

Figure 1. A schematic representation of idealized conformations of $(\text{CH}_3)_3\text{Z}$ groups in 1,8-bis(trimethylelement)naphthalenes, viewed down the C(9)–C(10) bond axis: A, **2** ($\text{Z} = \text{Ge}$) and **3** ($\text{Z} = \text{Sn}$); B, **1** ($\text{Z} = \text{C}$). The heavy horizontal line symbolizes the projection of the average plane of the naphthalene ring.

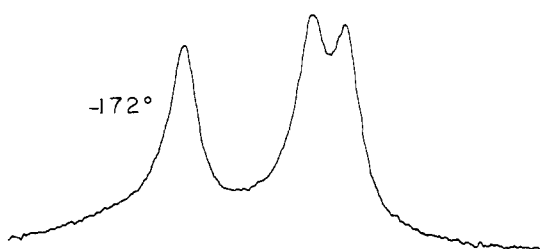


Figure 2. ^1H NMR spectrum (350.25 MHz, methyl region) of **2** in a 2:1 mixture of CHF_2Cl and CF_2Cl_2 at -172°C .

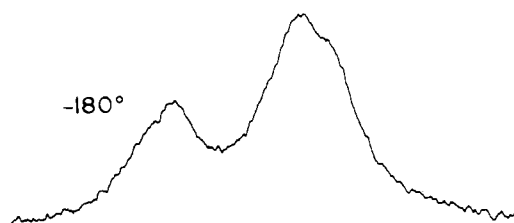


Figure 3. ^1H NMR spectrum (383.74 MHz, methyl region) of **3** in a 2:1 mixture of CHF_2Cl and CF_2Cl_2 at -180°C .

tions of **1**, **2**, and **3** in solution resemble those in the solid state (i.e., if the conformational differences are not merely induced by lattice forces), it can be predicted⁴ that the effect of the naphthalene ring on the chemical shifts of the three diastereotopic methyl groups in **2** and **3** at the slow exchange limit will differ markedly from that in **1**. We now report, first, an experimental verification of this prediction, and, second, the determination, by dynamic NMR, of the energy requirement for torsion about the $(\text{CH}_3)_3\text{Z}$ –C bonds in **2** and **3**.

The ^1H NMR spectrum of **2** near the slow exchange limit (Figure 2) features three singlets in the methyl region, two of which are closely spaced (0.11 ppm) while the third is 0.41 ppm downfield from the center peak. For **3** we were able to resolve only the widely separated (0.43 ppm) chemical shifts, and thus the spectrum appears as a 2:1 doublet with the high intensity component at high field (Figure 3).⁶ The downfield singlet in **2** and **3** is evidently due to the methyl groups which point toward the average plane of the naphthalene ring in conformation A (Figure 1).⁴ In contradistinction, the chemical shifts of the methyl protons in **1** and other substituted 1,8-di-*tert*-butylnaphthalenes exhibit the reverse pattern, corresponding to conformation B (Figure 1), with the downfield and upfield singlets separated from the center singlet by 0.26–0.38 and 0.79–0.80 ppm, respectively.^{1b} The different ground-state conformations (Figure 1) are therefore inherent molecular properties. It seems likely that the significantly greater crowding and internal strain in **1**, as compared with **2** and **3** (to judge by the skeletal deformations⁵), lies at the root of this distinction.

As determined by line shape analysis of the ^1H NMR spectra,⁷ the rate constant for $(\text{CH}_3)_3\text{Z}$ group rotation is 140

s^{-1} for **2** at -160°C and for **3** at -175°C ; $\Delta G^\ddagger = 5.4_5$ and 4.7 kcal/mol for **2** and **3**, respectively. For 1,8-di-*tert*-butylnaphthalenes, the corresponding barriers are ~ 6.5 kcal/mol at ca. -140°C .^{1b} It therefore seems reasonable to expect that the as yet unknown^{2b} 1,8-bis(trimethylsilyl)naphthalene will exhibit a $(\text{CH}_3)_3\text{Si}$ –C rotation barrier of ~ 6.0 kcal/mol, which is precisely the barrier recently predicted by Hutchings and Watt, using an EFF approach.⁸ However, the same calculations⁸ also predict a trend in $(\text{CH}_3)_3\text{Z}$ –C rotation barriers of 4.7, 6.0, and 6.9 kcal/mol for $\text{Z} = \text{C}$, Si, and Sn, respectively, which is the reverse of the trend observed for ΔG^\ddagger (6.5, 5.5, and 4.7 kcal/mol for $\text{Z} = \text{C}$, Ge, and Sn, respectively). The source of this discrepancy remains to be discovered.

