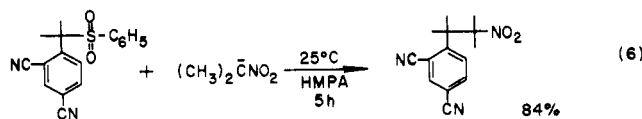
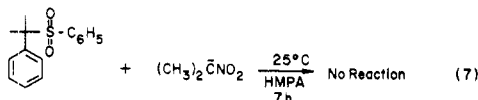


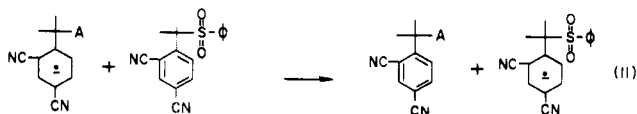
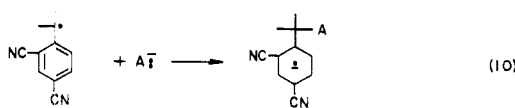
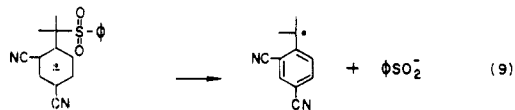
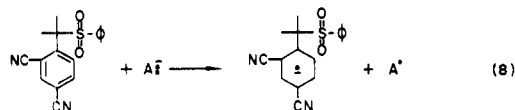
dicyano sulfone of eq 6 reacts rapidly with the lithium salt



of 2-nitropropane and gives an 84% yield of the pure product,¹³ there is no reaction when the unsubstituted sulfone of eq 7¹⁴ is treated with the lithium salt of 2-nitropropane.



The reactions of eq 4 and 5 presumably proceed via the mechanistic sequence of eq 8-11. It is also apparent from



the transformations of eq 2 and 3 that monocyano compounds readily accept one electron from nitro paraffin salts to give radical anions and that these readily lose trimethylamine, or chloride ion, thereby giving rise to the corresponding radicals; i.e., the monocyano compounds exhibit characteristics analogous to those described by eq 8 and 9.¹⁵

Facilitation by the cyano group of electron-transfer chain substitution must involve the cyano group's ability to delocalize an electron. That a cyano group is converted to a cyano radical anion on exposure to a "high-pressure" source of electrons such as metallic sodium or lithium anthracene is well-known.¹⁶ But the present studies do not involve potent one-electron donors and yet a chain reaction involving radical anions and free radicals is set up under very mild conditions. That this is so could not have been predicted since, electrochemically, cyano groups undergo one-electron reduction much more difficultly than nitro groups. That the capability of a single cyano group for fostering electron-transfer substitution may well be marginal is suggested by preliminary experiments in the *p*-cyanocumyl system using NaCN and NaN₃; in these two instances substitution has not been observed.¹⁷

(13) The reaction of eq 6 shows all the characteristics of an electron-transfer chain reaction; it is inhibited by *m*-dinitrobenzene and by di-*tert*-butyl nitroxide, and it is speeded up by light.⁷

(14) Unpublished work by Dr. P. Ackermann, Purdue University.

(15) The demonstration that with monocyano compounds processes analogous to those of eq 10 and 11 occur will require the use of a nucleophile other than a nitro paraffin salt.

(16) C. Fabre and Z. Welvart, *C. R. Hebd. Seances Acad. Sci.*, 270, 1887 (1970); H. D. Hartzler, *J. Am. Chem. Soc.*, 93, 4527 (1971); J.-P. Mazaleyrat and Z. Welvart, *C. R. Hebd. Seances Acad. Sci.*, 274, 800 (1972); J. H. Wieringa, H. Wynberg, and J. Strating, *Tetrahedron Lett.*, 2071 (1972).

Most important of all, it has now been demonstrated for the first time that electron-transfer chain substitution can occur at a saturated carbon atom in the complete absence of nitro groups and that these reactions are synthetically valuable. Aside from their intrinsic interest, the results herein presented lead one to anticipate that electron-attracting groups other than nitro and cyano, singly or in combination, will also be able to facilitate electron-transfer substitution at a saturated carbon—both chain and non-chain.

Acknowledgment. We thank the National Science Foundation for supporting this investigation.

