,0.528458166,0.5653705516,-0.2080900806\C,-0.5995033542,1.3198753466,0.046070294\S,2.1044879322,1.3869976929,-0.326393969\O,2.0321668549,2.6243666222,0.4231383892\O,3.1475424859,0.4129846681,-0.0785740525\H,-0.5116021228,2.3744162066,0.2206992896\H,-2.7096678455,1.2497785723,0.302744791\H,-2.8574026984,-1.1697020986,-0.0836830501\H,-0.8314068325,-2.4763435514,-0.5444787735\H,1.3652037781,-1.348697751,-0.6259431377\\Version=x86-Linux-G03RevB.04\HF=-780.1471426\S2=0.762163\S2-1=0.\S2A=0.750112\RMSD=0.000e+00\RMSF=1.223e-05\Dipole=-1.7182414,-0.7570231,-0.4822188\PG=C01 [X(C6H5O2S1)]\\@

7. $PhSO_2$-OO• (**16**)

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET20\FOpt\UBHandHLYP\CC-pVTZ\C6H5O4S1(2)\KJWTAN\15-May-2008\0\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=CHECKPOINT GUESS=READ\\Geometry optimization of PhSO2OOrad, input copied fr PhSO4rad5.chk\\0,2\C,-1.8860591446,0.5927353404,0.2150551874\C,-1.9734107082,-0.7743763208,0.0347293829\C,-0.834058839,-1.5362544297,-0.1462056277\C,0.4046235441,-0.9325600923,-0.1511911186\C,0.4742023636,0.4362116912,0.0281731478\C,-0.6538870676,1.2115683529,0.2132222084\O,1.9684904443,2.4881824165,0.6259611976\O,3.0736794521,0.2740465385,0.3165744585\H,-0.5588425926,2.2694277845,0.358099569\H,-2.7750540265,1.1763363941,0.3595949764\H,-2.9359263329,-1.2507711431,0.0390898932\H,-0.9101317819,-2.5985463227,-0.2787150079\H,1.3031019097,-1.5042258976,-0.278463433\O,2.3041152276,1.4644495517,-1.6340188183\S,2.0462987236,1.2071197409,0.0225005512\O,1.4709396782,2.3264029554,-2.1330162269\\Version=x86-Linux-G03RevB.04\HF=-930.4659833\S2=0.756243\S2-1=0.\S2A=0.750026\RMSD=7.748e-09\RMSF=3.497e-06\Dipole=-1.8895334,-1.0287095,-0.0060892\PG=C01 [X(C6H5O4S1)]\\@

8. PhS•=O

1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET21\FOpt\UBHandHLYP\CC-pVTZ\C6H5O1S1(2)\KJWTAN\26-Jul-2008\0\\#BHANDHLYP/CC-PVTZ OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=CHECKPOINT GUESS=CHECK\\Geom optn of PhSOrad, input PhSOrad4.chk\\0,2\C,-1.6857111318,-0.4104670153,-0.1121508337\C,-0.3191064663,-0.3225077864,-0.2683415526\C,0.2856078595,0.9219932386,-0.2292323392\C,-0.4650587083,2.0714308506,-0.0359417853\C,-1.8307613565,1.9710801931,0.1190077765\C,-2.4422648057,0.7313953018,0.0812183205\H,-2.1633705971,-1.3719399447,-0.1411776207\H,0.2865321778,-1.1953179251,-0.4194480134\H,0.0152275322,3.033212368,-0.0072876319\H,-2.417892577,2.8575616948,0.2689561481\H,-3.506545336,0.6553212479,0.2020062917\S,2.0253622332,1.0927433871,-0.4225400001\O,2.589633926,-0.2707625003,-0.6134494698\\Version=x86-Linux-G03RevB.04\HF=-704.9638525\S2=0.779524\S2-1=0.\S2A=0.75072\RMSD=6.720e-09\RMSF=1.764e-05\Dipole=-1.1653475,0.626709,0.1964351\PG=C01 [X(C6H5O1S1)]\\@

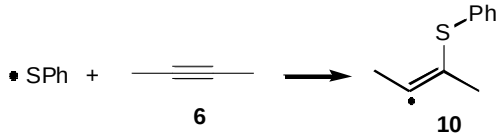
9. $PhSO_3$•

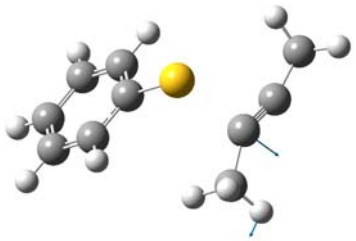
1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET21\FOpt\UBHandHLYP\CC-pVTZ\C6H5O3S1(2)\KJWTAN\27-Jul-2008\0\\#BHANDHLYP/CC-PVTZ OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=CHECKPOINT GUESS=CHECK\\Geom optn of PhSO3rad, input geom copied fr PhSO3rad4.chk\\0,2\C,-1.8840052933,0.5905254545,0.2096843179\C,-1.9766209353,-0.7776614274,0.0418648087\C,-0.8386048816,-1.5410198634,-0.1364831541\C,0.4014223892,-0.9385816502,-0.1524167276\C,0.4784382652,0.431146841,0.0102426922\C,-0.6499410719,1.2058420422,0.1957106857\O,1.9656696085,2.4780905396,0.612640357\O,3.0600570184,0.2540402

