connecting two states of differing orbital character should be large. These matrix elements should not be diminished by small FC factors owing to geometry differences between the T_1 and S_1 states. Conformational changes on electronic excitation may also accelerate other radiationless transitions, such as internal conversion and intramolecular vibrational relaxation.[15] The photochemical behavior of T_1 and S_1 acetophenone might also be quite different. Some of these issues are now being explored in our laboratories.

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[15] Moss, D. B.; Parmenter, C. S.; Ewing, G. E. *J. Chem. Phys.* **1987**, *86*, 51 and references therein.

Synthesis of Cyclopentenyl Sulfones via the [3 + 2] Cyclization–Elimination Reaction of (Phenylsulfonyl)allene

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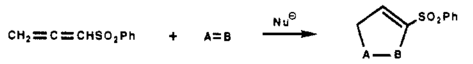
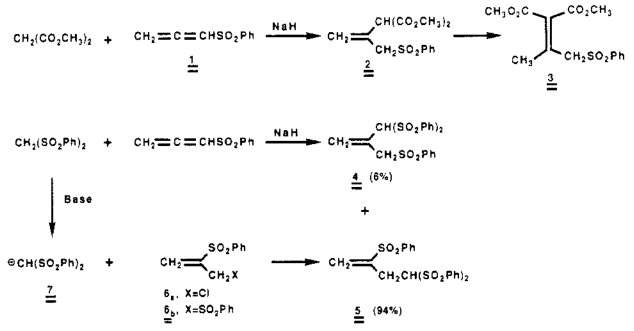
Approaches to carbocyclic systems wherein a five-membered ring is generated by means of a [3 + 2]-anionic cycloaddition reaction remain the focus of intense synthetic efforts.[1,2] As part of a program concerned with the chemistry of unsaturated sulfones,[3] we sought to develop a general strategy for five-ring construction which would allow direct entry into a variety of cyclopentenyl-substituted sulfones. In this communication we describe the stepwise reaction of (phenylsulfonyl)allene with activated olefins by using catalytic quantities of a nucleophilic reagent as a method for producing five-membered rings in high yield (eq 1).



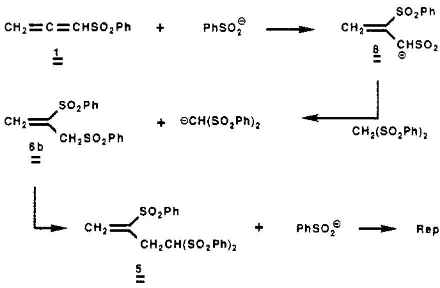
(1)

(Phenylsulfonyl)allene is highly activated toward nucleophilic addition because of its markedly lowered LUMO energy level compared with allene.[4] While the reactions with heteronucleophiles have been well investigated,[5] much less attention has been paid to the carbon–carbon bond-forming reactions of **1** with carbon nucleophiles.[6,7] We have studied the reaction of **1** with dimethyl malonate in the presence of a trace of sodium hydride and found that the expected Michael-type adduct **2** was isolated as the exclusive product (90%) (see Scheme I). This material readily rearranged to the thermodynamically more stable isomer **3** by stirring with potassium *tert*-butoxide in THF for longer periods of time. In marked contrast to this result, the reaction of **1** with bis(phenylsulfonyl)methane in the presence of a trace of base afforded the expected Michael-type adduct **4** in only 6% yield. Interestingly, the major product obtained (94%) corresponded to structure **5**.[8] All attempts to isomerize **4** to **5** under a variety of basic and thermal conditions failed. Structure **5** was independently synthesized by treating the anion derived from bis(phenylsulfonyl)methane (**7**) with either 3-chloro-2-(phenylsulfonyl)-1-propene (**6a**) or 2,3-bis(phenylsulfonyl)-1-propene (**6b**).

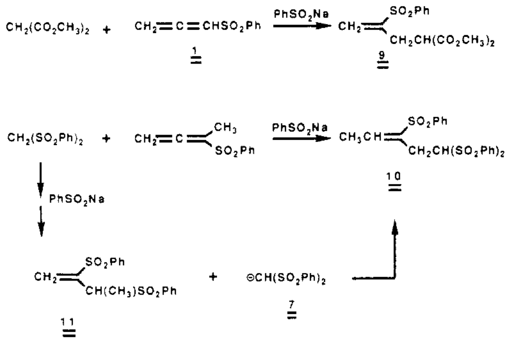
Scheme I



Scheme II



Scheme III



A mechanism which rationalizes the formation of **5** and which is consistent with all the data (vide infra) is outlined in Scheme II. Carbanion **8** is the probable key intermediate in this novel chain process. Proton transfer of **8** with bis(phenylsulfonyl)methane followed by an S_N2' reaction of the resulting carbanion with **6b** generates **5** and an additional quantity of benzenesulfinate anion. This material undergoes a subsequent nucleophilic addition with allene **1** and regenerates **7**. Presumably a trace of benzenesulfinate anion was present in the reaction mixture and served as the initiator for the chain reaction.[9]

