in the presence of a base (pyridine).[12]

Interestingly, the olefination of alkylidenemalonates[2d] with the 1,1-bimetallics **2** is also possible and the reaction of diethyl benzylidenemalonate (0.9 equiv) with **2a** in the presence of acetic anhydride (5 equiv, 25 °C, 0.5 h) gives cleanly 1-phenyl-1-nonene (78%; *E*/*Z* 65/35).

In summary, we have shown that zinc and zirconium heterobimetallic reagents of type **2** and **5** can be readily prepared by hydrozirconation. The reaction of organometallics **2** with aldehydes produces *with high stereoselectivity* (*E*)-disubstituted olefins whereas ketones give a *E*/*Z* mixture of stereoisomers. These new zinc and zirconium 1,1-bimetallic reagents show a good functional group compatibility and should become useful reagents for organic synthesis. The determination of the structure and the synthetic scope of these reagents is underway in our laboratories.[13]

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Supplementary Material Available: Spectra for new compounds (17 pages). Ordering information is given on any current masthead page.

(12) Strauss, D. A.; Grubbs, R. H. *Organometallics* **1982**, *1*, 1658.
(13) Presented in part at the ACS 1991 Joint-Central-Great Lakes Regional meeting, May, 1991, and at the OMCOS 6 meeting (Utrecht, The Netherlands, August 1991).

Electron Transfer vs Polar Mechanisms. Transition-State Structures and Properties for Reactions of a Cation Radical and a Nucleophile

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In response to the intense interest in the mechanistic dichotomy of polar vs electron transfer (ET) pathways in organic reactions,[1] and in a followup to our recent analysis of this dichotomy in reactions of radical ions,[2] we present for the first time ab initio computations of *the isomeric polar and ET transition states* for a nucleophile–electrophile pair modeled by H_2S and $C_2H_6^{\bullet+}$, the latter being in its one-electron σ-bond structure,[3] in eqs 1 and 2.[4] The computations show that the ET-TS does not follow the outer-sphere paradigm but is *inner-sphere and stereoselective* much like its isomer TS of the substitution (SUB-TS) pathway!

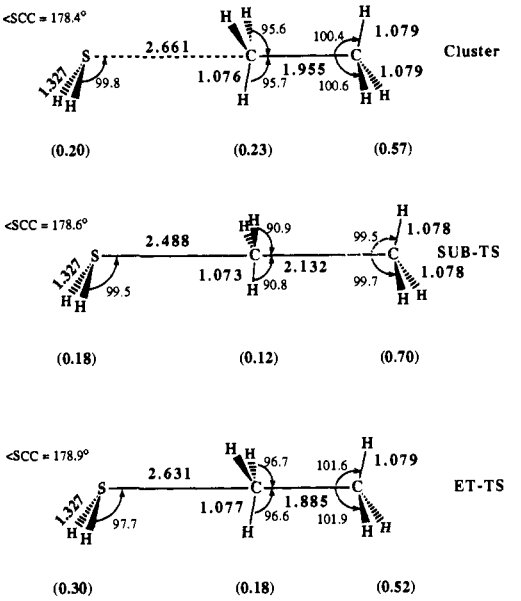
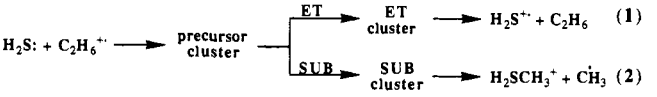


Figure 1. 3-21G*(p) optimized geometries for baskside precursor cluster, substitution TS (SUB-TS), and electron transfer TS (ET-TS). Group spin densities are shown in parentheses below their respective fragments. The $\langle S^2 \rangle$ values are 0.771 (Cluster), 0.775 (SUB-TS), and 0.773 (ET-TS).



The various species in eqs 1 and 2 were computed with the GAUSSIAN 86 and 88 series of programs,[5] using a 3-21G*(p) basis set. The basis set is the standard 3-21G* augmented with first-row polarization functions, taken from the 6-31G* basis set,[6] in order to achieve equivalent cation radical geometries obtained with the latter basis set.[7] Isotope effects were computed with Eyring's equation and analyzed in terms of the contributing components: masses and moments of inertia, excitation, and zero-point energy.[8] All geometries were gradient optimized at the UHF level and characterized by frequency analysis. The interconnection that exists between the critical points in a given pathway were ascertained following ref 9.

