later, the reaction was filtered through a Celite pad into 100 mL of 20% aqueous citric acid solution. The pad was washed with 50 mL of THF and the filtrate also added to the 20% aqueous citric acid solution. After being stirred for 10 min, the organic phase was separated and the aqueous extracted with EtOAc/THF (100 mL, 1:1). The combined organic phase was dried ($MgSO_4$), filtered, and evaporated to yield the crude product contaminated by citric acid and benzaldehyde. Silica gel flash chromatography of this crude product provided 0.96 g (54%) of (–)-1; mp 168–169 °C; $R_f$ (1/9 MeOH/$CHCl_3$) = 0.48; $[\alpha]^{30}_D = -58.9°$ ($c$ = 1.0, methanol); 99% ee; $^1H$ NMR ($d_6$-DMSO) same as (±)-(1); FDMS (DMSO) $m/e$ 323, 325 ($M^+$). Anal. Calcd for $C_{14}H_{14}Cl_1N_3O_2S_1$: C, 51.93; H, 4.36; N, 12.98. Found: C, 51.63; H, 4.21; N, 12.81. In a similar manner, 12 (2.50 g, 5.47 mmol) provided 1.05 g (59%) of (+)-1; mp 167–168 °C; $R_f$ (1/9 MeOH/$CHCl_3$) = 0.48; $[\alpha]^{30}_D = +58.8°$ ($c$ = 1.0, methanol); 95% ee; $^1H$ NMR ($d_6$-DMSO) same as (±)-(1); FDMS (DMSO) $m/e$ 323, 325 ($M^+$). Anal. Calcd for $C_{14}H_{14}Cl_1N_3O_2S_1$: C, 51.93; H, 4.36; N, 12.98. Found: C, 52.23; H, 4.20; N, 12.73. The enantiomeric purity of these samples was determined by their individual conversion (DMAP, $Et_3N$, and (–)-menthoxyacetyl chloride in $CH_2Cl_2$) to the diastereomeric amides, which were assayed by HPLC (system B) in duplicate. Chromatographic peak assignments were verified by doping experiments with the diastereomeric amides produced from racemic 1.[19]

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# Additions and Corrections

## Vol. 56, 1991

**Derrick L. J. Clive,* Chengzhi Zhang, K. S. Keshava Murthy, William D. Hayward, and Sylvain Daigneault.** New Low-Valent Titanium Reagents for Dicarbonyl Coupling and Their Use in a General Method of Annulation.

Page 6451, Table III. Entries o to s should refer to titanium tetrachloride and not to titanium trichloride.

## Vol. 57, 1992

**Scott McN. Sieburth* and Louis Fensterbank.** An Intramolecular Diels-Alder Reaction of Vinylsilanes.

Page 5281. The following note was inadvertently omitted.

**Note Added in Proof.** After submission of this manuscript, we learned of a contribution by the Stork group in this area (Stork, G.; Chan, T. Y.; Breault, G. A. *J. Am. Chem. Soc.* **1992**, *114*, 7578–7579). We would like to thank Professor Stork for sharing his manuscript prior to publication.

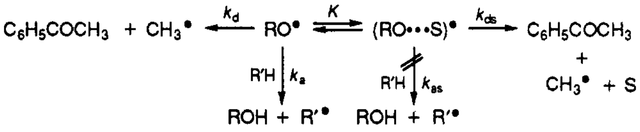
## Vol. 58, 1993

**Sung Soo Kim,* Sung Yeon Kim, Seung Sin Ryou, Choon Seung Lee, and Kwang Hee Yoo.** Solvent Effects in the Hydrogen Abstractions by *tert*-Butoxy Radical: Veracity of the Reactivity/Selectivity Principle.

Pages 192–196. Solvent effects on hydrogen abstractions by cumyloxyl radical have been recently investigated (Avila, D. V.; Brown, C. E.; Ingold, K. U.; Lusztyk, J. *J. Am. Chem. Soc.* **1993**, *115*, 466). The rate constants for the β-scission become larger with increasing solvent polarity, while those of hydrogen abstractions from cyclohexane stay essentially constant.

Those observations can be eminently rationalized by assuming equilibration between solvent-free and solvated cumyloxyl radicals, where the former either abstracts hydrogen from cyclohexane or experiences homolytic fragmentation while the latter solely undergoes β-scission as with Scheme I. The ratio of the products, i.e., 2-phenyl-2-propanol and acetophenone, can be equated with eq 1.

**Scheme I**[a]



[a] Key: $RO^\bullet$, cumyloxyl radical; $(RO\cdots S)^\bullet$, solvated cumyloxyl radical; S, solvent; R'H, cyclohexane; ROH, 2-phenyl-2-propanol; $K$, equilibrium constant; $k_a$ and $k_{as}$, rate constants for the abstractions by solvent-free and solvated cumyloxyl radicals, respectively, with $k_{as}$ negligibly small; $k_d$ and $k_{ds}$, rate constants for β-scission with solvent-free and solvated cumyloxyl radicals, respectively.

$$\frac{\Delta[\mathrm{ROH}]}{\Delta[\mathrm{C_6H_5COCH_3}]} = \frac{k_a[\mathrm{RO^\bullet}][\mathrm{R'H}]}{k_d[\mathrm{RO^\bullet}] + k_{ds}[(\mathrm{RO\cdots S})^\bullet]} \qquad (1)$$

Strong solvation of cumyloxyl radical could render $k_{ds} \gg k_d$ and $[(RO\cdots S)^\bullet] \gg [RO^\bullet]$, whereby eq 1 could be approximated to eq 2. Yield of the alcohol is then also controlled by an equilibrium constant $K$ which may be variable with solvents to disclose vigorous solvent interactions with the hydrogen abstractions. The rate constant for the abstraction involved with product ratio studies by Walling and Wagner may correspond thereby to $k_a/K$ in eq 2.

$$\frac{\Delta[\mathrm{ROH}]}{\Delta[\mathrm{C_6H_5COCH_3}]} = \frac{k_a[\mathrm{RO^\bullet}]}{k_{ds}[(\mathrm{RO\cdots S})^\bullet]}[\mathrm{R'H}] = \frac{k_a}{k_{ds}}\frac{1}{K}[\mathrm{R'H}] \qquad (2)$$

They proposed that only weakly solvated *tert*-butoxy radical should be capable of hydrogen abstraction at the slower rate, which must be kinetically equivalent to the previous equilibration regulating concentration of solvent-free *tert*-butoxy radical, the sole hydrogen abstractor.