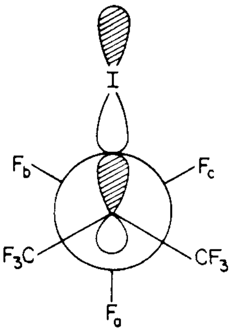
As indicated by the stick diagrams, the spectral features are readily analyzed into sets of parallel and perpendicular components resulting from hyperfine interaction with ^{127}I ($I = 5/2$), the substructure of each component consisting of a 1:3:3:1 line group characteristic of coupling to three equivalent ^{19}F's ($I = 1/2$) nuclei. The observation of significant interaction with only three out of the nine fluorines [$^{19}A_{\parallel}(3) = 121$; $^{19}A_{\perp}(3) = 109$ MHz] is accounted for by the preferred conformation **1** in which the C_β—F_a bond from each of the three CF_3 groups is aligned parallel to the C_α—I bond wherein most of the spin density is concentrated (vide infra). This is quite analogous to the most stable conformation of the perfluoroethyl radical resulting from hindered rotation about the C_α—C_β bond, the measured couplings for the three axial fluorines being very similar to that (113 MHz) for the unique β-fluorine of C_2F_5,[9] as expected for a largely isotropic interaction.



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The assignment of the spectrum to the $(CF_3)_3CI^-$ radical anion is established by the marked anisotropy of the **g** and ^{127}I hyperfine tensors which is characteristic of a large spin density in the $5p_\sigma$ orbital of the iodine atom.[10] A good least-squares fit of the line positions was obtained by a matrix diagonalization program without the inclusion of an iodine quadrupole interaction, the parameters and their standard deviations[11] being $g_{\parallel} = 1.9631$ (9), $g_{\perp} = 2.1651$ (13); $^{127}A_{\parallel} = 1282.9$ (6.9) and $^{127}A_{\perp} = 489.7$ (8.8) MHz. By including a correction for the orbital contribution to $^{127}A_{\perp}$,[10] values of $^{127}A_{\text{iso}} = 671.1$ and $^{127}B = 305.9$ MHz are derived for the isotropic and anisotropic ^{127}I hyperfine coupling constants. Accordingly, we obtain a ^{127}I (5p) contribution of 0.38 to the semioccupied orbital by taking $^{127}B_0$ for unit spin density to be 812.4 MHz.[12] The existence of such a large spin density on iodine points clearly to the stability of the $(CF_3)_3CI^-$ radical anion despite the near planarity of the $(CF_3)_3C$ radical; so one is forced to look elsewhere for an explanation of the factors governing the stability of RX^- radical anions.[13]

If the R group is considered as a pseudohalogen in a diatomic-like RX^-, it seems reasonable to propose that the stability of RX^- with respect to its dissociation modes ($R\cdot + X^-$ or $R^- + X\cdot$) is governed by the extent to which the spin density is shared between the atomic orbitals of the localized three-electron bond, the maximum stability being attained for homonuclear diatomics such as I_2^- and its congeners. This strongly suggests that relative electronegativity is likely to be an important factor, and this could well be the reason why the ^{127}I (5p) spin density of 0.38 for $(CF_3)_3CI^-$ is larger than the corresponding value (0.23) for CF_3I^-.[3,14,15]

Acknowledgments. We thank Dr. J. C. Walton for suggesting this experiment, Dr. D. Griller and Dr. K. U. Ingold for supplying us with a sample of perfluoro-*tert*-butyl iodide, and Dr. C. M. L. Kerr for the least-squares matrix diagonalization calculations. This research has been supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy (Document No. ORO-2968-121).

