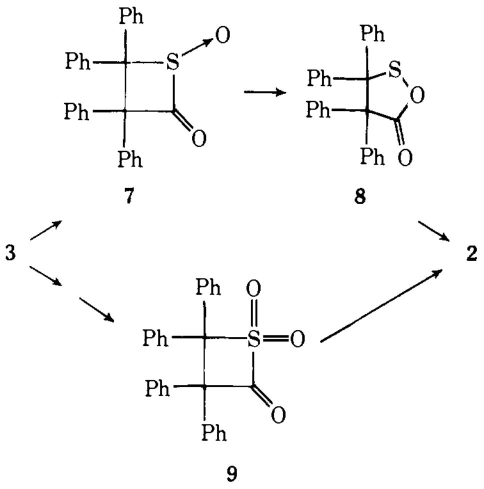
Scheme I



Preliminary experiments to determine the reactivity of **2** have been conducted. The anhydride **2** showed no evidence of decomposition at temperatures below 230 °C. Thermolysis of **2** at 240 °C (10 min) gave **4** (71%).[20] Mass spectral analysis of the gases liberated during thermolysis indicated that the major fragmentation pathway was the extrusion of SO_2 and CO rather than SO and CO_2.[21] Irradiation (medium-pressure mercury lamp, quartz, 1 h) of a degassed methylene chloride solution of **2** afforded exclusively 9,10-diphenylphenanthrene (73%).[20,23] Finally, treatment of anhydride **2** with an ether solution of $LiAlH_4$ (>10 equiv, 12 h) led to an immediate color change from colorless to blue to red and eventually to light green. Workup of the organic layer after addition of ethyl acetate and acidification with 6 N HCl led to a complex mixture (≥9 compounds by TLC). Purification by preparative thick-layer chromatography gave 2,2-diphenylethanol (50%).[20] The mechanism of these and related reactions are under investigation.

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(10) Use of conventional thick-layer chromatography led to decreased yields of **2** and increased yields of **4**, as well as the formation of tetraphenyl-β-lactone.
(11) Physical and spectral properties of 3,3,4,4-tetraphenyl-1,2-oxathiolan-5-one 2-oxide (**2**): mp 233–235 °C dec from hexanes; IR ($CHCl_3$) 1795, 1182, 1100 cm^{-1}; NMR ($CDCl_3$) δ 6.70–7.46 (m); ^{13}C NMR ($CDCl_3$) 67.8, 87.4, 127.6, 128.0, 128.1, 128.3, 128.4, 128.7, 129.3, 129.6, 131.1, 131.7, 132.2, 132.3, 133.7, 135.6, 139.4, 140.1, 173.2 ppm; MS (CI mode) P + 1 peak at *m/e* 425; MS (EI mode) *m/e* (rel intensity) 362 (0.1), 360 (0.1), 333 (28), 332 (100), 289 (6), 255 (13), 254 (20), 250 (8), 241 (11), 178 (10), 176 (10), 166 (12), 165 (33), 126 (11), 77 (14). Anal. ($C_{27}H_{20}O_3S$) C, H, S.
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(20) The experimentally obtained material proved to be identical with an authentic sample.
(21) The fragmentation pattern observed in this study is qualitatively similar to that observed for mandelic acid anhydride[12d] and acyclic carboxylic-sulfurous anhydrides.[22]
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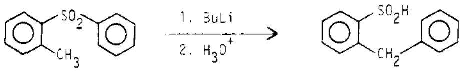
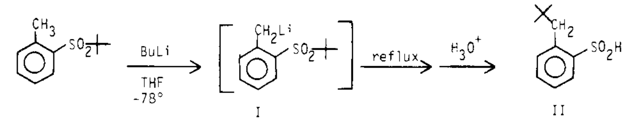
An Example of Alkyl Group Transfer in a Truce-Smiles Rearrangement

Sir:

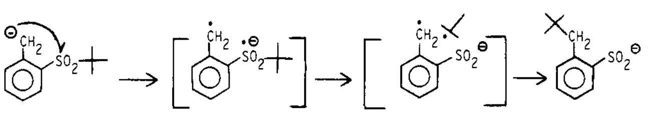
The extensively studied Truce-Smiles rearrangement has previously involved only diaryl sulfones, as with phenyl *o*-tolyl sulfone to form *o*-benzylbenzenesulfinic acid.[1]



We report here the first example of such rearrangement in which the migrating group is alkyl rather than aryl. In the course of investigating several reactions of metalated *o*-tolyl *tert*-butyl sulfone, it was found that refluxing the lithiated species I in THF for several hours led to formation of *o*-neopentylbenzenesulfinic acid (II) (the yield of which was increased from 40 to 75% by lengthening reflux time from 2 to 8 h). The structure of the product II has been confirmed by NMR of the methyl sulfone derivative and NMR and mass spectrum of the 2-hydroxy-3,5-dichlorobenzyl sulfone derivative. Particularly noteworthy is the fact that the alkyl group being transferred is tertiary.[2]

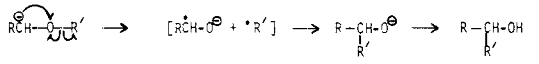


This novel rearrangement can be rationalized in terms of an electron-transfer-radical-anion reaction pathway. The close proximity of the $-SO_2-$ group should facilitate transfer of an

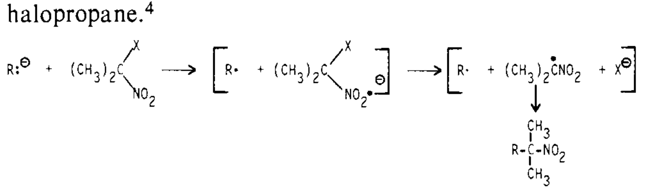


electron from the benzylic carbanion to form a stable benzylic radical and the sulfonyl radical anion. Subsequent or accompanying homolytic cleavage of the sulfur *tert*-butyl bond would generate the sulfinate anion and *tert*-butyl radical. Immediate radical combination, within the solvent cage, would give rise to the observed product.

