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ALLYLSULFONE IN FREE RADICAL REACTION

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Abstract: A sulfonyl radical induced addition-cyclization reaction of vinylcyclopropane and 1,6-diene by using allylsulfone as sulfonyl radical precursor to give functionalized cyclopentane is described.

The free radical cyclization reaction is increasingly being used in the formation of ring systems.[1] This reaction exhibits interesting regio- and stereo-selectivity. Allylsulfone undergoes 1,3-rearrangement under BPO-CCl_4 condition via an addition-elimination mechanism involving sulfonyl radical (Eq 1).[2] On the basis of mechanism proposed by Whitham, we believe that allylsulfone can be a potential sulfonyl radical precursor. This report describes our unexpected results on sulfonyl radical induced addition-cyclization reaction of

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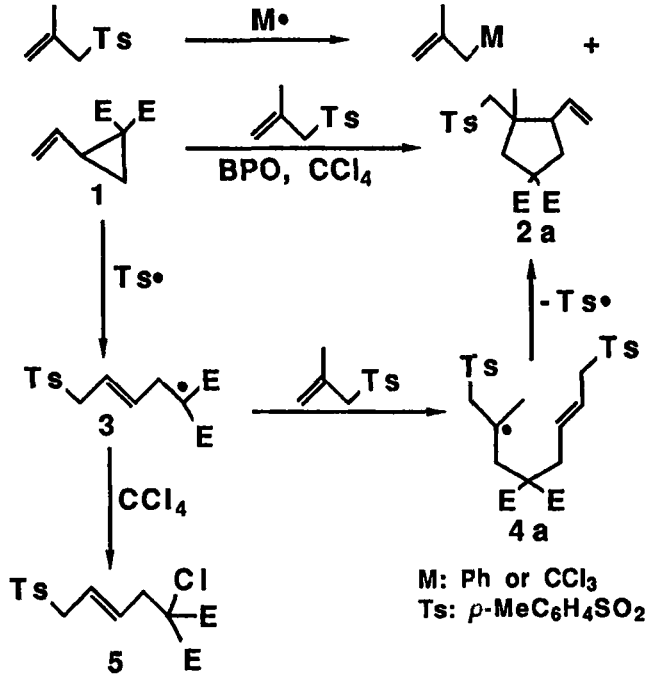
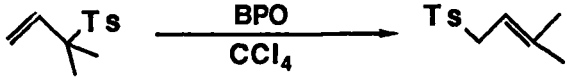
Scheme I



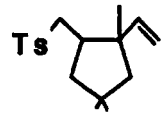
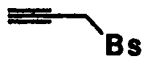
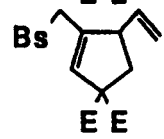
vinylcyclopropane and 1,6-diene by using allylsulfone as sulfonyl radical precursor.[3,4]



(Eq 1)

When vinylcyclopropane **1** was treated with methallyl tolyl sulfone (5 eq) and benzoylperoxide (BPO) in carbon tetrachloride, cyclopentane **2a** was obtained in 81% yield as 1.1:1 separable isomers and no trace of **5** could be found (Scheme I). The results with various sulfones are summarized in Table I. The radical intermediate **3** undergoes addition reaction to allylsulfone to give **4a** instead of chlorine atom abstraction from carbon tetrachloride to give **5**.

Table I: The Free Radical Addition-Cyclization Reaction of Vinylcyclopropane 1[a]

Entry	Allylsulfone	Product 2	Yield (Ratio)
a			81% (1.1:1)[b]
b			47%[c]
c			31%

a: E: CO_2Me, Ts: p-$MeC_6H_4SO_2$, Bs: $C_6H_5SO_2$
b: Ratios refer to isomeric products and are based on isolated yields.
c: One stereoisomer was obtained.

Treatment of diene with methallyl tolyl sulfone (1.2 eq) under BPO-CCl_4 condition gave the cyclopentyl chloride **7** in good yield and no **10** being found (Scheme II). In the presence of carbon tetrabromide (5 eq), the corresponding bromide was obtained under similar condition.[5] Most examples display a good preference for the cis isomer.[3a,3d] The results of this reaction are shown in Table II. The radical intermediate **9** undergoes halogen atom (Cl, Br) abstraction from carbon tetrahalides to give **7**.