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(13) There is a basic flaw in Symons' postulate that the tendency for RX^- dissociation is determined simply by the change of orbital hybridization at R in going from RX^- to $R\cdot + X^-$. For the reverse reaction, it could similarly be argued that rehybridization provides a driving force for the association of $R\cdot + X^-$ to form RX^-. Hence, opposite predictions are obtained according to the direction in which the reaction is being considered, in violation of the principle of microscopic reversibility. Clearly, the direction of a spontaneous reaction can only be predicted from a property change which has both magnitude and sign, as of course is the case for ΔG. We are indebted to Professor J. A. Pople for originally directing our attention to this general point.
(14) The value of the ^{127}I (5p) spin density for CF_3I^- in ref 2 and 3 was based on a $^{127}B_0$ value of 635 MHz[10] calculated from Froese's wave function: C. Froese, *J. Chem. Phys.*, **45,** 1417 (1966). If this value is used, the calculated ^{127}I (5p) spin densities for $(CF_3)_3CI^-$ and CF_3I^- become 0.48 and 0.29, respectively.
(15) Our proposal that a higher ^{127}I (5p) spin density promotes the stability of the R_fI^- radical anion to the dissociation path $R_f\cdot + I^-$ is supported by controlled annealing studies on the CF_3I^- and $(CF_3)_3CI^-$ radical anions. Thus, although CF_3I^- has been observed to dissociate into the CF_3 radical in the vicinity of 100 K,[3] the present work showed that the spectrum of the $(CF_3)_3C$ radical did not grow in when the matrix was annealed to 104 K at which temperature the $(CF_3)_3CI^-$ radical anion was observed to disappear gradually.

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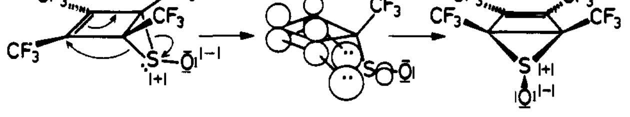
[1,3]-Sigmatropic Shifts for 5-X-Bicyclo[2.1.0]pent-2-enes. An Evaluation of the Pseudopericyclic Model[1]

Sir:

Perfluorotetramethyl (Dewar thiophene) *exo*-*S*-oxide (**1**) undergoes a remarkably facile degenerate rearrangement ($\Delta H^{\ddagger} = 6.6$ kcal/mol).[2,3] The small barrier has been interpreted by Lemal and co-workers[2,3] to exclude both a four-electron pericyclic [1,3]-sigmatropic shift and a biradical process as the reaction mechanism.[4] A six-electron process was proposed instead in which the endocyclic lone pair on sulfur participates nucleophilicly, with the result that bonding and nonbonding orbitals on sulfur interchange roles. The concept was generalized and the suggestion made that such transformations be designated as *pseudopericyclic.*[2]



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We point out that the quantum mechanical distinction between a "four-electron" pericyclic and a "six-electron" pseudopericyclic transition state is not clear-cut. This conclusion follows from the fact that the pericyclic-shift MO's of Figures

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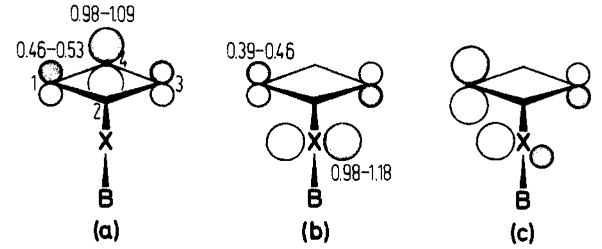
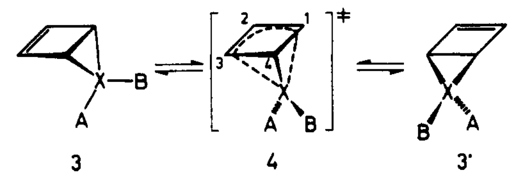


Figure 1. (a, b) PRDDO-Boys and CNDO/2-ER LMO's for pericyclic transition states **4**.[13] Mulliken atomic populations in the PRDDO-Boys calculations for **4a–f** are shown. (c) For **4d**, the Boys localization mixes the endo lone pair on O with LMO (b) to give the LMO shown plus its mirror image.