Registry No. *o,p*-Dicyano- α -phenylsulfonylcumene, 72214-06-3; diethyl methylmalonate sodium salt, 18424-77-6; diethyl (α,α -dimethyl-*o,p*-dicyanobenzyl)methylmalonate, 72206-82-7; sodium benzenethiolate, 930-69-8; *o,p*-dicyano- α -phenylsulfmethylmalonate, 72206-82-7; 2-nitropropane lithium salt, 3958-63-2; *o,p*-dicyano- α -(2-nitro-2-propyl)cumene, 72206-83-8; *p*-cyanobenzyl chloride, 874-86-2; *p*-cyanobenzaldehyde, 105-07-7; *N,N,N*-trimethyl-*p*-cyanobenzylammonium chloride, 70579-08-7; 2-methyl-2-nitro-*p*-cyanophenylpropane, 72206-84-9; *p*-cyano- α -chlorocumene, 72206-85-0; *p*-cyano- α -(1-nitroethyl)cumene, 65253-36-3; nitroethane ion, 25590-58-3.

(17) These and related reactions are being studied with a view to defining the similarities and differences in behavior of cyano and nitro compounds.

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Lanthanide-Induced Chemical Shifts of Sulfonium Salts

Summary: Lanthanide shift reagents may be used in the structural elucidation of trialkyl- and dialkylarylsulfonium salts.

Sir: The use of lanthanide shift reagents (LSR) as tools in the structural elucidation of organosulfur compounds is well documented.¹ These reagents have routinely been used in the analysis of numerous tricoordinate sulfur(IV) species such as sulfoxides and sulfilimines; however, their application to the structural elucidation of sulfonium salts is virtually unknown.^{2,3}

Lanthanide-induced shifts (LIS) have not been routinely applied to structural problems involving ionic moieties. The lack of work in this area is a result of the difficulty in obtaining solvents in which the shift reagent and sub-

(1) (a) W. H. Pirkle and D. L. Sikkenga, *J. Org. Chem.*, 40, 3430 (1975); (b) R. R. Fraser and Y. Y. Wigfield, *Chem. Commun.*, 1471 (1970); (c) R. M. Wing, J. J. Uebel, and K. K. Andersen, *J. Am. Chem. Soc.*, 95, 6046 (1973); (d) K. K. Andersen and J. J. Uebel, *Tetrahedron Lett.*, 5253 (1970); (e) R. R. Fraser, T. Durst, M. R. McClory, R. Viau, and Y. Y. Wigfield, *Int. J. Sulfur Chem.*, 1, 133 (1971).

(2) K. B. Lipkowitz, Ph.D. Dissertation, Montana State University, 1975 (Xerox University Microfilms No. 76-13,307). A LIS shift study on a sulfonium salt was performed; two modes of complexation were postulated, one involving complexation at the anion (iodide) and the second involving complexation at the electron pair on sulfur.

(3) (a) M. Casey, L. Blattner, and R. L. Caret, Abstracts, 12th Mid-Atlantic Regional Meeting of the American Chemical Society, Hunt Valley, MD, 1978, No. CU 2; (b) R. L. Caret, M. Casey, and A. Vennoe, Abstracts, 13th Mid-Atlantic Regional Meeting of the American Chemical Society, West Long Branch, NJ, 1979, No. ORGN 34 and CU 4.

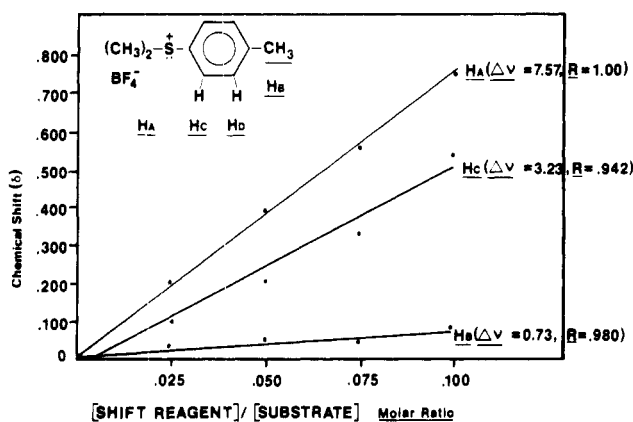
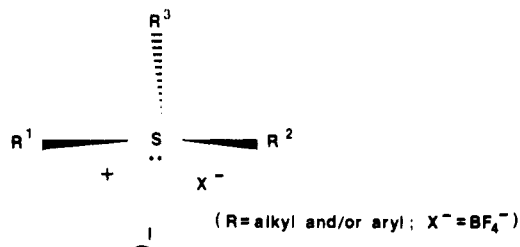


