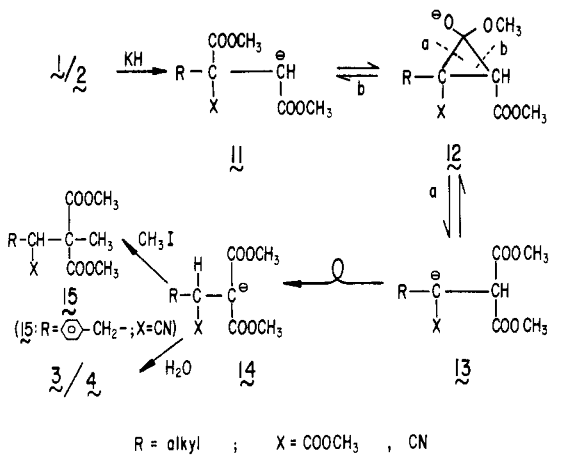
Scheme IV



was completed. To this mixture was added cold dilute hydrochloric acid until the reaction mixture was neutralized. This mixture was extracted several times with ether, and the combined organic layers were washed sequentially with cold sodium bicarbonate, water, and brine and then dried over magnesium sulfate. The solvent was removed. The desired products were obtained in about 80–88% yields. The materials were then used in the KH reactions without further purification. The physical and spectral data for these products are shown in Table I.

General Procedure for the KH Reactions. An excess amount of KH (35% in oil, 3 mmol) was washed several times with petroleum ether in a three-necked round-bottomed flask. After removal of petroleum ether, 3 mL of glyme was added. To this slurry was added dropwise a solution of 1.5 mmol of **1** (or **2**) in 3 mL of glyme. The reaction mixture was stirred at room temperature for 3 h or under reflux for 0.5 h. The resulting solution was then cooled in an ice bath before cold water or methyl iodide (1.7 mmol in 2 mL of glyme) was cautiously added. Workup as described in the above alkylation reactions gave 80–93% yields of essentially pure rearranged products. Table I lists the properties of the rearranged compounds.

Acknowledgment. We thank Drs. M. J. Holm and F. B. Zienty for their helpful discussions and encouragement. We are also indebted to Dr. K. Wood, Mr. R. C. Scheibel, and Mr. R. Fuhrhop for obtaining mass spectra and for valuable discussions.

Registry No. 1 (R = CH_2Ph), 84454-40-0; 2 (R = $CH(CH_3)Ph$), 84454-41-1; 3 (R = CH_2Ph), 84454-42-2; 4 (R = $CH(CH_3)Ph$) (isomer 1), 84454-43-3; 4 (R = $CH(CH_3)Ph$) (isomer 2), 84454-44-4; **6**, 40967-67-7; **7**, 6283-71-2; **8**, 84454-45-5; **9**, 84454-46-6; **10**, 84454-47-7; **15**, 84454-48-8.

Decomposition of *N*,*N*-Dialkylthiadiaziridine 1,1-Dioxides: A Mechanistic Revision

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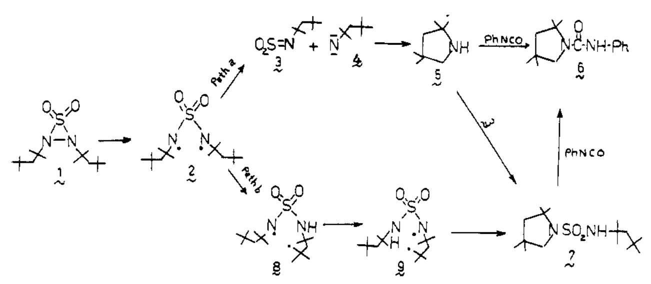
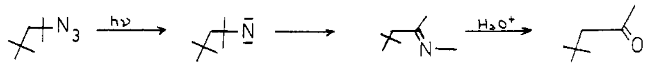
Recently,[1] we reported that the thermal decomposition of di-*tert*-octylthiadiaziridine 1,1-dioxide in benzene or toluene gives rise to a pyrrolidinyl sulfamide (**7**). At that time we thought that while it was possible to conceive of an intramolecular path for formation of this sulfamide (**7**), the fact that urea **6** was formed in presence of phenyl isocyanate provided evidence for the existence of free 2,2,4,4-tetramethylpyrrolidine (**5**). This pyrrolidine was thought to arise from *tert*-octylnitrene (**4**) by γ-hydrogen insertion since similar cyclizations of arylnitrenes and carbonylnitrenes were known[2] and since this *tert*-octylnitrene rearrangement conveniently explained the product distribution.[1] It was recognized, however, that no alkylnitrene insertions of this type had previously been substantiated.[2]

