ratio suggestive of an epoxide or dioxetane, but this material could not be isolated and identified.

The ozonolyses in reactive solvents (Table I) typically contained from 1.2 to 2 times excess aldehyde except for acetone, which was 5 times more abundant than the alkene. The solvent was stripped off on a rotary evaporator at room temperature. The products were separated from less volatile, peroxidic residues by using trap-to-trap distillations on a vacuum line from room temperature to −41 °C, −78 °C, and −196 °C. The cis and trans trioxolanes were usually found in the −78 °C traps and were not separated further. Yields were determined by NMR, using benzene as an internal standard. The assignment of the stereochemistry of the trioxolanes was determined by comparison with the chemical shifts for 3-ethoxy-5-methyl-1,2,4-trioxolane.[2]

***cis*-3-Methoxy-5-methyl-1,2,4-trioxolane (4)**: ^{1}H NMR ($CDCl_3$) δ 6.02 (s, 1 H), 5.26 (q, J = 5.0 Hz, 1 H), 3.41 (s, 3 H), 1.51 (d, J = 5.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 112.7 (dq, J = 200, 5 Hz), 101.31 (d, J = 171 Hz), 50.7 (qdd, J = 145, 51, 4 Hz), 14.1 (qd, J = 129, 5 Hz).

***trans*-3-Methoxy-5-methyl-1,2,4-trioxolane (5)**: ^{1}H NMR ($CDCl_3$) δ 6.02 (br s, 1 H), 5.67 (dq, J = 0.4, 5.0 Hz, 1 H), 3.42, (s, 3 H), 1.40 (d, J = 5.0 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 113.2 (dq, J = 203, 5 Hz), 101.6 (d, J = 171 Hz), 51.0 (dd, J = 146, 56, 4 Hz), 17.7 (qd, J = 129, 5 Hz).

Dimethoxymethyl hydroperoxide (6): ^{1}H NMR ($CDCl_3$) δ 5.30 (s, 1 H), 3.37 (s, 6 H); ^{13}C NMR ($CDCl_3$) 124.8, 51.2.

***cis*-3-Methoxy-5-isopropyl-1,2,4-trioxolane (7)**: ^{1}H NMR ($CDCl_3$) δ 5.98 (s, 1 H), 4.88 (d, J = 5.6 Hz, 1 H), 3.42 (s, 3 H), 2.44 (m, 1 H), 1.13 (d, J = 7.1 Hz, 3 H).

***trans*-3-Methoxy-5-isopropyl-1,2,4-trioxolane (8)**: ^{1}H NMR ($CDCl_3$) δ 5.99 (s, 1 H), 5.21 (d, J = 6.1 Hz, 1 H), 3.43 (s, 3 H), 2.44 (m, 1 H), 1.13 (d, J = 7.1 Hz, 3 H).

***cis*-3-Methoxy-5-*tert*-butyl-1,2,4-trioxolane (10)**: ^{1}H NMR ($CDCl_3$) δ 5.91 (s, 1 H), 4.81 (s, 1 H), 3.42 (s, 3 H), 0.95 (s, 9 H); ^{13}C NMR ($CDCl_3$) 113.5, 109.7, 51.4, 30.8, 24.2.

***trans*-3-Methoxy-5-*tert*-butyl-1,2,4-trioxolane (11)**: ^{1}H NMR ($CDCl_3$) δ 5.95 (s, 1 H), 5.13 (s, 1 H), 3.44 (s, 3 H), 1.03 (s, 9 H); ^{13}C NMR ($CDCl_3$) 114.0, 109.8, 51.7, 32.9, 24.7.

3-Methoxy-5,5-dimethyl-1,2,4-trioxolane (9): ^{1}H NMR ($CDCl_3$) δ 5.93 (s, 1 H), 3.40 (s, 3 H), 1.60, (dq, J = 0.6, 1.2 Hz, 3 H), 1.46 (q, J = 0.6 Hz, 3 H); ^{13}C NMR ($CDCl_3$) 115.4 (d, J = 205 Hz), 109.8 (s), 51.5 (q, J = 144 Hz), 24.4 (q, J = 127 Hz), 21.9 (q, J = 129 Hz).