1a,b can be transformed, *without changing the total wave function*, into an equivalent set of localized MO's in which three (pseudopericyclic)—rather than two (pericyclic)—MO's "carry" the electronic reorganization. The requisite transformation mixes the C_1-X-C_3 orbital (Figure 1b) with the endocyclic lone pair on X to produce localized C_1-X and X-C_3 orbitals (similar to Figure 1c and its mirror image) *qualitatively* appropriate for describing the forming and breaking X-C bonds of the pseudopericyclic transition state. (In either case, Figure 1a describes the migration of the π bond.) The two models therefore represent limiting extremes along a *mechanistic continuum*. The real distinction concerns the quantitative (not qualitative) nature of the MO's and rests largely on the extent to which the endocyclic lone pair can be rigorously localized on X in the transition state (limiting pericyclic) or, conversely, interacts in a *net bonding fashion* with the symmetric π-allyl MO's, thereby making the X-$C_{1,3}$ interactions more than the half-bonds of the pericyclic model (increasing pseudopericyclic character).

To examine the question raised by Lemal et al. from this perspective, we have computed the minimum-energy antarafacial pathways between model systems **3a–f** and **3′a–f** (cf. Table I) at the approximate ab initio PRDDO[6a] level via the synchronous-transit[6b] technique. End-point structures were first generated by complete MINDO/3 geometry optimization,[7,8] and PRDDO LST pathways were constructed between **3** and **3′**. PRDDO midpoint structures **4** were then optimized in C_s symmetry, and three-point-interpolation QST pathways were constructed.



3 **4** **3′**

To characterize the changes in electronic structure, PRDDO-Boys localizations[9] were performed for several structures on the QST pathways for **3a–f** → **3′a–f**, and CNDO/2-Edmiston-Ruedenberg localizations[10] were carried out for transition states **4a–f** and for the analogous sulfur-containing species **4g–i**,[11] where A-X-B = :S:, :S$^+$-O$^-$, and O$^-$-S$^+$:, respectively. With one exception, the calculations showed the lone pairs on **3b–i** to be transformed without change on going to transition states **4**[12] and produced the pericyclic shift LMO's shown in Figures 1a,b.[13] For **4d** (A-X-B = :O:) the PRDDO-Boys (but not the CNDO/2-ER) localization mixed the endocyclic lone pair on O with the antisymmetric pericyclic-shift MO to yield somewhat delocalized O-C_1 and O-C_3 LMO's (Figure 1c). This result, anticipated above, is, however, consistent with the known preference of the Boys criterion (maximal separation of orbital centroids) for equivalent "τ" (Figure 1c) over "σ,π" structures[9] and does not indicate significant lone-pair involvement in the electronic reorganization. Generation of the pericyclic-shift "σ,π" structure for **4d** as a saddle point on the Boys surface showed this structure to be nearly as well localized and produced an essentially rigorously localized endo lone pair on O.

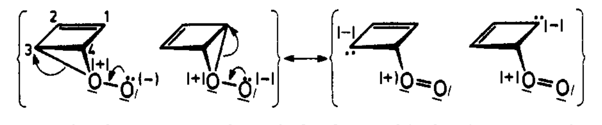
Table I. PRDDO Results for Rearrangement of Bicyclopentenes **3** via Antarafacial Transition States **4**

3	A-X-B	valency of X[a] 3	valency of X[a] 4	X-C index,[b] 4	θ[c]	ΔE(4-3)[d]
3a	H-C-H	3.98	3.99	0.48	95.2	78.9
3b	:N-H	3.00	3.03	0.50	80.7	68.3
3c	H-N:	3.03	2.98	0.47	97.3	87.5
3d	:O:	2.07	2.10	0.50	76.3	75.9
3e	:O$^+$-O$^-$	2.68	2.62	0.27	88.4	31.7
3f	O$^-$-O$^+$:	2.68	2.50	0.20	113.0	43.5

[a] APS valency of X calculated over Lowdin OAO's as described in ref 14. [b] X-C_1 and X-C_3 APS bond index in **4**. [c] Puckering angle in **4** (cf. Figure 2a). [d] In kilocalories/mole.