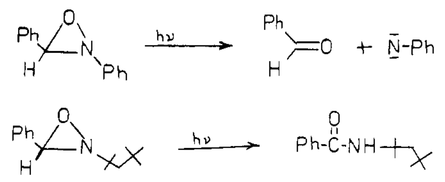
Scheme I



Scheme II



Scheme III



It now appears that the reaction sequence as illustrated in path a of Scheme I may be incorrect. When sulfamide **7** is heated in the presence of phenyl isocyanate under conditions identical with those for its formation, pyrrolidinylurea **6** is formed in 60% yield. Thus the formation of urea **6** is not singularly evidence of the existence free pyrrolidine **5** because sulfamide **7**, once formed, is capable of dissociation, presumably to **3** and **5**, and the latter is trapped by phenyl isocyanate.

In addition, attempts to independently generate *tert*-octylnitrene failed to produce any tetramethylpyrrolidine. For example, irradiation of *tert*-octyl azide in ether followed by aqueous acid workup gave methyl neopentyl ketone as the only isolated product. This is consistent with methyl migration (concerted or from nitrene) to give imine which is hydrolyzed to ketone in the workup (Scheme II) and is a well-known reaction.[3,4]

It has been reported that photochemical decomposition of oxaziridines produce nitrenes[3] (Scheme III). For this reason 3-phenyl-2-*tert*-octyloxaziridine was prepared via peracid oxidation of the imine. However, irradiation of this oxaziridine produced *N*-*tert*-octylbenzamide as the only isolated product.

We conclude that thiadiaziridines probably do not generate alkylnitrenes upon thermolysis but more likely rearrange by an intramolecular pathway, perhaps as indicated in path b in Scheme I.

Experimental Section

Reaction of *N*-(1,1,3,3-Tetramethylbutyl)-*N*-(2,2,4,4-tetramethyltetramethylene)sulfamide with Phenyl Iso-

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[1] Timberlake, J. W.; Alender, J. A.; Garner, A. W.; Hodges, M. L.; Özmeral, C.; Szilagyi, S.; and Jacobus, J. O. *J. Org. Chem.* **1981**, *46*, 2082.

[2] Lwowski, W. "Nitrenes"; Wiley: New York, 1970; pp 47–97.

[3] Splitter, J. S.; Calvin, M. *Tetrahedron Lett.* **1968**, 1445.

[4] Sasaki, T.; Eguchi, S. Katada, T.; Hiroaki, O. *J. Org. Chem.* **1977**, *42*, 3741.

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cyanate. A solution of sulfamide (2.26 g, 7.1 mmol) and phenyl isocyanate (1.1 g, 9.2 mmol) in 50 mL of benzene was heated to reflux and stirred for 72 h. Ethyl alcohol (11.8 g, 256 mmol) was added to react with excess isocyanate, and the solution was allowed to reflux for 1 h. The solvent was evaporated and the residue eluted through a silica gel column with a 1:1 hexane–ether mixture. Three fractions were collected: 1.04 g of unreacted starting material, 0.21 g of ethyl *N*-phenylcarbamate, and 0.64 g (68% yield based on consumed sulfamide) of urea: mp 157.5–158.5 °C (hexane) (lit.[1] mp 158.5–159.5 C); NMR ($CDCl_3$) δ 1.18 (s, 6 H), 1.56 (s, 6 H), 1.79 (s, 2 H), 3.37 (s, 2 H), 7.32–7.46 (s, 5 H).