Ozonolysis of Vinyl Acetate. In a typical experiment, 2.2 mmol of vinyl acetate in 2 mL of $CDCl_3$ was ozonized at −41 °C. After warm-up to room temperature, the reaction mixture was filtered in order to remove an insoluble, peroxidic, white solid, and CH_2Cl_2 was added to the NMR tube as an internal standard. 3-Acetoxy-1,2,4-trioxolane was formed in 34% yield and 3-acetoxy-1,2-dioxolane was obtained in 51% yield. Triphenylphosphine was added to the NMR tube in stoichiometric amounts to remove the trioxolane and isolate the dioxolane, which reacts more slowly.

3-Acetoxy-1,2-dioxolane (13): ^{1}H NMR ($CDCl_3$) δ 6.56 (ddd, J = 5.9, 1.4, 0.7 Hz, 1 H, H-3), 4.31 (dddd, J = 7.8, 7.1, 4.9, 0.7 Hz, 1 H, H-5), 4.09 (ddd, J = 8.5, 7.1, 7.1 Hz, 1 H, H-5′), 2.96 (dddd, J = 13.0, 8.5, 5.9, 4.9 Hz, 1 H, H-4′), 2.75 (dddd, J = 13.0, 7.8, 7.1, 1.4 Hz, 1 H, H-4), 2.13 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 170.0 (s), 95.0 (d, $J_{C(H)}$ = 178 Hz), 68.0 (t, $J_{C(H)}$ = 150 Hz), 42.3 (t, $J_{C(H)}$ = 136 Hz), 21.0 (qd, $J_{C(H)}$ = 130, 34 Hz).

3-Acetoxy-1,2,4-trioxolane (14): ^{1}H NMR ($CDCl_3$) δ 7.14 (d, J = 1.0 Hz, 1 H, H-3), 5.56 (d, J = 1.0 Hz, 1 H, H-5), 4.97 (s, 1 H, H-5′), 2.11 (s, 3 H, CH_3).

3,3-Dimethoxy-1,2-dioxolane (3). 1,1-Dimethoxyethene (2 mmol) in 10 mL of pentane was ozonized at 0 °C until completion. The solvent was removed on a rotary evaporator. The products were separated from an involatile, peroxidic residue by trap-to-trap distillation on a vacuum line from room temperature to −41 °C, −78 °C, and −196 °C traps. 3,3-Dimethoxy-1,2-dioxolane was collected in the −41 °C trap, dimethyl carbonate in the −78 °C trap, and pentane in the −196 °C trap. The dioxolane was isolated in 68% yield without further purification: ^{1}H NMR ($CDCl_3$) δ 4.24 (t, J = 7.1 Hz, 2 H, H-5), 3.29 (s, 6 H, OCH_3), 2.52 (t, J = 7.1 Hz, 2 H, H-4); ^{13}C ($CDCl_3$) δ 123.3 (s), 71.6 (t, $J_{C(H)}$ = 149 Hz), 50.9 (q, $J_{C(H)}$ = 144 Hz), 39.0 (t, $J_{C(H)}$ = 124 Hz); CIMS with isobutane and ammonia, obsd $M + NH_4^+$ 135.0670, calcd $M + NH_4^+$ 135.0657.

Reaction of 3,3-Dimethoxy-1,2-dioxolane (3) with Triphenylphosphine. 3,3-Dimethoxy-1,2-dioxolane (0.13 mmol) was dissolved in 0.5 mL of $CDCl_3$ and placed in an NMR tube. The tube was serum-capped and kept under N_2. Triphenylphosphine (0.14 mmol) dissolved in 0.5 mL of $CDCl_3$ under N_2 was added to the NMR tube. Dichloromethane was similarly added to the NMR tube as an internal standard. The tube was kept capped and the progress of the reaction was monitored for several hours by proton NMR spectroscopy. A 95% yield was obtained for the conversion of 3,3-dimethoxy-1,2-dioxolane to methyl acrylate. In a similar manner, 1,1-dimethoxyethene was ozonized in acetone-d_6 at −78 °C followed by triphenylphosphine reduction without isolation of the 1,2-dioxolane. The reaction occurred more slowly but with the same results; addition of trace acid did not accelerate the conversion. 3-Methoxy-1,2-dioxolane was similarly treated with triphenylphosphine to yield acrolein, methanol, and triphenylphosphine oxide.

Acknowledgment. This work was supported by Grant CHE-86-03834 from the National Science Foundation. We are grateful to Professor William Pearson for helpful suggestions.

