reagents whose special properties include having a very strong electrophilic center (E) and a much weaker nucleophilic center (Y).

With one exception, the compounds used in this study (Table I) have previously been synthesized and assigned absolute and relative configurations using the (+)-R₃Si*H configuration as the reference configuration.[2,7] The exception is (−)-α-naphthylphenylmethyl(p-tolylthio)silane, mp 87–88°, [α]D −67° (c 0.8, n-hexane).[8] The method of preparation for this compound and assignment of relative configuration paralleled those for (−)-R₃Si*SCH₃.[8]

Reactions in Table I were carried out under dry nitrogen and the reaction mixtures were colorless and homogeneous. Using 1 equiv of R₃Si*X and 1 equiv of i-Bu₂AlH (both ca. 0.5 M) in n-hexane, a wide range of reactivities has been found during preliminary studies.

The reactivity with i-Bu₂AlH in n-hexane was: R₃Si*OCH₃ > R₃Si*O(−)Men > R₃Si*OPh > R₃Si*F, R₃Si*SCH₃ > R₃Si*SC₆H₄-p-CH₃ > R₃Si*Cl.

From examination of the reactivity pattern it is clear that the concepts of "good" and "poor" leaving groups, which we (and others) base upon idealized (pure "push") nucleophilic attack reactions, certainly do not obtain for the reactions in Table I with a reagent such as i-Bu₂AlH in n-hexane. For such reactions, then, it is not too surprising to find R₃Si*Cl reacting with retention of configuration in apparent violation of the SN2-Si stereochemistry rule which really applies to reactions with reagents that are predominantly strong nucleophiles.

At room temperature in n-hexane, reaction with R₃Si*OCH₃ is complete in less than 2 min, and reaction with R₃Si*Cl is only 10% complete after 24 hr.

In sharp contrast to the above results, profound changes in stereochemistry result from use of the etherate complex of i-Bu₂AlH. The stereochemical results using i-Bu₂AlH–Et₂O in ether solvent are reported in Table II.

Table II. Reductions of R₃Si*X with i-Bu₂AlH–Et₂O in Ether

Reaction no.	Si*X	Product	Predominant stereochemistry, %
1′	(+)-Si*OCH₃	(+)-SiH	Retention, 99
2′	(−)-Si*O(−)Men	(+)-SiH	Retention, 96
3′	(+)-Si*OPh	(+)-SiH	Retention, 100
4′	(+)-Si*F	(−)-SiH	Inversion, 90
5′	(−)-SiSCH₃	(−)-SiH	Inversion, 98
6′	(−)-SiSC₆H₄-p-CH₃	(−)-SiH	Inversion, 98
7′	(−)-Si*Cl	(−)-SiH	Inversion, 90

Comparison of Tables I and II reveals dramatic stereochemistry crossover from retention of configuration for reactions 4–7 in Table I to inversion of configuration for reactions 4′–7′ in Table II. The stereochemical results in reactions 4′–7′ parallel those obtained with lithium aluminum hydride.[2a]

In addition to the etherate complex of i-Bu₂AlH, other donor–acceptor complexes of i-Bu₂AlH were

(7) L. H. Sommer and J. McLick, J. Amer. Chem. Soc., 89, 5806 (1967).

(8) Analyses for C, H, and S were satisfactory and spectral data were consistent with the assigned structure.

studied and gave stereochemical results paralleling those in Table II. Among the complexes studied was i-Bu₂AlH–TMEDA (TMEDA is tetramethylethylenediamine) in n-hexane solvent and with this reagent relative rates gave the reactivity pattern: R₃Si*Cl > R₃Si*OCH₃ > R₃Si*O(−)Men, R₃Si*F. This is a pattern to be expected from attack of a strong nucleophile at a silicon center.

We believe that reactions 1–7 in Table I proceed by a four-center SNi-Si mechanism (II) and that the poor leaving groups in reactions 1′–3′ in Table II also react by an SNi-Si mechanism which involves a preliminary fast displacement of an ether molecule from aluminum by the silicon reactant.