148,0.293870044\H,-0.5560266196,2.2646569499,0.3380072355\H,-2.7703474832,1.1778509732,0.3564516563\H,-2.9398459615,-1.2523958431,0.056129688\H,-0.915611231,-2.6047487438,-0.2575819609\H,1.2970076407,-1.51572922,-0.275190957\O,2.3231668517,1.5415718993,-1.5372573271\S,2.0523817038,1.2097568334,-0.0312653584\\Version=x86-Linux-G03RevB.04\HF=-855.3257356\S2=0.759974\S2-1=0.\S2A=0.750068\RMSD=5.159e-09\RMSF=8.891e-06\Dipole=-1.809957,-0.8555768,-0.2008962\PG=C01 [X(C6H5O3S1)]\\@

C.2 Addition to 2-butyne (**6**, R=Me)

11. Transition state for:

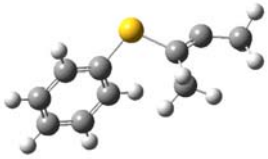




1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET17\FTS\UBHandHLYP\CC-pVTZ\C10H11S1(2)\KJWTAN\25-Dec-2003\0\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(TS,NOEIGENTEST,READFC) OPTCYC=500 NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Finding TS from vinyl rad (from PhS addn to 2-
butyne)\\0,2\S,0.1690077987,2.0443956421,0.2291259444\C,1.9400480274,0.8905035183,0.9967144225\C,2.7956905475,0.9580351716,0.1160951507\C,1.5623253671,0.3992542542,2.3295520179\C,3.4860466535,1.2778432848,-1.1161370719\C,-0.9023481686,0.7181734491,-0.1816547635\C,-1.8099159717,0.2274193598,0.7523345709\C,-2.6694005024,-0.7999494318,0.4230992291\C,-2.6339073749,-1.3576633534,-0.8405563082\C,-1.7370579304,-0.8772809269,-1.7768251424\C,-0.8807525091,0.1529468778,-1.4529381349\H,-1.8415078504,0.6678820241,1.7308475033\H,-3.3686258416,-1.1641353404,1.153010904\H,-3.3029884307,-2.1581778009,-1.0958192872\H,-1.7088164712,-1.3036894231,-2.7625748075\H,-0.190130244,0.5336008119,-2.1809876013\H,1.3420050782,1.2264669984,2.9910804455\H,0.6790651518,-0.2234867967,2.2707671012\H,2.3712795655,-0.1852065003,2.7494922453\H,3.7117097758,0.3820733177,-1.6822412082\H,2.8643397758,1.9235106422,-1.730398084\H,4.4170325534,1.7956862214,-0.9183811256\\Version=x86-Linux-G03RevB.04\HF=-785.6734298\S2=0.81146\S2-1=0.\S2A=0.752349\RMSD=7.155e-09\RMSF=3.032e-06\Dipole=0.4511189,-0.7005648,-0.0790227\PG=C01 [X(C10H11S1)]\\@

ν_{im} = -472.654 cm^{-1}

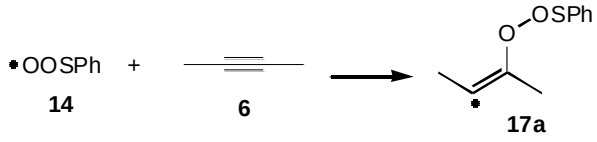
12. Vinyl radical **10**

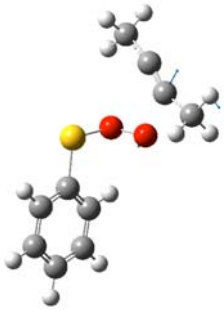


1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET21\FOpt\UBHandHLYP\CC-pVTZ\C10H11S1(2)\KJWTAN\13-Jan-2007\0\\#BHANDHLYP/CC-PVTZ SCF=(QC,DIRECT) OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Geometry optimization of vinyl radical from addition of PhSrad to 2-butyne\\0,2\S,-0.0173401089,1.9362077486,0.5967968426\C,1.596044766,1.1824028792,0.4522885851\C,2.4440054321,1.7402816817,-0.3615414155\C,1.8987848088,0.0291625429,1.3664338018\C,3.8382138005,1.6592253328,-0.7930931039\C,-1.1155235916,0.6228748589,0.1278687949\C,-2.3387132118,0.5351278287,0.7720481221\C,-3.2554404943,-0.4248075813,0.3933988186\C,-2.952858902,-1.3186686973,-0.6141279684\C,-1.729225857,-1.2378400876,-1.2500060614\C,-0.8175982329,-0.2661687354,-0.8913254607\H,-2.5671577807,1.214527804,1.571977148\H,-4.2025146226,-0.4808189388,0.8974747774\H,-3.6627419991,-2.0716999316,-0.9007487444\H,-1.4858908383,-1.9265512567,-2.0380038706\H,0.1224996803,-0.1923967863,-1.4045691291\H,1.8138251272,0.3402801473,2.4009856032\H,1.1950655595,-0.7793044375,1.2093351679\H,2.8977479354,-0.3523074853,1.1982483021\H,4.3642685788,0.8505982969,-0.2878338852\H,3.9036998189,1.4846687885,-1.861053006\H,4.3639501318,2.5834060283,-0.5809503185\\Version=x86-Linux-G03RevB.04\HF=-785.6870221\S2=0.765783\S2-

1=0.\S2A=0.750123\RMSD=0.000e+00\RMSF=2.158e-06\Dipole=0.5888482,-0.645023,-0.1081174\PG=C01 [X(C10H11S1)]\\@