Figure 1. LIS of dimethyl-*p*-tolylsulfonium tetrafluoroborate. The resonances of each of the protons are plotted as a function of the molar ratio of shift reagent, $\text{Pr}(\text{fod})_3$, to substrate in CD_2Cl_2 . The H_D protons were partially obscured by the H_C protons. The shifts of the H_D protons gave a poor correlation (0.772) and are not plotted. The induced shift at a 1:1 molar ratio of the shift reagent to substrate ($\Delta\nu$) and the correlation coefficient (R) of the respective line are given in parentheses.⁵

strate are sufficiently soluble for the investigation. The only known examples in which LIS studies have been carried out on ionic moieties involve ammonium salts.⁴ We have recently completed an LIS investigation employing trialkyl- and dialkylarylsulfonium salts (1). The results of these investigations are presented below.



Sulfonium salts, in a manner analogous to ammonium salts, do indeed give observable induced shifts when LSR are employed. Also, these salts are more strongly shifted by the LSR than are the corresponding neutral sulfides. The ammonium salts also exhibit this behavior when compared to the amines.⁴ Examples of the magnitudes of these induced shifts are provided in Figures 1 and 2. In these applications, the McConnell–Robertson equation holds. The closer the observed proton is to the site of complexation, the greater the induced shift.⁶

The origin of these shifts is primarily attributed to a pseudocontact interaction between the paramagnetic lanthanide shift reagent and the molecule being investigated.⁷ In the case of the ammonium salts, this interaction is attributed to a complexation between the LSR and the basic anion (iodide or chloride). In the case of the sulfo-

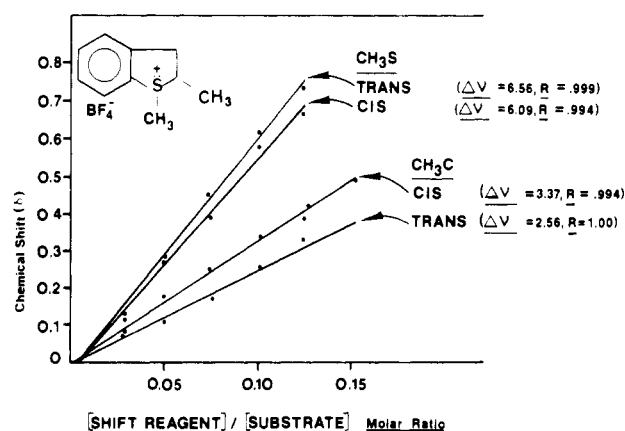
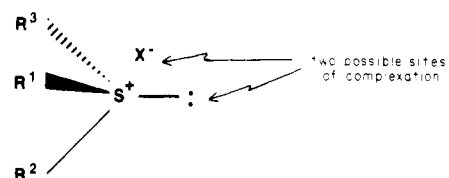
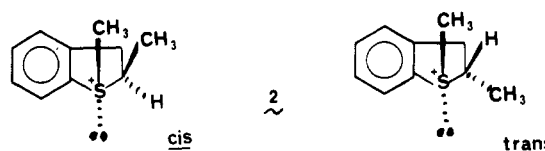


Figure 2. The LIS study of 1,2-dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate (2). The SCH_3 and CCH_3 resonances are plotted as a function of the molar ratio of shift reagent, $\text{Pr}(\text{fod})_3$, to substrate in CD_2Cl_2 . Note that only the methyl resonances are plotted for clarity. See ref 11 for additional data. The induced shift at a 1:1 molar ratio of shift reagent to substrate ($\Delta\nu$) is given in parentheses along with the correlation coefficient (R) of the respective line.⁵

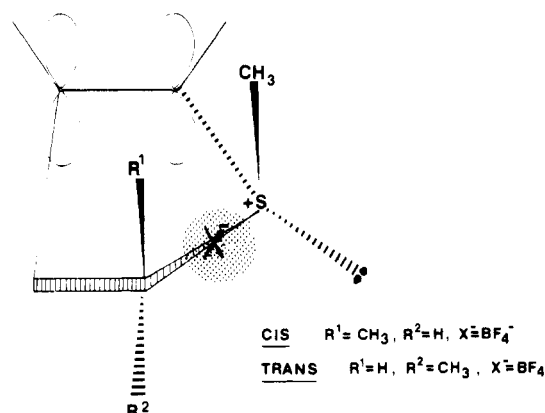
nium salts, however, two sites of complexation are possible, the electron pair on sulfur and/or the anion.