Registry No. 1, 115665-05-9; **2**, 115665-04-8; **3**, 124153-52-2; **4**, 124153-53-3; **5**, 124153-54-4; **6**, 124153-55-5; **7**, 124153-56-6; **8**, 124153-57-7; **9**, 124153-58-8; **10**, 124153-59-9; **11**, 124153-60-2; **13**, 124175-02-6; **14**, 101672-23-5; (*E*)-$H_3COCH{=}CHOCH_3$, 7062-97-7; (*Z*)-$H_3COCH{=}CHOCH_3$, 7062-96-6; CH_3CHO, 75-07-0; $(CH_3)_2CHCHO$, 78-84-2; $(CH_3)_3CCHO$, 630-19-3; $(CH_3)_2CO$, 67-64-1; $CH_3CO_2CH{=}CH_2$, 108-05-4; $H_2C{=}C(OMe)_2$, 922-69-0; $CO(OCH_3)_2$, 616-38-6; $H_2C{=}CHCO_2CH_3$, 96-33-3.

Thermochemistry of Molecular Complexes. 3. Molecular Complexes of I_2 with Halogenated Benzene Derivatives

Jorge J. Munoz, Raul Morales, Jose L. Martinez, and
Jeffrey A. Joens*

Department of Chemistry, Florida International University, Miami, Florida 33199

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Molecular complexes formed by noncovalent interactions have been the focus of experimental study for over 40 years.[1a-g] Recently, Morales and co-workers[2] developed a spectroscopic technique for determining thermodynamic parameters of weakly bound molecular complexes. For a 1:1 molecular complex between a donor (D) and acceptor (A) molecule

$$D + A \rightleftharpoons DA \tag{1}$$

the change in absorbance of the molecular complex with temperature is related to an apparent enthalpy of formation of the complex by the relationship:

$$\Delta H_{app} = -R\, \partial(\ln A_{CT})/\partial(1/T) \tag{2}$$

where A_{CT} is the absorbance due to the molecular complex. Morales and co-workers showed that under conditions where the equilibrium concentration of free donor mole-

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(1) See, for example: (a) Andrews, L. J.; Keefer, R. M. *Molecular Complexes in Organic Chemistry*; Holden-Day: San Francisco, 1964. (b) Briegleb, G. *Elektronen Donator Acceptor Komplexe*; Springer-Verlag: Berlin, 1964. (c) Foster, R. *Organic Charge Transfer Complexes*; Academic: New York, 1969. (d) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley: New York, 1969. (e) Foster, R. *Molecular Complexes*; Paul Elek: London, 1973. (f) *Spectroscopy and Structure of Molecular Complexes*; Yarwood, J., Ed.; Plenum: New York, 1973. (g) Connors, K. A. *Binding Constants: The Measurement of Molecular Complex Stability*; Wiley: New York, 1987.

(2) Morales, R.; Diaz, G. C.; Joens, J. A. *J. Phys. Chem.* **1988**, *92*, 4742.

0022-3263/90/1955-1122$02.50/0

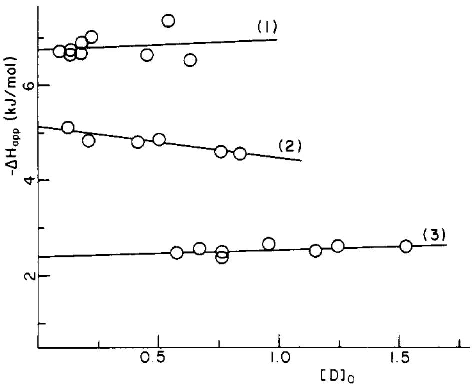

Figure 1. Plot of $-\Delta H_{app}$ vs initial donor concentration $[D]_0$ for (1) monoiodobenzene; (2) 1,2-dibromobenzene; (3) 1,2,4-trifluorobenzene. The intercept in the plot is equal to the formation enthalpy for the corresponding molecular complex, as discussed in the text.

cules is large compared to the concentration of bound donor molecules, a plot of ΔH_{app} versus initial donor concentration has an intercept equal to ΔH, the enthalpy of formation of the complex, and a limiting slope equal to $-K\Delta H$, where K is the formation constant for the complex. The advantage of this procedure over previous methods of studying molecular complexes is that the above method can be used to obtain accurate values of ΔH for cases where the donor–acceptor interaction is extremely weak ($|\Delta H| <$ 10 kJ/mol). This procedure has been tested by determining values for ΔH and K for complexes of molecular iodine with methyl-substituted benzene derivatives,[3] for which a large body of experimental data, obtained by a number of different techniques, is available for comparison. In general, good agreement was found between results obtained by the above procedure and results from previous studies.