13. Transition state for:

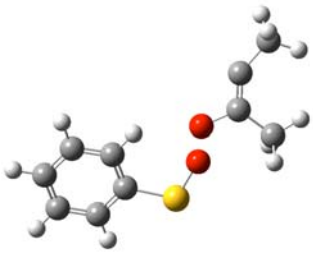




1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET3\FTS\UBHandHLYP\CC-pVTZ\C10H11O2S1(2)\KJWTAN\16-Feb-2007\0\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(TS,NOEIGENTEST,READFC) OPTCYC=500 NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Finding TS from vinyl radical (from PhSOOrad addn to 2-butyne): O-C bond lengthe\\0,2\C,-0.9516106197,-2.7929584105,-1.3352108004\C,-1.8873567208,-3.4477266727,-0.559741799\C,-2.6110979564,-2.7363805894,0.3772641134\C,-2.3985053286,-1.3838480664,0.5408153448\C,-1.4656426454,-0.7322434415,-0.2488821503\C,-0.739074654,-1.4366083046,-1.1902106067\S,-1.2911791546,1.0089708936,-0.0109219299\O,0.0315036026,1.3559663329,-0.9347649988\O,1.217437102,1.085470265,-0.2932054745\C,1.8821437552,2.5484181672,0.7136803138\C,1.3511043703,3.5850975526,0.3400703448\C,2.8145626312,1.7850555317,1.541048667\C,0.5439153752,4.5732062871,-0.3412183932\H,-0.0134595261,-0.9311062476,-1.7959181458\H,-0.3812899604,-3.3385626914,-2.0640871499\H,-2.0484220522,-4.5023318395,-0.6806536197\H,-3.3378450636,-3.2354991207,0.9909829722\H,-2.9531984975,-0.8394024583,1.2838874141\H,-0.061636699,4.0818071996,-1.0982300759\H,-0.1204889094,5.0827523965,0.3462450941\H,1.1619258192,5.3143161921,-0.8336626553\H,3.43805311,1.1575433478,0.9166487201\H,3.4473465249,2.45363506,2.108801964\H,2.273716497,1.1422286166,2.2232628514\\Version=x86-Linux-G03RevB.04\HF=-935.9618994\S2=0.804265\S2-1=0.\S2A=0.750791\RMSD=8.772e-09\RMSF=2.719e-06\Dipole=0.0691401,0.2858118,0.4114901\PG=C01 [X(C10H11O2S1)]\\@

ν_{im} = -616.614 cm^{-1}

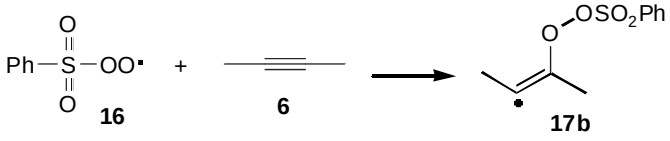
14. Vinyl radical **17a**

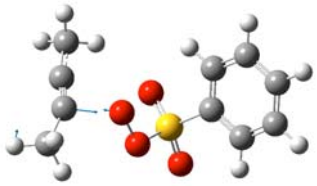


1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET4\FOpt\UBHandHLYP\CC-pVTZ\C10H11O2S1(2)\KJWTAN\20-Jan-2007\0\\#BHANDHLYP/CC-PVTZ SCF=(QC,DIRECT) OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=ALLCHECK GUESS=CHECK\\Geometry optimization of vinyl radical formed from addition of PhS-O-Orad to 2-b\\0,2\C,-2.1252861512,-1.9199879509,-1.5780470421\C,-2.3667968409,-3.2238147883,-1.1942804885\C,-2.0357804338,-3.6294217861,0.0840805504\C,-1.467892952,-2.7396914258,0.9709822899\C,-1.2351085455,-1.4321069964,0.5789639641\C,-1.5613621945,-1.0179717905,-0.6978866096\S,-0.5260442881,-0.3499022589,1.7823378591\O,-0.4141896579,1.0528412715,0.980428727\O,0.8279169112,1.1053867464,0.1934550327\C,1.333538318,2.3774442428,0.319913195\C,1.4505158508,3.0880976263,-0.7673692566\C,1.7794632205,2.7674550815,1.6913436202\C,2.0215229328,4.3399585826,-1.2517535456\H,-1.3697387889,-0.0071101881,-0.9983325671\H,-2.375794067,-1.597334987,-2.5716743681\H,-2.8060001649,-3.9187214992,-1.8849115363\H,-2.2166228127,-4.6421275946,0.39322371\H,-1.2073170173,-3.0633806031,1.962968276\H,2.777266924,4.1588563361,-2.0079658508\H,1.2581276297,4.9700918575,-

1.6938193771\H,2.4880227829,4.8989603807,-
0.4418622305\H,2.4870374726,2.0390111406,2.0712140289\H,2.2494869158,3.7408585119,1.6854947013\H,0.9359
349564,2.8004100911,2.3694969176\\Version=x86-Linux-G03RevB.04\HF=-935.9939831\S2=0.767555\S2-
1=0.\S2A=0.750137\RMSD=0.000e+00\RMSF=7.237e-07\Dipole=0.3558787,0.4722784,-0.1054467\PG=C01
[X(C10H11O2S1)]\\@

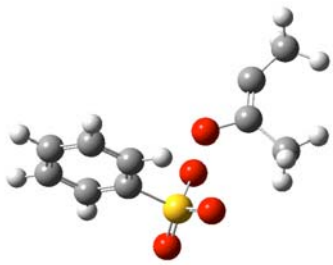
15. Transition state for:





1\1\GINC-AC29\FTS\UBHandHLYP\CC-pVTZ\C10H11O4S1(2)\KXT563\31-May-2008\0\\# BHandHLYP/cc-pVTZ
scf=verytight opt=(TS,Noeigentest,readFC) freq=noraman geom=checkpoint guess=read\\input geom copied fr
TSPhSO4addn2.chk\\0,2\C,-1.659340154,-0.3848147684,-1.5102227682\C,-1.5843652606,-1.3939056086,-
0.5698537763\C,-0.6147861219,-1.3639569469,0.4145048461\C,0.2887562477,-
0.3237110505,0.4612323799\C,0.2032201524,0.6774507081,-0.4866167932\C,-0.7618571794,0.6619994417,-
1.4731882884\O,0.8177736738,3.1271320753,-1.1066024249\O,1.892584762,2.1165081963,0.8917130672\H,-
0.8059165791,1.4588367738,-2.1883852148\H,-2.4170821817,-0.4107764842,-2.2702150803\H,-2.2872118977,-
2.205508895,-0.6013161669\H,-0.5648713385,-2.1469522888,1.1471727952\H,1.0419311634,-
0.2742872224,1.2231635544\O,2.6199191524,1.4220870168,-1.2595991819\S,1.3599699442,2.0008810603,-
0.4225628181\O,2.3147128206,1.2687236193,-2.6000632036\C,3.3609623088,2.5564084415,-
3.5552635763\C,2.5694501238,3.4417439588,-3.8408678359\C,1.4781628058,4.3697059034,-
4.0350503749\H,0.9274085972,4.1406806706,-4.9389682665\H,0.8087533866,4.3175472174,-
3.1842947783\H,1.8490616863,5.3859446117,-4.1100227771\C,4.6684588973,1.9074129063,-
3.5322589261\H,4.9862786499,1.7454953313,-2.5102577265\H,4.6223686008,0.945783414,-
4.0261758228\H,5.4002777399,2.5278549184,-4.0328598418\\Version=IA64L-G03RevD.01\State=2-A\HF=-
1086.3805997\S2=0.791351\S2-1=0.\S2A=0.750477\RMSD=6.137e-09\RMSF=9.110e-07\Thermal=0.\Dipole=-
0.5756781,-0.7435558,-1.1471415\PG=C01 [X(C10H11O4S1)]\\@
ν_{im} = -539.604 cm^{-1}

16. Vinyl radical **17b**

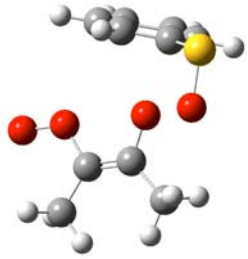


1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET16\FOpt\UBHandHLYP\CC-pVTZ\C10H11O4S1(2)\KJWTAN\21-
May-2008\0\\#BHANDHLYP/CC-PVTZ SCF=VERYTIGHT OPT=(READFC,MAXCYCLE=500) NOSYMM
FREQ=NORAMAN GEOM=CHECKPOINT GUESS=CHECK\\geom input copied fr addnPhSO4_5.chk\\0,2\C,-
1.6674348552,0.7878270958,0.2132581534\C,-1.9397271006,-0.5660510083,0.2304425545\C,-0.924221883,-
1.4886721841,0.0610801704\C,0.3716679601,-1.0601995158,-0.1294015406\C,0.6283549127,0.297304814,-
0.1475854803\C,-
0.3745079013,1.2297821151,0.0230716752\O,2.3966979902,2.194547846,0.0417004182\O,3.1958433156,-
0.1589118162,0.0433265842\H,-0.1372861537,2.2750099538,0.0126068649\H,-
2.4592994135,1.4995552649,0.3499055395\H,-2.9477173647,-0.9051924762,0.3807598671\H,-1.1407999253,-
2.5398232332,0.0820886869\H,1.176584763,-1.7587430269,-0.2500749509\O,2.4635117094,0.7785346969,-

1.9941003266\S,2.2813461744,0.842357936,-0.386565342\O,1.5916313603,1.7283606496,-
2.620053392\C,2.3496040565,2.5182577189,-3.4749346529\C,1.971167932,2.5345401983,-
4.7202526817\C,2.2235455562,3.2270484478,-5.9784725173\H,3.009501118,3.9720873905,-
5.8650184517\H,2.533966246,2.5308049424,-6.749053236\H,1.3330444522,3.7348307785,-
6.3315346857\C,3.4375070093,3.3233039445,-2.8489753343\H,3.048920432,3.8949605322,-
2.0158861275\H,4.2210125165,2.6804975934,-2.4682681243\H,3.8717046328,3.9962647522,-
3.5749238005\\Version=x86-Linux-G03RevB.04\HF=-1086.4086136\S2=0.766453\S2-
1=0.\S2A=0.750123\RMSD=7.592e-09\RMSF=9.678e-07\Dipole=-1.3258574,0.2823809,-0.9613563\PG=C01
[X(C10H11O4S1)]\\@

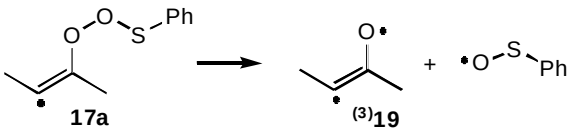
C.3 Reactions of **17a/b** involving O_2

