Elimination and Addition Reactions. 36.[1a,b] Acceleration of Nucleophilic Eliminative Ring Fission by Bond Strain

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Abstract: Rates of eliminative ring fission of cyclic ethers bearing carbanion stabilizing groups have been measured with a view to assessing the contribution of ring strain to the ease of cleavage of bonds in elimination reactions. (Ethylsulfonylmethyl)oxiran (**4**) undergoes eliminative ring fission probably by the E2 mechanism. This occurs at least 2.5 million times as rapidly as elimination of methoxide ion from the acyclic model **14**. In fission of the oxiran, at least one-third of the ring strain is expressed in reduction of the energy of activation of ring fission. Cyclic ethers of larger ring sizes also undergo elimination faster than the acyclic analogue, but ratios are small. In these ethers of larger ring size and in contrast to the oxiran, equilibrium constants for ring vs. chain isomers strongly favor the former. Deuterium-labeling studies show that sulfonyl, cyano, and carbalkoxy, but not carboxylate, groups activate ring closure by intramolecular nucleophilic addition.

This paper reports the first attempt to quantify the contribution of ring strain to enhancement of reactivity in an elimination reaction.

In reactions such as nucleophilic substitution and elimination, leaving groups are expelled with cleavage of the bond connecting the leaving group to the substrate. Although the quantification of leaving-group ability is an important objective in the understanding of reactivity of organic compounds, very few studies[2-5] have been made of systems capable of yielding information on leaving-group ability (nucleofugality). The problem is to isolate the process in which the leaving-group connection is broken from other processes which may produce differential effects. In nucleophilic aliphatic substitution reactions, for example, differential interactions between entering and leaving groups make the assessment of nucleofugalities difficult.

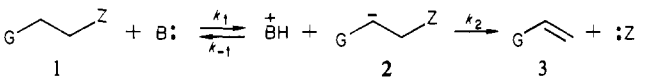
Elimination reactions offer the best prospect of accurate measurement of leaving-group abilities. This is because, in appropriate systems, equilibria which precede departure of the leaving group can be quantified. Hence the process of leaving-group departure in isolation becomes susceptible to observation.

Recent work on nucleofugality has been devoted to carbonyl-forming and related eliminations on the one hand[3,4] and to alkene-forming elimination on the other.[5,6] The latter system, involving the loss of leaving groups from stabilized carbanions, has been extensively investigated in these laboratories and quantitative ranking of leaving groups in systems spanning a range of 10^{14} in reactivity has been made.[5]

The ability of the systems we had studied (Scheme I) to yield absolute data on nucleofugality prompted an enquiry into factors which could alter nucleofugality and hence be subject, in our system, to quantification in absolute terms. Our studies have shown that the most important factor in determining nucleofugality is the charge on the leaving group.[6] Other factors such as the dissociation energy of the bond connecting the leaving group are less significant. A familiar and important but unquantified factor in altering leaving-group ability is *strain*.[7]

In nucleophilic substitution on an oxiran, for example, the ring strain[8] allows displacement of an "alkoxy" leaving group.[9] Such

Scheme I



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a reaction is unknown in unstrained systems. The only related exceptions are seen in reactions of Grignard[10] and other reagents[11] with acetals in apolar solvents. In the former case, coordination of the metal to the oxygen leaving group probably reduces electron density on the leaving atom and encourages its departure. Similarly, nucleophilic displacement of carbon leaving groups is unknown in acyclic systems. Many examples, however, are known of nucleophilic displacement on cyclopropanes which occur with ring cleavage, provided that the leaving carbanion is stabilized by appropriate groups such as carbalkoxy.[12]

This and later papers in the series deal with quantification of the effect of strain on leaving-group abilities using the types of system we have used earlier for ranking of leaving groups in unstrained systems.

Alkene-Forming Elimination of Alkoxy Groups and Eliminative Ring Fission of Oxirans

Results obtained from systems used for ranking of a wide variety of leaving groups (Scheme I) showed that methoxy was a middle ranked (6.1) group on a log scale extending from 10.4 to -2.9.[5,13] Comparison of the reactivity of an activated acyclic methyl ether (Scheme II) (**14**) with an activated oxiran (**4**) offered an opportunity of evaluating the accelerative effect of straining the bond to the leaving group. This process of eliminative ring fission is a diverse reaction of which a large number of examples has been collected in a recent review.[14] In connection with the present investigation, the literature shows that oxirans of type **4** are labile in even mildly basic conditions. Reactions involve removal of the β proton and not, as is more usual, attack at a carbon atom of the oxiran ring. Thus, as examples, cyanomethyloxirans are unstable to base,[15] and treatment of epihalohydrins with (arene)sulfinate ions gives not arylsulfonylmethyloxirans but γ-hy-