The UHF/3-21G*(p) optimized geometries and group spin densities of the lowest energy transition states for the ET and SUB pathways and their *common* ancestor precursor cluster are shown in Figure 1. Table I shows[10] corresponding energetics and

(1) For a sample of leading references, see: (a) Eberson, L. *Electron Transfer Reactions in Organic Chemistry*; *Springer Verlag*: Heidelberg, 1987. (b) Bank, S.; Noyd, D. A. *J. Am. Chem. Soc.* **1973**, *95*, 8303. (c) Pross, A. *Acc. Chem. Res.* **1985**, *18*, 212. (d) Kochi, J. K. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1227. (e) Chanon, M.; Tobe, M. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 1. (f) Chanon, M. *Bull. Chim. Soc. Fr.* **1982**, *209*. (g) Newcomb, M.; Curran, D. P. *Acc. Chem. Res.* **1988**, *21*, 206. (h) Ashby, E. C. *Acc. Chem. Res.* **1988**, *21*, 414. (i) Verhoeven, W. J.; Gersheim, W. V.; Martens, F. M.; van der Kerk, S. M. *Tetrahedron* **1986**, *42*, 975. (j) Lund, T.; Lund, H. *Tetrahedron Lett.* **1986**, *27*, 95. Lund, T.; Lund, H. *Acta Chem. Scand.* **1988**, *B42*, 269.
(2) Eberson, L.; Shaik, S. S. *J. Am. Chem. Soc.* **1990**, *112*, 4489.
(3) The one-electron bond structure of $C_2H_6^{\bullet+}$ is not the global minimum. See: Clark, T. *J. Am. Chem. Soc.* **1988**, *110*, 1672.
(4) For polar and ET pathways in radical cation chemistry, see: (a) Dinnocenzo, J. P.; Todd, W. P.; Simpson, T. R.; Gould, I. R. *J. Am. Chem. Soc.* **1990**, *112*, 2462. (b) Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1989**, *111*, 8. (c) Tholmann, D.; Grutzmacher, H.-Fr. *Chem. Phys. Lett.* **1989**, *163*, 225. (d) Tholmann, D.; Grutzmacher, H.-Fr. *Org. Mass. Spectrom.* **1989**, *24*, 439. (e) Hammerich, O.; Parker, V. D. *Adv. Phys. Org. Chem.* **1984**, *20*, 55. (f) Eberson, L.; Nyberg, K. *Acta Chem. Scand.* **1978**, *B32*, 235.
(5) (a) Frisch, M. J.; Binkley, J. S.; Schlegel, H. B.; Raghavachari, K.; Melius, R.; Martin, L.; Stewart, J. J. P.; Bobrowicz, F. W.; Rohlfing, C. M.; Kahn, L. R.; DeFrees, D. J.; Seeger, R.; Whiteside, R. A.; Fox, D. J.; Fluder, E. M.; Pople, J. A. *Gaussian 86*; Gaussian, Inc.: Pittsburgh, PA 15213. (b) Frisch, M. J.; Head-Gordon, M.; Schlegel, H. B.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A. Seeger, R.; Melius, R.; Baker, J.; Martin, R.; Stewart, J. J. P.; Fluder, E. M.; Topiol, S.; Pople, J. A. *Gaussian 88*; Gaussian, Inc.: Pittsburgh, PA 15213.
(6) (a) 3-21G*: Pietro, W. J.; Francl.; M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039. (b) 6-31G*: Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1982**, *77*, 3654.
(7) (a) Bouma, W. J.; Poppinger, D.; Radom, L. *Isr. J. Chem.* **1983**, *23*, 21. (b) Bellville, D. J.; Bauld, N. L. *J. Am. Chem. Soc.* **1982**, *104*, 5700.
(8) (a) Bigeleisen, J.; Wolfsberg, M. *Adv. Chem. Phys.* **1958**, *1*, 15. (b) Halevi, E. A. *Prog. Phys. Org. Chem.* **1963**, *1*, 109. (c) Melander, L.; Saunders, W. H. *Reaction Rates of Isotopic Molecules*; Wiley: New York, 1980.
(9) Williams, I. H.; Miller, A. B.; Maggiora, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 530.
(10) (a) Dinnocenzo, J. P. Private compilation of thermochemical data. (b) Meot-Ner, M.; Karpas, Z.; Deakyne, C. A. *J. Am. Chem. Soc.* **1986**, *108*, 3915. (c) Turner, D. W.; Baker, C.; Baker, A. D.; Brundle, C. R. *Molecular Spectroscopy*; Wiley: New York, 1970.

