

S-2

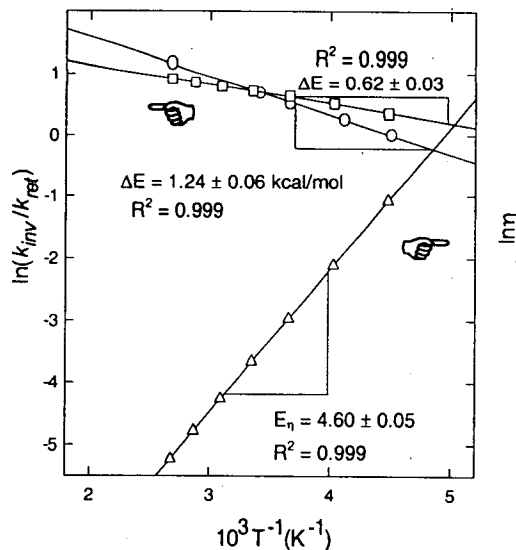


Figure S-1. Arrhenius plots (E in kcal/mol) of the k_{inv}/k_{ret} ratio in the photolysis of the azoalkanes **1a** (\square) and **1c** (\circ) and of the *n*-butanol (Δ) viscosity (η in P) [cf. Fig. 2 in ref 5a].

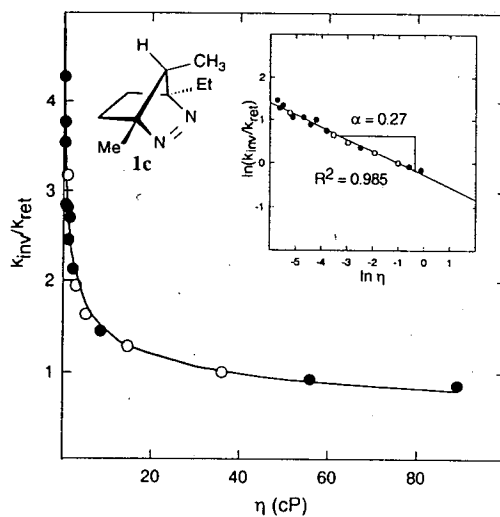


Figure S-2. Viscosity dependence of the k_{inv}/k_{ret} ratio for the photolysis of azoalkane **1c** as a function of solvent (\bullet) and temperature in *n*-butanol (\circ); the insert displays the double-logarithmic dependence (η in P) [cf. Fig. 1 in ref 5b].

S-3e

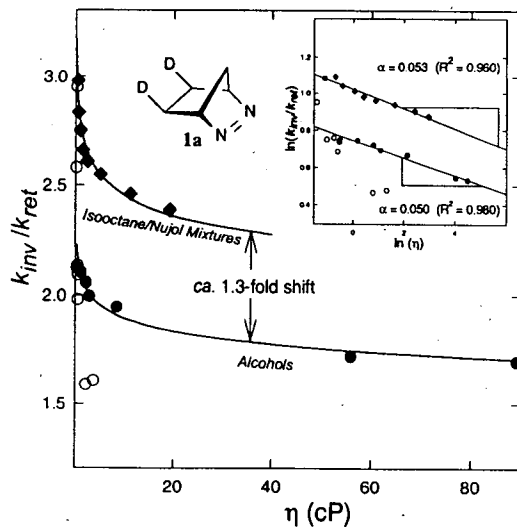


Figure S-3. Viscosity dependence of the k_{inv}/k_{ref} ratio in the DBH (**1a**) photolysis ($\lambda = 333$ nm) for alcohols (\bullet), isooctane/nujol mixtures (\blacklozenge) and aprotic solvents of different polarity (\circ) [cf. Fig. 1 in ref 5d].

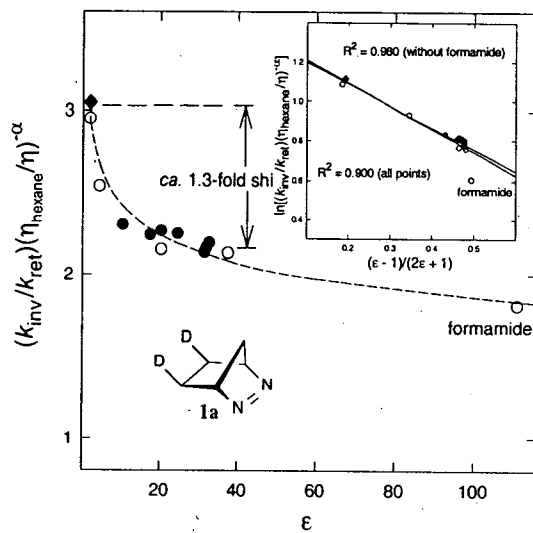


Figure S-4. Isoviscosity plot of the k_{inv}/k_{ref} ratio for the DBH (**1a**) photolysis ($\lambda = 333$ nm) in alcohols (\bullet), isooctane/nujol mixtures (\blacklozenge), and aprotic solvents (\circ) [cf. Figs. 2 and 3 in ref 5d].