The present paper reports the results of an investigation of the properties of molecular complexes of I_2 with halogenated benzene derivatives. Formation enthalpies have been determined for complexes of I_2 with 11 of the 12 fluorobenzene derivatives, seven bromobenzene derivatives, and three iodobenzene derivatives, using carbon tetrachloride as the solvent. The results have been combined with previous measurements of formation enthalpies for complexes of I_2 with chlorobenzene derivatives[2] to develop a simple relationship between the formation enthalpy of the complex and the degree of substitution in the donor molecule. Exceptions to this relationship are discussed. Values of λ_{max}, the wavelength maximum for the near UV absorption band of the molecular complex, are also reported for a number of the iodine-donor molecular complexes.

Results and Discussion

Figure 1 presents a plot of ΔH_{app} versus donor concentration for a representative set of the donor molecules used in the present study. For each donor molecule, the apparent enthalpy of formation has been found for several different donor concentrations. The actual value for the formation enthalpy is then determined by fitting the data to a line, with the formation enthapy equal to the intercept of the line.

Table I Enthalpy of Formation for Donor–I_2 Molecular Complexes (T = 25 °C)

donor	N^a	$-\Delta H$,^{b} kJ/mol
monofluorobenzene	10	5.7 ± 0.4
1,2-difluorobenzene	9	4.6 ± 0.3
1,3-difluorobenzene	7	3.5 ± 0.6
1,4-difluorobenzene	7	3.5 ± 0.4
1,2,3-trifluorobenzene	4	2.8 ± 0.9
1,2,4-trifluorobenzene	8	2.4 ± 0.3
1,3,5-trifluorobenzene	9	28.9 ± 1.3
1,2,3,4-tetrafluorobenzene	3	2.0 ± 0.9
1,2,4,5-tetrafluorobenzene	4	1.3 ± 0.9
pentafluorobenzene	7	2.4 ± 0.8
hexafluorobenzene	4	1.73 ± 0.1
monobromobenzene	6	6.1 ± 0.2
1,2-dibromobenzene	6	5.1 ± 0.2
1,3-dibromobenzene	6	4.8 ± 0.2
1,4-dibromobenzene	11	5.7 ± 0.6
1,2,4-tribromobenzene	5	4.4 ± 0.3
1,3,5-tribromobenzene	5	2.7 ± 0.8
1,2,4,5-tetrabromobenzene	5	2.4 ± 0.3
monoiodobenzene	9	6.7 ± 0.4
1,2-diiodobenzene	7	5.5 ± 0.5
1,4-diiodobenzene	7	7.7 ± 0.3

[a] Number of measurements. [b] Error limits for this work reported at the 95% confidence limits.

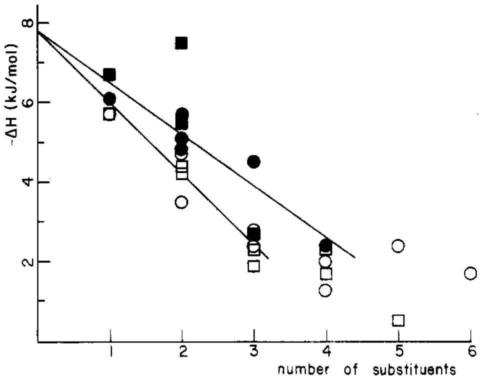

Figure 2. Plot of $-\Delta H$ vs number of substituent groups for (○) fluorine-substituted, (□) chlorine-substituted, (●) bromine-substituted, and (■) iodine-substituted benzene donor molecules. The lower line represents a decrease in the magnitude of ΔH of 1.8 kJ/mol per substituent, as found for fluorine- and chlorine-substituted donor molecules, while the upper line represents a decrease in the magnitude of ΔH of 1.3 kJ/mol per substituent, as found for bromine-substituted donor molecules.