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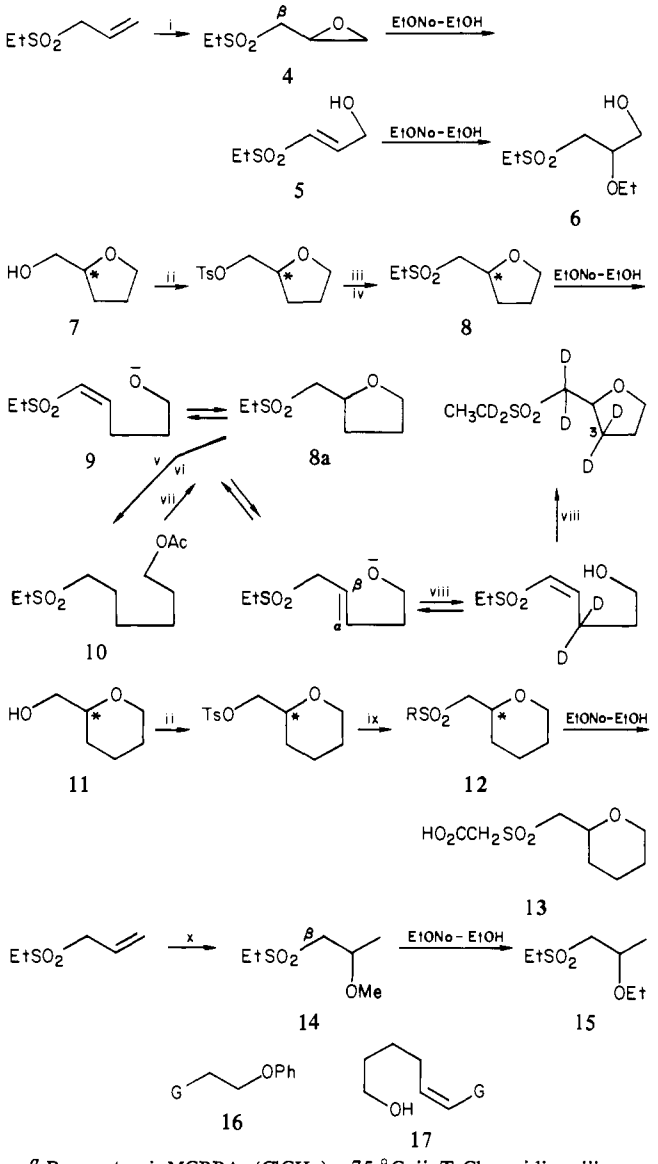
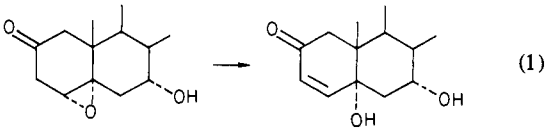
Scheme II[a]



[a] Reagents: i, MCPBA, $(ClCH_2)_2$, 75 °C; ii, TsCl-pyridine; iii, PhSNa-EtOH; iv, H_2O_2-MeOH-NH_4MoO_7; v, EtMgBr-Et_2O; vi, Ac_2O; vii, NaOH-EtOH-H_2O; viii, EtONa-EtOD, ix, R-SH-EtONa-EtOH; x, MeONa-MeOH.

droxy, α,β-unsaturated sulfones.[16] The most significant previous work is that of Barton,[17] who showed that in reactions of the steroidal oxiran (see eq 1), rapid formation of the diol occurred



(1)

on treatment with base. Furthermore, the rate of nucleophilic eliminative ring fission was depressed when protium at C_3 was replaced by deuterium. This indicates that the mechanism was probably E2 rather than $(E1cB)_1$ with deprotonation rate determining, $k_{obsd} \gg k_{deprotonation}$ being calculated roughly from deprotonation rates of ketones in basic media.[18]

Table I. Rates of Elimination[a] in Sulfones

sulfone[b]	$k^{c,d}$	k_H/k_D[e]
4	185	2.5
8	1.39×10^{-3}	0.95
12, R = $HO_2C{\cdot}CH_2$	8.81×10^{-4}	
16, G = $HO_2C{\cdot}CH_2SO_2$	3.59×10^{-2}	*f*
16, G = $MeSO_2$	8.15×10^{-2}	*f, g*
12, R = $EtSO_2$	2.0×10^{-3} *h*	
14	7.5×10^{-5}	*f*

[a] Reactions in EtONa-EtOH at 25 °C. [b] See Scheme II. [c] Units M^{-1} s^{-1}. [d] Mean. [e] Uncorrected for secondary isotope effect. [f] For G = $PhSO_2$, reaction shows $k_{elimination} << k_{H\text{-}D}$ exchange.[5] [g] Reference 22a. [h] Estimated.

The objective of the present work was to compare the reactivity in elimination reactions of acyclic unstrained ethers with that of cyclic systems of varying degrees of strain and hence to evaluate the contribution to leaving-group ability (nucleofugality) of strain in the bond to the leaving group.

