cysteine methylenes), 4.5 (m, 1 H, α-H), 5.5 (br d, 1 H, NH). The oil was used in subsequent reactions without further purification.

N-(Benzyloxycarbonyl)-L-cysteine Ethyl Ester (20). To *N,N'*-bis(benzyloxycarbonyl)-L-cystine diethyl ester (1.69 g, 3.0 mmol) dissolved in a 5% solution of acetic acid in diethyl ether (100 mL), and cooled to 0 °C in an ice–salt bath, was added zinc dust (5.81 g, 180 mmol) slowly, in portions, over a period of 15 min. The mixture was stirred at 0 °C for 2 h and at room temperature for 1 h. The reaction mixture was filtered and the precipitate washed well with acetic acid–ether. The combined filtrate and washings were concentrated in vacuo, and the residue was dissolved in 1 N HCl (50 mL). The aqueous solution was saturated with NaCl and extracted with ethyl acetate (3 × 25 mL). The organic phase was dried over Na_2SO_4 to yield 1.69 g (100%) of title compound as an oil. This oil was used without further purification for subsequent reactions: TLC (solvent A) R_f 0.3; ^1H NMR (60 MHz, $CDCl_3$) 1.3 (t, 3 H, ethyl ester Me), 1.9 (d, 1 H, SH), 3.1 (dd, 2 H, cysteine methylenes), 4.3 (q, 2 H, ester methylenes), 4.8 (m, 1 H, α-H), 5.2 (s, 2 H, benzyloxycarbonyl methylenes), 5.9 (br d, 1 H, NH), 7.4 (s, 5 H, benzyloxycarbonyl aromatic).

N-[[(2,2,2-Trichloroethyl)oxy]carbonyl]-L-cysteine *tert*-Butyl Ester (21). To 13 (0.37 g, 0.53 mmol) in 90% aqueous methanol (5 mL) was added tri-*n*-butylphosphine (0.312 g, 1.05 mmol) and the reaction mixture was stirred at room temperature for 5 h. The solvent was removed in vacuo and the residue triturated with ether (10 mL). Removal of ether led to an oil which was purified on a silica gel gravity column with 5% acetone in hexane as the elutant. Compound 21 was obtained, 0.33 g (89%), as an oil: TLC (solvent hexane–acetone, 9:1) R_f 0.3; ^1H NMR (60 MHz, $CDCl_3$) δ 1.5 (s, 9 H, *tert*-butyl ester Me's), 1.9 (d, 1 H, SH), 3.2 (dd, 2 H, cysteine methylenes), 4.8 (s, 2 H, trichloroethyloxycarbonyl methylenes).

N¹-(Benzyloxycarbonyl)-N²-(*tert*-butoxycarbonyl)-L,L-lanthionine Ethyl *tert*-Butyl Diester (2). Cystine 14 (0.96

g, 1.74 mmol) and hexaethylphosphorus triamide (0.47 g, 1.91 mmol) in 25 mL of benzene were stirred at room temperature under an atmosphere of nitrogen for 5 h. The solvent was removed in vacuo and the product mixture was purified by MPLC with hexane as the eluting solvent to yield 0.47 g (52%) of lanthionine 2 as an oil: TLC (solvent B) R_f 0.31; $[\alpha]^{25}_D$ +2.3° (c 7.9, $CHCl_3$); ^1H NMR (60 MHz, $CDCl_3$) δ 1.3 (t, 3 H, ethyl ester methyl), 1.5 (s, 18 H, Boc and *t*-Bu Me's), 3.0 (t, 4 H, lanthionine methylenes), 4.3 (q, 2 H, ethyl ester methylenes), 5.2 (s, 2 H, benzyloxycarbonyl methylenes), 5.4–5.8 (d, 2 H, NH), 7.4 (s, 5 H, benzyloxycarbonyl aromatics). Anal. Calcd for $C_{25}H_{38}O_8N_2S$: C, 57.03; H, 7.22; N, 5.32; S, 6.08. Found: C, 56.90; H, 7.31; N, 5.30; S, 6.09.