Supporting evidence for the proposed mechanism is provided by the observation that the reaction of dimethyl malonate with allene **1** in the presence of added sodium benzenesulfinate afforded

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[1] Boche, G.; Martens, D. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 724. Kolobielski, M.; Pines, H. *J. Am. Chem. Soc.* **1957**, *79*, 5820. Eidenschink, R.; Kauffmann, T. *Angew. Chem., Int. Ed. Engl.* **1972**, *11*, 292. Klumpp, G. W.; Schmitz, R. F. *Tetrahedron Lett.* **1974**, 2911. Luteri, G. F.; Ford, W. F. *J. Organomet. Chem.* **1976**, *105*, 139. Kauffmann, T. H. *Top Curr. Chem.* **1980**, *92*, 109 and references cited therein.

[2] Kempf, D. J.; Wilson, K. D.; Beak, P. *J. Org. Chem.* **1982**, *47*, 1610. Beak, P.; Burg, D. A. *Tetrahedron Lett.* **1986**, 5911. Beak, P.; Wilson, K. D. *J. Org. Chem.* **1986**, *51*, 4627; **1987**, *52*, 218.

[3] Padwa, A.; Bullock, W. H.; Dyszlewski, A. D. *Tetrahedron Lett.* **1987**, 3193. Padwa, A.; Carter, S. P.; Chiacchio, U.; Kline, D. *Tetrahedron Lett.* **1986**, 2683.

[4] Hayakawa, K.; Nishiyama, H.; Kanematsu, K. *J. Org. Chem.* **1985**, *50*, 512.

[5] Stirling, C. J. M. *J. Chem. Soc. C* **1964**, 5863. Appleyard, G. D.; Stirling, C. J. M. *J. Chem. Soc. C* **1967**, 2686. Horner, L.; Lindel, H. *Phosphorus Sulfur* **1984**, *20*, 165. McMullen, C. H.; Stirling, C. J. M. *J. Chem. Soc. B* **1966**, *1217*, 1221. McDowell, S. T.; Stirling, C. J. M. *J. Chem. Soc. C* **1967**, 351. Fujii, I.; Ryu, K.; Hayakawa, K.; Kanematsu, K. *J. Chem. Soc., Chem. Commun.* **1984**, 844. Thyagarajan, B. S.; Wood, B. F.; Glowienka, J. A.; Delgado, P. *Phosphorus Sulfur* **1985**, *25*, 1.

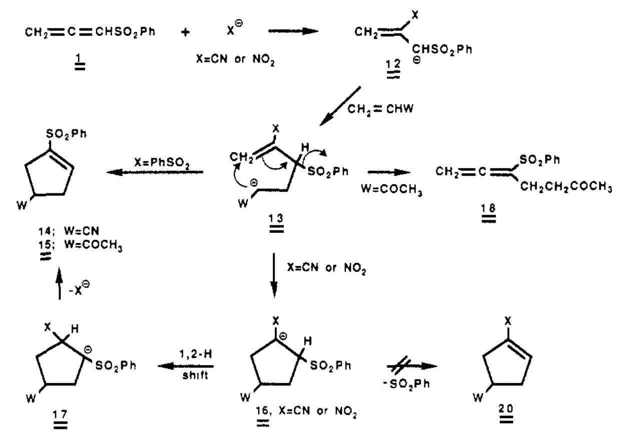
[6] Landor, S. R. In *The Chemistry of Allenes*; Landor, S. R., Ed.; Academic Press: New York, NY, 1982. Schuster, H. F.; Coppola, G. M. *Allenes in Organic Synthesis*; J. Wiley, Inc.: New York, NY, 1984.

[7] Ohmori, M.; Yamada, S.; Takayama, H. *Tetrahedron Lett.* **1982**, 4709. Hayakawa, K.; takewaki, M.; Fujimoto, I.; Kanematsu, K. *J. Org. Chem.* **1986**, *51*, 5100.