17. Peroxyl radical **18a**



1\1\ CHEMISTRY CLUSTER KIRKLAND-KNET18\FOpt\UBHandHLYP\CC-pVTZ\C10H11O4S1(2)\KJWTAN\28-Jul-2008\0\\#BHANDHLYP/CC-PVTZ OPT=(READFC,MAXCYCLE=500) NOSYMM FREQ=NORAMAN GEOM=CHECKPOINT GUESS=CHECK\\Geom optn of PhSOOvinyl + O2, input copied fr O2vinylPhSOO3.chk\\0,2\C,-1.237064551,-1.7972881767,-1.8105497033\C,-2.4954474131,-2.0872431284,-1.3190880239\C,-2.708365385,-2.1747778347,0.0431417229\C,-1.6619726831,-1.9648477568,0.9174123643\C,-0.3981930184,-1.6771938238,0.4266048201\C,-0.1844932328,-1.6022427869,-0.940653055\S,0.9458148306,-1.4462523874,1.5527510074\O,0.991396825,0.1784611583,1.7271504347\O,1.8208764069,0.7636122786,0.6592838045\C,1.4405686367,2.0596678884,0.5099280512\C,1.577408374,2.9184195815,1.7156889239\C,0.7604811691,3.8142238625,-1.1837178621\H,0.7958115253,-1.3764061134,-1.311864881\H,-1.0737294897,-1.723849309,-2.8691924963\H,-3.3117597537,-2.2457765927,-1.9992584636\H,-3.686926821,-2.401292757,0.4232768283\H,-1.8172183113,-2.0211503503,1.9780601157\H,1.4179830006,4.0900565939,-1.99898707\H,-0.2522412037,3.8666061519,-1.5637945715\H,0.8730911239,4.5275844659,-0.384512558\H,2.5983852847,2.8731320559,2.0783184143\H,1.321384871,3.94739964,1.5213596581\H,0.9361707579,2.5497890333,2.5060288908\C,1.065853453,2.4465064746,-0.7099886834\O,0.9958934424,1.4362587371,-1.6509702799\O,0.6289127618,1.8169966052,-2.8324326983\\Version=x86-Linux-G03RevB.04\HF=-1086.3636282\S2=0.773107\S2-1=0.\S2A=0.750287\RMSD=3.773e-09\RMSF=1.248e-06\Dipole=-0.676218,0.64401,0.2168789\PG=C01 [X(C10H11O4S1)]\\@

18. Transition state for:



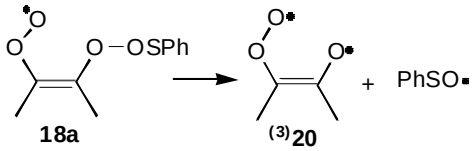
1\1\GINC-AC23\FTS\UBHandHLYP\CC-pVTZ\C10H11O2S1(2)\KXT563\02-Aug-2008\0\\# BHandHLYP/cc-pVTZ scf=verytight opt=(TS,Noeigentest,readFC,MaxCyc
le=500) freq=noraman geom=checkpoint guess=check\\input geom copied fr TSvinylPhSO-O3.chk\\0,2\C,-2.0244019551,-1.6863110042,-1.5813643466\C,-2.3243336553,-3.0125662099,-1.3390283884\C,-2.0809300367,-3.5508948356,-0.0903959395\C,-1.5399404732,-2.7697946189,0.9089326941\C,-1.2509772929,-1.4389272131,0.6595441402\C,-1.4900061788,-0.8925561107,-0.5869175345\S,-0.5880412147,-0.4920634346,1.994902467\O,-0.3201739162,0.9258217693,1.357039817\O,1.1351608289,0.9480530402,0.6235094363\C,1.4688168603,2.2376635823,0.4910107999\C,1.4145937428,2.7818996934,-0.7086516292\C,1.9211881925,2.9341165531,1.7372657158\C,1.7644481266,4.0132622079,-1.4065348441\H,-1.251857895,0.1362990004,-0.7715321324\H,-2.2066020143,-1.2634809326,-2.5520021696\H,-2.7407224213,-3.6232590164,-2.1178760458\H,-2.3068168444,-4.5824271212,0.106229136\H,-1.3420181831,-3.1952121942,1.8766526686\H,2.4906534496,3.8257552011,-2.190097423\H,0.8901088275,4.4562425852,-1.8710642117\H,2.189528688,4.7477004073,-0.7245190795\H,2.7502163272,2.394581698,2.1802451177\H,2.2300634615,3.951782761,1.5421586106\H,1.1129425764,2.9521121921,2.4584951413\\Version=IA64L-G03RevD.01\State=2-A\HF=-935.9909516\S2=0.926684\S2-1=0.\S2A=0.760354\RMSD=4.887e-09\RMSF=1.728e-06\Thermal=0.\Dipole=0.1637264,0.5267621,-0.3923906\PG=C01 [X(C10H11O2S1)]\\@

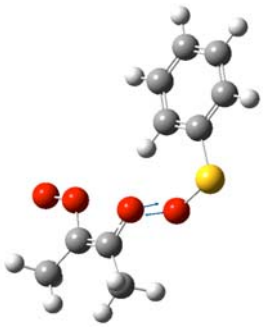
ν_{im} = -856.094 cm^{-1}

19. Biradical $^{(3)}$**19**

1\1\GINC-AC25\FOpt\UBHandHLYP\CC-pVTZ\C4H6O1(3)\KXT563\18-Aug-2008\0\\# BHandHLYP/cc-pVTZ opt=(calcFC,MaxCycle=500) freq=noraman\\input copied fr harvey/vrtb-prod2_5.out at bhlyp/6-311g**\\0,3\C,-0.015587837,0.157290323,0.1118021441\C,2.6398715673,-0.1419870333,-0.0462441588\H,3.2923650685,0.7255161547,-0.0075202438\H,2.656362104,-0.6182330958,0.9319538783\H,3.0715386951,-0.8343651042,-0.7632423663\C,-0.1655600998,-0.4821687976,1.4752919697\H,-1.2099577165,-0.4669741195,1.7489991019\H,0.187888151,-1.5069764562,1.4640903586\H,0.409011595,0.0553262863,2.2211125877\O,-0.9860639086,0.5857877279,-0.4890287885\C,1.2867373809,0.2377731147,-0.4347094829\\Version=IA64L-G03RevD.01\State=3-A\HF=-231.084489\S2=2.038488\S2-1=0.\S2A=2.000378\RMSD=5.591e-09\RMSF=6.345e-07\Thermal=0.\Dipole=1.2817421,-0.5537712,0.7684374\PG=C01 [X(C4H6O1)]\\@

