The solution was warmed to room temperature over 12-16 h. Quench and workup were identical to that described above for DEAC.

Deprotection of Lactam 4c: Formation of 6. Lactam 4c (0.100 g, 0.30 mmol) was dissolved in 20 mL of liquid ammonia. Sodium metal (0.069 g, 3.0 mmol, 10 equiv) was added, and a deep blue color was obtained. The solution was allowed to reflux for 1 h with the persistence of blue color. The reaction was quenched with ammonium chloride (0.200 g, 13 equiv) and allowed to warm to room temperature in a hood. The residue was triturated with acetonitrile (5 mL), and the decanted solution was concentrated to a residue. The residue was triturated with methanol (5 mL) and was filtered through cotton. The filtrate was concentrated to yield an oil. The oil was purified by column chromatography (silica gel, $CHCl_3$/MeOH, 9/1) to yield 0.030 g of semisolid (57% yield). Purity was >90% as established by TLC: ^{1}H NMR ($CDCl_3$) δ 6.20 (bs, 1-H), 3.79 (m, 2-H), 3.35 (s, 3-H), 3.12 (bs, 1-H), 2.54 (t, 1-H), 2.46 (d, J = 4.1 Hz, 1-H), 2.06 (dt, J = 1.0, 13.5 Hz, 1-H), 1.74 (ddd, J = 2.4, 11.1, 13.5 Hz, 1-H), 0.996 (s, 9-H).

Preparation of 7. Deprotected compound 6 (0.030 g, 0.14 mmol) was dissolved in anhydrous THF (1 mL). 1,1'-Carbonyldiimidazole (0.024 g, 0.14 mmol) was added, and the solution was warmed to 35-40 °C for 24 h. The solution was concentrated in vacuo, and the crude oil was purified by column chromatography (silica gel 230 m, $CHCl_3$/MeOH, 9/1). The desired fractions were combined and concentrated to yield 15 mg of oil (50% yield). Purity was >90% as determined by TLC: exact mass calculated for $C_{12}H_{20}NO_4$ (M + 1), 242.13923, exact mass found (Cl, M + 1), 242.1400; MS (Cl) 242.210 128; ^{1}H NMR ($CDCl_3$) δ 4.25 (ddd, J = 3.00, 9.40, 11.1 Hz, 1-H), 3.90 (d, J = 9.40 Hz, 1-H), 3.85 (m, J = 3.00, 3.30, 5.10 Hz, 1-H), 3.36 (s, 3-H), 2.75 (dd, J = 3.00, 5.10 Hz, 2-H), 2.30 (ddd, J = 3.00, 3.30, 13.8 Hz, 1-H), 1.75 (ddd, J = 3.30, 11.1, 13.8 Hz, 1-H), 1.03 (s, 9-H); ^{13}C NMR ($CDCl_3$) δ 166.6, 150.9, 87.3, 72.5, 56.3, 51.7, 38.6, 33.8, 33.3, 25.1.

Nuclear Overhauser Effect (NOE) Spectroscopy. Homonuclear decoupling was first performed (QE 300 NMR spectrometer) to identify irradiation frequencies. The irradiation power was 2900, and the offset was determined from chloroform at 7.26 ppm. Irradiation and pulse length were 20 s followed by a 0.5-s delay. The spectrum was obtained after 24 pulses. The NOE experiment was performed with irradiation power of 3200 under identical pulse conditions. The reference spectrum was obtained with a 10 000-Hz offset.

Acknowledgment. Financial support of the University of California, Riverside, Committee on Research is gratefully acknowledged.

Registry No. 1, 74272-66-5; **2a**, 96759-99-8; **2b**, 96925-01-8; **2c**, 128495-75-0; **3a**, 137869-45-5; **3b**, 137869-46-6; **3c**, 137869-47-7; **4a**, 137869-48-8; **4b**, 137869-49-9; **4c**, 137869-50-2; **5a**, 137895-23-9; **5b**, 137869-51-3; **5c**, 137869-52-4; **6**, 137869-53-5; **7**, 137895-24-0; $SnCl_4$, 7646-78-8; $PhCH_2NH_2$, 100-46-9; diethylaluminum chloride, 96-10-6.

Supplementary Material Available: Spectral data for compounds **3a-c**, **4a-c**, **5a-c**, and 7 (16 pages). Ordering information is given on any current masthead page.

Tunable Regioselectivity Associated with the Reaction of 2,3-Dihalo-1-(phenylsulfonyl)-1-propenes with Ambident Nucleophilic Reagents

Albert Padwa,* David J. Austin, Masaru Ishida,† Cheryl L. Muller,‡ S. Shaun Murphree, and Philip E. Yeske

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received September 10, 1991

2,3-Dihalo-1-(phenylsulfonyl)-1-propenes, obtained by the addition of bromine or iodine onto (phenylsulfonyl)propadiene, were found to exhibit interesting reactivity as both mono- and dielectrophiles, with the mode of reactivity depending upon the nature of the nucleophile as well as the reaction conditions. Thus, amines or thiophenols smoothly effected substitution at the allylic site, while sodium methoxide reacted at the vinylic position through an addition-elimination process. In the realm of ambident nucleophiles, β-dicarbonyl compounds in a medium of NaH/*tert*-butoxide/THF gave 2-alkyl-3-acyl-4-[(phenylsulfonyl)methyl]furans, produced by initial allylic S_N2 displacement followed by 5-*exo-trig* cyclization. Conversely, such β-dicarbonyls in a methoxide/methanol system yielded 2-alkyl-4-[(phenylsulfonyl)methyl]furans, where reaction proceeds by initial addition-elimination on the vinyl sulfone moiety. In contrast, silyl enol ethers in the presence of silver tetrafluoroborate resulted in products derived from S_N2 displacement at the allylic site. Thioamides could be used to form 2-substituted thiazoles by initial allylic displacement by the sulfur atom followed by an addition-elimination reaction. Thus, a variety of compounds were prepared from 2,3-dihalo-1-(phenylsulfonyl)-1-propenes by the proper choice of reagents and reaction conditions.

Allenes play an important role in many aspects of organic chemistry.[1-3] Their ability to enter into reactions as either a nucleophile or an electrophile provides the synthetic chemist with a variety of methods for preparing more complex compounds.[4] The addition of electrophilic reagents to allenes is a well-studied process,[5] as is the synthesis of alkene-substituted heterocycles via intramolecular nucleometallations of allenes using mercury(II) or silver(I) salts.[6-9] For simple alkyl-substituted allenes,

† Current address: Department of Chemistry, Faculty of Engineering, Gifu University Yanagido, Gifu 501-11, Japan.

‡ C.L.M. is pleased to acknowledge the NIH for a postdoctoral fellowship (CA-08845-01).

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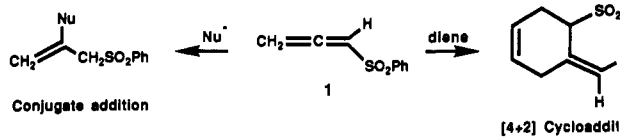
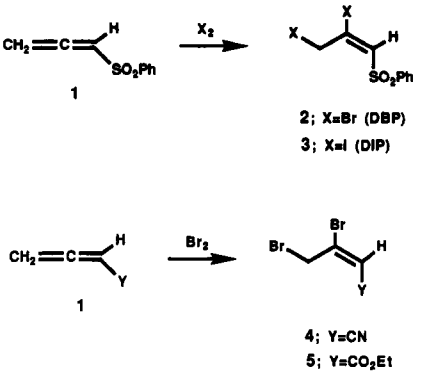
electrophilic attack generally occurs on the terminal position, since the central carbon is electrophilic in nature.[10] However, the allene framework is very delicately balanced, so that small changes in steric or electronic factors greatly affect the orientation of addition. Thus, an allenic moiety conjugated to an electron-withdrawing substituent readily undergoes nucleophilic addition reactions.[11-17] 1-(Phenylsulfonyl)-1,2-propadiene (1) represents one of the more intriguing allenes known.[18] This material readily undergoes Michael addition with various nucleophiles across the C_1–C_2 activated π-bond.[19-23] (Phenylsulfonyl)allene is also a useful reagent in cycloaddition chemistry, owing to an enhanced reactivity as a consequence of a low lying LUMO.[24,25]



As part of our continuing involvement with the chemistry of allenic sulfones,[26] we became interested in examining the reactivity of the "nonactivated" C_2–C_3 π-bond of 1 with various electrophilic reagents. Inasmuch as this π-bond lies in a plane orthogonal to the orbitals of the *activated* olefin, the distal π-bond should experience very little electronic influence from the pendant sulfone functionality. Bearing this in mind, we chose to examine a familiar reaction associated with simple allenes, namely halogen addition.[27-33] Indeed, we have found that the addition of bromine or iodine to allene 1 proceeds smoothly at 25 °C and can be controlled so that the reaction may be terminated after 1 equiv of halogen is consumed.[34] The resulting dihalides (2 and 3) are stable, highly crystalline compounds requiring no special precautions to prevent decomposition. This is particularly remarkable consid-



ering that these substrates contain an allyl halide, a vinyl halide, and a vinyl sulfone functionality all attached to only a three-carbon array. The related nitrile 4[30] and ester[31] 5 dibromides have been reported in the literature, but relatively little use[32] has been made of this class of reagents. The dihalo sulfones 2 and 3 can be viewed as multielectrophilic reagents, with great potential as nucleophilic acceptors for sequential addition.[34] Consequently, we decided to examine the behavior of these interesting reagents toward various ambident nucleophiles. The present paper documents the results of these studies.