The relative stereochemistry of the isomeric products was determined by ^{13}C NMR spectroscopy. The γ gauche interaction in the cis configuragation contributes to a significant shielding effect of both methylene carbons bearing p-toluenesulfonyl and halo groups.[6] The ^{13}C chemical shifts data of these two carbons are listed in Table III. We believe that the major product should be cis isomer.

Scheme II

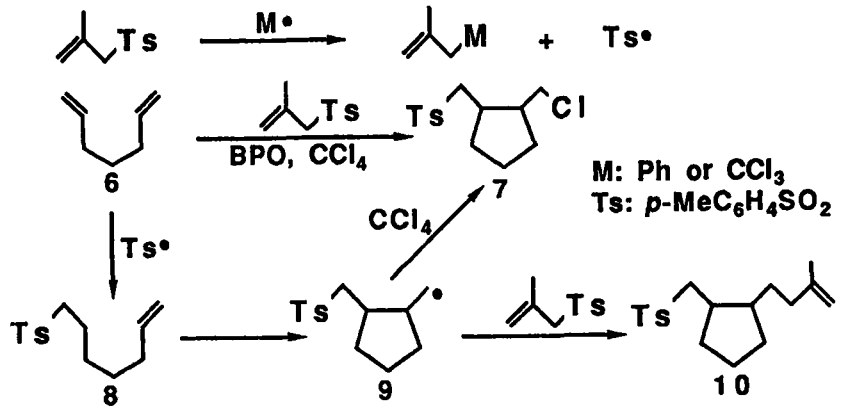
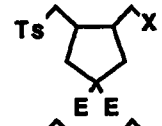
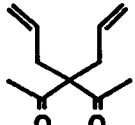
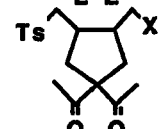
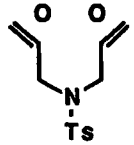
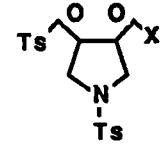
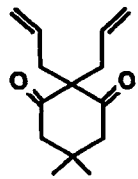
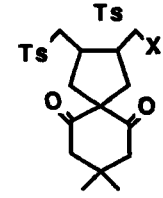
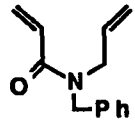
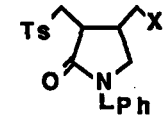


Table II: Free Radical Cyclization Reaction Of 1,6-Dienes[a]

Entry	Substrate 6	Halide	Product 7	X	Yield	(Ratio)[b]
a		CCl_4		Cl	65%	(6.3:1)
b		CBr_4		Br	85%	(5:1)
c		CCl_4		Cl	70%	(4.8:1)
d		CBr_4		Br	64%	(4.4:1)
e		CCl_4		Cl	77%	(2.7:1)
f		CBr_4		Br	74%	(2.5:1)
g		CCl_4		Cl	79%	(3.7:1)
h		CBr_4		Br	70%	(3.7:1)
i		CCl_4		Cl	48%	(3.2:1)
j		CBr_4		Br	47%	(3.1:1)

a: E: CO_2Me, Ts: p-$MeC_6H_4SO_2$

b: Ratios refer to isomeric products are based on HPLC analysis.

Table III: ^{13}C Chemical Shifts In Cis And Trans Isomers

Product	CH_2Ts	CH_2X (X=Br, Cl)
cis -7b	55.1	32.5
trans -7b	59.7	34.8
cis -7c	55.6	44.3
trans -7c	59.8	45.7
cis -7e	54.3	42.3
trans -7e	58.9	44.7
cis -7f	53.6	29.9
trans -7f	58.9	32.8
cis -7g	54.8	43.8
trans -7g	59.9	45.9
cis -7h	54.4	32.2
trans -7h	59.8	34.5

These results suggest that for the electron rich carbon centered radical the halogen atom abstraction proceeds at a much faster rate than the addition to unsatuated carbon-carbon bond. On the other hand, for electron poor carbon centered radical the rate for the addition reaction to unsatuated carbon-carbon bond is much faster than halogen atom abstraction.