N¹-(Benzyloxycarbonyl)-N²-[[(2,2,2-trichloroethyl)oxy]carbonyl]-L,L-lanthionine Ethyl *tert*-Butyl Diester (3). To a solution of 15 (0.33 g, 0.54 mmol) in benzene (15 mL) was added hexaethylphosphorus triamide (0.34 g, 1.36 mmol) dropwise, with stirring, under nitrogen. The reaction mixture was stirred at room temperature overnight, and the solvent was evaporated in vacuo. The oil obtained was purified by MPLC, with 10% acetone in hexane as the eluting solvent, to yield 0.18 g (58%) of 3 as an oil: TLC (solvent hexane–acetone, 9:1) R_f 0.22; $[\alpha]^{25}_D$ +2.4° (c 5.7, $CHCl_3$); ^1H NMR (90 MHz, $CDCl_3$) δ 1.3 (t, 3 H, ethyl ester Me), 1.5 (s, 9 H, *tert*-butyl ester Me), 3.0 (d, 2 H, lanthionine methylenes), 4.2 (q, 2 H, ethyl ester methylenes), 4.6 (m, 2 H, α-H's), 4.8 (s, 2 H, [(trichloroethyl)oxy]carbonyl methylenes), 5.2 (s, 2 H, benzyloxycarbonyl methylenes), 5.9 (dd, 2 H, NH's), 7.4 (s, 5 H, benzyloxycarbonyl aromatics). Anal. Calcd for $C_{23}H_{31}N_2O_8Cl_3S$: C, 45.88; H, 5.15; N, 4.66; S, 5.32. Found: C, 47.16; H, 5.27; N, 4.75; S, 5.59. Two attempts to obtain satisfactory analysis for 3 resulted in % C found to be higher than the calculated value.

A Theoretical Study of the Homolytic Abstraction of Benzylic Hydrogen
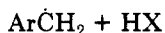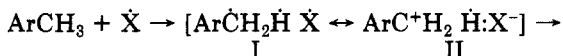
Richard D. Gilliom

Department of Chemistry, Rhodes College, Memphis, Tennessee 38112

The activation energies for the abstraction of a hydrogen atom from toluene, 4-chlorotoluene, and *p*-xylene by chlorine and bromine atoms and a methyl radical from toluene have been calculated with the MNDO approximation of molecular orbital theory with complete geometric optimization of both the reactants and the transition states. The results indicate that electron transfer to the attacking radical occurs but that the usual explanation of the polar effect in radical abstraction reactions is not complete.

The most common reaction of free radicals is the abstraction of hydrogen.[1] This reaction has been widely studied. When toluenes serve as the hydrogen donors in this reaction a Hammett correlation is observed.[1] While some radicals give better correlations with σ and others with σ^+, the interpretation of the "polar effect" as generally accepted was first given by Russell.[2] This explanation of the polar effect rests upon the idea of stabilization of the transition-state structure by a polar canonical structure

$$ArCH_3 + \dot{X} \rightarrow [Ar\dot{C}H_2\dot{H}\ \dot{X} \leftrightarrow ArC^+H_2\ \dot{H}:X^-] \rightarrow$$
$$\qquad\qquad\qquad \mathrm{I} \qquad\qquad\qquad \mathrm{II}$$

$$Ar\dot{C}H_2 + HX$$

This interpretation was based upon the observation that

most abstracting radicals correlate with a negative value for ρ in Hammett-type plots; i.e. electron-withdrawing substituents slow the reaction.[3] This polar interpretation of substituent effects seemed strengthened by the discovery that radicals of low electronegativity, *tert*-butyl,[4] 3-heptyl,[5] and undecyl,[6] afforded Hammett correlations with a positive ρ value.

Zavitsas and Pinto[7] proposed that charge separation in the transition state either does not occur or is an unnecessary assumption. These workers argued that the differences in reactivities of a series of substituted toluenes

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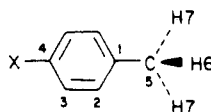(4) Pryor, Wm. A.; Davis, Wm. H.; Stanley, J. P. *J. Am. Chem. Soc.* 1973, 95, 4754.
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Table I. Significant MNDO Properties of Toluenes