Results and Discussion

The formation of 1-(phenylsulfonyl)-1,2-propadiene (1) has been elaborated in earlier work by Stirling,[18] where it was shown that propargyl sulfone readily isomerized under basic conditions to the thermodynamically more stable allene species 1. Once formed, bromine was added across the C_2C_3 π-bond of this allene to give dibromide 2 (DBP) as a crystalline solid, mp 62–63 °C, in 85% yield. The related diiodide 3 (DIP) was prepared by sunlamp irradiation of 1 in a benzene solution of iodine and was isolated as yellow crystals, mp 91–92 °C, in 85% yield. The stereochemistry about the π-bond was established as the *E* isomer, with the halide trans to the sulfonyl group. The assignment rests on the absence of an NOE effect between the methylene and vinyl hydrogens as well as an X-ray single-crystal structure analysis. This stereochemistry is consistent with formation of a bromonium or iodonium ion on the least hindered side of the allene, followed by attack of the halide on the terminal carbon.

Our initial efforts toward unlocking the synthetic potential of these halo sulfones centered around the reaction with heteronucleophiles. Since there exist two available sites for reaction, two distinct regioisomeric products are possible. A simple S_N2 displacement of the terminal halide would produce compounds such as 6, while attack at the vinylic position would lead to compounds 7. The latter

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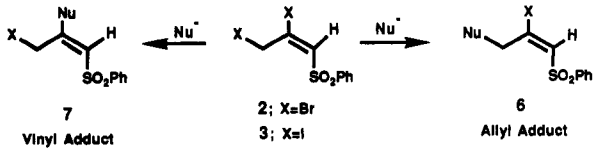
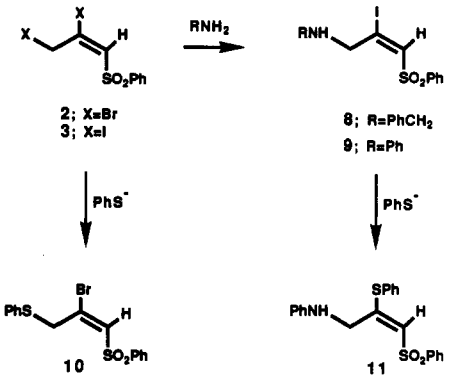


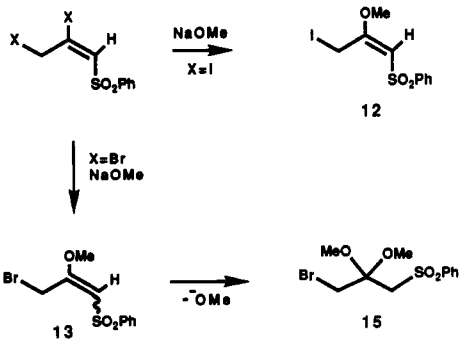
reaction pathway most likely would involve an initial Michael addition to the vinyl sulfone followed by elimination of halide to regenerate the double bond. Such a mechanism has been suggested to be operative in the addition of cuprates to β-acetoxy,[35] β-alkylthio,[36] and β-halo enones[37] to form β-alkyl-substituted enones.

Some interesting trends in reactivity were immediately evident. For example, while the dibromo compound **2** underwent clean allylic substitution when treated with thiophenol in the presence of triethylamine to give adduct **10**, DIP (**3**) was unstable toward these conditions giving rise to intractable material. However, treatment of **3** with nitrogen nucleophiles (e.g., benzylamine, aniline) smoothly effected substitution at the allylic site to give adducts **8** and **9**. These intermediate iodo sulfones are less reactive than DIP itself, so that further manipulation on the second electrophilic site is quite manageable. Thus, treatment of the aniline adduct **9** with thiophenoxide produced thioenol **11** in good yield.

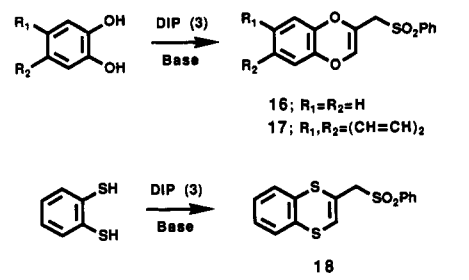


The reactivity encountered with sodium methoxide diverged from the other heteronucleophiles, adding predominantly in an addition–elimination sense. Thus, treatment of DIP (**3**) with methoxide ion produced **12** as the major product. Reaction of DBP with sodium methoxide provided a 2.6:1 mixture of the *E*/*Z* isomers of **13** as well as a small amount (10%) of the S_N2 displacement product **14**. Treatment of DBP with excess methoxide ion led to the formation of the dimethoxy adduct **15** in 47% yield.

By connecting two nucleophilic sites with a carbon-chain tether, it was possible to induce cyclization to produce six-ring heterocycles. Thus, catechol and 2,3-dihydroxynaphthalene were found to react with DIP (**3**) to give 1,4-benzodioxins **16** and **17** in 55% and 58% yield, respectively. Similarly, 1,2-benzenedithiol cleanly afforded



18 in high yield when treated with DIP.



We also envisioned using the above multifunctional sulfones as acceptors for sequential addition with ambident nucleophiles such as ketones.[38] By first alkylating a ketone enolate at the α-carbon atom, then effecting ring closure on the oxygen atom, furans could be formed.[39] An example of this concept is provided in the reaction of DBP with dimethyl malonate using NaH/t-BuOK in THF. The major product isolated in 77% yield was a crystalline solid whose structure was identified as furan **19**. A similar transformation occurred with 2,4-pentanedione, producing furan **20** in 80% yield. By carrying out the dimethyl malonate addition for short periods of time, it was possible to isolate the product of allylic displacement (i.e. **22**). This material was readily converted to furan **19** in 85% yield by treatment with potassium *tert*-butoxide. This transformation proceeds by a 5-*exo*-*trig* addition–elimination sequence,[40] producing **23** as a transient species which rapidly isomerizes to the furan.

Methyl acetoacetate represents an interesting substrate since it provides nonequivalent carbonyls and thus divergent routes to two different furans. However, treatment of DIP with the sodium salt of methyl acetoacetate in THF gave rise to a single furan (87%) whose structure was

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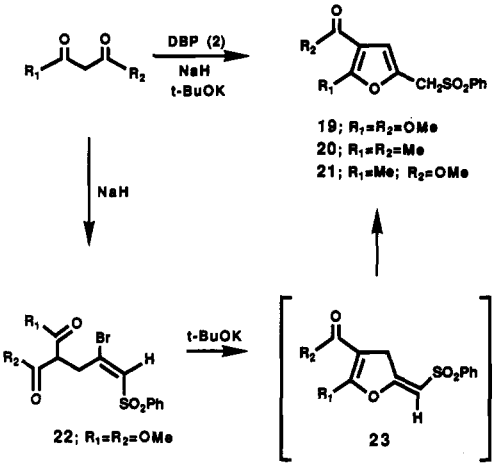
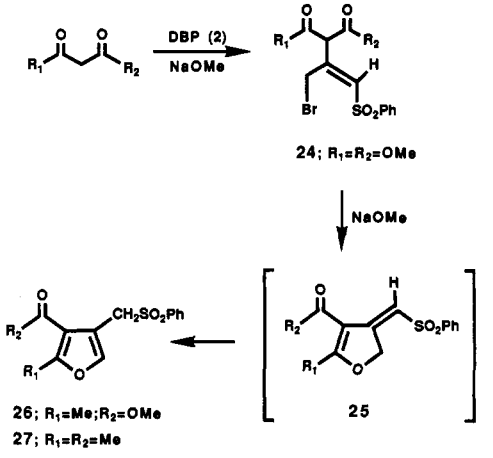
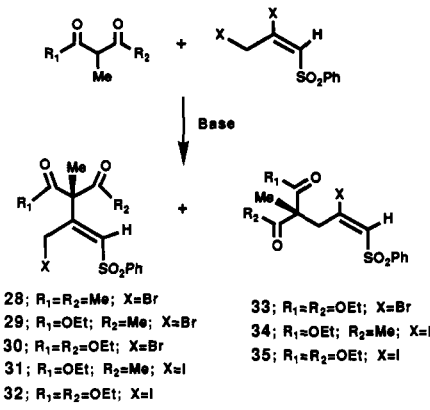


assigned as methyl 2-methyl-5-[(phenylsulfonyl)-methyl]-3-furanoate (21).

Simply changing the solvent from THF to methanol (or acetonitrile) resulted in a dramatic crossover in the regioselectivity of the reaction. Thus, when the β-dicarbonyl additions are carried out in methanol, β-bromo sulfones 24 are formed by an addition–elimination reaction of the enolate onto the activated π-bond of DBP.[41] When the initially formed adduct contains an acetyl group (i.e. methyl acetoacetate, 2,4-pentanedione adducts), spontaneous cyclization occurs to yield the 2,3,4-substituted furans 26 and 27 (see Table I).