[8] **5**: NMR ($CDCl_3$, 300 MHz) δ 3.21 (d, 2 H, J = 6.0 Hz), 5.57 (t, 1 H, J = 6.0 Hz), 6.07 (s, 1 H), 6.49 (s, 1 H), and 7.5–7.8 (m, 15 H).

[9] Even when a highly purified sample of bis(phenylsulfonyl)methane was used, the reaction still produced compound **5** in high yield. More than likely, the phenyl sulfinate anion is derived from some equilibrium between the bis-sulfone and the base.

Scheme IV



the abnormal adduct **9** as the major product (60%)[10] (see Scheme III). This is perfectly compatible with the reaction sequence outlined in Scheme II. An additional piece of data which supports the SN'_2 sequence was obtained by carrying out the reaction of bis(phenylsulfonyl)methane with 3-(phenylsulfonyl)-buta-1,2-diene in the presence of sodium benzenesulfinate. The major product isolated here corresponded to structure **10**.[11] The formation of **10** is readily explained in terms of an attack of anion **7** onto the methylene carbon of the initially formed disulfone **11**.

Considering the great utility of vinyl sulfones in organic synthesis,[12] we sought to develop an annulation strategy for cyclopentenyl sulfone formation which involves treating (phenylsulfonyl)allene with an activated olefin in the presence of a nucleophilic reagent (see Scheme IV). In this approach, generation of carbanion **12** by reaction of the nucleophile with **1** is followed by a cyclization–elimination sequence[2] to provide the five-membered ring. Indeed, when allene **1**, acrylonitrile, and sodium benzenesulfinate (trace) are stirred in THF at ambient temperature, cycloadduct **14**[13] was isolated in 73% yield. Similar results were obtained when sodium cyanide or sodium nitrite were used as catalysts. Addition of these reagents to the allene generates a cyclized intermediate (i.e., **16**) which undergoes a 1,2-proton shift to give **17** prior to sulfinate ejection. A subsequent elimination of cyanide (or nitrite) ion generates the observed product (Scheme IV).

A similar set of reactions takes place when methyl vinyl ketone was used as the trapping agent.[14] Addition of sodium nitrite to **1** and MVK gave **15** in 75% yield in addition to allene **18** (8% yield).[15] The formation of **18** involves intramolecular proton transfer of the hydrogen adjacent to the sulfonyl group to the enolate oxygen followed by loss of sulfinate.

The high efficiency of this novel five-membered ring-forming process, coupled with the simplicity of the procedure, promises to provide an efficient route to a variety of cyclopentenyl-substituted sulfones. We are continuing to explore the scope and mechanistic details of this novel annulation reaction and will report additional findings at a later date.

Acknowledgment. We thank the National Science Foundation for generous support of this work.

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(10) **9**: NMR ($CDCl_3$, 300 MHz) δ 2.83 (d, 2 H, J = 7.6 Hz), 3.69 (s, 6 H), 3.83 (t, 1 H, J = 7.6 Hz), 5.83 (s, 1 H), 6.41 (s, 1 H), and 7.5–7.8 (m, 5 H).

(11) **10**: NMR ($CDCl_3$, 300 MHz) δ 2.04 (d, 3 H, J = 7.2 Hz), 3.23 (d, 2 H, J = 6.4 Hz), 5.85 (t, 1 H, J = 6.4 Hz), δ 7.20 (q, 1 H, J = 7.2 Hz), and 7.4–7.8 (m, 15 H).

(12) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.

(13) **14**: NMR ($CDCl_3$, 300 MHz) δ 2.80–3.1 (m, 4 H), 3.30 (p, 1 H, J = 6.9 Hz), 6.68 (s, 1 H), and 7.5–7.9 (m, 5 H).

(14) The cycloaddition proceeded smoothly with use of ethyl (or phenyl) vinyl ketone. Reaction with acrolein or methyl acrylate, on the other hand, led to polymer. Further work is currently underway so as to ascertain the scope and generality of the reaction.

(15) **15**: NMR ($CDCl_3$, 300 MHz) δ 2.10 (s, 3 H), 2.65–2.90 (m, 4 H), 3.40 (p, 1 H, J = 7.6 Hz), 6.63 (s, 1 H), and 7.5–7.9 (m, 5 H). **18**: NMR ($CDCl_3$, 300 MHz) δ 2.08 (s, 3 H), 2.44–2.50 (m, 2 H), 2.62 (t, 2 H, J = 7.1 Hz), 5.35 (t, 2 H, J = 3.3 Hz) and 7.5–7.9 (m, 5 H).