***tert*-Octyl Azide.** A modification of the literature procedure was employed.[4] Diisobutylene (22.4 g, 0.20 mol) in a mixture of 57% H_2SO_4 (200 mL), $CHCl_3$ (200 mL), and 10 drops of Aliquat 336 was cooled in an ice–water bath. Sodium azide (19.5 g, 0.30 mol) was added over a period of 5 min, and the mixture was stirred for 12 h. The mixture was separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts were washed with H_2O (200 mL), 5% $NaHCO_3$ (200 mL), and H_2O (200 mL) and dried ($MgSO_4$). The solvent was removed to give 31.1 g (100%) of *tert*-octyl azide which was distilled under reduced pressure: 90–92 °C (62 mm); IR (neat) 2100 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 9 H), 1.31 (s, 6 H), 1.52 (s, 2 H). Anal. Calcd for $C_8H_{17}N_3$: C, 61.90; H, 11.04; N, 27.07. Found: C, 61.94; H, 11.08; N, 27.17.

Photochemical Decomposition of *tert*-Octyl Azide. Azide (1.00 g, 6.5 mmol) dissolved in benzene (400 mL) was placed in an Hanovia reactor, degassed with N_2 for 20 min, and irradiated with a 450-W Hg lamp for 1 h. The reaction mixture was extracted with 5% HCl (3 × 100 mL). The HCl extract was made basic with NaOH and extracted with ether (3 × 75 mL). The ether extracts were dried (K_2CO_3) and the ether was removed in vacuo at 0 °C to give 0.39 g (53%) of 4,4-dimethyl-2-pentanone: IR (neat) 1720 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.02 (s, 9 H), 2.06 (s, 3 H), 2.28 (s, 2 H).

The benzene layer was dried (K_2CO_3) and the benzene was removed in vacuo to give a dark oil (0.20 g, 24% based on loss of N_2 from the azide), but no further attempts were made to identify the components of this mixture.

***tert*-Octylbenzaldimine.** Benzaldehyde (22.39 g, 0.211 mol) and *tert*-octylamine (32.25 g, 0.25 mol) were dissolved in benzene (100 mL) and heated to reflux in a flask fitted with a Dean–Stark trap. After the stoichiometric amount of H_2O was collected, the benzene and the excess amine were removed in vacuo. The imine was distilled (0.1 mm, 98–101 °C) to give a light yellow viscous liquid: 39.03 g (85%); IR (neat) 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.95 (s, 9 H), 1.31 (s, 6 H), 1.69 (s, 2 H), 7.3–7.85 (m, 5 H), 8.24 (s, 1 H).

3-Phenyl-2-*tert*-octyloxazirane. Imine (21.70 g, 0.10 mol) was dissolved in benzene (100 mL) and cooled in an ice–water bath. *m*-Chloroperbenzoic acid (22.4 g, 0.13 mol) was added over a 30-min period, and the mixture was allowed to warm to room temperature. After 6 h the reaction mixture was filtered, and the filtrate was washed with saturated K_2CO_3 solution (3 × 100 mL), 5% HCl (100 mL), saturated $NaHSO_3$ solution (100 mL), and water (100 mL) and dried ($MgSO_4$). The solvent was removed in vacuo to give oxazirane: 15.58 g, (67%); IR (neat) 1710 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.01 (s, 9 H), 1.13 (s, 3 H), 1.25 (s, 3 H), 1.69 (s, 2 H), 4.70 (s, 1 H), 7.3–7.5 (m, 5 H). Anal. Calcd for $C_{15}H_{23}NO$: C, 77117; 9.95, N, 6.03. Found: C, 77.01; H, 9.81.