20. Transition state for:





1\1\GINC-AC23\FTS\UBHandHLYP\CC-pVTZ\C10H11O4S1(2)\KXT563\14-Aug-2008\0\\# BHandHLYP/cc-pVTZ scf=verytight opt=(TS,Noeigentest,calcFC) freq=noraman\\input geom fr copied kirkland/2008_2/TSaddedO2_PhSO-O4.out\\0,2\C,2.5698993224,1.8743867141,-0.144602766\C,3.9052557689,1.6562584169,0.1308447198\C,4.3710070258,0.3638731265,0.2764450908\C,3.507681069,-0.703387822,0.1476563235\C,2.1722162432,-0.4741259349,-0.1368297745\C,1.6959815594,0.8145070571,-0.2813410444\S,1.1364555388,-1.8961173572,-0.3025836258\O,-0.2850047347,-1.2886771244,-0.6640290644\O,-1.0591789199,-0.8728473961,0.6529972998\C,-2.345069981,-0.7532698055,0.3127532466\C,-3.1092612012,-2.0274742722,0.2199731311\C,-4.2238388705,0.8863194262,-0.1764800096\H,0.6577597749,0.9857910787,-0.484095551\H,2.1989392786,2.8767395906,-0.2515032884\H,4.5777747903,2.4867210184,0.2354071658\H,5.4073874356,0.184181632,0.4939241643\H,3.8729294862,-1.7078611212,0.2678619528\H,-4.5718604513,1.5792228833,0.5798306698\H,-4.2868942996,1.403221707,-1.1266196617\H,-4.8728240242,0.0271767279,-0.1954687583\H,-3.058871551,-2.5530841192,1.1666141817\H,-4.1454817538,-1.8876565561,-0.044395512\H,-2.6490525235,-2.6619450684,-0.5288245515\C,-2.8294064082,0.4830601139,0.0976238732\O,-1.8992166555,1.488542792,0.1671508624\O,-2.3655109186,2.6827452925,-0.017033074\\Version=IA64L-G03RevD.01\State=2-A\HF=-1086.3633223\S2=0.838229\S2-1=0.\S2A=0.753542\RMSD=3.452e-09\RMSF=1.416e-06\Thermal=0.\Dipole=-0.5899002,-0.4689237,-0.0325371\PG=C01 [X(C10H11O4S1)]\\@

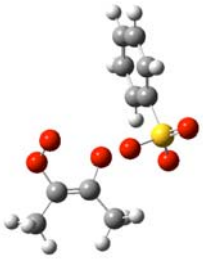
ν_{im} = -633.764 cm^{-1}

21. Biradical $^{(3)}$**20**

1\1\GINC-AC7\FOpt\UBHandHLYP\CC-pVTZ\C4H6O3(3)\HXL563\30-Jul-2008\0\\# BHandHLYP/cc-pVTZ scf=direct opt=(maxcycle=500,calcFC) freq=noraman\\preTS2\\0,3\C,-1.0065116983,-0.3573151043,-0.017280687\C,0.5940930317,1.7200041772,-0.1015221696\H,0.9584472435,2.0680618412,-1.0647242581\H,-0.2614292985,2.3131158583,0.180655836\H,1.3893614371,1.8819295216,0.618875048\C,-2.219359487,0.5084245743,0.1979002618\H,-2.3437872804,1.222516472,-0.6078152852\H,-3.0869001471,-0.1314269958,0.244463607\H,-2.1404844635,1.0670624692,1.1235808817\O,-1.0929802587,-1.5676367803,-0.0671462092\C,0.2688540544,0.2857365454,-0.1665085963\O,1.3248163324,-0.5549822639,-0.4541773557\O,2.2150165344,-0.5449293148,0.5097789266\\Version=IA64L-G03RevD.01\State=3-A\HF=-

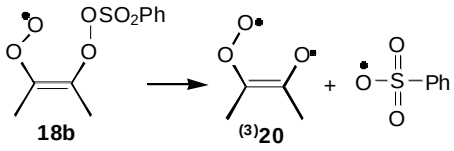
381.4483787\S2=2.038502\S2-1=0.\S2A=2.000546\RMSD=5.459e-09\RMSF=1.491e-06\Thermal=0.\Dipole=-0.4651221,1.7706641,-0.0117223\PG=C01 [X(C4H6O3)]\\@