First Simultaneous Observation of the ^{133}Cs NMR from Cs$^+$, Cs$^-$, and Cs$^+$e$^-$ in a Metal Solution

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There is much current interest in the preparation and study of solutions of alkali metals in nonaqueous solvents containing either crown ethers or cryptands.[1] The observation of nuclear magnetic resonance (NMR) signals from all the alkali anions (except lithium) in these systems has provided detailed information about these intriguing species.[2-8] By comparison, in these metal solutions, the characterization of species based on either the alkali metal cation (M$^+$) or the electron–cation species (M$^+$e$^-$) has been largely neglected. Here we report the first NMR observation of all three cesium species, Cs$^+$, Cs$^+$e$^-$, and Cs$^-$, present in the same metal solution.

No ^{133}Cs NMR signals could be detected from solutions of cesium metal in the pure crown ether solvents, 12-crown-4 (12C4) and 15-crown-5 (15C5), even though the optical spectra of these blue solutions reveal the presence of the Cs ions.[9,10] The failure to observe such NMR signals suggests that they are broadened beyond detection either by chemical exchange processes or by a highly efficient relaxation mechanism. Unfortunately, these two liquid crown ethers have only a very narrow temperature range because of their relatively high freezing points (>260 K). However, as illustrated by Dye,[1] the accessible liquid temperature range can be increased by the addition of a cosolvent such as tetrahydrofuran (THF).

Figure 1 shows ^{133}Cs NMR spectra at 193 K for three saturated cesium metal solutions containing different proportions of the liquid crown ethers 12C4 and 15C5, in THF. Solutions which contain low crown ether content (<5% v/v), Figure 1 (parts a and b), yield spectra which consist of either two or three signals. The signals at chemical shifts (δ, see caption to Figure 1) of −300 and −280 ppm for 12C4 and 15C5 solutions, respectively, can be assigned[2] to the cesium anion (Cs$^-$). For the cesium–THF solution containing 5% 12C4 (Figure 1a) there are two additional signals, having chemical shifts of +1.9 and +65.9 ppm, which we assign to cation-based species. The signal at +1.9 ppm is assigned to the species (Cs$^+$(12C4)$_2$) consisting of a Cs$^+$ ion complexed by two 12C4 molecules. This assignment is unambiguous because signals having similar chemical shifts (δ = −4 ppm) and line widths ($\Delta\nu_{1/2}$, approximately 50 Hz) are observed from solutions of cesium halides (CsX; X = Cl, Br, I) in neat liquid 12C4. There are two compelling reasons for assigning the broader signal located at +65.9 ppm to the paramagnetic complex Cs$^+$(12C4)$_2$e$^-$. First, the NMR signal from the solid electride Cs$^+$(12C4)$_2$e$^-$, whose crystal structure has been characterized, occurs at almost the identical chemical shift.[11] Secondly, the shift difference between the Cs$^+$(12C4)$_2$ and Cs$^+$(12C4)$_2$e$^-$ signals is a Knight shift

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(1) Dye, J. L. *Prog. Inorg. Chem.* **1984**, *32*, 327.

(2) Edwards, P. P.; Ellaboudy, A. S.; Holton, D. M.; Pyper, N. C. *Annual Reports on NMR Spectroscopy*; Webb, G. A., Ed.; Academic Press: in press.

(3) Ceraso, J. M.; Dye, J. L. *J. Chem. Phys.* **1974**, *61*, 1585.

(4) Dye, J. L.; Andrews, C. W.; Ceraso, J. M. *J. Phys. Chem.* **1975**, *79*, 3076.

(5) Holton, D. M.; Ellaboudy, A. S.; Pyper, N. C.; Edwards, P. P. *J. Chem. Phys.* **1986**, *84*, 1089.

(6) Tinkham, M. L.; Dye, J. L. *J. Am. Chem. Soc.* **1985**, *107* 6129.

(7) Edwards, P. P.; Ellaboudy, A. S.; Holton, D. M. *Nature (London)* **1985**, *317*, 242.

(8) Tinkham, M. L.; Ellaboudy, A. S.; Dye, J. L.; Smith, P. B. *J. Phys. Chem.* **1986**, *90*, 14.

(9) Edmonds, R. N.; Holton, D. M.; Edwards, P. P. *J. Chem. Soc., Dalton Trans.* **1986**, 323.

(10) Holton, D. M.; Ellaboudy, A. S.; Edmonds, R. N.; Edwards, P. P. *Proc. Roy. Soc.* **1987**, in press.

(11) Ellaboudy, A. S.; Dye, J. L., unpublished observations.