We also feel that reactions 4′–7′ in Table II probably proceed by an SN2-Si mechanism because the reducing H in i-Bu₂AlH–Et₂O is far more hydridic and nucleophilic than the bridge H's in trimeric i-Bu₂AlH.[9]

Detailed studies of rates and rate law for retentive and invertive reductions of R₃Si*X by i-Bu₂AlH, complexed and uncomplexed with donor substances, are presently under way.

(9) Support for the assumption of more nucleophilic character of H in donor–acceptor complexes of i-Bu₂AlH, compared to trimeric i-Bu₃AlH, is found in metalation of monoalkylacetylenes with i-Bu₃AlH–Et₃N compared to hydroalumination with trimeric i-Bu₂AlH; work of G. S. Zweifel and R. B. Steele; R. B. Steele, Ph.D. Thesis, University of California at Davis, 1966.

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Electrical Conductivity by the Bis-1,3-dithiole–Bis-1,3-dithiolium System[1]

Sir:

Recently we reported the isolation and structure determination of bis-1,3-dithiolium chloride[2] (1) and also published an X-ray structure determination[3] of 2.

In this communication we present some more intriguing properties of these molecules.

We were prompted to examine the electrical properties of 2 because X-ray crystallography revealed that, in a single crystal, the molecules were found to have their central double bonds (C₁–C₁′) lined up along one of the crystal's axes.[3] Thus, if the crystals were placed

(1) Research supported by the Petroleum Research Fund administered by the American Chemical Society and by the Research Corporation.

(2) F. Wudl, G. M. Smith, and E. J. Hufnagel, Chem. Commun., 1435 (1970). (b) Professor S. Hünig (Würzburg) also prepared bis-1,3-dithiolium chloride (private communication). (c) In ref 2a, the nmr chemical shift of 2 is in error; it should read CCl₄ (δ relative to TMS) 6.15 (s).

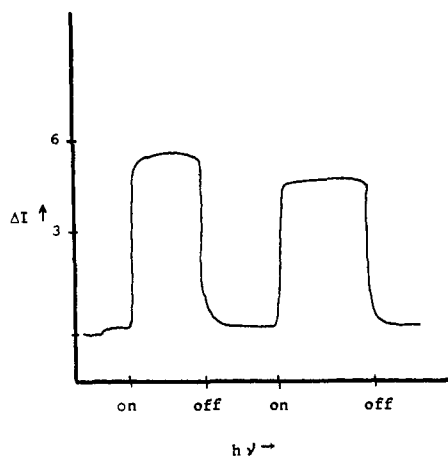(3) W. F. Cooper, N. C. Kenny, J. W. Edmonds, A. Nagel, F. Wudl, and P. Coppens, ibid., 889 (1971).

Figure 1. ΔI = photocurrent (10^{-12} A).

Figure 2. ΔI = photocurrent (10^{-12} A).

in an electric field, conduction may be possible by a process in which an electron could be transferred from a surface molecule to the anode and be replaced by another electron from a neighboring molecule along the axis.

Indeed, 2 proved to be a semiconductor at room temperature in the dark (ρ (25°) = 10^{12} Ω cm). This measurement was performed on a single crystal (in an inert atmosphere) by the four-electrode method[4] using platinum electrodes and silver–base adhesive. No noticeable electrolysis was detected after prolonged passage of current (at 5–10 V) indicating that the conduction mechanism was electronic.[4] As a single crystal, 2 is a better conductor than anthracene (ρ = 10^{22} Ω cm)[10] or ferrocene (ρ = 10^{14} Ω cm).[5] Consequently, the intermolecular barriers to the mobility of charge carriers appeared to be lower in 2 (however, vide infra) than in other comparable organic solids.

Since it is necessary to excite 2 with light in order to achieve removal of an electron by molecular oxygen, we presumed that photopromotion of an electron from the valence band to the conduction band in 2 may be quite efficient with concomitant enhancement of electrical conductance. Figure 1 depicts the photocurrent pattern of 2. Clearly, it appeared as though 2 was a photoconducting molecule.