Since we were intrigued by this unusual regiochemical crossover, we sought to discover if this effect might also be substrate dependent as well as a function of the experimental conditions used. This led us to study the reaction of several 2-methyl-substituted β-dicarbonyl anions with DBP and DIP. As with the unsubstituted 1,3-dicarbonyl compounds, generation and reaction of the anion in polar solvents results in almost exclusive attack at C_2 to give vinyl addition products (i.e. 28–32). In nonpolar solvents, however, the expected changeover to reaction at the allylic site was not observed. Thus, using sodium hydride as the base and either DMF or THF/HMPA as solvent, vinyl adducts 28–32 were isolated as the major products. Only trace amounts of the product derived from allylic attack could be detected in the reaction between ethyl methylacetoacetate and DBP (2). Under certain conditions, however, up to 30% of allylic attack (i.e. 33)



occurred using DBP and the anion derived from diethyl methylmalonate. The same anion with the diiodo reagent 3 produced a 1:1 mixture of vinyl vs allylic adducts (32/35); a similar result was obtained using the anion of ethyl methylacetoacetate. A variety of counterions and solvents were examined (Table II) for their effect on the product ratio.

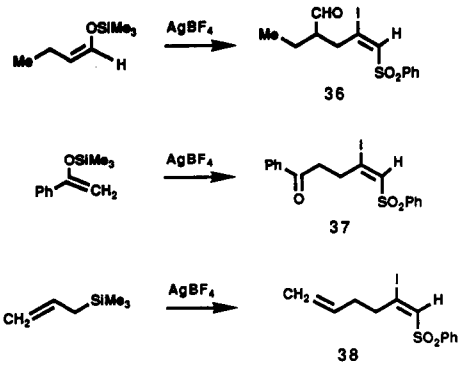
The difference in product distribution as a function of the solvent and nucleophile can be related to several factors. Nucleophilic substitution reactions carried out in aprotic solvents often occur more readily than comparable reactions in protic solvents since, in hydrogen bonding solvents, the enolate anion is subject to strong solvation forces that lower its ground-state energy.[42] Also, hydrogen bonding of methanol onto the sulfonyl group might be expected to lower the LUMO of the π-bond and thereby enhance the conjugate addition pathway. Soft nucleophiles such as thiophenoxide or amines would be expected to undergo reaction at the softer allylic site. With methoxide ion, the extensive hydrogen-bonding network is interrupted in the transition state for the displacement reaction; consequently the addition–elimination process predominates. As might be expected, the diiodo reagent DIP give slightly higher ratios of allylic attack than the corresponding dibromide due to the enhanced leaving group ability of iodide over bromide. Complete crossover, however, has not been achieved. The substituted β-dicarbonyl anions are apparently inhibited from reacting at the allylic site perhaps as a consequence of the stringent steric requirements of the S_N2 reaction. The conjugate addition/β-halide elimination path is presumably less sensitive to steric effects and proceeds in competition with the S_N2 displacement.

A method permitting reaction exclusively at the allylic site would improve the usefulness of these reagents. Additionally, if a compound with a single activating group could be induced to react with DIP or DBP, the method would become much more versatile. Attempted alkylation of simple ketones or aldehydes with either dihalo reagent (2 or 3) resulted in the formation of complex reaction mixtures. Fortunately, it was possible to modify the procedure by reacting DIP (3) with enol silyl ethers in the presence of silver tetrafluoroborate. Thus, the silyl enol ethers derived from butyraldehyde and acetophenone were successfully alkylated with DIP to give products derived exclusively from allylic attack (i.e. 36 and 37). Allyltrimethylsilane was also found to act as a nucleophile, producing 38 in good yield when treated with DIP and silver tetrafluoroborate. It is important to note that $AgBF_4$ was

(41) For some related work on β-functionalized vinyl sulfones, see: Matcalfe, B. W.; Bonilavri, E. *J. Chem. Soc., Chem. Commun.* **1978**, 914. Back, T. G.; Collins, S.; Law, K. W. *Tetrahedron Lett.* **1984**, *25*, 1689. Giblin, G. M. P.; Simpkins, N. S. *J. Chem. Soc., Chem. Commun.* **1987**, 207.

(42) Reichardt, C. In *Solvents and Solvent Effects in Organic Chemistry*; VCH: Weinheim, 1990; Chapter 5, pp 208–239.

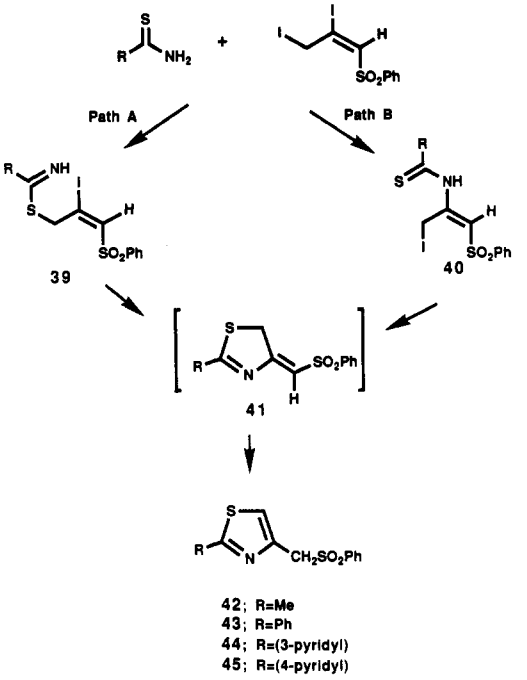
(43) Duval, D.; Geribaldi, S. In *The Chemistry of Enones*; Wiley-Interscience: New York, 1989; pp 357–378.



critical to the success of the alkylation;[44] without it, the reaction did not proceed. The reaction of TMS enol ethers with DIP using other Lewis acids ($TiCl_4$, $ZnCl_2$) led only to the destruction of the enol silyl ether (DIP was recovered unchanged). We believe that $AgBF_4$ not only acts as a Lewis acid to activate the allylic position but also assists in the desilylation step. This presumably occurs by attack of fluoride ion on the silicon atom. The resulting enolate then reacts to give products formally derived from S_N2 displacement on the terminal halide. The regioselectivity of alkylation using these conditions nicely complements that encountered with β-dicarbonyl anions which gives products derived from vinylic displacement.

The regiochemistry observed in the reaction of DBP (2) and DIP (3) with various nucleophiles has important consequences for their use as reagents in the synthesis of other heterocycles. As demonstrated above, conditions can be chosen to funnel the reaction of some diactivated carbanions exclusively to the vinylic or allylic positions. By taking advantage of this *tunable* regioselectivity, trisubstituted furans of two different substitution patterns may be formed. In addition to using carbon/oxygen nucleophiles as precursors for furans, this protocol is adaptable to the synthesis of other heterocyclic systems. Another reaction which appeared suitable for exploration involved the addition of DIP with thioamides. For a test case, one of the simplest thioamides, namely thioacetamide, was chosen. Treatment of DIP with this ambident nucleophile in DMF using pyridine as the base resulted in the formation of a single thiazole (75%), whose structure was assigned as 2-methyl-4-[(phenylsulfonyl)methyl]thiazole (**42**) on the basis of its spectroscopic properties. Related transformations also occurred using thiobenzamide as well as 3- and 4-pyridyl carbothioamides. In all cases, only the 2-substituted thiazole ring was observed in the reaction products (i.e. **43–45**). Two different paths can be put forth to rationalize the formation of the 2-substituted thiazole ring. One route (path A) involves displacement of the allylic iodide by the sulfur atom of the thioamide to produce **39**, which subsequently cyclizes to thiazole **42** via the intermediacy of **41**. The alternate path B occurs by an initial addition–elimination reaction involving the nitrogen atom of the thioamide at the vinylic site. The intermediate so produced (i.e. **40**) undergoes a subsequent cyclization under the reaction conditions. Although both pathways are possible, path A is more consistent with the known propensity of thioamides to alkylate on the sulfur atom.[45]

In conclusion, the work reported herein establishes the usefulness of 2,3-dihalo-1-(phenylsulfonyl)-1-propenes as reagents for the synthesis of arylsulfonyl-substituted



heterocycles. In addition, the pendant sulfone group present in the final product may be removed easily or used as a convenient and versatile site for further elaboration (via alkylation[46] or Julia coupling[47]). Extensions of the scope and synthetic potential of these reactions are being investigated further. This strategy toward the synthesis of furans has been applied to more complex targets and is described in the accompanying paper.

Experimental Section

Melting points are uncorrected. Mass spectra were determined at an ionizing voltage of 70 eV. Unless otherwise noted, all reactions were performed in oven-dried glassware under an atmosphere of extra dry nitrogen. Solutions were evaporated under reduced pressure with a rotary evaporator, and the residue was chromatographed on a silica gel column using an ethyl acetate–hexane mixture as the eluent unless specified otherwise. NaH (60% in mineral oil) was placed under N_2 and washed with several milliliter portions of hexane prior to use.

Preparation of (*E*)-2,3-Dibromo-1-(phenylsulfonyl)-1-propene (DBP, 2). To a solution containing 10.0 g of (phenylsulfonyl)allene[18] (1) in 60 mL of glacial acetic acid was slowly added 2.5 mL of bromine at rt. The reaction mixture was allowed to stir overnight at 25 °C, poured into 200 mL of ice water, and carefully neutralized with a 50% NaOH solution. The aqueous mixture was extracted with CH_2Cl_2, washed with water, a saturated $NaHCO_3$ solution, and brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was subjected to flash silica gel chromatography. Slow evaporation of the major fraction induced the precipitation of (*E*)-2,3-dibromo-1-(phenylsulfonyl)-1-propene (2) (85%) as white prisms: mp 62–63 °C; IR (neat) 3050, 1605, 1445, 1325, 1160, 1080, and 750 cm^{-1}; ^{1}H-NMR (90 MHz, $CDCl_3$) δ 4.96 (s, 2 H), 6.78 (s, 1 H), and 7.50–8.15 (m, 5 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 29.8, 127.8, 129.6, 133.7, 134.4, 137.6, 139.6; Anal. Calcd for $C_9H_8Br_2O_2S$: C, 31.79; H, 2.37. Found: C, 31.86; H, 2.36.