To gain insight into the origin of this complexation, we chose the 1,2-dimethyl-2,3-dihydrobenzothiophenium tetrafluoroborate system (2). The *cis* and *trans* isomers



of 2 had been synthesized and their configurations assigned previously.⁸ By this method, the two isomers of 2 were synthesized for use in this investigation. The *cis/trans* isomerism present in 2 provides a convenient "handle" for determining the site of complexation between the salt and the shift reagent. The salient geometric features of the two isomers are summarized in the following drawing.



Note the position of the anion with respect to the methyl

(4) J. I. Seeman and R. L. Bassfield, *J. Org. Chem.*, **42**, 2337 (1977), and references cited therein.

(5) A least-squares analysis was performed twice on five to seven points, each at varying percentages of shift reagent to substrate and with between 0 and 15 mol % of $\text{Pr}(\text{fod})_3$.

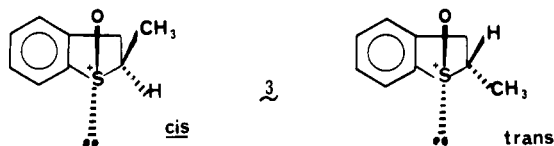
(6) The McConnell–Robertson equation may be expressed as $\Delta\nu = K \cdot (3 \cos^2 \theta - 1) / R^3$ where $\Delta\nu$ is the induced shift in parts per million, R is the distance from the observed nucleus to the lanthanide ion in angstroms, θ is the angle between the principal magnetic axis of the complex (usually assumed to be colinear with the bond between the lanthanide ion and the site of complexation) and a line drawn from the lanthanide ion to the nucleus being observed, and K is a constant which depends on the system being investigated.

(7) R. E. Cramer, R. Dubois, and K. Seff, *J. Am. Chem. Soc.*, **96**, 4125 (1974).

(8) K. K. Andersen, I. K. Nielsen, and R. L. Caret, *J. Am. Chem. Soc.*, **96**, 8026 (1974).

groups in each isomer. From X-ray data of analogous cyclic sulfonium salts,⁹ the anion would be predicted to be oriented in an area roughly in the plane of the thiophene ring as close to the positive sulfur as is sterically allowable. In addition, the negatively charged anion would remain oriented as far away as possible from the π -electron cloud of the aromatic ring and the electron pair on sulfur.

The results of the LIS study on **2** are given in Figure 2. These results are consistent with a complexation at or with the anion and not with the lone pair on sulfur.¹⁰ If the lone pair is the site of complexation, then the SCH₃ of both the cis and trans isomers would be approximately equidistant from the LSR, but the CCH₃ of the trans isomer would be much closer to the praseodymium than would the CCH₃ of the cis isomer. There should be a large difference in shift between these latter two methyl groups.¹² Note for comparison the difference in shift of the C-methyl groups of the corresponding sulfoxides **3**. The $\Delta\Delta\nu$ at a



1:1 molar ratio of the shift reagent to the substrate for the C-methyl of each of the isomers is ca. 5 ppm.⁸ As we see from Figure 2, the sulfonium salts do not exhibit shift differences of this magnitude ($\Delta\Delta\nu = 0.47$ ppm for S-methyl and 0.81 ppm for C-methyl). If, on the other hand, the complexation were occurring at the anion, the results would be expected to be quite different. In this case, the SCH₃ groups of both the cis and trans isomers would be approximately equidistant from the anion as would be the CCH₃ groups of both of these isomers. No significant difference in the magnitude of the shifts of these two isomeric methyl pairs would be observed. This is consistent with our findings. It appears that the site of complexation is at the anion. The nature of this complexation is presently under investigation in our laboratories. Preliminary UV results indicate that no direct covalent complex is forming but do not disprove the possible involvement of a weak complexation between the lanthanide ion and the tetrafluoroborate anion. We hope to have answers to these questions in the near future.

In summary, LIS studies may be used in the investigation of the structure of sulfonium salts. In these applications, the McConnell-Robertson equation holds, with the complexation apparently occurring primarily at the anion of the salt.

Acknowledgment. The authors wish to express their appreciation to Ms. Moira Casey and Mr. L. Blattner for their help on this project. Also, thanks are extended to Mr. J. Gaudiello, Mr. A. Fierschnaller, and Mr. J. Sosnowski for their help in the synthesis of 2,3-dihydrobenzothiophene. This project was supported by a grant from the Towson State University Faculty Research Committee; their aid is greatly appreciated.