Results and Discussion

The Systems. The reactivities of ethylsulfonylmethyloxiran (**4**), tetrahydrofuran (**8**), and tetrahydropyran (**12**) (R = $HO_2C{\cdot}CH_2$) have been compared with that of the acyclic analogue **14**. Outlines of their preparations and the products obtained in the standard base–solvent system sodium ethoxide–ethanol are in Scheme II.

In reactions with the oxiran **4**, isolation of the primary product **5** was only possible by very rapid quenching of the reaction. It undergoes further fast reaction, giving the ethoxy adduct **6**.

In reactions with the tetrahydrofuran **8**, no reaction could be detected even under conditions in which it was obvious from earlier results[5] that elimination must be occurring. When optically active substrate was used, racemization occurred on treatment with base in conditions in which the alcohol **7** and the sulfide **8** ($EtSO_2$ = EtS) were completely optically stable. It was concluded, therefore, that racemization was the result of eliminative ring fission activated by carbanion stabilization giving **9** which recloses rapidly with formation of racemic ether **8a**. It was important to strengthen this conclusion; two lines of evidence do so. Treatment of **8** with ethylmagnesium bromide in ether and subsequent reaction of the product with acetic anhydride give the acetate **10** derived from the anion **9**. When the acetate is saponified, the product is **8a**. When **8a** is treated with sodium deuteroxide in D_2O, exchange of deuterium for hydrogen occurs rapidly adjacent to the sulfonyl group and slowly at C_3 but nowhere else. This behavior is consistent only with ring opening to **9** and equilibration with the more thermodynamically stable β,γ-unsaturated hydroxysulfone.[19,20] This sulfone, in the course of equilibration, picks up deuterium at C_3. The favorable thermodynamic stability of the nonconjugated sulfone permits observation of deuterium–hydrogen exchange; when other activating groups are used, deuterium–hydrogen exchange at C_3 occurs more slowly (below). There seems little doubt, therefore, that racemization of **8** in base is the result of eliminative ring fission notwithstanding our inability to trap the intermediate **9** by addition of nucleophiles such as piperidine[21] and cyanide ion.

In the case of the tetrahydropyranyl system, it was again found that no ring opening could be directly observed with the sulfone **12** (R = Et). Attempts to use resolved material as for the tetrahydrofuran system were frustrated by racemization which occurred during the insertion of the sulfonyl group. After many attempts to obtain material on which kinetic measurements could be made, it was decided to place a resolving handle in the sulfone **12** and use appropriate calibration of the effect of these structural alterations on rates. Sulfone **12** (R = $HO_2C{\cdot}CH_2$) was obtained from the alcohol **11** via the tosylate and resolved with phenylethylamine. The effect of change of the group attached to sulfur

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in the sulfone was estimated by comparing the effect, on the rate of elimination of phenoxide ion, of change of activating group G in ether **16** from $EtSO_2$ to $HO_2C{\cdot}CH_2SO_2$.[22]

The acyclic ether **14** was considered the closest approach to an unstrained but structurally analogous system. Reaction rates in this case were determined by following by GLC the disappearance of methoxy compound **14** and its conversion to the ethoxy derivative **15**.

Mechanism and Reactivity in Ring Fission. Table I shows that eliminative ring fission in the oxiran is very rapid by comparison with the same process in the much less strained five- and six-membered ring homologues and the acyclic unstrained analogue. Strain in the bond connecting the leaving group, occasioned by its incorporation in a strained ring, promotes cleavage of this bond.

Precise evaluation of the extent of acceleration requires knowledge of the rate-determining step of the reaction. This information emerges from values of primary deuterium isotope effects. For the 5-membered ring substrate **8**, the primary kinetic deuterium isotope effect is close to unity. This is consistent with the $(E1cB)_R$[5] mechanism in which the deprotonation equilibrium is rapidly established before rate-determining expulsion of the leaving group from the carbanion. Similarly, the six-ring substrate **12** deprotonates[18] much more rapidly than elimination occurs, and it has been established earlier for the acyclic analogue **14** (Et = Ph and Me = H) that deuterium–hydrogen exchange at C_β is very much more rapid than elimination. By contrast, eliminative ring fission of the oxiran **4** shows a primary deuterium isotope effect of 2.5. Deprotonation is involved in the rate-determining step, pointing either to E2 or $(E1cB)_1$ mechanisms.