X	bond	length[a]	bonds	angle[b]	atom	charge density[c]	heat of formation[d]
H	1–5	1.503	1–5–6	110.3	1	−99	11.3
	5–6	1.111	1–5–7	112.0	2	−44	
	5–7	1.110			3	−62	
	X–4	1.090			4	−56	
					5	80	
					6	2	
					7	4	
					X	60	
CH$_3$	1–5	1.503	1–5–6	110.3	1	−95	3.3[e]
	5–6	1.111	1–5–7	111.9	2	−47	
	5–7	1.110			3	−47	
	X–4	1.503			4	−95	
					5	80	
					6	−1	
					7	−4	
					X	80	
Cl	1–5	1.504	1–5–6	110.3	1	−92	3.2
	5–6	1.111	1–5–7	111.9	2	−41	
	5–7	1.109			3	−44	
	X–4	1.750			4	7	
					5	78	
					6	2	
					7	−1	
					X	−110	

[a] Angstroms. [b] Degrees. [c] Charge $\times$ 10^3. [d] Kilocalories/mole. [e] Energy is minimized when the H atom of the substituent methyl is perpendicular to the ring and on the same side of the ring as H6.

toward a radical were due to differences in the bond-dissociation energies, BDE, of the benzylic C–H bonds in each of the substrates. This argument depends upon the assumption that electron-withdrawing substituents increase the BDE and was based upon the observation of only negative values of ρ for several abstracting radicals. This proposition was questioned by the finding of positive values of ρ for abstraction reactions.[4-6] The Pryor group concluded that both the polar effect upon the transition state and upon bond-dissociation energies must be considered.[8]

A more recent study also attempted to resolve the role of charge separation in the transition state of hydrogen abstraction reactions.[9] In this later work the Swain and Lupton[10] equation, using the positional weighting factors of Williams and Norrington,[11] was used to attempt to study substituent effects in terms of field and resonance effects. The authors concluded that polar structures contribute to the transition state for abstraction reactions and that "resonance" contributions to the stability of the transition state of the abstraction reaction, except for *tert*-butoxy radical, were not very significant. They concluded that the transition state is predominantly described by polar structures such as II.[9]

Most recently Dust and Arnold have presented a σ· scale based upon benzylic α-hydrogen electron-spin resonance hyperfine coupling constants.[12] This work reexamined a series of radical reactions by using an extended Hammett relation to attempt to assess the relative importance of spin delocalization (radical stabilization) vs. polar effects in

radical reactions. They concluded that polar effects were dominant in the bromine atom abstraction of hydrogen from substituted toluenes. Recently it was reported[13] that this reaction has a "two-point" isokinetic temperature[14] of 276 K, a result consistent with an entropic, not an enthalpic, interpretation.

In an attempt to understand these contradictory results we have located the transition state on the MNDO surface in order to examine the geometry and electron distribution for the abstraction of benzylic hydrogen. The transition states have been located not only for toluene but also for 4-chlorotoluene and *p*-xylene so that the role of substituents could be examined.

Methods

Molecular orbital calculations were carried out with the MNDO[15] approximation as supplied in the Quantum Chemistry Program Exchange program QCPE 428[16] for chlorine and methyl, while MOPAC, QCPE 455,[17] was used for bromine abstraction. Geometrical optimization was performed using all independent internal coordinates for the optimization of the reactants and all except the bond lengths of the breaking C–H bond and the incipient H–X bond for the transition state. The unrestricted SCF option was employed for all optimizations. The transition-state structure was located on the MNDO energy surface by methods previously described.[18] The MNDO method was chosen because it is much less costly than ab initio

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Table II. MNDO Transition States for Hydrogen Abstraction from Toluenes by Chlorine Atom[a]

X	bond	length	bonds	angle	atom	charge density	heat of formation
H	1–5	1.502	1–5–6	110.1	1	−105	42.4
	5–6	1.124	1–5–7	112.5	2	−40	
	5–7	1.110	5–6–Cl	180.0	3	−61	
	X–4	1.090			4	−53	
	6–Cl	2.199			5	101	
					6	−11	
					7	4	
					X	61	
					Cl	−46	
CH_3	1–5	1.503	1–5–6	110.5	1	−104	35.2[b]
	5–6	1.123	1–5–7	112.0	2	−41	
	5–7	1.110	5–6–Cl	180.0	3	−44	
	X–4	1.500			4	−101	
	6–Cl	2.220			5	98	
					6	−9	
					7	2	
					X	76	
					Cl	−42	
Cl	1–5	1.500	1–5–6	109.7	1	−97	34.4
	5–6	1.127	1–5–7	112.6	2	−36	
	5–7	1.108	5–6–Cl	184.8	3	−45	
	X–4	1.747			4	9	
	6–Cl	2.170			5	101	
					6	−7	
					7	8	
					X	−101	
					Cl	−48	

[a] Positions and units as in Table I. [b] Energy is minimized when the H atoms of the substituent methyl is perpendicular to the ring and on the side opposite to H6; it is 0.2 kcal/mol greater when on the same side.