Furthermore, as Table I shows, the automerizations of the lone-pair-containing species **3b–d** resemble that of the lone-pair-free hydrocarbon **3a**, which serves as our pericyclic-shift model, both energetically and in other important respects. In particular, the presence of an endo lone pair on X in **3b** and **3d** produces only a small increase (~0.03) in the calculated Armstrong-Perkins-Stewart (APS)[14] valency at X and only slightly strengthens the X-$C_{1,3}$ interaction in **4** as measured by the APS bond indices. The large changes implied by the pseudopericyclic model are not observed in these systems.

The *O*-oxide systems **3e** and **3f**, on the other hand, behave quite differently. While the PRDDO minimum-basis-set barriers evidently are much too large, the calculated lowering of the barrier for *exo-O*-oxide **3e** relative to that for the Dewar furan **3d** clearly parallels that observed experimentally for *exo-S*-oxide **1** ($\Delta H^{\neq}$ = 6.6 kcal/mol) relative to the parent Dewar thiophene (ΔH = 18.8 kcal/mol).[3] We suggest that these facilitations arise primarily from a *preferential stabilization* of the transition state (**2** or **4e**) relative to **1** or **3e** by the *exo-oxide substituent*. Thus, as depicted below, **4e** can substitute O-O π bonding for the weak, strained O-$C_{1,3}$ bonding.



As a result, the computed APS O-O bond index increases from 0.86 e in **3e** to 1.14 e in **4e**, the O-$C_{1,3}$ bond index falls substantially relative to that in **4d**, and the puckering angle, θ, opens, relieving angle strain at C_4 (cf. Table I).

The observation that exo orientation of the substituent H on N in **4b,c** or O$^-$ on O$^+$ in **4e,f** lowers the PRDDO barrier by 12–19 kcal/mol suggests the operation of an additional factor.[15] As Figure 2 shows, **4b** and **4c** differ significantly in their N-$C_{1,3}$ distances and in the associated puckering angles θ_{4b} and θ_{4c}. We attribute this difference to a combination of the endo-H-$C_{1,3}$ nonbonded repulsion in **4c**, which increases θ_{4c}, and to the exo-H-N-C_4-H nonbonded repulsion between

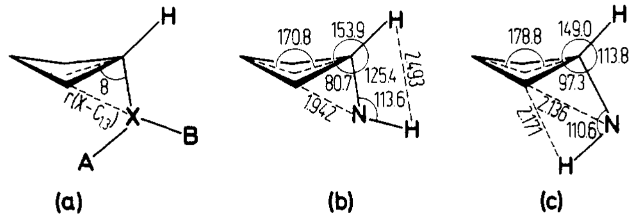


Figure 2. (a) Puckering angle θ; (b, c) PRDDO optimized structures for **4b** and **4c** (angles in degrees, distances in ångstroms). The sum of the H- -H and C- -H van der Waals radii are, by comparison, 2.40 and 2.90 Å,[20] respectively.

cis hydrogens in **4b**, which decreases θ_{4b}. Better N-$C_{1,3}$ overlap is thus achieved, and the pericyclic shift is facilitated. The same factor apparently operates in the *O*-oxides, and presumably in the *S*-oxides as well.[16]

In summary, we find no evidence in the bicyclo systems **3b–i** for the lone-pair participation implied by the pseudopericyclic concept. The idea that pericyclic transformations may experience secondary perturbations by nonbonding electrons, or conceivably may be strongly influenced by electron-deficient centers,[2,18] nevertheless appears to be a useful one. However, it needs to be appreciated that such effects, in general, can be expected to express themselves strongly only in special cases. In the systems considered here, the pseudopericyclic concept is redundant and possibly misleading.

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(11) Obtained from PRDDO-optimized **4d–f** by incrementing the C–O and O–O bonds: **4g**, r_{C-S} = 1.819; **4h,i**, r_{C-S} = 1.822, r_{S-O} = 1.483 Å. Variations of the C–S–O bond angle produced no significant changes in the LMO populations.