The values for the formation enthalpies for the iodine–donor molecular complexes studied here are given in Table I. All data have been reported at T = 25 °C. Error limits are reported at the 95% confidence limits, using standard statistical techniques.[4] To our knowledge, the data represent the first experimental determinations of formation enthalpies for these complexes.

A plot of the experimental values for the enthalpy of formation for molecular complexes of iodine with halogenated benzene molecules is given in Figure 2. Data are taken from the present study for fluorine-, bromine-, and iodine-substituted donor molecules, and from a previous study[2] for chlorine-substituted molecules.

If the molecule 1,3,5-trifluorobenzene is excluded from consideration, the dependence of formation enthalpy on degree of substitution is almost identical for fluorine- and chlorine-substituted donor molecules. For both sets of molecules, the enthalpy of formation appears, to a first approximation, to depend only on the number of fluorine or chlorine atoms attached to the benzene ring, and to be nearly independent of the location of the substituent groups. For donors with three or fewer fluorine or chlorine atoms, the dependence of formation enthalpy on degree

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(4) Bevington, P. R. *Data Reduction and Error Analysis for the Physical Sciences*; McGraw-Hill: New York, 1969.

of donor substitution is linear, with the formation enthalpy becoming less exothermic by about 1.8 kJ/mol per added fluorine or chlorine atom. After this point, increasing the number of fluorine or chlorine atoms attached to the donor molecule has a smaller effect on the formation enthalpy of the corresponding molecular complex than predicted by the linear relationship.

For bromine- and iodine-substituted donor molecules, it is more difficult to describe the dependence of the enthalpy of formation on the degree of donor substitution because of the small number of molecules that have been studied. For bromine-substituted donor molecules, it appears that there is again a linear relationship between ΔH and the degree of substitution, with the formation enthalpy for complexes with bromine-substituted donor molecules becoming less exothermic by about 1.3 kJ/mol per bromine atom. For iodine-substituted donor molecules, there is a general decrease in the magnitude of the formation enthalpy as the number of iodine atoms attached to the benzene ring increases, but the scatter in the results and the limited number of donor molecules studied makes it impossible to give a systematic relationship between degree of substitution and enthalpy of formation. The situation is complicated by the additional possibility of formation of molecular complexes between I_2 and iodine atoms attached to the benzene ring, with the iodine atoms on the ring acting as n-donors for the complex.[1a]

The above results can be explained in terms of a model previously developed to describe complexes of molecular iodine with chlorine-substituted[2] and methyl-substituted[3] benzene molecules. In this model, it is assumed that for weakly perturbing substituent groups the electron-donating or electron-withdrawing effect of the groups are, to first order, additive, and dependent only on the number and type of substituent. If the enthalpy of formation for the complex is proportional to the available π-electron density of the donor molecule, the model predicts a linear relationship between formation enthalpy and degree of substitution for benzene derivatives with a single type of substituent. For electron-withdrawing groups it also appears that once the π-electron density of the benzene ring has been reduced to a certain point, increasing the number of electron-withdrawing groups on the benzene ring has only a small effect on the π-electron density of the ring.

Of the molecular complexes between iodine and halogenated benzene derivatives that have been studied, only the complex of iodine with 1,3,5-trifluorobenzene shows anomolous behavior. The experimental value for the formation enthalpy of this complex is −28.9 kJ/mol, much larger in magnitude than the value found for the other trifluorobenzene complexes. The reason for this difference is not known, but does not appear to be due to an impurity in the chemicals used in the measurements or a chemical reaction between 1,3,5-trifluorobenzene and molecular iodine. The absorption spectrum of the molecular complex of iodine with 1,3,5-trifluorobenzene also shows unusual behavior, as noted below.

In principle, the slope of the line in a plot of ΔH_{app} versus donor concentration can be used to find the formation constant for a molecular complex. However, because the formation constants for iodine–halogentated benzene complexes are small ($K < 0.1$ M^{-1}), the experimental values for the slope are also small relative to their uncertainties. It has therefore not been possible to directly determine values for the formation constants by this method for the donor molecules used in the present study.