Table III. MNDO Transition States for Hydrogen Abstraction from Toluenes by Bromine Atom[a]

X	bond	length	bonds	angle	atom	charge density	heat of formation
H	1–5	1.452	1–5–6	106.6	1	−81	50.3
	5–6	1.430	1–5–7	118.0	2	−35	
	5–7	1.097	5–6–Br	176.4	3	−58	
	X–4	1.090			4	−45	
	6–Br	1.575			5	39	
					6	105	
					7	43	
					X	66	
					Br	−244	
CH_3	1–5	1.453	1–5–6	106.3	1	−73	42.2
	5–6	1.429	1–5–7	118.6	2	−39	
	5–7	1.097	5–6–Br	176.5	3	−43	
	X–4	1.503			4	−84	
	6–Br	1.554			5	14	
					6	120	
					7	45	
					X	76	
					Br	−241	
Cl	1–5	1.449	1–5–6	105.8	1	−74	42.9
	5–6	1.453	1–5–7	118.7	2	−33	
	5–7	1.096	5–6–Br	176.5	3	−41	
	X–4	1.746			4	13	
	6–Br	1.565			5	24	
					6	112	
					7	47	
					X	−94	
					Cl	−235	

[a] Positions and units as in Table I.

methods, thereby permitting much more extensive geometrical optimization. We,[18] as well as others,[19] have found that semiempirical methods are as accurate as small basis set ab initio calculations for predicting activation energies; large basis set calculations are too costly. While MINDO/2 and MINDO/3 may predict somewhat more accurate activation energies for homolytic reactions than does MNDO,[18] MNDO is slightly more successful in obtaining geometries in accord with those given by the BEBO method that has been shown to successfully give the reaction path and geometries obtained by ab initio methods for simpler reactions.[20]

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Table IV. MNDO Transition State for Hydrogen Abstraction from Toluene by Methyl Radical[a]

X	bond	length	bonds	angle	atom	charge density	heat of formation
H	1–5	1.475	1–5–6	109.5	1	–85	60.9
	5–6	1.252	1–5–7	115.3	2	–47	
	5–7	1.103	5–6–C(H$_3$)	183.3	3	–61	
	X–4	1.090			4	–5	
	6–CH$_3$	1.308			5	1	
					6	61	
					7	13	
					X	59	
					C(H$_3$)	–25	

[a] Positions and units as in Table I.

Results

The MNDO optimized geometries, charge densities, and heats of formation of the toluenes are given in Table I. The geometries of the transition states optimized for all internal coordinates except the incipient H6–X bond and the breaking C5–H6 bond are given in Table II, along with other relevant properties, for chlorine, in Table III for bromine, and in Table IV for methyl-radical abstraction.

Discussion

It will be noted that the length of the C5–H6 bond, which is perpendicular to the plane of the aryl ring, is calculated to be slightly longer than the other C5–H bonds in the toluenes. If it is assumed that free rotation of the methyl group occurs, the C–H bond length in the methyl group would be a weighted average of the values in Table I. Thus the C5–H bond in 4-chlorotoluene is slightly shorter than in toluene. Since 4-chlorotoluene reacts with chlorine 0.79 times slower than does toluene,[21] the rationale of Zavitsas and Pinto would seem to be supported, assuming a direct relationship between bond length and bond strength. This reasoning, however, gives no explanation of why p-xylene is 1.6 times more reactive than toluene.[21] It may also be noted that the C1–C5–H bond angles are somewhat distorted from the tetrahedral angle with the perpendicular H6 less distorted than the others. This appears to occur because of overlap between the C–H6 bond electrons and those of the π-system of the aryl ring. This is supported by the decreased electron density at H6 relative to the other hydrogens and at C5 relative to the ring carbons and is probably related to the hyperconjugative electron supply effect of a methyl group. This electron supply can be seen in Table I to decrease with distance so that the para C atom is the least negatively charged of the aryl carbons, although all received increased electron density. In p-xylene the electron supply of one methyl group is sufficient to increase the electron density on the hydrogens of the other methyl group enough to make them slightly negative although no effect is noticed at the carbon atom. The effect of a chlorine atom, as shown by 4-chlorotoluene, is to decrease the electron density on the hydrogen atoms of the methyl group relative to those of unsubstituted toluene.