The X-ray structure of DBP (2) was solved by direct methods using the SHELXTL program. Following anisotropic refinement of the skeleton atoms, all other hydrogen atoms were fixed into position. The final discrepancy index and weighted discrepancy index were R = 5.8% and R_w = 5.7%, respectively. The final positional and thermal parameters as well as the experimental data for the X-ray diffraction study are given in the supplementary material.

(44) Silver triflate was tried as well but yields for the alkylation were significantly reduced (ca. 20%).
(45) Harada, T.; Tamaru, Y.; Yoshida, Z. *Tetrahedron Lett.* **1979**, 3525.
(46) Magnus, P. D. *Tetrahedron* **1977**, *33*, 2019.
(47) Julia, M.; Stacino, J. *Tetrahedron* **1986**, *42*, 2469.

Table I. Reaction of β-Dicarbonyl Compounds with 2,3-Dihalo-1-(phenylsulfonyl)-1-propene

nucleophile	reagent	base	solvent	regiochemistry	product (%)
methyl acetoacetate	DBP (2)	NaH	THF	allyl	21 (76)
methyl acetoacetate	DIP (3)	NaH	THF	allyl	21 (87)
methyl acetoacetate	DBP (2)	K_2CO_3	CH_3CN	vinyl	26 (65)
2,4-pentanedione	DBP (2)	NaH	THF	allyl	20 (71)
2,4-pentanedione	DIP (3)	NaH	THF	allyl	20 (80)
2,4-pentanedione	DBP (2)	K_2CO_3	CH_3CN	vinyl	27 (77)
dimethyl malonate	DBP (2)	NaH	THF	allyl	22 (62)
dimethyl malonate	DBP (2)	MeONa	MeOH	vinyl	24 (68)

Table II. Reaction of Substituted β-Dicarbonyl Compounds with 2,3-Dihalo-1-(phenylsulfonyl)-1-propene

nucleophile	reagent	base	solvent	product (%)	vinyl/allyl ratio
3-methyl-2,4-pentanedione	DBP (2)	NaH	THF	28 (59)	100/0
ethyl methylacetoacetate	DBP (2)	NaH	THF	29 (87)	100/0
ethyl methylacetoacetate	DIP (3)	NaH	THF	31/34 (84)	50/50
ethyl methylacetoacetate	DIP (3)	NaH	THF/HMPA	31 (64)	100/0
diethyl methylmalonate	DBP (2)	NaH	THF	30/33 (89)	95/5
diethyl methylmalonate	DBP (2)	KH	THF	30/33 (95)	70/30
diethyl methylmalonate	DBP (2)	LDA	THF	30 (68)	100/0
diethyl methylmalonate	DBP (2)	*t*-BuOK	*t*-BuOH	30 (62)	100/0
diethyl methylmalonate	DIP (3)	NaH	THF	32/35 (85)	66/33
diethyl methylmalonate	DIP (3)	NaH	benzene	32/35 (94)	33/66
diethyl methylmalonate	DIP (3)	NaH	DMF	32 (55)	100/0
diethyl methylmalonate	DIP (3)	KH	THF	32/35 (87)	90/10
diethyl methylmalonate	DIP (3)	KH	benzene/18-crown-6	32/35 (82)	55/45

Preparation of (*E*)-2,3-Diiodo-1-(phenylsulfonyl)-1-propene (DIP, 3). A stirred solution containing 6.68 g of allene 1 and 8.18 g of iodine in 320 mL of benzene was irradiated with a 250-W sunlamp for 1 h under N_2. After removal of the solvent under reduced pressure, the crude residue was taken up in CH_2Cl_2 and washed with a 10% $Na_2S_2O_3$ solution. The organic layer was dried over Na_2SO_4, and the solvent was removed under reduced pressure to leave behind a crude yellow residue which crystallized on standing. Recrystallization from CH_2Cl_2/hexane gave 11.81 g (85%) of bright yellow crystals of (*E*)-2,3-diiodo-1-(phenylsulfonyl)-1-propene (DIP, 3): mp 91–92 °C; IR (KBr) 1595, 1450, 1285, 1085, 750, and 665 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 5.10 (s, 2 H), 6.86 (s, 1 H), 7.60 (m, 2 H), 7.70 (m, 1 H), and 7.97 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 8.3, 117.1, 127.6, 129.5, 134.1, 137.9, and 139.2. Anal. Calcd for $C_9H_8I_2O_2S$: C, 24.91; H, 1.86. Found: C, 25.01; H, 1.90.

3-(Benzylamino)-2-iodo-1-(phenylsulfonyl)-1-propene (8). To a stirred solution containing 200 mg of DIP (3) in 5 mL of CH_2Cl_2 was added 0.10 mL of benzylamine. The reaction mixture was stirred at 25 °C for 14 h under N_2 and then poured into water. The solution was extracted with CH_2Cl_2, and the resulting solution was washed with water, a 10% $Na_2S_2O_3$ solution, and brine and dried over anhydrous Na_2SO_4. Removal of the solvent under reduced pressure left a crude residue which was subjected to silica gel chromatography. The major fraction contained 146 mg (77%) of 8: IR (neat) 1605, 1225, 1155, 1090, and 700 cm^{-1}; ^1H-NMR ($CDCl_3$, 90 MHz) δ 1.91 (s, 2 H), 3.60 (s, 2 H), 4.02 (s, 2 H), and 7.20–7.98 (m, 11 H). Anal. Calcd for $C_{16}H_{16}INO_2S$: C, 46.49; H, 3.90. Found: C, 46.31; H, 3.87.

3-(Phenylamino)-2-iodo-1-(phenylsulfonyl)-1-propene (9). To a stirred solution containing 200 mg of DIP (3) in 5 mL of CH_2Cl_2 was added 84 μL of aniline dropwise via syringe. The reaction was protected from light and was stirred for 12 h at rt under N_2. The mixture was poured into water and extracted with CH_2Cl_2. The combined organic extracts were washed with water, a 10% $Na_2S_2O_3$ solution, and brine. The solution was dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure. Recrystallization of the residue from CH_2Cl_2–hexane gave 158 mg (86%) of 9: mp 116–117 °C; IR (KBr) 1610, 1515, 1325, 1140, 835, and 695 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 4.25 (s, 1 H), 4.48 (s, 2 H), 6.62 (d, 2 H, *J* = 7.4 Hz), 6.76 (t, 1 H, *J* = 7.4 Hz), 7.15 (t, 2 H, *J* = 7.4 Hz), 7.21 (s, 1 H), 7.57–7.62 (m, 2 H), 7.67–7.72 (m, 1 H), and 7.94–7.97 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 48.1, 113.4, 118.5, 127.4, 129.1, 129.3, 133.9, 139.5, 139.8, and 145.9. Anal. Calcd for $C_{15}H_{14}INO_2S$: C, 45.13; H, 3.53; N, 3.51. Found: C, 45.03; H, 3.55; N, 3.53.

2-Bromo-3-(phenylthio)-1-(phenylsulfonyl)-1-propene (10). To a solution containing 200 mg of DBP (2) and 0.06 mL of thiophenol in 2.5 mL of absolute methanol at 0 °C was added 0.09 mL of triethylamine. After the mixture was stirred overnight at rt, the solvent was removed under reduced pressure and the residue was extracted with CH_2Cl_2 and washed with water. Evaporation of the solvent afforded 200 mg (92%) of 2-bromo-3-(phenylthio)-1-(phenylsulfonyl)-1-propene (10) as a white solid: mp 95–96 °C; IR (KBr) 1445, 1325, 1145, 920, 745, and 695 cm^{-1}; NMR (90 MHz, $CDCl_3$) δ 4.17 (s, 2 H), 6.79 (s, 1 H), 7.20–7.45 (m, 5 H), and 7.50–8.10 (m, 5 H). Anal. Calcd for $C_{15}H_{13}BrO_2S_2$: C, 48.79; H, 3.55. Found: C, 48.86; H, 3.58.

3-(Phenylamino)-1-(phenylsulfonyl)-2-(phenylthio)-1-propene (11). To a stirred ice-cold solution containing 100 mg of 9 and 28 μL of thiophenol in 3 mL of THF was added 80 μL of triethylamine dropwise via syringe. The mixture was stirred under an argon atmosphere at 0 °C for 2 h and was then allowed to warm to rt over 12 h. The mixture was poured into water and extracted with CH_2Cl_2, and the combined extracts were washed with water and brine. The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed under reduced pressure to leave behind a crude residue which was subjected to silica gel chromatography to give 72 mg (76%) of 11: IR (neat) 1605, 1505, 1280, 1085, 760, and 695 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 4.53 (s, 2 H), 5.59 (s, 1 H), 6.50 (d, 2 H, *J* = 7.4 Hz), 6.75 (t, 1 H, *J* = 7.4 Hz), 7.13 (t, 2 H, *J* = 7.4 Hz), 7.35–7.43 (m, 5 H), 7.48–7.54 (m, 2 H), 7.58–7.63 (m, 1 H), and 7.81–7.84 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 45.0, 112.9, 118.4, 119.3, 126.8, 128.4, 129.2, 130.1, 130.3, 130.4, 133.1, 135.4, 142.1, 146.8, and 164.7; HRMS calcd for $C_{21}H_{19}NO_2S_2$ 381.0857, found 381.0859.