(9) For example, S. M. Johnson, C. A. Maier, and I. C. Paul, *J. Am. Chem. Soc.* **B**, 1603 (1970).

(10) This investigation does not rule out the possibility of complexation occurring at both sites [see, for example, C. C. Hinkley, M. R. Klotz, and F. Patil, *J. Am. Chem. Soc.*, **93**, 2147 (1971)].

(11) All spectra were recorded as mixtures of the cis and trans isomers, consisting of an ca. 80:20 trans/cis ratio as determined by NMR.

(12) When the radial (*R*) and angular (θ) factors are taken into account, and if complexation is occurring solely at the lone pair on sulfur, calculations show that the induced shift of the CCH₃ of the trans isomer should be larger than that of the cis by a factor of ca. 1.2 cis/trans.

Registry No. *cis*-2 BF₄⁻, 55563-68-3; *trans*-2 BF₄⁻, 55563-67-2; dimethyl-*p*-tosylsulfonium tetrafluoroborate, 51404-78-5.

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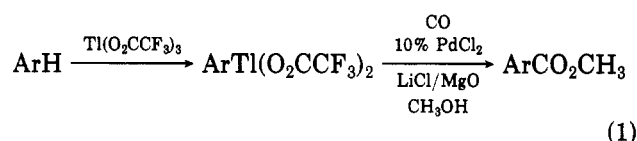
Received May 29, 1979

Synthesis of Aromatic Esters, Lactones, Anhydrides, and Heterocycles via Thallation-Carbonylation of Arenes

Summary: The thallation and subsequent palladium-catalyzed carbonylation of simple arenes, benzylic and β -phenethyl alcohols, benzoic and phenylacetic acids, benzamide, and acetanilide afford benzoate esters, phthalides, 3,4-dihydroisocoumarins, phthalic and homophthalic anhydrides, phthalimide, and acetylanthranil, respectively. The carbonylation reaction proceeds in excellent yield at room temperature and atmospheric pressure and is highly stereo- and regioselective.

Sir: In recent years a substantial number of important new synthetic procedures have been developed which utilize organothallium intermediates.^{1,2} Our interest in the application of carbonylation reactions in organic synthesis,³ and particularly in the synthesis of biologically active lactones,⁴ prompted us to examine the carbonylations of arylthallium compounds. At this time we wish to report that thallation and subsequent palladium-catalyzed carbonylation of arenes provides a highly convenient new route to a wide variety of aromatic esters, lactones, anhydrides, and heterocycles.

The direct carbonylation of arylthallium compounds has been studied and requires high temperatures and pressures.⁵ We have observed, however, that carbonylation can be effected at room temperature under 1 atm of carbon monoxide simply by employing catalytic amounts of palladium chloride. Thus by utilizing essentially the same thallation conditions as Taylor and McKillop,^{6,7} replacing the solvent by methanol, adding lithium chloride, magnesium oxide, and 10% palladium chloride, and flushing with carbon monoxide, we observe the facile conversion of arenes to the corresponding methyl benzoate esters (eq 1). Some representative examples are presented in Table



I (entries 1 and 2). It is particularly noteworthy that only catalytic amounts of palladium chloride are required and that no additional reoxidant for palladium need be added.

(1) McKillop, A.; Taylor, E. C. *Chem. Br.* **1973**, 9, 4-11.

(2) McKillop, A.; Taylor, E. C. *Adv. Organomet. Chem.* **1973**, *11*, 147-206.

(3) Larock, R. C. *J. Org. Chem.* **1975**, *40*, 3237-42.

(4) Larock, R. C.; Riefling, B.; Fellows, C. A. *J. Org. Chem.* **1978**, *43*, 131-7.

(5) Davidson, J. M.; Dyer, G. *J. Chem. Soc. A* **1968**, 1616-7.

(6) McKillop, A.; Hunt, J. D.; Zelesko, M. J.; Fowler, J. S.; Taylor, E. C.; McGillivray, G.; Kienzle, F. *J. Am. Chem. Soc.* **1971**, *93*, 4841-4.

(7) Taylor, E. C.; Kienzle, F.; Robey, R. L.; McKillop, A.; Hunt, J. D. *J. Am. Chem. Soc.* **1971**, *93*, 4845-50.