(12) Interestingly, the canonical (delocalized) MO eigenvalues indicated that the endo lone pairs are destabilized relative to exo lone pairs without any compensating drop in the π_s(allyl) orbital of the same symmetry. For example, the (π + n) S and A combinations for **4b** and **4c** are split by 3.47 and 3.43 eV, respectively.

(13) For **4a–c,e,f**, The Boys localization actually yields somewhat asymmetric versions of the LMO's shown in Figures 1a,b. Analysis shows, however, that this asymmetry is a mathematical artifact of the Boys criterion and is of no chemical significance.

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(15) The orientation of the substituent principally affects the transition-state energy. Thus, the PRDDO and MINDO/3 energies for **3b,c** and **3e,f** differ by only 0.2–3.1 kcal/mol.

(16) To more fully examine the sulfur-containing systems, semiempirical MNDO[17]-optimized structures were determined for **3a–i** and **4a–i**. More facile rearrangements were indeed predicted for the *exo*- and *endo*-*S*-oxides [ΔE(**4–3**) = 18.4 and 17.0 kcal/mol] than for Dewar thiophene (ΔE = 32.9 kcal/mol), and rearrangement of exo-NH 3b (ΔE = 44.7 kcal/mol) was favored over that of endo-NH **3c** (ΔE = 55.3 kcal/mol). Unfortunately, certain results pertaining to the analogous oxygen systems seem implausible. Thus, further computational study of the relationship between the S and O rearrangements will have to be deferred until more sophisticated methods can be employed.

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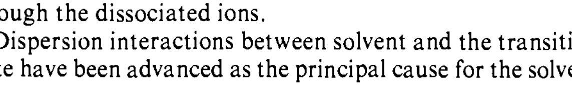
Decarboxylation Reactions: Reactivity of a Free Carboxylate Anion in Ethereal Solvents

Sir:

Because of their biological significance and synthetic prominence, decarboxylation reactions have been extensively studied in both protic and aprotic media. Studies by Verhoek et al.[1-3] showed that, in water mixtures with dioxane or alcohol, acids such as trinitrobenzoic acid or trichloroacetic acid decompose through the free carboxylate anion. More recent work by Kemp et al.[4,5] has demonstrated the unusually high solvent sensitivity of the decarboxylation of the tetramethylguanidinium (TMG) salt of benzisoxazole-3-carboxylic acids (I). This solvent sensitivity was also noticed by Hunter et al.[6] in crown ether induced decarboxylations of alkali salts of triphenylacetic acid and other carboxylic acids. In the latter system, ion pairing was found to be important since the reaction appears to proceed through the dissociated ions.

Dispersion interactions between solvent and the transition state have been advanced as the principal cause for the solvent sensitivity of the decarboxylation of benzisoxazole-3-carboxylates in aprotic media.[4] Similarities were noted in the solvent effects reported by Parker[7] for anionic reactants, although evidence was found that in the less polar solvents ion pairing of the TMG salt of I contributed to its reactivity in these solvents. In a recent study[8] on the decarboxylation of crown ether and cryptand complexes of the potassium salt of 6-nitrobenzisoxazole-3-carboxylic acid (II), we showed that the rate constant of the cryptated ion pair in benzene is nearly three orders of magnitude higher than the decarboxylation rate constant previously reported for the TMG^+ salt of II. It approaches the rate constant found for the latter salt in Me_2SO, suggesting that ion pairing plays a major role in determining the reactivity of these carboxylates in less polar solvents. We have now been able to determine the absolute rate constant of the free carboxylate anion of II in ethereal solvents. The results imply that the solvent effects in media such as benzene, tetrahydrofuran, and glymes are almost exclusively caused by ion pairing, the free ion rate constant of II in THF being even higher than in hexamethylphosphoramide.

In tetrahydrofuran, acid II itself slowly decomposes to form 2-cyano-5-nitrophenol, a product which can be monitored spectrophotometrically at 340 nm. However, while in benzene the decarboxylation kinetics for the crown complexed alkali carboxylates are perfectly first order,[8] a ln C_0/C vs. *t* plot for acid II in THF and other ethers curves upward. The reaction



II