3-Iodo-2-methoxy-1-(phenylsulfonyl)-1-propene (12). A 230-mg (0.52-mmol) sample of DIP (3) was dissolved in 10 mL of methanol and was stirred at 0 °C. To this solution was added 0.4 mL of a 0.5 M NaOMe solution, and the mixture was stirred at 0 °C for 30 min. An additional 0.6-mL aliquot of NaOMe solution was added, and the reaction mixture was allowed to stir for an additional 2 h. The reaction was quenched with aqueous hydrochloric acid and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure to give 97 mg (55%) of 3-iodo-2-methoxy-1-(phenylsulfonyl)-1-propene (12) as a white solid: mp 114–115 °C; IR (neat) 1601, 1447, 1335, 1130, and 1082 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.65 (s, 6 H), 4.78 (s, 2 H), 5.52 (s, 2 H), 7.60 (m, 3 H), and 7.98 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ −5.4, 56.5, 102.8, 127.0, 129.2, 133.1, 142.4, and 167.3. Anal. Calcd for $C_{10}H_{11}IO_3S$: C, 35.51; H, 3.28. Found C, 35.59; H, 3.31.

Reaction of DBP (2) with Sodium Methoxide in Methanol. To a solution containing 200 mg of DBP (2) in 2.5 mL of absolute methanol at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir overnight at rt and then quenched with a saturated NH_4Cl solution. The methanol was removed under reduced pressure, and the residue was extracted

with CH_2Cl_2 and washed with water. After removal of the solvent, the crude reaction mixture was subjected to silica gel chromatography to give 135 mg (78%) of a 2.6:1 *E,Z* mixture of 3-bromo-2-methoxy-1-(phenylsulfonyl)-1-propene (**13**): IR (neat) 1630, 1450, 1330, 1160, 1090, and 720 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) major *E* isomer δ 3.44 (s, 3 H), 4.17 (s, 2 H), 5.36 (s, 1 H), and 7.4–8.0 (m, 5 H); minor *Z* isomer δ 3.61 (s, 3 H), 4.49 (s, 2 H), 5.53 (s, 1 H), and 7.4–8.0 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) major *E* isomer δ 55.2, 58.7, 84.2, 127.9, 128.4, 133.3, 138.3, and 149.1; HRMS calcd for $C_{10}H_{11}BrO_3S$ 289.9612, found 289.9621.

The second fraction isolated from the column contained 28 mg (10%) of 2-bromo-3-methoxy-1-(phenylsulfonyl)-1-propene (**14**): IR (neat) 1620, 1450, 1150, 1090, and 760 cm^{-1}; ^1H-NMR (90 MHz, $CDCl_3$) δ 3.80 (s, 3 H), 3.87 (s, 2 H), 5.86 (s, 1 H), and 7.50–8.15 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 24.3, 55.7, 110.7, 127.0, 128.1, 132.4, 141.5, and 160.5; HRMS calcd for $C_{10}H_{11}BrO_3S$: 289.9612, found 289.9619.

To a stirred solution containing 269 mg (4.98 mmol) of NaOMe in 120 mL of anhydrous MeOH at 0 °C was added 857 mg (2.52 mmol) of DBP (**2**) in 3 mL of THF. The solution was stirred at 0 °C for 3.5 h, and the methanol was removed under reduced pressure. The residue was partitioned between CH_2Cl_2 and a pH 7 buffer, and the combined organic fractions were washed with brine and dried over $MgSO_4$. Removal of the solvent followed by silica gel chromatography provided 379 mg (47%) of 3-bromo-2,2-dimethoxy-1-(phenylsulfonyl)propane (**15**): mp 118–119 °C; IR (neat) 3000, 1315, 1150, 1085, 760, and 730 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.09 (s, 6 H), 3.57 (s, 2 H), 3.80 (s, 2 H), and 7.40–7.95 (m, 5 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 31.2, 48.3, 55.4, 98.7, 127.4, 128.6, 133.2, and 139.9. Anal. Calcd for $C_{11}H_{15}BrO_4S$: C, 40.88; H, 4.68. Found: C, 40.79; H, 4.66.

Reaction of (*E*)-2,3-Diiodo-1-(phenylsulfonyl)-1-propene (3) with Catechol, 2,3-Naphthalenediol, and 1,2-Benzenedithiol. To a solution containing 0.43 g (1.0 mmol) of DIP (**3**) and 1.2 mmol of the appropriate arene in 10 mL of DMF was added 0.16 g (2.0 mmol) of pyridine (or 0.28 g of K_2CO_3) under N_2. The mixture was stirred at 25 °C for 12 h, the solvent was removed, the residue was dissolved in 50 mL of CH_2Cl_2, washed with 50 mL of 1% Na_2SO_3 and then water, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure was followed by purification by silica gel chromatography. On the basis of the above procedure, the following compounds were obtained:

2-[(Phenylsulfonyl)methyl]-1,4-benzodioxin (16) (55%): mp 126–127 °C; IR (KBr) 1702, 1497, 1308, 1293, 1254, 1136, 1084, and 758 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.71 (s, 2 H), 5.89 (s, 1 H), 6.25 (dd, 1 H, J = 7.5 and 1.8 Hz), 6.59 (dd, 1 H, J = 7.5 and 1.8 Hz), 6.70–6.85 (m, 2 H), 7.47–7.60 (m, 2 H), 7.60–7.70 (m, 1 H), and 7.92–8.00 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 57.4, 116.0, 124.2, 124.4, 127.9, 128.1, 128.5, 129.0, 133.8, 138.3, 141.3, and 141.7; *m/e* (relative intensity) 288 (M^+, 9), 147 (100), 121 (18), 91 (21). Anal. Calcd for $C_{15}H_{12}O_4S$: C, 62.49; H, 4.20. Found: C, 62.59; H, 4.22.

2-[(Phenylsulfonyl)methyl]naphtho[2,3-*b*]-1,4-dioxin (17) (58%): mp 172–173 °C; IR (KBr) 1708, 1511, 1308, 1279, 1260, 1142, and 747 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 3.79 (s, 2 H), 6.03 (s, 1 H), 6.65 (s, 1 H), 6.98 (s, 1 H), 7.23–7.35 (m, 2 H), 7.45–7.70 (m, 5 H), and 7.95–8.00 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 57.4, 111.8, 125.3, 125.4, 126.6, 126.7, 127.5, 127.6, 128.5, 129.0, 130.9, 131.0, 133.8, 138.3, 140.7 and 141.2; *m/e* (relative intensity) 338 (M^+, 8), 197 (100), 141 (42), 115 (33), and 77 (28). Anal. Calcd for $C_{19}H_{14}O_4S$: C, 67.44; H, 4.17. Found: C, 67.54; H, 4.13.

2-[(Phenylsulfonyl)methyl]-1,4-benzodithiin (18) (71%): mp 108–109 °C; IR (KBr) 1557, 1449, 1171, 1136, 756, and 737 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 4.12 (s, 2 H), 6.44 (s, 1 H), 7.00–7.07 (m, 1 H), 7.15–7.30 (m, 3 H), 7.35–7.45 (m, 2 H), 7.55–7.62 (m, 1 H), and 7.70–7.77 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 62.9, 126.4, 127.7, 127.8, 127.9, 128.4, 128.5, 128.7, 128.9, 132.9, 133.2, 133.9, and 137.2; *m/e* (relative intensity) 320 (M^+, 14), 179 (100), 135 (66), 115 (9), 91 (24), and 77 (39). Anal. Calcd for $C_{15}H_{12}O_2S_3$: C, 56.22; H, 3.77. Found: C, 56.33; H, 3.81.

Methyl 2-Methoxy-5-[(phenylsulfonyl)methyl]-3-furanoate (19). To a stirred suspension containing 141 mg of NaH in 2.5 mL of dry THF at 0 °C was added 0.09 mL of dimethyl malonate. The mixture was allowed to stir at rt for 30 min, cooled to 0 °C, and treated with a solution containing 200 mg of DBP (**2**) in 2.5 mL of dry THF. After stirring at rt overnight, the reaction mixture was quenched with a saturated NH_4Cl solution. Removal of the solvent followed by silica gel chromatography of the residue gave 143 mg (62%) of 4-bromo-2-carbomethoxy-5-(phenylsulfonyl)-4-pentenoate (**22**): IR (neat) 1735, 1450, 1330, 1155, and 765 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 3.67 (d, 2 H, J = 7.4 Hz), 3.70 (s, 6 H), 3.81 (t, 1 H, J = 7.4 Hz), 6.76 (s, 1 H), and 7.50–8.05 (m, 5 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 34.3, 50.0, 52.3, 127.1, 128.9, 133.4, 139.6, 139.7, and 167.3. Anal. Calcd for $C_{14}H_{15}BrO_6S$: C, 43.08; H, 3.88; Found: C, 42.91; H, 3.72.

To a stirred solution containing 140 mg of **22** in 2.5 mL of dry THF under N_2 was added 39 mg of t-BuOK. The reaction mixture was stirred for 15 h at rt and was then quenched with a saturated NH_4Cl solution. The mixture was concentrated under reduced pressure and extracted with CH_2Cl_2. The organic layer was washed with water, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to leave behind a crude residue which was subjected to silica gel chromatography to give 125 mg (85%) of furan **19**: mp 124–125 °C; IR ($CHCl_3$) 1790, 1705, 1615, 1595, 1150, 1080, and 780 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 3.73 (s, 3 H), 3.83 (s, 3 H), 4.26 (s, 2 H), 6.47 (s, 1 H), 7.48–7.53 (m, 2 H), 7.61–7.69 (m, 1 H), and 7.73–7.75 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 51.3, 55.6, 57.9, 92.4, 114.3, 128.4, 129.2, 131.9, 134.0, 138.0, 162.0, and 162.7. Anal. Calcd for $C_{14}H_{14}O_6S$: C, 53.52; H, 4.55. Found: C, 53.66; H, 4.49.