Finally, values for λ_{max}, the wavelength of maximum absorbance for the iodine-donor molecular complex, have been determined for several of the complexes of iodine with halogenated benzene derivatives. The results are reported in Table II. Because of overlap between the absorption of the molecular complex and that of the donor molecule, it was only possible to determine λ_{max} for donor molecules with a low degree of substitution. In general, the wavelength of maximum absorbance decreases with increasing halogen substitution on the benzene ring, as would be expected based on the correlation between λ_{max} and the ionization potential of the donor molecule that has been previously observed for molecular complexes of iodine.[1a,1d,5-7] Again, the complex between iodine and 1,3,5-trifluorobenzene appears to be an exception to this general trend. The molecular complexes of iodine with iodobenzene donor molecules also show irregular behavior, which may be due to the presence of both n-donor and π-donor complexes.

Table II. Wavelength Maximum for Near UV Absorption Band of Donor–I_2 Molecular Complexes

donor	λ_{max}, nm
benzene	292
monofluorobenzene	282
1,4-difluorobenzene	278
1,2,4-trifluorobenzene	278
1,3,5-trifluorobenzene	302
monochlorobenzene	282
monobromobenzene	286
1,2-dibromobenzene	286
1,3,5-tribromobenzene	276
monoiodobenzene	266
1,2-diiodobenzene	288

Experimental Section

Halogenated benzene compounds used in the present study were purchased from Aldrich at a minimum purity of 97% and used without further purification, except for 1,3,5-tribromobenzene (98%) and 1,2,4,5-tetrabromobenzene (98%), which were further purified by sublimation. Iodine (Mallinkrodt, 99.8%) and carbon tetrachloride (Fisher, spectral grade) were also used without further purification. Solutions of iodine and donor molecules were prepared in carbon tetrachloride using quantitative techniques.

For determination of ΔH_{app}, the apparent enthalpy of formation of the molecular complex, a Shimadzu 265 UV–visible spectrophotometer with temperature regulated cell holder was used. For each solution, absorbances were measured at five wavelengths in the range 320–380 nm. Wavelengths were selected to minimize absorbance by the donor molecule and obtain the largest possible absorbance by the molecular complex. Data were taken at approximately 5-deg intervals in the range 20–40 °C, with absolute values of temperature determined to an accuracy of ±0.1 °C using a thermocouple sensor. Experimental absorbances were corrected for absorbance of free iodine and donor molecule and for changes in absorbance due to changes in solution density with temperature. Values for ΔH_{app} were then found from a plot of ln A_{CT} versus $1/T$. Further details of the experimental procedure for determination of the enthalpy of formation and formation constant for molecular complexes are given in ref 2.

For determination of λ_{max}, the location of the peak in the absorption band of the molecular complex, a Cary 2300 UV–visible spectrophotometer interfaced to a DS-15 data station was used. Measurements were made in the double beam mode, using a solution of iodine and donor molecule in the sample cuvette, and donor molecule, at the same concentration as in the sample cuvette, in the reference cuvette. Because the donor molecules all possess a strong absorption band in the region 260–320 nm that overlaps the absorption band from the molecular complex, short

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(5) McConnell, H.; Ham, J. S.; Platt, J. R. *J. Chem. Phys.* **1953**, *21*, 66.

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pathlength (0.1 cm) matched quartz cuvettes were used in the measurements. No attempt was made to determine the extinction coefficient of the absorption band of the molecular complex at λ_{max}.

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A One-Pot Synthesis of α-Ester Sulfones

Andrew S. Kende* and José S. Mendoza

Department of Chemistry, University of Rochester, Rochester, New York 14627

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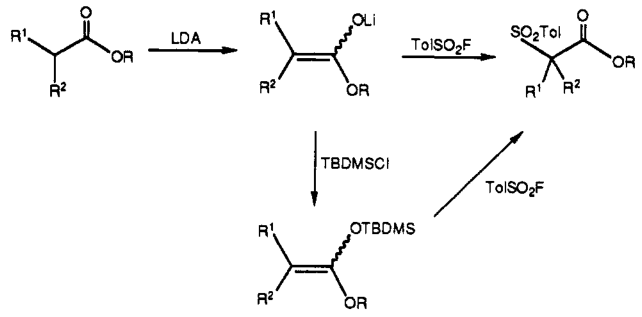
The sulfonyl group is increasingly attracting attention as a useful functionality in organic synthesis. Of particular interest are the applications of the sulfonyl group as a temporary transformer of chemical reactivity in the synthesis of eventually sulfur-free compounds.[1] As part of our research program on the synthesis of ambruticin,[2] we required a method to introduce the sulfone functionality α to an ester group. α-Ester sulfones are generally prepared by oxidation of the corresponding sulfides or sulfoxides,[3,4] or by alkylation of benzenesulfinate salts with α-halo esters.[5]

In this paper we present an alternate and a very facile procedure which enables the one-pot preparation of α-ester sulfones under mild conditions. This new route involves the direct sulfonylation of esters by reaction of the ester lithium enolate or the silyl ketene acetal with *p*-toluenesulfonyl fluoride[6] (Scheme I).