This mechanism has precedence in the Wittig rearrangement of metalated ethers. Although an early mechanism involved an intramolecular carbanion S_N2 displacement, more recent evidence for the Wittig rearrangement favors an electron-transfer-radical-anion mechanism.[3] A related mechanism



has also been suggested in the intermolecular coupling of alkyllithium reagents with 2,2-dinitropropane and 2-nitro-2-halopropane.[4]



Further work on this type of alkyl transfer in Truce-Smiles rearrangements is currently underway in this laboratory and will be reported on at a later date.

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Unequivocal Determination of the Site of Metal-Carbonyl Bond Breaking in Tetracarbonylchromium(0) Complexes of *o*-Phenanthroline and 2,2'-Dipyridyl

Sir:

Since it became evident that five-coordinate intermediates derived through metal-ligand bond breaking in octahedral metal-carbonyl complexes could undergo stereochemical rearrangement on the time scale of the ligand-substitution process,[1] there has been great interest in the determination of the site of such M-L bond fission, where equivocal, so that possible correlation between structure and reactivity both of the substrates and intermediates could be attempted.[2]

In general, isotopic labeling studies have been employed to this end where the ligand is CO. These have involved either determination of the rates of formation and disappearance of labeled species[3] or of the identity of products formed via reaction of stereospecifically labeled substrates.[4]

One method, employed in the analysis of the *cis*-(diphos)-$Mo(CO)_4$ system (diphos = 1,2-bis(diphenylphosphino)ethane) employed Fourier transform (FT) NMR studies of ^{13}CO distribution, but also required a ^{13}C "internal standard" to be present in the molecules studied. Solubility and stability problems, as well as the lack of a sufficient amount of natural isotropic abundance noncarbonyl carbon-13 in many stystems of interest, have severely limited the applicability of this approach.

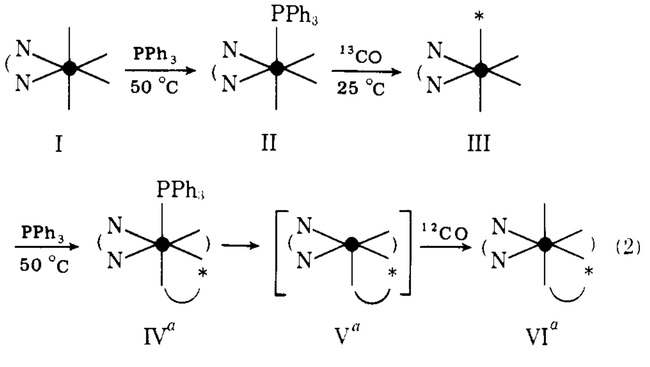
The communication describes an alternative approach, of much broader applicability, through which the site of initial M-CO bond breaking, as well as the degree of fluxionality of the five-coordinate intermediate thus formed *under the normal conditions employed in the ligand-substitution process,* can be determined. The systems chosen for study,

$$cis\text{-}(L_2)Cr(CO)_4 + L' \rightarrow fac\text{-}(L_2)Cr(CO)_3L' + CO \quad (1)$$

L_2 = *o*-phenanthroline (phen) and 2,2'-dipyridyl (dpy)
L' = phosphine, phosphite

have been studied in this context in two previous reports;[5,6] the present results, which are unequivocal and are quantitative, reveal loss to occur exclusively at an axial position (cis to L_2), with *complete scrambling of label during the ligand-substitution process.*

The preparation of a stereospecifically labeled *cis*-$(L_2)Cr(CO)_4$ molecule and the subsequent ligand-substitution process employed, similar to those employed in the *cis*-(diphos)$Mo(CO)_4$ system,[4] are illustrated in eq 2. The key to the

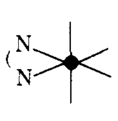


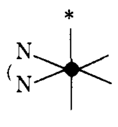
— = CO
*— = ^{13}CO
• = Cr
NN = phen, dipy

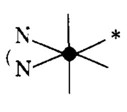
[a] In IV–VI the label need no longer be stereospecific.

application of the chemical transformations outlined there is choice of $(L_2)Cr(CO)_3(L')$ species (II, IV) exhibiting significantly greater instability than the tetracarbonyl complex from which they are formed, e.g., I and III; thus species containing more than one isotopic label are produced only to the extent that enrichment takes place in a molecule containing the natural isotopic abundance label. This greatly simplifies data in comparison with studies in which continuous introduction of a label in a substrate such as I can lead to successive enrichment and the production in significant quantities of as many as 12 species.[3,6]

The question of the site of initial Cr-CO bond breaking and the extent of scrambling during the ligand-substitution process (III to IV) rests with the determination of the quantity of label found in the various positions in VI, i.e., the relative quantities of the three species VIa-c present upon completion of the li-


VIa


VIb


VIc