The rate of deprotonation of the oxiran can be calculated approximately from earlier measurements.[18] Detritiation rates of sulfones, $PhSO_2CH_2CH_2Z$, have been measured, and deprotonation rates were derived from parallel deuterium–hydrogen-exchange experiments. A Taft plot for deprotonation allows derivation of the deprotonation rate of sulfone **4** by using the σ_1 value measured for the oxiranyl group.[23] In the present work, ethyl sulfones have been used instead of phenyl sulfones used earlier. Replacement of an alkyl by an aryl group lowers the pK_a of the sulfone (viz., pK_a's of $PhSO_2Me$ = 26.7 and of $MeSO_2Me$ = 28.8).[24] The deprotonation rate constant derived from the Taft plot for phenyl sulfones will therefore be higher than for the corresponding ethyl sulfone, and hence this derived value will be a maximum. This interpolated value (2.5×10^{-1} M^{-1} s^{-1} at 25 °C) is well below that of the measured elimination rate (185 M^{-1} s^{-1}), and tentatively, therefore, we assign the E2 mechanism to this reaction.

Assignment of the E2 (concerted) mechanism to eliminative ring fission in the oxiran implies that ring fission is not the sole rate-determining process; deprotonation is concerted with it. An objective of this work, namely, to quantify the effect of oxiran ring strain on reactivity in a bond cleavage process, is thus partially frustrated in this instance. This is because the specific process of ring fission cannot be studied in isolation. It is clear, however, that ring strain in the oxiran so much increases leaving-group ability of the "alkoxy group" that this group behaves like bromo or iodo when situated β to a sulfonyl group in an acyclic sulfone.[18] It has been noticed before that in acyclic activated eliminations[18] change of leaving group from methoxy through, e.g., fluoro or acetoxy to bromo or iodo produces a mechanism change from $(E1cB)_R$ through $(E1cB)_1$ to E2. The E2 mechanism is apparently characteristic of those leaving groups which give higher reactivities in S_N2 reactions.

The overall ratio of reactivities of the oxiran (strained) and the open-chain (unstrained) model, notwithstanding the fact that a single stage concerted process is being compared with a multistage process, is 2.46×10^6. A minimum of 8.7 kcal·mol^{-1} or roughly one-third of the ground-state ring strain energy is thus being expressed in lowering the energy of activation for the reaction in the strained cyclic system.

While the acyclic analogue **14** provides the obvious comparison for the strained cyclic systems, it was important to check, however, that in relatively unstrained cyclic systems, no special effect on reactivity peculiar to cyclic systems was operating. The rate constants for the five- and six-membered substrates (Table I) show that their reactivity is slightly greater than that of the acyclic compound and the primary deuterium isotope effects show that ring fission is rate determining. A small degree of ring strain is thus apparently being expressed in the small accelerations relative to the acyclic model. It is surprising, however, that the estimated reactivity of the unstrained six-membered ring system is greater than that of the tetrahydrofuran because tetrahydrofuran is slightly strained relative to tetrahydropyran.

Ring Chain Isomerism. There is no detectable amount of alcohol **5** in equilibrium with the oxiran **4**. It would be surprising if there were but the reverse of eliminative ring fission could, nevertheless, be quite a rapid reaction and this aspect of eliminative ring fission is under investigation. The very high equilibrium constants in favor of the cyclic structures **8** and **12** are striking, particularly as, in the case of the five-membered ring, this is slightly strained. To our knowledge there is not much precedent for such preference for cyclic forms. Another example has, however, been reported by Schweizer and his collaborators[25] for the phosphonium salt **8** ($EtSO_2$ = Ph_3P^+). This salt is shown to undergo nucleophilic eliminative ring fission by the observation of deuterium–hydrogen exchange at C_3. Curiously, however, only *one* proton at C_3 is exchanged for deuterium. H–D exchange at C_3 depends upon α,β–β,γ equilibration and hence rapid formation of the nonconjugated tautomer. When the nitrile **8** ($EtSO_2$ = CN) is treated with sodium deuteroxide in deuterium oxide, H–D exchange occurs rapidly adjacent to the cyano group but no deuterium appears at C_3 during the lifetime ($t_{1/2} \approx 1$ h in molar NaOD–D_2O at 100 °C) of the nitrile which hydrolyzes to the acid under the reaction conditions. The equilibrium between α,β- and β,γ-unsaturated nitriles lies overwhelmingly on the side of the conjugated isomer[19,20] in contrast to the sulfone analogues, and the result suggests that not only is the equilibrium unfavorable but also very slowly attained. By contrast, when the same nitrile is treated with molar sodium ethoxide in EtOD, the product obtained after 160 h at 80 °C is the ester **8** ($EtSO_2$ = CO_2Et) and protons at C_3 were completely replaced by deuterons. In this case a carbanion-stabilizing group survives the reaction conditions and promotes α,β–β,γ equilibration.

In the case of six-membered cyclic ethers, the cyclic and open-chain forms[26] **12** (RSO_2 = CO_2Me) and **17** (G = CO_2Me), respectively, are of comparable energy as both are present in observable amounts at equilibrium. The acid **12** ($EtSO_2$ = CO_2H) showed no deuterium–hydrogen exchange at any carbon atom under conditions comparable with those used in the five-ring series, and the open-chain acid **17** (G = CO_2H) neither underwent H–D exchange at carbon nor cyclization. In confirmation of earlier work,[26] the ester **17** (G = CO_2Me), on reaction with aqueous sodium hydroxide at room temperature, gave a quantitative yield of the ring-closed acid **12** (RSO_2 = CH_2CO_2H), indicating a rapid activated cyclization followed by a slower hydrolysis.