In order to gain better insight into the mechanism of photoconduction, we studied the wavelength dependence of the photocurrent (cf. Figure 2). However, the maximum in Figure 2 does not correspond to any of the absorption maxima in the electronic absorption spectrum of 2. On the other hand, 1 exhibits a strong absorption at 575 nm (ϵ 1.6 × 10^4). Therefore, we were forced to conclude that 2 was not responsible for the photocurrent but that it was contaminated with a trace of 1. Furthermore, the dark conductance measurements performed on "pure" 2 (vide supra[6]) should now be considered with suspicion.

Finally, we directed our attention to the electrical properties of 1 and found it to be an excellent organic solid-state semiconductor. It exhibits a room temperature resistivity of 3.7 ± 1 Ω cm (E = 10 V). The

(4) F. Gutmann and L. E. Lyons, "Organic Semiconductors," Wiley, New York, N. Y., 1967.
(5) D. O. Cowan and F. Kaufman, J. Amer. Chem. Soc., 92, 219, 6198 (1970).
(6) Pure 2 used in the conductance measurements had a mp of 118.5–119° and was purified by recrystallization from distilled cyclohexane.
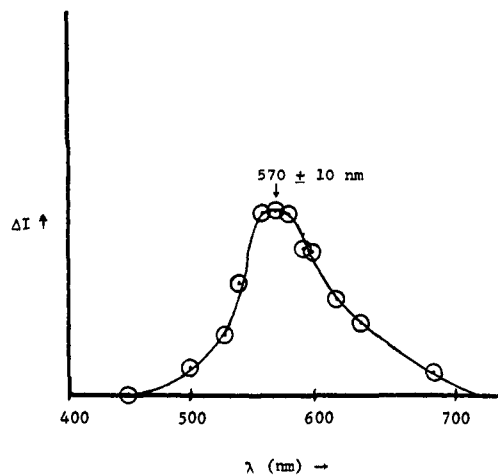
temperature dependence of conductance followed the familiar relation[4] ρ = $\rho_0 e^{-E_a/kt}$ where E_a was found to be 0.19 eV. About 10^3 mol equiv of current were passed through the sample without change in resistivity or appearance, indicating that the conduction mechanism is based on electronic charge carriers.[7] Since the above measurements were performed on compressed pellets, it is not unreasonable to surmise that electrical conductance by 1 will be even higher in the single crystal. Unfortunately, 1 exists (so far) only in microcrystalline form.

The above results show that 1 behaves in a manner strikingly similar to that of mixed valence organometallics such as biferrocenium picrate[5] 3.

3
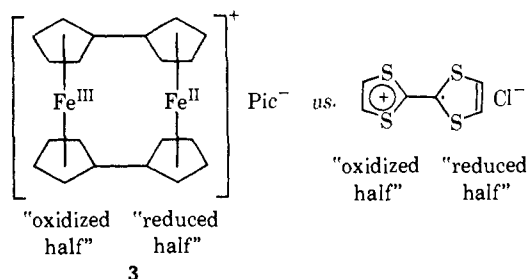
Ferrocene exhibits a room temperature resistivity 10^6 times higher than the room temperature resistivity of the mixed valence state derivative 3. More recently, Perlstein and Minot[8] made similar observations on another mixed valence transition metal complex.

Contrary to the organometallic systems, bis-1,3-dithiolium chloride is a considerably better conductor and its derivatives are prepared easily and in good yield. These features should make compound 1 and its derivatives amenable to systematic studies of conductivity in the organic solid state. We are currently investigating the intriguing possibility of including moieties such as 1 in a polymer and also the effect of

(7) Interestingly, the resistivity of salt 1 increases drastically upon exposure to moisture. The above measurements were performed on samples prepared in a glove box under dry nitrogen.
(8) J. H. Perlstein and M. J. Minot, Phys. Rev. Lett., 26, 371 (1971).

Communications to the Editor

substitutents on conductance and other physical properties of **1** as well as **2**.