2-Acetyl-1-methyl-4-[(phenylsulfonyl)methyl]furan (20). Under conditions similar to those used for **21** (vide infra), the reaction between 2,4-pentanedione and DIP resulted in the formation of **20** in 80% yield: mp 115–116 °C; IR ($CHCl_3$) 1690, 1570, 1330, 1240, 1095, 970, and 700 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 2.29 (s, 3 H), 2.37 (s, 3 H), 4.32 (s, 2 H), 6.48 (s, 1 H), 7.44–7.49 (m, 2 H), 7.58–7.62 (m, 1 H), and 7.69–7.72 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.1, 29.0, 55.4, 112.6, 122.4, 128.3, 129.0, 133.9, 138.0, 140.1, 159.3, and 193.4. Anal. Calcd for $C_{14}H_{14}O_4S$: C, 60.42; H, 5.07. Found: C, 60.19; H, 5.07.

Methyl 2-Methyl-5-[(phenylsulfonyl)methyl]-3-furanoate (21). A 252-mg (2.17-mmol) sample of methyl acetoacetate in 2 mL of THF was added to 76 mg (1.9 mmol) of NaH in 6 mL of THF at 0 °C. The mixture was stirred for 30 min at 0 °C, and then 357 mg of DIP (**3**) in 2 mL of THF was added and the mixture was allowed to stir for 3 h at 0 °C. The solution was quenched with pH 7 buffer and extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The resulting residue was chromatographed on silica gel to give 184 mg (76%) of methyl 2-methyl-5-[(phenylsulfonyl)methyl]-3-furanoate (**21**): mp 98–99 °C; IR ($CHCl_3$) 1715, 1575, 1450, 1330, 1260, 1090, and 695 cm^{-1}; NMR ($CDCl_3$, 360 MHz) δ 2.43 (s, 3 H), 3.79 (s, 3 H), 4.36 (s, 2 H), 6.52 (s, 1 H), 7.50–7.54 (m, 2 H), 7.66–7.68 (m, 1 H), and 7.75–7.77 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 13.3, 51.1, 55.3, 112.6, 114.4, 128.2, 128.8, 133.8, 137.8, 140.2, 160.0, and 163.5. Anal. Calcd for $C_{14}H_{14}O_5S$: C, 57.13; H, 4.79. Found: C, 57.00; H, 4.84.

Methyl 3-(Bromomethyl)-2-carbomethoxy-4-(phenylsulfonyl)-3-butenoate (24). To a solution containing 200 mg of DBP (**2**) and 0.09 mL of dimethyl malonate in 2.5 mL of absolute methanol at 0 °C was added 1.4 mL of a 0.5 N methanolic NaOMe solution. The mixture was allowed to stir at rt for 5 h and was then quenched with a saturated NH_4Cl solution. The solvent was removed under reduced pressure, and the residue was extracted with CH_2Cl_2 and washed with water. Evaporation of the solvent afforded a dark oil which was subjected to silica gel chromatography to give 156 mg (68%) of **24**: IR (neat) 1750, 1455, 1330, 1150, and 760 cm^{-1}; ^1H-NMR (90 MHz, $CDCl_3$) δ 3.83 (s, 6 H), 4.20 (s, 2 H), 4.84 (s, 1 H), 6.76 (s, 1 H), and 7.40–8.05 (m, 5 H); HRMS calcd for $C_{14}H_{15}BrO_6S$ 389.9773, found 389.9819.

Methyl 2-Methyl-4-[(phenylsulfonyl)methyl]-3-furanoate (26). A 246-mg (2.12-mmol) sample of methyl acetoacetate was combined with 680 mg (4.2 mmol) of K_2CO_3 in 5 mL of acetonitrile at rt. To this mixture was added 25 mg of Et_3N and 680 mg (2.0 mmol) of DBP (**2**), and the solution was allowed to stir at 25 °C for 16 h. The reaction was quenched by the addition of 15 mL of pH 7 buffer, and the CH_3CN was removed under reduced pressure. The crude residue was partitioned between ether and the aqueous buffer. The organic fraction was washed with brine and dried over $MgSO_4$. The resulting residue was chromato-

graphed on silica gel to give 382 mg (65%) yield of methyl 2-methyl-4-[(phenylsulfonyl)methyl]-3-furanoate (**26**): mp 104–105 °C; IR (neat) 1717, 1447, 1308, 1155, and 1099 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.49 (s, 3 H), 3.65 (s, 3 H), 4.57 (s, 2 H), 7.32 (s, 1 H), 7.49 (m, 2 H), 7.62 (m, 1 H), and 7.78 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 14.2, 51.1, 51.7, 112.3, 112.9, 128.5, 128.9, 133.6, 138.2, 141.8, 160.2, and 163.7. Anal. Calcd for $C_{14}H_{14}O_5S$: C, 57.13; H, 4.79. Found: C, 57.02; H, 4.77.

3-Acetyl-2-methyl-4-[(phenylsulfonyl)methyl]furan (27). Under conditions similar to those used above for furan **26**, the reaction between 2,4-pentanedione and DBP (**2**) resulted in the formation of furan **27** in 77% yield: mp 138–139 °C; IR (KBr) 1660, 1415, 1310, 155, and 1085 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.28 (s, 3 H), 2.56 (s, 3 H), 4.65 (s, 2 H), 7.37 (s, 1 H), 7.50 (m, 2 H), 7.62 (m, 1 H), and 7.83 (m, 2 H). Anal. Calcd for $C_{14}H_{14}O_4S$: C, 60.42; H, 5.07. Found: C, 60.37; H, 5.06.

3-Acetyl-4-(bromomethyl)-3-methyl-5-(phenylsulfonyl)-4-penten-2-one (28). A 342-mg (3.0-mmol) sample of methyl-2,4-pentanedione in 2 mL of THF was added to 138 mg (3.3 mmol) of NaH in 5 mL of THF and 10 mL of DMF, and the mixture was stirred at 0 °C. A 1.02-g (3.0-mmol) sample of DBP (**2**) was dissolved in 5 mL of THF and added via syringe to the reaction mixture. The mixture was allowed to stir at 0 °C, warming slowly to 25 °C over a 14-h interval. The solution was then partitioned between ether and water. The combined ether layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was chromatographed on silica gel to provide 663 mg (59%) of **28**: IR (KBr) 3080, 1710, 1310, and 1140 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.89 (s, 3 H), 2.24 (s, 6 H), 4.30 (s, 2 H), 6.39 (s, 1 H), 7.56 (m, 2 H), 7.62 (m, 1 H), and 7.91 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 20.4, 27.1, 57.4, 70.6, 118.4, 128.5, 129.3, 130.4, 134.1, 139.3, 204.5. Anal. Calcd for $C_{15}H_{17}BrO_4S$: C, 48.27; H, 4.59. Found: C, 48.18; H, 4.63.

4-(Bromomethyl)-3-carbethoxy-3-methyl-5-(phenylsulfonyl)-4-penten-2-one (29). A solution containing 149 mg (1.03 mmol) of ethyl methyl acetoacetate in 1 mL of THF was added slowly via syringe to 63 mg (1.5 mmol) of NaH in 5 mL of THF at 0 °C. The solution was allowed to stir at 0 °C for 30 min. To this mixture was added 346 mg (1.02 mmol) of DBP (**2**) in 3 mL of THF via syringe, and the mixture was allowed to stir at 0 °C for 6 h. The reaction was quenched with a saturated NH_4Cl solution and extracted with two portions of CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was chromatographed on silica gel to give 356 mg (87%) of **29**: IR (neat) 3070, 1740, 1701, 1600, and 1450 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 3 H, J = 7.0 Hz), 1.80 (s, 3 H), 2.28 (s, 3 H), 4.28 (q, 2 H, J = 7.0 Hz), 4.37 (s, 2 H), 6.53 (s, 1 H), 7.56 (m, 2 H), 7.70 (m, 1 H), and 7.93 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.8, 21.1, 26.6, 57.7, 62.3, 65.1, 118.2, 128.5, 129.2, 130.6, 133.9, 139.5, 170.1, and 202.8. Anal. Calcd for $C_{16}H_{19}BrO_5S$: C, 47.63; H, 4.75. Found: C, 47.72; H, 4.79.

Ethyl 3-(Bromomethyl)-2-carbethoxy-2-methyl-4-(phenylsulfonyl)-3-butenoate (30). A solution containing 340 mg (1.95 mmol) of diethyl methylmalonate in 1 mL of THF was added slowly via syringe to 79 mg (1.88 mmol) of NaH in 5 mL of THF. The solution was allowed to stir at 0 °C for 30 min, and 0.3 mL of HMPA was added. To this mixture was added 614 mg (1.80 mmol) of DBP (**2**) in 3 mL of THF via syringe, and the mixture was allowed to stir for at 0 °C for 12 h. The reaction was quenched with a saturated NH_4Cl solution and extracted with two portions of CH_2Cl_2. The combined organic layer was washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was chromatographed on silica gel to give 693 mg (89%) of **30**: IR (neat) 1732, 1450, 1250, 1107, 1018, 755, and 688 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.30 (t, 6 H, J = 7.0 Hz), 1.85 (s, 3 H), 4.26 (q, 4 H, J = 7.0 Hz), 4.37 (s, 2 H), 6.70 (s, 1 H), 7.55 (m, 2 H), 7.66 (m, 1 H), and 7.96 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.8, 21.3, 58.2, 59.6, 62.3, 118.3, 128.7, 129.1, 130.8, 133.8, 139.7, and 169.7. Anal. Calcd for $C_{17}H_{21}BrO_6S$: C, 47.12; H, 4.88; Found: C, 47.07; H, 4.90.