S-4e

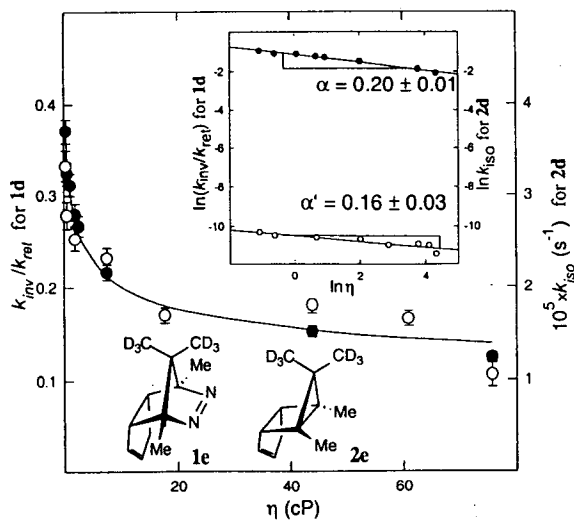


Figure S-5. Viscosity dependence for the k_{inv}/k_{ret} ratio (*cf.* Scheme 2) of the azoalkane (**1e**) photolysis (●) and k_{iso} for the thermal *syn*-to-*anti* isomerization of housane **2e** (○); the insert displays the respective double-logarithmic plots (*cf.* Fig. 1 in ref 5e).

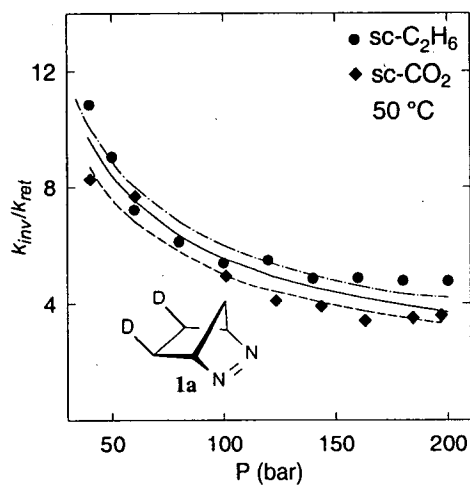


Figure S-6. Pressure dependence of the k_{inv}/k_{ret} ratio for the photolysis ($\lambda = 333$ nm) of DBH (**1a**) in *sc*-CO₂ (◆) and *c*-C₂H₆ (●) solid line refers to all data points together (*cf.* Fig. 1 in ref. 5c).

S-5-e

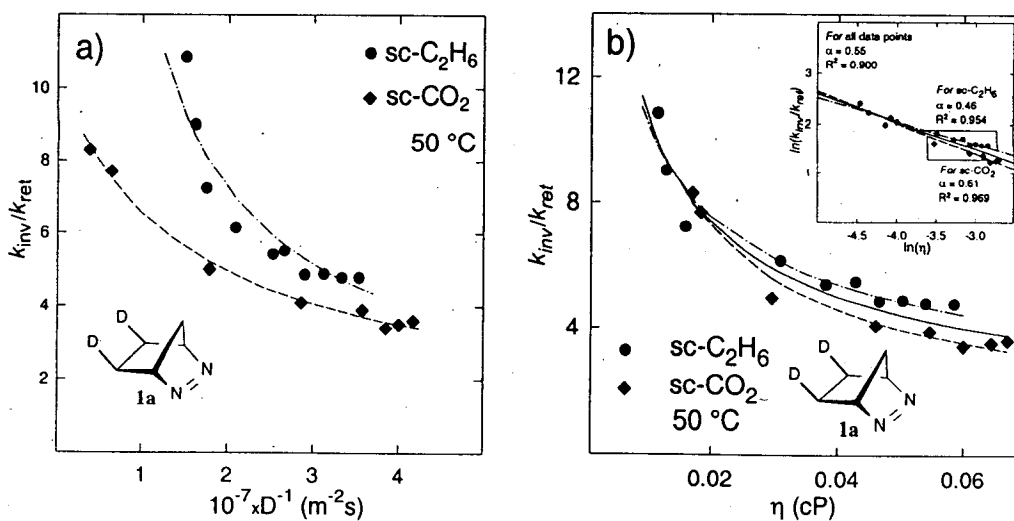


Figure S-7. Dependence of the experimental k_{inv}/k_{ret} ratio on the inverse of the self-diffusion coefficient (a) and on the viscosity (b) in $sc-CO_2$ (\blacklozenge) and $sc-C_2H_6$ (\bullet) for the photolysis ($\lambda = 333$ nm) of DBH (**1a**); the solid line refers to all data points and the insert displays the respective double-logarithmic plots (cf. Figs. 2 and 3 in ref 5c).

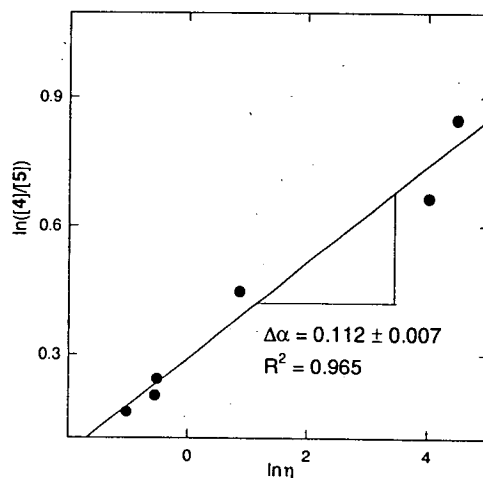


Figure S-8. Double-logarithmic plot for the viscosity dependence of the $[4]/[5]$ ratio in the electron-transfer-induced rearrangement of housane **3** (cf. Fig. 1 in ref 6a).