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Steric Driving Forces in Perester Decomposition. *tert*-Butylperoxy Di-*tert*-butylacetate[1]

Sir:

The question of concerted cleavage of both O–O and C–CO$_2$ bonds during the thermal reactions of *tert*-butyl peresters has been of considerable interest. This problem has been examined recently by the study of the effect of solvent viscosity,[2] secondary isotope effects,[3] bridgehead strain,[4] and pressure[5] on the rates and products of perester decomposition.[6]

This report presents a new approach for investigating transition-state structure in perester decompositions, the steric driving force for the reaction. This method has been utilized to great advantage for the study of ionization processes;[7] for example, the relative rates of solvolysis (eq 1) of di-*tert*-butylcarbinyl tosylate (**1a**) and

$$R_2CHOTs \longrightarrow [R_2CH\cdots OTs]^* \xrightarrow{-OTs} R_2C^+H \qquad (1)$$

1a, R = *t*-Bu
b, R = Me
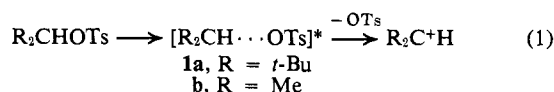
isopropyl tosylate (**1b**) have been measured to be 630 in 97% trifluoroethanol, and calculated to be 120,000 in trifluoroacetic acid.[7b] This rate acceleration was ascribed largely to relief of steric strain for **1a** on ionization, with a possible additional contribution from methyl participation.

To examine the occurrence of steric acceleration in perester reactions we prepared *tert*-butylperoxy di-*tert*-butylacetate (**2a**). Reaction of di-*tert*-butylacetyl chloride[8] with *t*-BuOOH–pyridine gave **2a** as a pale yellow oil: ir (cumene) 1764 cm^{-1} (C=O); nmr (CCl$_4$) δ 1.10 (s, 18, CH-*t*-*Bu*$_2$), 1.28 (s, 9, O-*t*-Bu), and 1.97 (s, 1, CH-*t*-Bu).[9] The kinetics of thermal decomposition of **2a** were examined in cumene solution and the measured rate constants are given in Table I along with suitable data for comparison.[10] The products of the reaction at 70° are given in Table II.

(1) Supported by the U. S. Army Research Office—Durham. Part V in the series "Steric Crowding in Organic Chemistry"; part IV: G. J. Abruscato, R. G. Binder, and T. T. Tidwell, *J. Org. Chem.*, submitted for publication.

(2) W. A. Pryor and K. Smith, *J. Amer. Chem. Soc.*, **92**, 5403 (1970).

(3) T. Koenig, J. Huntington, and R. Cruthoff, *ibid.*, **92**, 5413 (1970).

(4) (a) R. C. Fort, Jr., and R. E. Franklin, *ibid.*, **90**, 5267 (1968); (b) J. P. Lorand, S. D. Chodroff, and R. W. Wallace, *ibid.*, **90**, 5266 (1968); (c) L. B. Humphrey, B. Hodgson, and R. E. Pincock, *Can. J. Chem.*, **46**, 3099 (1968); (d) G. A. Razuvajev, L. S. Boguslavskaya, V. S. Etlis, and G. V. Brovkina, *Tetrahedron*, **25**, 4925 (1969); (e) S. F. Nelsen and E. F. Travecedo, *J. Org. Chem.*, **34**, 3651 (1969).

(5) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, **36**, 54, 57 (1971).

(6) For a general review of the relation between perester structure and reactivity, see C. Rüchardt, *Angew. Chem., Int. Ed. Engl.*, **9**, 830 (1970).

(7) (a) P. D. Bartlett and T. T. Tidwell, *J. Amer. Chem. Soc.*, **90**, 4421 (1968); (b) S. H. Liggero, J. J. Harper, P. v. R. Schleyer, A. P. Krapcho, and D. E. Horn, *ibid.*, **92**, 3789 (1970).

(8) M. S. Newman, A. Arkell, and T. Fukunaga, *ibid.*, **82**, 2498 (1960).