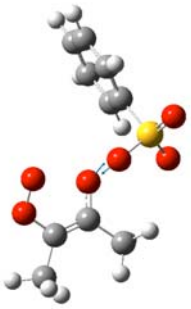
22. Peroxyl radical **18b**



1\1\GINC-AC25\FOpt\UBHandHLYP\CC-pVTZ\C10H11O6S1(2)\KXT563\27-Jul-2008\0\\# BHandHLYP/cc-pVTZ opt=(readFC, maxcycle=500) freq=noraman geom=checkpoint guess=check\\input geom copied from O2vinylPhSO4_3.chk\\0,2\C,-1.6544473336,0.7785212482,0.3127539663\C,-1.9201611404,-0.5761728703,0.2821340411\C,-0.9041453408,-1.4867954816,0.0577598041\C,0.3858084208,-1.0452753391,-0.1394082802\C,0.6355903671,0.3137299072,-0.1102079848\C,-0.3673612081,1.2343314777,0.1146626848\O,2.3819512907,2.23791283
86,0.0304516619\O,3.2114713352,-0.1049457168,0.08069398\H,-0.1355243275,2.2805707955,0.1397444614\H,-2.4467458955,1.4803205676,0.4913730582\H,-2.9238018662,-0.9259661723,0.4367375976\H,-1.1163028485,-2.5388096445,0.0396209169\H,1.1902075311,-1.7353874617,-0.3042326732\O,2.4601581601,0.7749419867,-1.9729752245\S,2.2799069482,0.8738622671,-0.3614073885\O,1.5806726934,1.7048149156,-2.6126959824\C,2.3109062323,2.4603666633,-3.4964018798\C,2.3781659095,3.2509674752,-5.8970409928\H,3.0281747091,4.0500006329,-5.5796619498\H,2.8954441107,2.6497607363,-6.6369137041\H,1.5104688108,3.6849678309,-6.3812676948\C,3.3688975822,3.320084175,-2.9093745139\H,2.9560263529,3.9193760677,-2.1079586528\H,4.1528573462,2.7075534803,-2.4817390452\H,3.8138136209,3.9662502835,-3.6490391392\O,0.9454572607,1.5135399971,-5.1758779514\O,1.2037286902,0.2653388926,-4.9060295293\C,1.9411362585,2.3992835369,-4.7658815455\\Version=IA64L-G03RevD.01\State=2-A\HF=-1236.7714101\S2=0.757181\S2-1=0.\S2A=0.750036\RMSD=6.475e-09\RMSF=1.210e-06\Thermal=0.\Dipole=-1.0396463,0.676866,-0.5123579\PG=C01 [X(C10H11O6S1)]\\@

23. Transition state for:





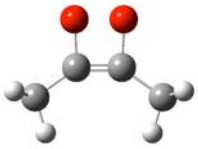
1\1\GINC-AC14\FTS\UBHandHLYP\CC-pVTZ\C10H11O6S1(2)\KXT563\02-Aug-2008\0\\# BHandHLYP/cc-pVTZ scf=verytight opt=(TS,Noeigentest,readFC,MaxCycle=500) freq=noraman geom=checkpoint guess=check\\input geom copied fr TSaddedO2_PhSO3LG3.chk\\0,2\C,3.0630359818,-1.2288232069,1.6216699636\C,3.7455122449,-1.8737713309,0.6095194463\C,3.5684218716,-1.4933494669,-0.7079393724\C,2.7050666582,-0.4654568473,-1.0188194337\C,2.0244444027,0.167880662,0.0034173476\C,2.193773382,-0.1994552993,1.322070846\O,0.5947715406,2.1906882449,0.7953535339\O,1.4044604245,2.1753720919,-1.5489377819\H,1.6588792042,0.3212210481,2.091400623\H,3.2080408027,-1.5238321371,2.6436820101\H,4.421719678,-2.6738100613,0.8470232727\H,4.1055347777,-1.9940672961,-1.4910215027\H,2.5638396476,-0.1472283651,-2.033420344\O,-0.363299736,0.7454870609,-0.9649817278\S,0.9250813815,1.4820153995,-0.3971722078\O,-1.0297150627,-0.1474660736,0.2705042158\C,-2.2874545111,0.1720140959,0.3848628827\C,-4.6636693898,-0.7287392697,0.3321504109\H,-4.8749900524,-0.0826252101,1.1679376745\H,-5.2574240787,-0.4092643157,-0.5186700251\H,-4.9716525758,-1.7365927563,0.5815685699\C,-2.6130434789,1.476445746,1.0295981553\H,-2.1986172967,1.5136737928,2.0293452026\H,-2.1404538143,2.2697796936,0.4648093145\H,-

3.6732255864,1.6706110043,1.0707592324\O,-2.9285495361,-1.8695525394,-0.7097084805\O,-1.9207113626,-1.8220440189,-1.5312723165\C,-3.2233025164,-0.7323586455,-0.0200865093\\Version=IA64L-G03RevD.01\State=2-A\HF=-1236.7605954\S2=1.046714\S2-1=0.\S2A=0.77094\RMSD=5.887e-09\RMSF=1.876e-06\Thermal=0.\Dipole=-1.1398612,-1.2925478,1.1066776\PG=C01 [X(C10H11O6S1)]\\@

ν_{im} = -840.902 cm^{-1}

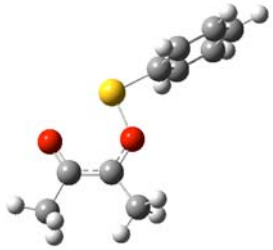
C.4 Reactions of **17a**/**b** without O_2