Experimental Section

For general instructions and kinetic methods, see part 30.[5] Hydrogen peroxide refers to 30% aqueous solution.

Allyl Ethyl Sulfone. Allyl ethyl sulfide[27] (6.79) in methanol (100 mL) was kept with hydrogen peroxide (200 mL) and ammonium molybdate

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(1.5 g) for 16 h. Dilution with saturated brine and extraction with dichloromethane gave the sulfone (5.1 g): bp 124 °C (14mmHg); n^{22}_D 1.4721; lit. bp 129 °C (11mmHg).

The α,α'-bis(deuterio) compound was prepared by treatment of allyl ethyl sulfone (3 g) with sodium hydroxide (0.92 g) in D_2O–dioxan, 30:50 v/v. After 50 min, extraction gave the sulfone (95%): bp 132 °C (13mmHg); n^{19}_D 1.4744; ^{1}H NMR ($CDCl_3$) τ 8.62 (t, 3 H), 7.0 (q, 2 H), 4.45 (t + q, 3 H).

(Ethylsulfonylmethyl)oxiran (4). The preceding isotopically normal sulfone (5.5 g) in 1,2-dichloroethane (250 mL) was refluxed with *m*-chloroperoxybenzoic acid (10.6 g) for 23 h. The mixture was washed with saturated aqueous sodium hydrogen carbonate and evaporation gave the *oxiran* (4.1 g): bp 80 °C (0.04mmHg); mp 54 °C (from toluene–light petroleum); ^{1}H NMR τ 8.65 (t, 3 H), 6.5–7.45 (m, 7 H); IR. Anal. ($C_5H_{10}O_3S$): C, H.

Reactions of the Oxiran (4) with Ethanolic Sodium Ethoxide. (a) The oxiran (0.5 g) was treated with 2 M ethanolic sodium ethoxide at 20 °C. After 16 h, dilution with brine and extraction gave a residue (0.45 g) which, on distillation, gave **ethyl 2-ethoxy-3-hydroxypropyl sulfone** (0.227 g): bp 130 °C (0.2mmHg); ^{1}H NMR ($CDCl_3$) τ 8.6 (t, 6 H), 7.25 (s, 1 H), 6.9 (q, 3 H), 6.3 (m, 7 H); IR 1060 (m), 1110 (s), 1130 (s) cm^{-1}.

(b) The oxiran (1 g) in ethanol (20 mL) was treated with 0.01 M ethanolic sodium ethoxide (20 mL), and the mixture was immediately (5 s) acidified (HNO_3). Dilution with water and extraction gave a crystalline residue (490 mg), crystallized from toluene to give **ethyl 3-hydroxyprop-1-enyl sulfone** (161 mg): mp 64 °C; ^{1}H NMR ($CDCl_3$) τ 8.7 (t, 3 H), 7.0 (q, 2 H), 6.6 (s, 1 H), 5.65 (s, 1 H); IR. Anal. ($C_5H_{10}O_3S$): C, H.

(+)-Ethyl Tetrahydrofurfuryl Sulfone (8). Tetrahydrofurfuryl alcohol was resolved *via* the half phthalate[29] and converted into the tosylate.[30]

Ethanethiol (9.6 mM) was injected into nitrogen-flushed 0.3 M methanolic sodium methoxide (30 mL). Tetrahydrofurfuryl tosylate (6.8 mM) was added, and after 18 h at 60 °C, dilution with water and extraction gave the sulfide (89%): bp 104 °C (29mmHg); n^{23}_D 1.4838; ^{1}H NMR ($CDCl_3$) τ 8.8 (t, 3 H), 8.2 (m, 4 H), 7.2–7.8 (m, 4 H), 5.9–6.6 (m, 3 H). Oxidation of the sulfide with methanolic hydrogen peroxide–ammonium molybdate gave the *sulfone* (89%): bp 131 °C (0.07mmHg) n^{20}_D 1.4807; $[\alpha]^{20}_D$ 6.9°; ^{1}H NMR τ 8.8 (t, 3 H), 7.7–8.5 (m, 4 H), 6.6–7.4 (m, 4 H), 6.3 (t, 2 H), 5.85 (m, 1 H); IR 1120 (s), 1300 (s) (SO_2) cm^{-1}. Anal. ($C_7H_{14}O_3S$): C, H.

The sulfone (231 mM) was kept at 80 °C in 0.054 M ethanolic sodium ethoxide for 1.5 h. The solution showed no optical rotation. Dilution of the solution with brine and reextraction gave recovered sulfone (88%): bp 170 °C (10mmHg); n^{23}_D 1.4790.