(9) Satisfactory carbon and hydrogen analyses were obtained for **2a**.

(10) P. D. Bartlett and L. B. Gortler, *J. Amer. Chem. Soc.*, **85**, 1864 (1963).

Table I. Rates of Decomposition of *tert*-Butylperoxy Di-*tert*-butylacetate (**2a**) in Cumene[a]

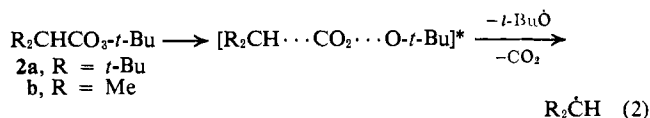| Perester	Temp, °C	k_1(sec^{-1}) × 10^6	k_{rel}	ΔH^*, kcal/mol	ΔS^*, eu
2a	85.4	24.4		29.9	7.9
	70.2	3.56			
	54.7	0.438			
	90.6[b]	44.6	6.7		
	60.0[b]	0.915			
2b[c]	90.6	6.67	1.0	31.8	9.4
	60.0[b]	0.106			

[a] Rates were measured by the infrared method using 0.09 *M* solutions, and the reported values are the averages of two runs at each temperature. Excellent first-order rate plots were obtained for at least two half-lives, and duplicate runs agreed within less than ±2% in all cases. [b] Calculated from data at other temperatures. [c] Reference 10.

Table II. Products of Decomposition of *tert*-Butylperoxy Di-*tert*-butylacetate (**2a**) at 70° in Cumene[a]

Product	Mol/mol of perester	Product	Mol/mol of perester
CO$_2$	0.89	*t*-BuOH	0.84
CH$_4$	0.01	*t*-Bu$_2$CH$_2$	0.74[b]
		Acetone	0.17

[a] Determined using 0.4 *M* solutions. [b] Products derived from combination of *t*-Bu$_2$CH groups with solvent were also detected.

The similarity in reactivity of **2a** and **2b** indicates that both of these peresters are reacting by the same mechanism, and a concerted two-bond cleavage (eq 2) is most

$$R_2CHCO_3\text{-}t\text{-Bu} \longrightarrow [R_2CH\cdots CO_2\cdots O\text{-}t\text{-Bu}]^* \xrightarrow[-CO_2]{-t\text{-Bu}\dot{O}}$$

2a, R = *t*-Bu
b, R = Me

$$R_2\dot{C}H \qquad (2)$$

consistent with the observed results.[6,11] The most telling piece of evidence for the concerted cleavage is the 50-fold greater rate of reaction of *tert*-butylperoxy isobutyrate (**2b**) over *tert*-butylperoxy acetate.[10,11a]

The remarkable feature of the reactivity of the di-*tert*-butylperacetate **2a** is the small rate enhancement (a factor of 6.7 at 90.6°) relative to the dimethylperacetate **2b**. The corresponding factor for trifluoroacetolysis of the structurally related tosylates was 120,000. This latter comparison was made under conditions where backside solvent participation, which accelerates the reactivity of the less highly substituted derivatives, is minimized, but backside solvent displacement could not be involved in the perester reactions. Steric repulsion of the leaving group may also be a factor in cleavage reactions of highly substituted substrates, and while the relative magnitudes of this interaction are difficult to assess, it appears the potential relief of strain from this cause is at least as great in the perester system. Furthermore inductive acceleration of the rate of **2a** could account for a major fraction of the **2a**/**2b** rate ratio.[4a] Thus the rate acceleration due to relief of steric strain in the dialkylperacetates is remarkably small. This result strongly suggests that rather little rehybridization of the carbon bonded to the carboxy group occurs in the transition state of perester decompositions leading to secondary radicals, and is in accord with the description of the

(11) (a) P. D. Bartlett and R. R. Hiatt, *ibid.*, **80**, 1398 (1958); (b) L. A. Singer in "Organic Peroxides," Vol. 1, D. Swern, Ed., Wiley, New York, N. Y., 1970.