The reaction was also carried out using KH as the base. This resulted in a 4:1 ratio of **30** and ethyl 4-bromo-2-carbethoxy-2-methyl-5-(phenylsulfonyl)-4-pentenoate (**33**): ^1H-NMR (300 MHz, $CDCl_3$) δ 1.28 (t, 3 H, J = 7 Hz), 1.48 (s, 3 H), 3.92 (s, 2 H), 4.21 (q, 2 H, J = 7 Hz), 6.90 (s, 1 H), 7.5 (m, 2 H), 7.6 (m, 1 H), 7.9 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.65, 18.4, 40.0, 52.6, 61.7, 127.4, 129.4, 133.9, 135.4, 139.2, 140.3, and 170.6.

3-Carbethoxy-4-(iodomethyl)-3-methyl-5-(phenylsulfonyl)-4-penten-2-one (31). A 224-mg (1.55-mmol) sample of ethyl methylacetoacetate in 2 mL of THF at 0 °C under N_2 was added dropwise via syringe to 68 mg (1.62 mmol) of NaH in 5 mL of THF, and then 0.5 mL of HMPA was added to the solution. To this mixture was added via syringe a 314-mg (0.72-mmol) sample of DIP (**3**) dissolved in 2 mL of THF. The resulting solution was stirred for 16 h at 0 °C, warming gradually to rt. The reaction mixture was diluted with ether and washed with a pH 7 buffer solution. The combined organic fractions were washed with brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was chromatographed on silica gel to give 205 mg (64% yield) of **31**: IR (neat) 1734, 1717, 1450, 1321, and 1258 cm^{-1}; NMR (300 MHz, $CDCl_3$) δ 1.31 (t, 3 H, J = 7 Hz), 1.85 (s, 3 H), 2.27 (s, 3 H), 4.28 (q, 2 H, J = 7 Hz), 4.26 (d, 1 H, J = 18 Hz), 4.32 (d, 1 H, J = 18 Hz), 6.81 (s, 1 H), 7.56 (m, 2 H), 7.65 (m, 1 H), and 7.96 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.8, 21.6, 26.7, 61.3, 62.3, 65.9, 93.3, 128.7, 129.3, 134.0, 136.0, 139.4, 170.1, 202.8; HRMS calcd for $C_{16}H_{19}IO_5S$ ($M^+ - C_2H_2O$) 407.9894, found 407.9892.

The reaction was also carried out using NaH and THF as solvent without any HMPA. This resulted in a 1:1 ratio of **31** and 3-carbethoxy-5-iodo-3-methyl-6-(phenylsulfonyl)-5-hexen-2-one (**34**): NMR (300 MHz, benzene-d_6) δ 0.89 (t, 3 H, J = 7 Hz), 1.53 (s, 3 H), 1.88 (s, 3 H), 3.65 (d, 1 H, J = 14 Hz), 3.93 (q, 2 H, J = 7 Hz), 4.52 (d, 1 H, J = 14 Hz), 6.80–7.05 (m, 3 H), 7.07 (s, 1 H), and 7.70 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.7, 17.5, 25.8, 41.5, 59.1, 62.1, 115.8, 127.6, 128.2, 129.6, 140.2, 142.4, 171.2, and 202.9.

Ethyl 2-Carbethoxy-3-(iodomethyl)-2-methyl-4-(phenylsulfonyl)-3-butenoate (32). A sample containing 165 mg (0.95 mmol) of diethyl methylmalonate in 2 mL of DMF was added dropwise via syringe to 41 mg (0.97 mmol) of NaH in 5 mL of DMF at 0 °C. A solution containing 33 mg of DIP (**3**) was dissolved in 2.5 mL of THF, and this was added to the above mixture via syringe. The solution was stirred for 14 h at 0 °C, warming gradually to rt, and was then quenched with aqueous hydrochloric acid. The organic layer was washed with several portions of water and brine, dried over $MgSO_4$, and concentrated under reduced pressure. The crude oil was chromatographed on silica gel to give 200 mg (55% yield) of **32**: IR (neat) 1730, 1450, 1323, 1250, 1138, 1105, and 686 cm^{-1}; ^1H-NMR (300 MHz, $CDCl_3$) δ 1.29 (t, 6 H, J = 7.0 Hz), 1.85 (s, 3 H), 4.26 (q, 4 H, J = 7.0 Hz), 4.37 (s, 2 H), 6.99 (s, 1 H), 7.56 (m, 2 H), 7.66 (m, 1 H), and 7.98 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.8, 21.7, 60.4, 61.8, 62.2, 93.3, 128.9, 129.3, 133.9, 135.9, 139.5, and 169.8. Anal. Calcd for $C_{17}H_{21}IO_6S$: C, 42.51; H, 4.41. Found: C, 42.58; H, 4.41.

The reaction was also carried out using KH as the base. This resulted in a 1:1 ratio of **32** and ethyl 2-carbethoxy-4-iodo-2-methyl-5-(phenylsulfonyl)-4-pentenoate (**35**): ^1H-NMR (300 MHz, $CDCl_3$) δ 1.35 (t, 3 H, J = 7 Hz), 1.47 (s, 3 H), 3.94 (s, 2 H), 4.25 (q, 2 H, J = 7 Hz), 7.20 (s, 1 H), 7.65 (m, 2 H), 7.74 (m, 1 H), and 7.90 (m, 2 H); ^{13}C-NMR (75 MHz, $CDCl_3$) δ 13.8, 18.4, 42.3, 53.1, 61.8, 115.0, 127.6, 129.5, 133.9, 139.4, 142.5, and 170.6.

General Procedure for the Reaction of (*E*)-2,3-Diiodo-1-(phenylsulfonyl)-1-propene (DIP) (3) with Trimethylsilyl Enol Ether in the Presence of Silver Tetrafluoroborate. To a solution containing 434 mg (1.0 mmol) of DIP **3** and 2.0 mmol of the appropriate trimethylsilyl enol ether in 40 mL of CH_2Cl_2 was added 389 mg (2.0 mmol) of $AgBF_4$ under a N_2 atmosphere. The reaction mixture was stirred at 25 °C in the dark for 20 h with monitoring by TLC. The reaction mixture was filtered, and the precipitate was washed with 80 mL of CH_2Cl_2. The combined CH_2Cl_2 layer was washed successively with a 5% NaCl solution, 1% sodium bisulfite solution, and water and then dried over $MgSO_4$. Removal of the solvent under reduced pressure followed by purification by silica gel chromatography gave pure material whose structure was assigned on the basis of its spectral properties.

(*E*)-2-Ethyl-4-iodo-5-(phenylsulfonyl)-4-pentenal (36) was prepared from the silyl enol ether of butyraldehyde (32%): clear oil; IR (neat) 1723, 1598, 1447, 1152, 1084, and 749 cm^{-1}; ^1H-NMR ($CDCl_3$, 300 MHz) δ 1.00 (t, 3 H, J = 7.5 Hz), 1.60–1.85 (m, 2 H), 2.58–2.70 (m, 1 H), 3.25 (dd, 1 H, J = 14.7 and 7.0 Hz), 3.40 (dd, 1 H, J = 14.7 and 6.6 Hz), 7.05 (s, 1 H), 7.50–7.70 (m, 3 H),

7.90–8.00 (m, 2 H) and 9.68 (d, 1 H, J = 2.1 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 11.3, 21.4, 37.9, 53.6, 121.3, 127.5, 129.5, 133.9, 140.2, 141.1, and 202.2; m/e (relative intensity) 251 (M^+ – I, 16), 237 (8), 223 (5), 143 (22), 125 (35), 109 (69), and 77 (100).

Pentanal **36** was converted into the corresponding 2,4-dinitrophenylhydrazone by treatment with 2,4-dinitrophenylhydrazine in ethanol (41%): mp 159–160 °C; IR (KBr) 1619, 1590, 1519, 1148, 1082, 1071, and 754 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 1.03 (t, 3 H, J = 7.4 Hz), 1.65–1.80 (m, 2 H), 2.75–2.90 (m, 1 H), 3.04 (dd, 1 H, J = 14.1 and 5.1 Hz), 3.68 (dd, 1 H, J = 14.1 and 9.5 Hz), 7.02 (s, 1 H), 7.36 (d, 1 H, J = 6.9 Hz), 7.50–7.70 (m, 3 H), 7.80–7.90 (m, 2 H), 7.92 (d, 1 H, J = 9.6 Hz), 8.30 (dd, 1 H, J = 9.6 and 2.4 Hz), 9.12 (d, 1 H, J = 2.4 Hz), and 11.01 (s, 1 H); m/e (relative intensity) 431 (M^+ – I, 17), 289 (32), 125 (69), 110 (57), 97 (21), and 77 (100). Anal. Calcd for $C_{19}H_{19}IN_4O_6S$: C, 40.87; H, 3.43; N, 10.03. Found: C, 41.02; H, 3.45; N, 9.98.