The sulfone (2.8 mM) was deuteriated by treatment with sodium ethoxide (14 mM) in ethanol-*O*-*d* (3 mL) at 25 °C. After 10 min, reisolation gave sulfone completely deuterated adjacent to the sulfonyl group (^{1}H NMR τ 7.0 (q, 2 H) absent) but racemized to the extent of 31.5%.

Trapping of the Ring-Opened Product. The sulfone (16.8 mM) in anhydrous ether (75 mL) was treated with 0.337 M ethereal ethylmagnesium bromide (17 mM). The mixture was refluxed for 1.5 h when acetic anhydride (10 mL) in ether (20 mL) was added. After 18 h, dilution with water and extraction gave a mixture which, on fractional distillation, gave first recovered sulfone (1.4 g, bp 116–150 °C (0.2mmHg)) and then a fraction (1.05 g, bp 150–153 °C (0.2mmHg)). This was purified by preparative GLC on SE 30 at 170 °C. ^{1}H NMR: τ 8.7 (t, 3 H), 8.0 (s, 3 H), 7.5–8.4 (m, 4 H), 7.05 (q, 2 H), 5.9 (t, 2 H), 3.6 (m, 2 H). IR: 1130 (s), 1250 (s), 1740 (s) cm^{-1}. The material was free (^{1}H NMR and GLC) of starting sulfone. This product (4.2 mM) was boiled with molar aqueous methanolic sodium hydroxide. After 1 h, neutralization (H_2SO_4) and extraction gave recovered ethyl tetrahydrofurfuryl sulfone (53%): bp 111 °C (0.1mmHg); n^{19}_D 1.4810; ^{1}H NMR and IR identical with those of an authentic specimen.

Hydrogen–Deuterium Exchange. The sulfone (0.93 mM) in molar aqueous sodium deuteroxide in D_2O was sealed in an NMR tube and kept at 100 °C. The spectrum was recorded at intervals. The protons adjacent to the sulfonyl group exchanged rapidly while those at C_3 exchanged with $t_{1/2}$ of ca. 2 h. No further change occurred after 4.75 h. The sulfone was recovered in 60% yield: bp 145 °C (1mmHg); n^{22}_D 1.4733.

Tetrahydropyranyl Series. (a) 2-(Ethylsulfonylmethyl)tetrahydropyran. 2-(Hydroxymethyl)tetrahydropyran was converted into the half phthalate with phthalic anhydride as in the tetrahydrofuran series. The *ester* had mp 74 °C (from diisopropyl ether). Anal. ($C_{14}H_{16}O_5$): C, H. The ester was resolved with brucine, giving 2-(hydroxymethyl)tetrahydropyran with $[\alpha]^{20}_{436}$ 0.69°.

The alcohol was converted into the tosylate, mp 74 °C (lit.[30] mp 74 °C), which on treatment with sodium ethanethiolate in ethanol gave **2-(ethylthiomethyl)tetrahydropyran** (31%): bp 106 °C (20mmHg); n^{18}_D 1.4870; $[\alpha]^{20}_{436}$ 1.82°. Anal. ($C_8H_{16}OS$): C, H. Oxidation of the sulfide with hydrogen peroxide–ammonium molybdate gave the *sulfone* (71%), mp 56 °C (from diisopropyl ether–petrol). Anal. ($C_8H_{16}O_3S$): C, H. The sulfone was optically inactive. It was established that the sulfide does not racemize on treatment with methanolic ammonium molybdate in the absence of hydrogen peroxide. The reason for racemization during oxidation thus remains obscure.

The sulfone was kept with an excess of molar NaOD–D_2O at 100 °C. Determination of the ^{1}H NMR spectrum at intervals showed that exchange at C_3 was essentially complete in 3 h and that $t_{1/2}$ was ca. 40 min.

(b) 2-(Carboxymethylsulfonylmethyl)tetrahydropyran (12, R = CH_2CO_2H). Ethyl thiolacetate (37 mM) was added to 0.5 M ethanolic sodium ethoxide (37 mM) followed by 2-(tosyloxymethyl)tetrahydropyran (37 mM) in methanol under nitrogen. The mixture was refluxed for 6 h when extraction gave crude methyl ester sulfide (90%), bp 100 °C (0.4mmHg). Oxidation gave the *sulfone* (98%): bp 147 °C (0.1mmHg); n^{17}_D 1.4856. Anal. ($C_{10}H_{18}O_5S$): C, H. Hydrolysis of the ester with aqueous methanolic sodium hydroxide gave the *acid* (65%), mp 116 °C (from ethyl acetate). Anal. ($C_8H_{14}O_5S$): C, H. The acid was partially resolved by using (+)-α-phenylethylamine. The material used in kinetic work had mp 112 °C and $[\alpha]^{20}_D$ 2.78°.