In conclusion, allylsulfone is a potential sulfonyl radical precursor. This reaction provides a method for the preparation of functionalized cyclopentane system from both vinylcyclopropane and 1,6-dienes.

Experimental:

General procedure: A solution of 103 mg (0.49 mmol) of dimethyl diallylmalonate, 123 mg (0.59 mmol) of methallyl

tolyl sulfone and 43 mg (0.18 mmol) of benzoylperoxide in 6 ml of carbon tetrachloride was heated under reflux for 7 h. The reaction mixture was diluted with 50 ml of ethyl acetate, washed with two 25-mL portions of saturated aqueous sodium bicarbonate, three 25-mL portions of water, dried (Na_2SO_4) and concentrated in vacuo. The residue was chromatographed over 20 g of silica gel (230-400 mesh) (eluted with ethyl acetate-hexane, 1:3.5) to give 128 mg (65%) of **7a** as 6.3:1 partial separable isomers.

Spectra data for the major isomers:

2a: IR (neat) 2956, 1731, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.4 (s, 3H, CH_3), 2.25-2.55 (m, 3H), 2.44 (s, 3H, CH_3), 2.38 and 3.12 (AB system, J=14Hz, 2H, CH_2), 2.68 and 3.32 (AB system, J=14Hz, 2H, CH_2SO_2), 3.74 (s, 3H, CH_3O), 3.79 (s, 3H, CH_3O), 4.9-5.2 (m, 2H, =CH), 5.4-5.8 (m, 1H, =CH), 7.34 (d, J=8.0Hz, 2H, ArH), 7.78 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$), δ 21.5(q), 24.8(q). 37.0(t), 43.7(t), 45.6(s), 52.8(q), 52.9(q), 56.0(d), 57.4(s), 59.7(t), 118.1(t), 127.5(d), 129.7(d), 134.7(d), 139.0(s), 144.2(s), 172.8(s), 173.2(s), and IR (neat) 2974, 1734 and 1149 cm-1; ^1H NMR ($CDCl_3$) δ 1.12 (s, 3H, CH_3), 2.2-2.5 (m, 3H), 2.45 (s, 3H, CH_3), 2.66 (s, 2H, CH_2), 2.98 and 3.2 (AB system, J=14Hz, 2H, CH_2SO_2), 3.73 (s, 3H, CH_3O), 3.74 (s, 3H, CH_3O), 4.85-5.2 (m, 2H, =CH), 5.4-5.85 (m, 1H, =CH), 7.35 (d, J=8.0Hz, 2H, ArH), 7.8 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 19.8(q), 21.4(q), 36.6(t), 44.8(s), 45.5(t), 52.7(q), 52.8(q), 54.3(d), 57.9(s), 66.2(t), 118.2(t), 127.5(d), 129.8(d), 135.3(d), 138.5(s), 144.4(s), 172.3(s), 173.3(s).

2b: IR (neat) 2956, 1728, 1437, 1269 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.7-3.4 (m, 8H), 2.45 (s, 3H, CH_3), 3.72 (s, 6H, CH_3O), 4.8-5.2 (m, 2H, =CH), 5.25-5.8 (m, 1H, =CH), 7.35 (d, J=8.0Hz, 2H, ArH),

7.78 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 37.0(d), 38.2(t), 38.3(t), 46.3(d), 52.7(t), 58.5(s), 117.4(t), 127.8(d), 129.8(d), 136.1(d), 137.9(s), 144.6(s), 172.3(s), 172.4(s).

2c: IR ($CHCl_3$) 2956, 1734, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.1 (dd, J=13Hz, 6Hz, 1H), 2.8 (dd, J=13Hz, 7.8Hz, 1H), 3.2-3.55 (m, 1H), 3.7 (s, 6H, CH_3O), 3.86 (s, 2H, CH_2SO_2), 4.85-5.75 (m, 4H, =CH), 7.4-8.1 (m, 5H, ArH); ^{13}C NMR ($CDCl_3$) δ 38.2(t), 50.8(d), 52.7(q), 55.4(t), 65.3(s), 118.1(t), 128.5(d), 128.9(d), 131.9(d), 133.6(d), 138.1(d), 138.1(s), 170.0(s), 170.9(s).