24. Oxetene **21**



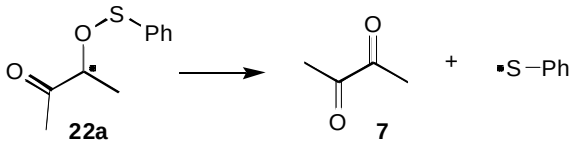
1\1\GINC-AC28\FOpt\RBHandHLYP\CC-pVTZ\C4H6O2\KXT563\16-Aug-2008\0\\# BHandHLYP/cc-pVTZ scf=verytight opt=(calcFC,MaxCycle=500) freq=noraman\\input copied fr dioxetane5.out\\0,1\C,-0.6594721671,-0.1238642577,0.0000057623\C,0.6594721728,-0.1238642514,0.0000340071\O,0.7155090806,1.2685536857,-0.0001473566\O,-0.7155090819,1.2685536751,-0.0001778347\C,1.850674614,-0.9778964267,0.0001715208\H,2.4617884743,-0.8002834158,-0.8775760356\H,2.4617441357,-0.8000642586,0.8779057562\H,1.5497652126,-2.0169863197,0.0002937122\C,-1.8506746097,-0.9778964357,0.0000943787\H,-2.46175823,-0.8002744676,-0.8776724735\H,-1.5497652306,-2.0169863304,0.0002160837\H,-2.4617743708,-0.8000731971,0.8778093274\\Version=IA64L-G03RevD.01\State=1-A\HF=-306.2671822\RMSD=7.750e-09\RMSF=9.352e-05\Thermal=0.\Dipole=0.,-1.2545535,0.000165\PG=C01 [X(C4H6O2)]\\@

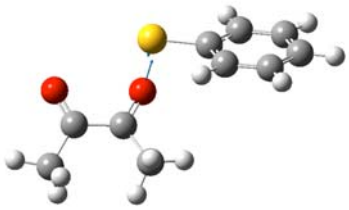
25. Radical **22a**



1\1\GINC-AC51\FOpt\UBHandHLYP\CC-pVTZ\C10H11O2S1(2)\KXT563\24-Aug-2007\0\\# BHandHLYP/cc-pVTZ scf=verytight opt=(readFC,MaxCycle=1000) freq=noraman geom=checkpoint guess=check\\Geom optn of MeC(O)-C(OSPh)Me -- after 2nd O transfer\\0,2\C,-1.9372634343,0.9183370651,0.2904200071\O,-0.6484150636,0.6139202111,0.2418395323\C,-2.1442562831,2.3857349342,0.3829693564\S,-0.0241242966,-0.9687278692,0.1328149684\C,1.6605562332,-0.4348479953,0.125276908\C,2.3033035886,-0.1790246553,-1.0756389043\C,2.359124972,-0.3213193383,1.3168669719\C,3.6310368634,0.1958349665,-1.0834288035\H,1.7585242935,-0.2781977673,-1.9952261102\C,3.6868103928,0.0536593363,1.3072974845\H,1.8574041577,-0.5302543829,2.2425466514\C,4.3212890479,0.3126066637,0.1076524195\H,4.1269665066,0.3927968765,-2.0154790442\H,4.2260614988,0.1401945079,2.2320558036\H,5.3560363666,0.6013101786,0.1006817749\H,-1.6574149551,2.7785484881,1.2696945552\H,-3.1914412367,2.6403111223,0.4229853662\H,-1.698702075,2.8826259185,-0.4727080432\C,-4.4016722114,0.3602918822,0.3151269371\H,-4.6644254652,1.002742502,-0.5173024231\H,-5.0102325524,-0.5302061352,0.2761858146\H,-4.6232610626,0.8982198875,1.2295955646\C,-2.956150814,-0.0654296184,0.2555927003\O,-2.6666327423,-1.2565118413,0.1775198092\\Version=IA64L-G03RevD.01\State=2-A\HF=-936.1427484\S2=0.772266\S2-1=0.\S2A=0.750172\RMSD=1.665e-09\RMSF=1.555e-06\Thermal=0.\Dipole=0.567515,1.3084291,0.0650452\PG=C01 [X(C10H11O2S1)]\\@

26. Transition state for:





1\1\GINC-AC26\FTS\UBHandHLYP\CC-pVTZ\C10H11O2S1(2)\KXT563\27-Aug-2007\0\\# BHandHLYP/cc-pVTZ scf=verytight opt=(TS,Noeigentest,readFC,MaxCycle=500) nosymm freq=noraman geom=checkpoint guess=check\\TS for MeC(O)-C(OSPh)Me -- PhS-O bond 2.0A\\0,2\C,-1.764826927,1.2521454252,-0.0637221371\O,-0.794275702,1.9060555668,0.4316683503\C,-1.5401988062,0.3884598442,-1.2559622084\S,0.220880606,1.0855655865,1.8980988206\C,1.65975701,0.6466441888,1.0150545837\C,2.6449059881,1.5976424927,0.7672798054\C,1.8474826555,-0.6578986605,0.5691741263\C,3.7884068122,1.2503294312,0.081749574\H,2.5000897733,2.6017420631,1.1170402272\C,2.9978834186,-1.003820008,-0.1066377345\H,1.0896477824,-1.3921573924,0.7662125741\C,3.9672010677,-0.0498116605,-0.3542054284\H,4.5435524864,1.9900902648,-0.1079681716\H,3.139040858,-2.0146822233,-0.4410925601\H,4.8622495517,-0.3196398114,-0.8832743507\H,-0.630584996,0.6886343383,-1.7554484763\H,-2.3664345025,0.4377449694,-1.9533604273\H,-1.4347628765,-0.6532889583,-0.9580201996\C,-4.2651351373,0.6805906969,-0.0005905781\H,-4.1087545118,-0.3742233999,-0.1983619727\H,-5.1143953643,0.800412905,0.6541942685\H,-4.4718990691,1.159332147,-0.9514156599\C,-3.0570469579,1.2885599409,0.6558178848\O,-3.1133961593,1.7865892536,1.7498776898\\Version=IA64L-G03RevD.01\HF=-936.128471\S2=0.81884\S2-1=0.\S2A=0.752914\RMSD=8.471e-09\RMSF=1.505e-06\Thermal=0.\Dipole=0.5254364,-1.0902276,-1.5841276\PG=C01 [X(C10H11O2S1)]\\@

ν_{im} = -617.812 cm^{-1}