Ethyl 2-Methoxypropyl Sulfone. Allyl ethyl sulfone (11.2 mM) in methanol (40 mL) was treated with sodium methoxide (112 mM) in methanol (72 mL). The mixture was refluxed for 1.5 h when dilution with water and extraction gave the ether (68%): bp 88 °C (0.2mmHg); n^{20}_D 1.4532. Anal. ($C_6H_{14}O_3S$): C, H.

The sulfone (1.26 mM) and methyl phenyl sulfone as internal GLC standard, in ethanol (12 mL), were treated with molar ethanolic sodium ethoxide (12 mL), and the mixture was kept at 25 °C. At intervals over 22 h, 0.2-mL aliquots were removed, neutralized with weak acid ion-exchange resin, and analyzed by GLC (SE30 at 160 °C) for loss of substrate.

2-(Phenoxyethylsulfonyl)acetic Acid. Ethyl thiolacetate was heated with equimolecular amounts of methanolic sodium methoxide and 1-bromo-2-phenoxyethane. After 2 h at reflux, dilution with brine and extraction gave the crude ester (90%) which was hydrolyzed in a 1:1:1 mixture of ethanol, water, and concentrated sulfuric acid at reflux for 8 h. Extraction gave the *sulfide–acid* (83%): mp 49 °C (from carbon tetrachloride–light petroleum). Anal. ($C_{10}H_{12}O_3S$): C, H. Oxidation of the acid with hydrogen peroxide in methanolic ammonium molybdate gave the *sulfone–acid* (80%): mp 85 °C (from carbon tetrachloride–chloroform). Anal. ($C_{10}H_{12}O_5S$): C, H.

Treatment of the acid with 0.2 M sodium ethoxide in 50:50 v/v ethanol–water gave the phenol, mp and mixture mp 41 °C.

Reactions with Other Tetrahydrofurfuryl Derivatives. (a) 2-Cyanomethyltetrahydrofuran. The nitrile (185 mg, bp 91 °C (13mmHg), n^{16}_D 1.4470, lit.[31] 92.4 °C (13mmHg); n^{13}_D 1.4476) was kept in molar sodium deuteroxide in D_2O (2 mL) at 100 °C for 580 h in a sealed NMR tube. Protons adjacent to the cyano group exchanged rapidly, but no other changes in integral were detected. Working up by addition to saturated brine, acidification, and extraction gave a residue (156 mg) which on distillation yielded tetrahydrofurfurylacetic acid (102 mg): bp 104 °C (1mmHg); n^{16}_D 1.4573 (lit.[32] bp 140 °C 11mmHg). In separate experiments, the hydrolysis was followed by titration and found to have a half-life of about 30 min.

When the nitrile was treated under similar conditions with molar sodium ethoxide in ethanol-*O*-*d*, recovery after 160 h at 80 °C gave a mixture of original nitrile and ester (below) (IR and NMR). The integral of protons at C_3 showed that exchange by deuterium and hence also ring opening had occurred.

(b) 2-(Methylcarboxymethyl)tetrahydrofuran (8, $EtSO_2$ = CO_2Me). The ester[32] showed no evidence for ring opening after 45 h in molar sodium ethoxide at 25 °C.

Reactions with other Tetrahydropyranyl Derivatives. (a) With Tetrahydropyranylacetic Acid 12 (RSO_2 = CO_2H). The acid, mp 56.5 °C (lit.[33] mp 55 °C), was kept with an excess of 0.5 M NaOD–D_2O solution at 100 °C for 20 h. ^{1}H NMR spectra showed no deuterium exchange either adjacent to the carboxyl group or at C_3.

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(b) With 7-Hydroxyhept-2-enoic Acid (17, G = CO_2H). The acid[33] underwent no ^1H NMR spectroscopic change (except at OH) on being kept at 100 °C with 0.5 M NaOD-D_2O for 6 h.

(c) With Methyl 7-hydroxyhept-2-enoate (17, G = CO_2Me). The ester was kept with an excess of 0.5 molar aqueous sodium hydroxide at 20 °C for 6 h. Acidification and extraction gave tetrahydropyranylacetic acid (97%).