Photochemical Decomposition of Oxazirane. Oxazirane (1.00 g, 4.29 mmol) dissolved in ether (400 mL) was placed in an Hanovia reactor, degassed with N_2 for 20 min, and irradiated with a 450-W Hg lamp for 1 h. The ether was removed in vacuo, and the remaining oil (a mixture of two compounds by TLC) was eluted through a silica gel preparative LC column with 60:40 pentane/ether. The first fraction proved to be starting material, and the second fraction was identified as *tert*-octylbenzamide: mp 70–71 °C (lit.[5] mp 68.5 °C); IR ($CHCl_3$) 3500–3300 (br, s), 1650 (s) cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.04 (s, 9 H), 1.53 (s, 6 H), 1.87 (s, 2 H), 6.0 (s, 1 H), 7.20–7.85 (m, 5 H).

Acknowledgment. We appreciate helpful comments by Professors Fred Greene, Walter Lwowski, and Rudy Abramovich regarding the nature of alkylnitrenes. Financial support was supplied by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the UNO Research Council.

Registry No. 4, 84499-88-7; 7, 76613-37-1; phenyl isocyanate, 103-71-9; *tert*-octyl azide, 35426-97-2; diisobutylene, 25167-70-8; 4,4-dimethyl-2-pentanone, 590-50-1; benzaldehyde, 100-52-7; *tert*-octylamine, 107-45-9; *tert*-octylbenzaldimine, 49707-52-0; 3-phenyl-2-*tert*-octyloxazirane, 61457-73-6; *tert*-octylbenzamide, 34021-55-1.

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(5) Lacey, R. N. *J. Chem. Soc.* **1960**, 1633.

Communications

Verification and Characterization of the E2C Mechanism. The Weak Base Catalyzed Elimination Reaction of β-Phenylethyl Substrates

Summary: Through application of the TDKIE criteria, a bent TS of H transfer has been characterized in the fluoride ion promoted E2C elimination reaction of β-phenylethyl substrates in aprotic solvent. The angle of H transfer of this TS is found to be a sensitive function of the nucleofugal properties of the leaving group.

Sir: The two most prominent proposals[1-5] accounting for the many rate and structural effects observed in weak base catalyzed β-elimination processes are readily distinguished by the geometries of their respective transition states. The Bunnett[5] E2 TS essentially requires linear H transfer between the substrate C_β and the base B; the Winstein–Parker[1-4] E2C-like TS provides for nonlinear H transfer in a rectangular concert of bond making and breaking. Bunnett and others[5] have advanced arguments against the viability of an E2C mechanism based on apparently sound experimental evidence. However, among the manifold criteria that have been applied in the effort (Brönsted equation considerations,[5b,c,6,7] rate–structure correla-

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(1) Winstein, S.; Darish, D.; Holness, N.J. *J. Am. Chem. Soc.* **1956**, *78*, 2915.

(2) de la Mare, P. B. D.; Vernon, C. A. *J. Chem. Soc.* **1956**, 41.

(3) Parker, A. J.; Ruane, M.; Biale, G.; Winstein, S. *Tetrahedron Lett.* **1968**, 2113.

(4) Biale, G.; Cook, D.; Lloyd, D. J.; Parker, A. J.; Stevens, I. D. R.; Takahashi, J.; Winstein, S. *J. Am. Chem. Soc.* **1971**, *93*, 4725.

(5) (a) Bunnett, J. F. *Surv. Prog. Chem.* **1969**, *5*, 53. (b) Eck, D.; Bunnett, J. F. *J. Am. Chem. Soc.* **1969**, 91, 3009. (c) Baciocchi, E.; Bunnett, J. F. *J. Org. Chem.* **1967**, *32*, 11. (d) McLennan, D. J., *J. Chem. Soc. c* **1966**, 705, 709.

(6) Parker, A. J.; Ruane, M.; Palmer, D. A.; Winstein, S. *J. Am. Chem. Soc.* **1972**, *94*, 2228.

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