0002-7863/91/1513-9890$02.50/0

Table I. Computed Energetics and Isotope Effects for the Substitution (SUB) and Electron Transfer (ET) Pathways in Equations 1 and 2[a]

reaction	$-\Delta E_{rxn}$	$\Delta E^{\ddagger}$(c,c)[c]	$\Delta G^{\ddagger}$(c,c)[c]	$\Delta S^{\ddagger}$[e]	α-D[e,f]	β-D[e,f]
SUB	26.3; 33 ± 3[b]	0.53; 0.071[d]	0.53	−27.9	0.582	1.080
					(0.679)	(1.062)
ET[g]	22.5; 24 ± 2[b]	0.05; 0.104[d]	0.72	−18.7	0.634	0.837
					(0.730)	(0.893)

[a] Energies in kcal/mol and entropies in eu. All thermodynamic quantities and isotope effects refer to a standard state of an ideal gas at 1 atm and T = 298.15 K. [b] Experimental ΔH° datum, based on data in ref 10. [c] Central barriers between precursor cluster and product cluster. [d] ZPE (scaled by 0.9) is included. [e] These quantities refer to the overall step from reactants to the TS. [f] α-D refers to the CH_3/CD_3 group in the α position to the nucleophile. β-D refers to the terminal CH_3/CD_3 group. Values in parentheses are obtained with *frequencies* scaled by 0.8. [g] ET without change in the original structures is endothermic by 28.25 kcal/mol at the cluster geometry and 22.5 kcal/mol at the geometry of the separated reactants.

deuterium isotope effects for the two pathways.

An important feature in Figure 1 is the clear stereochemical identities[11] of the two transition states, both belonging to the backside variety. Frontside type structures were found to be significantly higher in energy. For the ET pathway this stereospecificity is inconsistent with the idealized outersphere ET mechanism[1a] and points to a *significant innersphere character* as predicted recently on the basis of a curve-crossing analysis.[2]

Indeed, all the features of the ET-TS in the figure and table project the innersphere character of this TS. First, the spin density is delocalized and indicates significant orbital interaction between the nucleophilic and electrophilic portions of the TS. This is verified by the delocalized MO's of the species as well as by Hoffmann's fragment orbital analysis,[12] which shows a significant and dominant interaction between the HOMO (H_2S) and the SOMO ($C_2H_6^{\bullet+}$). Second, the *unusually inverse* α-D isotope effect, Table I, is dominated by bending-type modes (wagging and twisting) of the α-CH_3/CD_3 group, as expected from a "tight" TS, in the area of S_N2 TS's.[8b,13]

The entropy of activation $\Delta S^{\neq}$ serves normally as a potent mechanistic probe of polar vs ET pathways.[14] Surprisingly, $\Delta S^{\neq}$(ET) is seen to be more negative than the corresponding quantity for the SUB (polar) mechanism, contrary to what is observed in some cases and generally expected. A component analysis of $\Delta S^{\neq}$ reveals that it is the vibrational contribution which dominates the trend, $\Delta S^{\neq}$(ET) < $\Delta S^{\neq}$(SUB). The *molecular origin of this effect is the shorter bond in the ET-TS* which possesses thereby fewer accessible vibrational degrees of freedom. It seems worthwhile therefore to explore whether the opposite trend observed in ET-polar reactions of radical anions and alkyl halides does not have other origins than the postulated[14] outersphere character of the ET-TS.