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Ground- and Excited-State Oxidation-Reduction Chemistry of (Triphenyltin)- and (Triphenylgermanium)tricarbonyl(1,10-phenanthroline)-rhenium and Related Compounds

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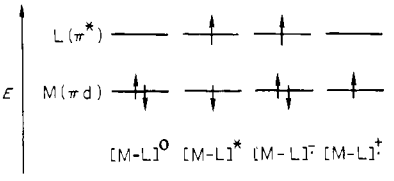
Abstract: Optical absorption and emission spectroscopy and the photochemistry and electrochemistry are reported for complexes of the general formula $R_3EM(CO)_3L$ (R = Ph or Me; E = Ge or Sn; M = Mn or Re; L = 1,10-phenanthroline, 2,2′-bipyridine, or 2,2′-biquinoline). The lowest excited state in each system results from charge-transfer, $(E-M)\sigma_b \rightarrow \pi^*L$, absorption. Several of the Re complexes (R = Ph; E = Ge or Sn; L = 2,2′-bipyridine or 1,10-phenanthroline) exhibit optical emission from the lowest excited state at 298 K in fluid solution; emission lifetimes under such conditions for these complexes are $\sim 10^{-6}$ s. These excited complexes can be quenched by both electron-donor quenchers and by electron-acceptor quenchers. Detailed quenching studies of $Ph_3SnRe(CO)_3(phen)$ (phen = 1,10-phenanthroline) have been carried out, and quenching obeys Stern-Volmer kinetics. Electron donors, Q, for which $E°(Q^+/Q)$ is more negative than $\sim +0.2$ V vs. SCE quench at an essentially diffusion-controlled rate. Electron acceptors, P^+, for which $E°(P^+/P)$ is more positive than ~ -1.0 V vs. SCE also quench at nearly a diffusion-controlled rate. Cyclic voltammetry of the complexes in CH_3CN/0.1 M $[n\text{-}Bu_4N]ClO_4$ typically shows a one-electron, reversible reduction in the -1.1 to -1.7 V vs. SCE range associated with the population of the lowest available π^* orbital principally localized on L. An irreversible oxidation current peak is observed in the range +0.5 to +0.8 V vs. SCE. The M-containing oxidation product is *fac*-$[(CH_3CN)M(CO)_3L]^+$. Consistent with the ground state electrochemistry, quenching by reversible electron-donor quenchers (e.g., *N,N,N′,N′*-tetramethyl-*p*-phenylenediamine) results in no net photoredox reaction ($\Phi < 10^{-3}$) whereas quenching by reversible electron-acceptor quenchers (e.g., *N,N′*-dimethyl-4,4′-bipyridinium) results in net redox chemistry to reduce the quencher and to form *fac*-$[(CH_3CN)M(CO)_3L]^+$ from the complex. The data are consistent with primary formation of $R_3E\cdot$ and the 16-valence electron $[M(CO)_3L]^+$ from cleavage of the $[R_3EM(CO)_3L]^{+\cdot}$ formed by excited-state electron transfer. Rate of $[R_3EM(CO)_3L]^{+\cdot}$ cleavage is similar to the dissociative E-M bond cleavage induced by the $(E-M)\sigma_b \rightarrow \pi^*L$ optical excitation.

A molecule in its lowest one-electron excited state should have reactivity properties related to the ground state of the one-electron oxidized molecule and the ground state of the one-electron reduced molecule. This statement follows from the simple orbital diagrams in Scheme I for a metal complex having a lowest metal to ligand charge-transfer excited state. The excited species has a "hole" in the lowest orbital like the one-electron oxidized molecule, and simultaneously the excited species has an electron in the highest orbital like the one-electron reduced molecule. Though such schemes are an oversimplification of the situation, such a view of excited-state reactivity leads to some fairly straightforward expectations. Such schemes should have particular value for many inorganic and organometallic molecules where the HOMO and LUMO of the molecule often play a very different role in the bonding.[1]

As an example of the value of such one-electron considerations in inorganic systems consider the six-coordinate, low-spin d^6 complexes that have been studied with respect to photosubstitution.[1,2] In all of these systems that are photosubstitution labile the HOMO is a π d orbital that is either nonbonding or weakly π bonding. By way of contrast, the LUMO is a σ d orbital that is strongly antibonding with respect to the metal-ligand bond. The lowest one-electron excited state then involves population of an orbital which is strongly σ antibonding, resulting in a very labile excited species. The "hole" generated in the π d level is not too consequential with respect to lability. These excited-state expectations are consistent with the existence, and indeed isolability, of various pairs of d^5/d^6 systems, e.g., $Fe(CN)_6^{3-/4-}$, $V(CO)_6^{0/-}$, and $Ru(NH_3)_6^{3+/2+}$, whereas attempted addition of an electron to the simple low-spin d^6 systems does not seem to result in an isolable d^7, six-coordinate complex. Presumably, the lowest orbital available in the low-spin d^6 system is a strongly σ-antibonding level whose occupation results in loss of a ligand; e.g., $Co(CN)_6^{3-} \xrightarrow{+e^-} Co(CN)_5^{3-} + CN^-$.

Scheme I. One-Electron Orbital Diagrams for a Metal Complex, M-L, in Its Ground State, and in Its MLCT Excited State, Reduced by One Electron and Oxidized by One Electron



In this article we wish to report the results of a study of the ground-state electrochemistry and excited-state electron transfer of the organometallic complexes $Ph_3ERe(CO)_3(phen)$ (E = Sn, Ge; phen = 1,10-phenanthroline) and related species. The results

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