7a: IR (neat) 2954, 1731, 1437 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0-2.9 (m, 6H), 3.0-3.33 (m, 2H, CH_2SO_2), 3.33-3.6 (m, 2H, CH_2Cl), 3.73 (s, 6H, CH_3O), 7.37 (d, J=8.2Hz, 2H, ArH), 7.79 (d, J=8.2Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.5(q), 35.7(d), 36.9(t), 38.4(t), 43.5(d), 44.2(t), 52.9(q), 55.7(t), 58.3(s), 127.9(d), 129.9(d), 136.3(s), 144.8(s), 172.1(s), 172.2(s).

7b: IR (neat) 2956, 1731, 1269 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.0-2.9 (m, 6H), 2.9-3.5 (m, 4H), 3.73 (s, 6H, CH_3O), 7.37 (d, J=8.1Hz, 2H, ArH), 7.79 (d, J=8.1Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.3(q), 32.5(t), 36.1(d), 37.7(t), 43.7(d), 52.7(q), 55.1(t), 58.0(s), 127.6(d), 129.7(d), 136.0(s), 144.6(s), 171.8(s), 172.0(s).

7c: IR ($CHCl_3$) 3022, 1698, 1314, 1146 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 2.0-2.8 (m, 6H), 2.9-3.6 (m, 4H), 7.37 (d, J=8.4Hz, 2H, ArH), 7.79 (d, J=8.4Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.5(q), 25.9(q), 26.7(q), 33.2(t), 34.8(t), 35.7(d), 43.5(d), 44.3(t), 55.6(t), 73.5(s), 127.8(d), 129.9(d), 136.3(s), 144.9(s), 203.6(s), 204.4(s).

7d: IR ($CHCl_3$) 3022, 1698, 1317, 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.09 (s, 3H, CH_3), 2.12 (s, 3H, CH_3), 1.8-3.7 (m, 6H), 2.8-3.4 (m, 4H), 7.37 (d, J=8.0Hz, 2H, ArH), 7.78 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.3(q), 25.8(q), 26.5(q), 32.6(t), 34.0(t), 34.1(t), 36.1(d), 43.7(d), 55.1(t), 73.1(s), 127.6(d), 129.8(d), 136.0(s), 144.7(s), 203.4(s), 204.2(s).

7e: IR ($CHCl_3$) 3028, 1305, 1158 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 6H, CH_3), 2.1-3.8 (m, 10H), 7.53 (d, J=8.0Hz, 2H, ArH), 7.82 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.7(q), 21.8(q), 35.5(d), 42.3(t), 43.4(d), 50.4(t), 51.3(t), 54.3(t), 127.7(d), 128.1(d), 130.0(d), 130.3(d), 133.4(s), 136.2(s), 144.2(s), 145.5(s).

7f: IR ($CHCl_3$) 3022, 1290, 1161 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.44 (s, 6H, CH_3), 2.4-3.7 (m, 10H), 7.34 (d, J=8.0Hz, 2H, ArH), 7.71 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.3(q), 21.4(q), 29.9(t), 35.6(d), 43.2(d), 50.6(t), 50.9(t), 53.6(t), 127.3(d), 127.7(d), 129.7(d), 129.9(d), 133.0(s), 135.6(s), 143.7(s), 145.1(s).

7g: IR ($CHCl_3$) 2962, 1731, 1695, 1146 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (s, 3H, CH_3), 1.03 (s, 3H, CH_3), 2.0-3.0 (m, 10H), 2.45 (s, 3H, CH_3), 3.0-3.25 (m, 2H, CH_2SO_2), 3.3-3.55 (m, 2H, CH_2Cl), 7.34 (d, J=8.0Hz, 2H, ArH), 7.77 (d, J=8.0Hz, 2H, ArH);^{13}C NMR ($CDCl_3$) 21.5(q), 27.6(q), 28.7(q), 30.3(s), 32.9(t), 36.4(d), 37.4(t), 43.8(t), 45.0(d), 51.1(t), 51.6(t), 54.8(t), 69.5(s), 127.8(d), 129.9(d), 136.4(s), 144.8(s), 206.8(s), 207.5(s).