It may be noted that the transition state for chlorine atom is reached with very little movement of atoms other than the hydrogen being abstracted. Even the breaking bond is lengthened only slightly, implying an early transition state on the reaction coordinate. It may also be noted that the closer the abstracting atom approaches the departing hydrogen at the transition state the longer is the breaking bond. The transition state occurs earliest for a p-methyl substituent, the more reactive of the three toluenes, while a p-chloro substituent, the least reactive of

Table V. MNDO Energies of Activation for Benzylic Hydrogen Abstraction of Toluenes

substituent	relative rate	E_a, kcal/mol
Chlorine Atom[a]		
hydrogen	1.00	2.1
4-methyl	1.57	2.9
4-chloro	0.79	2.2
Bromine Atom[b]		
hydrogen	1.00	12.3
4-methyl	2.42	12.2
4-chloro	0.73	13.0
Methyl Radical		
toluene		25.0

[a] Reference 20. [b] Reference 25.

the toluenes, leads to a later forming transition state. Similar observations are seen for bromine atom although the later transition state for bromine results in greater atomic movement.

While the above observations are consistent with our usual view of reaction mechanisms, based upon Hammond's postulate,[22] they do not explain the role of substituents in determining reactivity. As the reactant bond strengthening and weakening explanation of Zavitsas and Pinto[7] has been questioned (vide supra), we may turn to the polar explanation.[2] Tables II–IV show that MNDO does indeed predict that electron density is transferred from the reacting toluene to the abstracting radical at the transition state. The electron-donating methyl group affords less electron transfer at the transition state than does toluene, while the electron-withdrawing chlorine substituent gives the most electron transfer for chlorine and the least for bromine as is shown by the charge density on the abstracting radical. The site of electron transfer appears to be principally from the C atom of the methyl group. The effects of substituents upon electron density in the transition state appears to agree with traditional chemical reasoning. There is, without doubt, a polar effect in the abstraction reaction but the usual explanation is that the transition state is stabilized by polar canonical structures (vide supra). This, it is argued, leads to lower energies of activation and increased reactivity.

The energies of activation as calculated by MNDO are given in Table V. The energies of reactants were taken as the sum of the heats of formation of the separated, optimized species. While the "energies" given in Table V are actually enthalpies, this procedure is generally accepted.[23] As calculated by MNDO, both electron-supplying and -withdrawing substituents increase the energy of activation for chlorine atom abstraction, while for the bromine atom the electron-supplying p-methyl only slightly decreases the energy of activation. The methyl

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radical, while generally observed to be the least selective and hence most reactive of the three abstracting radicals considered in this study, has the largest computed energy of activation.

Conclusions

The generally accepted explanations of the polar effect in hydrogen-abstraction reactions are based upon enthalpic arguments. On the basis of the empirical results obtained by us[13] and others[24] for the bromination reaction, it appears

that these arguments are unsatisfactory and that an entropic effect must be considered. Now, based upon the semiempirical MNDO method, theoretical results are presented that also suggest that reasoning based upon only enthalpic arguments is inadequate.

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7-Oxabicyclo[2.2.1]hept-2-ene and Related Materials by Reductive Elimination

Seid Mirsadeghi[†] and Bruce Rickborn*

Department of Chemistry, University of California, Santa Barbara, California 93106

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The cycloadduct 1 of furan and (E)-1,2-bis(phenylsulfonyl)ethylene has been converted to various derivatives, which in turn have been subjected to sodium amalgam reductive elimination conditions. Some of these procedures constitute useful methods for the preparation of the title olefin. The amalgam reduction of 1 provides modest yields of 7-oxabicyclo[2.2.1]hepta-2,5-diene. The cycloadduct of isobenzofuran and the reactive dienophile was prepared and subjected to analogous reactions. Various reaction steps which compete with reductive elimination have been identified.