Comparing the isotope effects in Table I, the largest qualitative difference is observed in the β-D isotope effect which is inverse for the ET pathway but normal for the SUB pathway. Consistent with Streitwieser's analysis,[15] this difference was found to originate in the bending-type modes of the terminal β-CH_3/CD_3 group whose frequencies increase in the ET-TS but decrease in the SUB-TS. These trends in the frequencies reflect the short C–C bond of the ET-TS as opposed to the long C–C bond in the SUB-TS (Figure 1). Indeed if it were possible to measure isotope effect, the total (α and β) effect for the ET reaction would still be inverse, while for the SUB reaction a resolution of the isotope effect would have revealed the inverse α effect as opposed to the normal β effect. Thus, the β-D isotope effect is a possible *probe of TS structure for the ET and SUB mechanisms* in our example. The applicability of this probe may carry over to other cases as well.[16]

Thus, our modeling of the polar-ET dichotomy projects an important conclusion, that the ET-TS, in organic reactions of radical cations,[2] may well possess a definite structure and robust stereochemistry which may be probed. This conclusion joins similar evidence in the literature.[2,17] and while many efforts have focused on the ET-polar dichotomy in reactions with an even number of electrons in the nucleophile and electrophile,[1a–c,g–j,18] it is in the area of odd-electron reactions[2] where possibilities lie in eventually basing the structure of the ET-TS on principles of bonding in common with the "conventional" TS's of polar mechanisms.

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Registry No. H_2S, 7783-06-4; $C_2H_6^{\bullet+}$, 34488-65-8; D_2, 7782-39-0.

(11) Shaik, S. S.; Dinnocenzo, J. P. *J. Org. Chem.* **1990**, *55*, 3434.
(12) Libit, L.; Hoffmann, R. *J. Am. Chem. Soc.* **1974**, *96*, 1370.
(13) (a) Gray, C. H.; Coward, J. K.; Schowen, K. B.; Schowen, R. L. *J. Am. Chem. Soc.* **1979**, *101*, 4351. (b) Wong, O. S.-L.; Schowen, R. L. *J. Am. Chem. Soc.* **1983**, *105*, 1951. (c) Harris, J. M.; Paley, M. S.; Prasthofer, T. W. *J. Am. Chem. Soc.* **1981**, *103*, 5915. (d) Rodgers, J.; Femec, D. A.; Schowen, R. L. *J. Am. Chem. Soc.* **1982**, *104*, 3263.
(14) (a) Daasberg, K.; Pedersen, S. U.; Lund, H. *Acta Chem. Scand.* **1991**, *45*, 424. (b) Lexa, D.; Saveant, J.-M.; Su, K.-B.; Wang, D.-L. *J. Am. Chem. Soc.* **1988**, *110*, 7617.
(15) Streitwieser, A., Jr.; Jagow, R. H.; Fahey, R. C.; Suzuki, S. *J. Am. Chem. Soc.* **1958**, *80*, 2326.
(16) Yamataka, H.; Matsuyama, T.; Hanafusa, T. *J. Am. Chem. Soc.* **1989**, *111*, 4912.
(17) (a) Eberson, L. *New J. Chem.* **1991**, in press. (b) Stanbury, D. M.; DeMaine, M. M.; Goodloe, G. *J. Am. Chem. Soc.* **1989**, *111*, 5496. (c) Stanbury, D. M.; Martinez, R.; Tseng, E.; Miller, C. E. *Inorg. Chem.* **1988**, *27*, 4277. (d) Benauer, K.; Monzione, M.; Schurmann, P.; Viette, V. *Helv. Chim. Acta* **1987**, *91*, 401. (e) Ohta, K.; Morokuma, K. *J. Phys. Chem.* **1987**, *91*, 401.
(18) In reactions with an even number of electrons the ET-TS is enforced to be outersphere. See: Shaik, S. S. *Acta Chem. Scand.* **1990**, *44*, 205.

Timing and Mechanistic Implications of Regiospecific Carbonyl Oxygen Isotope Exchange during Vitamin B_{12} Biosynthesis

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It has recently been shown[1] by ^{18}O labeling that during the biosynthesis of vitamin B_{12} (**1**; cyanocobalamin) almost complete $^{18}O/^{16}O$ exchange of the carbonyl oxygen of one of the three acetamido groups takes place, a result which has profound bearing on the mechanism of corrin biosynthesis. Thus in one hypothesis[2] δ-lactone formation from the ring-A acetate group (C-27) to C-20 has been proposed to rationalize the ring contraction of the

(1) Kurumaya, K.; Okazaki, T.; Kajiwara, M. *Chem. Pharm. Bull.* **1989**, *37*, 1151.
(2) Eschenmoser, A. *Angew. Chem., Int Ed. Engl.* **1988**, *27*, 6–39 and references cited therein. The mechanism suggested for the ring-contraction step is a stereoelectronically dictated dyotropic 1,2-migration of antiperiplanar groups within the dilactonic ensemble.

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