7h: IR ($CHCl_3$) 2962, 1731, 1695, 1149 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.92 (s, 3H, CH_3), 1.02 (s, 3H, CH_3), 1.9-2.9 (m, 10H), 2.45 (s, 3H, CH_3), 3.0-3.2 (m, 2H, CH_2SO_2), 3.2-3.4 (m, 2H, CH_2Br),

7.37 (d, J=8.0Hz, 2H, ArH), 7.78 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.4(q), 27.6(q), 28.5(q), 30.1(s), 32.2(t), 34.0(t), 36.7(t), 36.7(d), 45.0(d), 50.9(t), 51.4(t), 54.4(t), 69.3(s), 127.7(d), 130.0(d), 136.2(s), 144.6(s), 206.6(s), 207.4(s).

7i: IR (neat) 3060, 1694, 1300 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 2.6-4.1(m, 8H), 4.43 (s, 2H, CH_2N), 7.05-7.5 (m, 5H, ArH), 7.37 (d, J=8.0Hz, 2H, ArH), 7.82 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.6(q), 39.5(d), 40.2(d), 46.3(t), 47.0(t), 48.5(t), 57.5(t), 127.8(d), 128.0(d), 128.1(d), 128.8(d), 130.0(d), 135.6(s), 136.1(s), 145.1(s), 171.6(s).

7j: IR ($CHCl_3$) 3010, 1692, 1317, 1152 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.45 (s, 3H, CH_3), 2.6-4.05 (m, 8H), 4.44 (s, 2H, CH_2N), 7.05-7.5 (m, 5H, ArH), 7.37 (d, J=8.0Hz, 2H, ArH), 7.83 (d, J=8.0Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 21.5(q), 35.5(t), 39.3(d), 41.4(d), 47.0(t), 49.7(t), 57.4(t), 127.7(d), 127.9(d), 128.0(d), 128.7(d), 130.0(d), 135.4(s), 136.0(s), 146.1(s), 171.6(s).

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References and Notes:

1.(a)Hart, D.J. *Science* (washington, D.C.), **1984**, *223*, 883. (b)Neumann, W.P. *Synthesis* **1987**, 665. (c)Curran, D.P. *Synthesis*, **1988**, 417 and 489.

2.Knight, D.J.; Lin, P.; Whitham, G.H. *J. Chem. Soc. Perkin Trans. I*, **1987**, 2707.

3.(a)De Riggi, I.; Surzur, J.-M.; Bertrand, M.P. *Tetrahedron*, **1988**, *44*, 7119. (b)Serra, A.C.; da Silva Corra, C.M.M. *J. Chem. Research(S)*, **1989**, 85. (c)Chuang, C.-P.; Ngoi, T.H.J. *Tet. Lett.* **1989**, *30*, 6369.(d)Chuang, C.-P. and Wang, R.-Z. *J.*

Chinese Chem. Soc., **1990**, *37*, 89. (e)Nouguier, R.; Lesueur, C.; De Riggi, E. and Bertrand, M.P., *Tet. Lett.*, **1990**, *31*, 3541 (f)De Riggi, I; Surzur, J.-M. and Bertrand, M.P. *Tetrahedron*, **1990**, *46*, 5285. (g)Chuang, C.-P. *Synlett*, **1990**, *9*, 527.

4.(a)Miura, K.; Fugami, K.; Oshima, K.; and Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 5135. (b)Chuang, C.-P.; Hou, S.-S. and Ngoi, T.H.J. *J. Chinese Chem. Soc.*, **1990**, *37*, 85. (c)Feldman, K.S. and Romanelli A.L. *Tetrahedron Lett.* **1990**, 823.

5.In the presence of iodoform, the corresponding iodide was obtained in poor yield.

6.Christl, M.; Reich, H.J. and Roberts, J.D. *J. Am. Chem. Soc.*, **1971**, *93*, 3463.

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