(*E*)-4-Iodo-1-phenyl-5-(phenylsulfonyl)-4-penten-1-one (37) was prepared from the silyl enol ether of acetophenonone (50%): mp 95–96 °C; IR (KBr) 1688, 1598, 1451, 1289, 1150, 1084, and 743 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 3.23 (t, 2 H, J = 7.7 Hz), 3.46 (t, 2 H, J = 7.7 Hz), 7.09 (s, 1 H), 7.40–7.70 (m, 6 H), and 7.90–8.00 (m, 4 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 35.3, 38.2, 123.3, 127.4, 128.0, 128.6, 129.5, 133.3, 133.8, 136.2, 139.6, 140.5, and 196.7; m/e (relative intensity) 299 (M^+ – I, 11), 157 (60), 128 (30), 105 (77), and 77 (100). Anal. Calcd for $C_{17}H_{15}IO_3S$: C, 47.90; H, 3.55. Found: C, 47.86; H, 3.52.

(*E*)-2-Iodo-1-(phenylsulfonyl)-1,5-hexadiene (38). A mixture containing 434 mg (1.0 mmol) of DIP (**3**), 228 mg (2.0 mmol) of allyltrimethylsilane, and 389 mg of $AgBF_4$ in 40 mL of CH_2Cl_2 was stirred at 25 °C for 120 h. The usual workup afforded 150 mg (43%) of (*E*)-2-iodo-1-(phenylsulfonyl)-1,5-hexadiene (**38**) as a clear oil: IR (neat) 1642, 1596, 1447, 1150, 1084, and 747 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 2.28 (td, 2 H, J = 7.2 and 6.9 Hz), 3.14 (t, 2 H, J = 7.2 Hz), 5.00 (dd, 1 H, J = 10.1 and 1.0 Hz), 5.08 (dd, 1 H, J = 16.8 and 1.0 Hz), 5.73 (ddt, 1 H, J = 16.8, 10.1, and 6.9 Hz), 7.02 (s, 1 H), 7.50–7.70 (m, 3 H), and 7.85–7.94 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 33.6, 37.0, 116.4, 124.5, 127.4, 129.4, 133.7, 135.2, 139.0, and 140.7; m/e (relative intensity) 221 (M^+ – I, 5), 207 (48), 143 (32), 125 (21), and 77 (100). Anal. Calcd for $C_{12}H_{13}IO_2S$: C, 41.39; H, 3.76. Found: C, 41.43; H, 3.77.

General Procedure for the Synthesis of Heterocycles from the Reaction of DIP (3) with Thioamides. To a solution containing 0.43 g (1.0 mmol) of DIP (**3**) and 1.2 mmol of the appropriate substrate in 10 mL of DMF was added 0.28 g (2.0 mmol) of K_2CO_3 (or 0.16 g of pyridine) under N_2. The mixture was stirred at 25 °C for 12 h, and the solvent was removed under reduced pressure. The residue was dissolved in 50 mL of CH_2Cl_2, was washed with 50 mL of 1% Na_2SO_4 and water, and dried over anhydrous $MgSO_4$. Removal of the solvent under reduced pressure was followed by purification by silica gel chromatography. On the basis of the above procedure, the following compounds were obtained:

2-Methyl-4-[(phenylsulfonyl)methyl]thiazole (42) (75%): mp 126–127 °C; IR (KBr) 1513, 1447, 1331, 1248, 1152, 891, and 689 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 2.58 (s, 3 H), 4.51 (s, 2 H), 7.14 (s, 1 H), 7.46–7.55 (m, 2 H), 7.55–7.65 (m, 1 H), and 7.70–7.77 (m, 2 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 18.8, 58.0, 119.7, 128.4, 128.8, 133.6, 138.3, 142.6, and 165.9; m/e (relative intensity) 189 (M^+ – SO_2, 14), 147 (6), and 112 (100). Anal. Calcd for $C_{11}H_{11}NO_2S_2$: C, 52.15; H, 4.38; N, 5.53. Found: C, 52.21; H, 4.33; N, 5.43.

2-Phenyl-4-[(phenylsulfonyl)methyl]thiazole (43) (60%): mp 106–107 °C; IR (KBr) 1513, 1447, 1262, 1146, 1084, 796, and 766 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.61 (s, 2 H), and 7.30–7.80 (m, 11 H); ^{13}C-NMR ($CDCl_3$, 75 MHz) 58.2, 120.0, 126.3, 128.6, 128.7, 128.8, 130.1, 132.8), 133.6, 138.3, 144.3 and 167.9; m/e (relative intensity) 315 (M^+, 6), 251 (9), 174 (100), and 110 (22). Anal. Calcd for $C_{16}H_{13}NO_2S_2$: C, 60.93; H, 4.15; N, 4.44. Found: C, 60.80; H, 4.08; N, 4.34.

2-(3-Pyridyl)-4-[(phenylsulfonyl)methyl]thiazole (44) (47%): mp 138–139 °C; IR (KBr) 1513, 1304, 1260, 1148, 1125, 1084, and 1001 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 4.62 (s, 2 H), 7.32 (dd, 1 H, J = 7.8 and 5.0 Hz), 7.42 (s, 1 H), 7.45–7.55 (m, 2 H), 7.55–7.65 (m, 1 H), 7.70–7.80 (m, 2 H), 7.97 (ddd, 1 H, J = 7.8, 2.1, and 1.8 Hz), 8.61 (dd, 1 H, J = 5.0 and 1.8 Hz), and 8.89 (d, 1 H, J = 2.1 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 58.0, 120.8, 123.5, 128.5, 128.9, 133.5, 133.8, 138.2, 144.9, 147.3, 150.8, and 164.4; m/e (relative intensity) 316 (M^+, 1), 252 (16), 175 (100), and 105 (19). Anal. Calcd for $C_{15}H_{12}N_2O_2S_2$: C, 56.94; H, 3.82; N, 8.85. Found: C, 56.85; H, 3.82; N, 8.77.

2-(4-Pyridyl)-4-[(phenylsulfonyl)methyl]thiazole (45) (56%): mp 172–173 °C; IR (KBr), 1596, 1304, 1262, 1148, 1125, 1084, and 828 cm^{-1}; NMR ($CDCl_3$, 300 MHz) δ 4.62 (s, 2 H), 7.42–7.52 (m, 3 H), 7.52–7.65 (m, 3 H), 7.70–7.75 (m, 2 H), and 8.63 (dd, 2 H, J = 4.5 and 1.5 Hz); ^{13}C-NMR ($CDCl_3$, 75 MHz) δ 58.0, 120.0, 121.8, 128.5, 128.9, 133.8, 138.2, 139.4, 145.3, 150.5, and 164.9; m/e (relative intensity) 316 (M^+, 0.3), 252 (20), 175 (100), 105 (16), and 71 (72). Anal. Calcd for $C_{15}H_{12}N_2O_2S_2$: C, 56.94; H, 3.82; N, 8.85. Found: C, 56.91; H, 3.83; N, 8.82.

Acknowledgment. We gratefully acknowledge support of this work by the National Institutes of Health (CA-26750). Use of the high-field NMR spectrometer used in these studies was made possible through equipment grants from the NIH and NSF.

Registry No. **1**, 2525-42-0; **2**, 128496-94-6; **3**, 137929-74-9; **8**, 138286-87-0; **9**, 138286-88-1; **10**, 138286-89-2; **11**, 138286-90-5; **12**, 138286-91-6; (*E*)-**13**, 138286-92-7; (*Z*)-**13**, 138286-93-8; **14**, 138286-94-9; **15**, 138286-95-0; **16**, 138286-96-1; **17**, 138286-97-2; **18**, 138286-98-3; **19**, 128496-95-7; **20**, 128496-96-8; **21**, 128496-97-9; **22**, 128497-00-7; **24**, 138286-99-4; **26**, 138287-00-0; **27**, 138287-01-1; **28**, 138287-02-2; **29**, 138287-03-3; **30**, 138287-04-4; **31**, 138287-05-5; **32**, 138287-06-6; **33**, 138287-07-7; **34**, 138287-08-8; **35**, 138287-09-9; **36**, 137929-86-3; **36** DNP hydrazone derivative, 138287-10-2; **37**, 137929-87-4; **38**, 137929-88-5; **42**, 138287-11-3; **43**, 138287-12-4; **44**, 138287-13-5; **45**, 138287-14-6; $H_3CCH_2CH{=}CHOTMS$, 19980-22-4; $PhC(OTMS){=}CH_2$, 13735-81-4; $CH_2{=}CHCH_2TMS$, 762-72-1; thioacetamide, 62-55-5; thiobenzamide, 2227-79-4; 3-pyridinethiocarboxamide, 4621-66-3; 4-pyridinethiocarboxamide, 2196-13-6; benzylamine, 100-46-9; aniline, 62-53-3; thiophenol, 108-98-5; catechol, 120-80-9; 2,3-naphthalenediol, 92-44-4; 1,2-benzenedithiol, 17534-15-5; dimethyl malonate, 108-59-8; 2,4-pentanedione, 123-54-6; methyl acetoacetate, 105-45-3; methyl-2,4-pentanedione, 815-57-6; ethyl methyl acetoacetate, 609-14-3; diethyl methylmalonate, 609-08-5.

Supplementary Material Available: ^{1}H NMR and ^{13}C NMR (75 MHz) spectra for all compounds with high-resolution mass spectra, tables of the final positional and thermal parameters and related experimental data for the X-ray diffraction study of DBP (**2**), and an ORTEP drawing of **2** (9 pages). Ordering information is given on any current masthead page.