The oxygen analogue of norbornene, 7-oxabicyclo-[2.2.1]hept-2-ene (**3**), is potentially useful as a dienophile and in other applications. It has received little attention, however, since it is relatively inaccessible. The only open literature preparative method,[1] the direct Diels–Alder reaction of furan and ethylene, requires the use of pressure apparatus and suffers from very low yield and a tedious isolation procedure.[2]

De Lucchi and co-workers have recently reported the use of (E)-1,2-bis(phenylsulfonyl)ethylene as a very reactive "acetylene equivalent" dienophile[3] and shown that it will react cleanly with furan to form the adduct **1**. Since at least three distinct pathways (all of which have been described by De Lucchi for carbocyclic materials) could be envisioned (see Scheme I) for converting **1** to **3**, this obvious extension seemed worth pursuing. It was recognized that cleavage of the oxa bridge in **1** might intervene, since there is precedent for such behavior in reactions involving presumed anionic intermediates with the analogous 1,4-dihydro-1,4-epoxynaphthalene[4] and reductive elimination of β-alkoxy sulfones occurs readily under the conditions needed to effect removal of a phenylsulfonyl group.[5] We report here conditions which are useful for the preparation of **3** as well as the results of studies which shed some light on the various reactions that **1** and related materials undergo.

Results and Discussion

The most direct method by which **1** can be converted to **3** involves catalytic reduction of the double bond to give

2, followed by reductive elimination (path A, Scheme I). The first step was accomplished in CHCl$_3$ solvent, Parr shaker, with Pd/C catalyst (quantitative). De Lucchi[3] has commented on the failure of several reducing agents to effect reductive elimination of a model bis-sulfone and settled on sodium amalgam (6% Na, used in large excess) with solid NaH$_2$PO$_4$·H$_2$O as a buffer in methanol solvent as the most efficient method for carrying out this step. When we employed this procedure with **2**, the desired product **3** was indeed formed, along with the overreduced material 7-oxabicyclo[2.2.1]heptane (**6**) in combined 30–50% yield. The yields were determined, after pentane extraction and careful evaporation of most of the solvent,

(1) Nudenberg, W.; Butz, L. W. J. Am. Chem. Soc. **1944**, 66, 307. The preparation of **3** by an electrochemical oxidation method is also claimed in a Japanese patent (T. Shono, Japan Patent 72 27 511; Chem. Abstr. **1972**, 77: 139803x), but details, including starting material, are not obvious from the abstract.

(2) Several years ago we repeated the literature procedure[1] and obtained **1** in ca. 1 % yield, contaminated with furan (unpublished work with J. Staroscik). Considerable furan polymerization occurs, and careful fractionation is needed to isolate **1** from the large excess of furan that is employed.

(3) (a) De Lucchi, O.; Modena, G. Tetrahedron Lett. **1983**, 24, 1653. (b) De Lucchi, O.; Lucchini, V.; Pasquato, L.; Modena, G. J. Org. Chem. **1984**, 49, 596. (c) De Lucchi, O.; Pasquato, L. Gazz. Chim. Ital. **1984**, 114, 349.

(4) Caple, R.; Chen, G. M. S.; Nelson, J. D. J. Org. Chem. **1971**, 36, 2874. See also: Jeffrey, A. M.; Yeh, H. J. C.; Jerina, D. M.; DeMarinis, R. M.; Foster, C. H.; Piccolo, D. E.; Berchtold, G. A. J. Am. Chem. Soc. **1974**, 96, 6929. Brion, F. Tetrahedron Lett. **1982**, 23, 5299.

(5) For example, Kocienski[6] has utilized this approach to convert epoxy sulfones to allylic alcohols. We have also been unable to prevent reductive elimination of a cyclic β-methoxy sulfone when the desired reaction was simple reduction (unpublished work with R. J. Moss).

(6) Kocienski, P. J. Tetrahedron. Lett. **1979**, 441.

† Formerly known as Bagher Mir-Mohamad-Sadaghy.