Scheme I



The silyl ketene acetal is prepared[7] by treating the ester with 1.2 equiv of LDA in dry tetrahydrofuran at −78 °C. The resulting solution is stirred for 1 h, after which *tert*-butyldimethylchlorosilane in THF is added dropwise to the anion. The reaction mixture is stirred at −78 °C for 30 min and at 0 °C for an additional 30-min period. The *p*-toluenesulfonyl fluoride is added all at once to the silyl ketene acetal at −78 °C and then warmed to room temperature. Our method is experimentally simple, and yields range from moderate to good (Table I).

Reaction of *p*-toluenesulfonyl fluoride with either the ester enolate or the silyl ketene acetal derived from α,-α′-disubstituted esters gave good yields of the corresponding α-ester sulfones (entries 1 and 3). On the other hand, reaction of *p*-toluenesulfonyl fluoride with the ester enolate derived from α-monosubstituted esters gave only moderate yields of the sulfonylated product. Under these conditions once the α-ester sulfone is formed, it presumably is deprotonated by any unreacted ester enolate.

When the ester enolate derived from ester **5** was treated in a comparable manner with *p*-toluenesulfonyl chloride, no sulfonylation occurred. Instead the α-chloro ester was formed as the sole product, as observed earlier for ketone enolates by Hünig.[6c]

Experimental Section

Melting points are uncorrected. ^{1}H NMR spectra were recorded on a Nicolet QE-300 spectrometer, and chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane. ^{13}C NMR spectra were recorded on a Nicolet QE-300 spectrometer at 75.5 MHz and are reported in ppm from the center line of the chloroform-*d* triplet (77.0 ppm). Infrared spectra were recorded on a Perkin-Elmer 1310 spectrophotometer. Nominal and accurate mass spectra were obtained by electron impact on a VG-7035 mass spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc.

All reactions were run in flame-dried flasks under an atmosphere of nitrogen. Tetrahydrofuran was distilled from sodium and benzophenone prior to use. Unless otherwise mentioned, the chemicals were used as received from commercial sources.

General Procedure. Two general procedures were employed for the formation of α-ester sulfones. The following experimental procedures are representative.

Method A. Preparation of 2-Methyl-2-[(4-methylphenyl)sulfonyl]propanoic Acid Methyl Ester (2). A solution of diisopropylamine (4.8 mmol, 0.67 mL) in THF (4.0 mL) was treated with *n*-butyllithium (2.5 M in *n*-hexane, 4.8 mmol, 1.92 mL), at 0 °C, under nitrogen, with stirring. After 20 min at 0 °C, the solution was cooled to −78 °C, and a solution of 2-methylpropanoic acid methyl ester (1) (4.0 mmol) in THF (3.0 mL) was slowly added. After 1.0 h at −78 °C, *tert*-butyldimethylchlorosilane (4.8 mmol) in THF (2.0 mL) was added dropwise. After 30 min at −78 °C, the mixture was warmed to 0 °C, stirred for 30 min, and then cooled again to −78 °C, and *p*-toluenesulfonyl fluoride (5.74 mmol) in THF (3.0 mL) was added all at once. The reaction mixture was allowed to warm to room temperature and stirred for 3 h. The reaction was cooled to 0 °C, quenched with saturated ammonium chloride solution (5.0 mL) and then water (5.0 mL), and extracted with ethyl acetate several times. The combined organic extracts were washed with water and brine, dried ($MgSO_4$), and concentrated in vacuo. The residue was recrystallized from ethyl acetate–hexane to give 0.891 g (87%) of **2** as colorless crystals: mp 70–71 °C; IR ($CHCl_3$) 2960, 1735, 1600, 1470, 1440, 1315, 1302, 1270, 1160, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.70 (2 H, d, J = 8.1 Hz), 7.33 (2 H, d, J = 8.1 Hz), 3.68 (3 H, s), 2.44 (3 H, s) 1.59 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 169.05,

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