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References and Notes

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- (2) (a) Seyferth, D.; Vick, S. C. *J. Organomet. Chem.* **1977**, *141*, 173. (b) Wroczynski, R. J.; Baum, M. W.; Kost, D.; Mislow, K.; Vick, S. C.; Seyferth, D. *Ibid.* **1979**, *170*, C29.
- (3) Cozzi, F.; Sjöstrand, U.; Mislow, K. *J. Organomet. Chem.* **1979**, *174*, C1.
- (4) Blount, J. F.; Cozzi, F.; Damewood, J. R., Jr.; Iroff, L. D.; Sjöstrand, U.; Mislow, K. *J. Am. Chem. Soc.* **1980**, *102*, 99.
- (5) The extent of skeletal distortion may be gauged by the artificial torsion angle $\text{Z}(1)$ – $\text{C}(1)$ – $\text{C}(8)$ – $\text{Z}(2)$ (68.6, 54.3, and 53.1° for $\text{Z} = \text{C}$, Ge, and Sn, respectively), by the average values of $\text{Z}(1)$ – $\text{C}(1)$ – $\text{C}(4)$ and $\text{Z}(2)$ – $\text{C}(8)$ – $\text{C}(5)$ (150.9, 155.8, and 156.3° for $\text{Z} = \text{C}$, Ge, and Sn, respectively), by the average values of $\text{C}(1)$ – $\text{C}(9)$ – $\text{C}(10)$ – $\text{C}(4)$ and $\text{C}(8)$ – $\text{C}(9)$ – $\text{C}(10)$ – $\text{C}(5)$ (19.3, 11.2, and 9.3° for $\text{Z} = \text{C}$, Ge, and Sn, respectively), and by the spread in the $\text{C}(1)$ – $\text{C}(9)$ – $\text{C}(8)$ angle (129.9, 126.1, and 125.6° for $\text{Z} = \text{C}$, Ge, and Sn, respectively).
- (6) The barrier for methyl exchange is lower in **3** than in **2** and as a result different temperatures are required for slow exchange conditions in the two compounds. The viscosity of the solvent increases rapidly as the temperature is lowered and this leads to increased dipole–dipole relaxation and broader lines in **3** compared with **2**. It is remarkable that compounds of molecular weights of the order of 400 give resolved NMR spectra at temperatures near -180°C . The success achieved with **2** and **3** can be attributed to the very high spectrometer frequency used to measure the NMR spectra and presumably also to the presence of internal rotation in the methyl groups. This internal rotation can give rise to nonexponential relaxation and non-Lorentzian line shapes: Matson, G. B. *J. Chem. Phys.* **1976**, *65*, 4147. Werbelow, L. G.; Grant, D. M. *J. Magn. Reson.* **1978**, *29*, 603. However, the broad base on the peaks in Figure 2 is at least partly instrumental in origin.
- (7) Chemical shifts of **2** and **3** in CF_2Cl_2 – CHFCl_2 show negligible temperature dependence, i.e., <2 Hz in the range -50 to -100°C for **2** and in the range -100 to -140°C for **3**, as measured relative to the Freon 21 doublet.
- (8) Hutchings, M. G.; Watt, I. *J. Organomet. Chem.* **1979**, *177*, 329. We thank the authors for communicating their results prior to publication.

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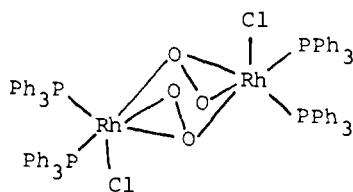
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Preparation and Reactions of New Dioxygen Complexes of Rhodium

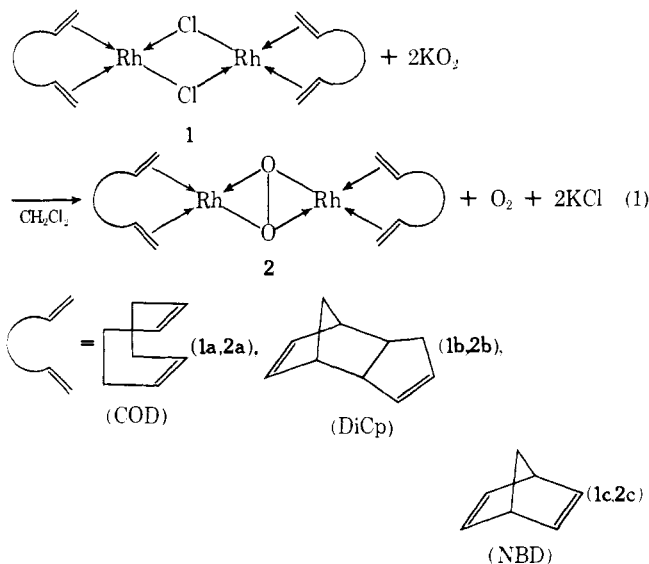
Sir:

Traditionally, dioxygen complexes of transition metals have been prepared by the oxidative addition of molecular oxygen to the low valent metal complexes stabilized by phosphine or isonitrile ligands.¹ We recently reported a new preparative method of dioxygen complexes of palladium using superoxide ion as a dioxygen source.² Extension of the work has led to the formation of dioxygen complexes of various transition metals having olefinic ligands or π -allyl ligands.³ Dioxygen complexes of rhodium thus prepared have only π -coordinated ligands

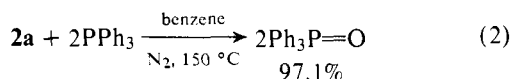
except for dioxygen which serves as a bridging ligand in the complexes. The structure of the complexes⁴ differs from that of ordinary mononuclear dioxygen complexes of rhodium,⁵ although they are somewhat analogous to the complex $[(\text{Ph}_3\text{P})_2\text{RhClO}_2]_2$ ⁶ whose structure was determined by Bennett et al.⁷



Experimentally dioxygen complexes of rhodium were prepared by the anion exchange reaction (eq 1). The reaction

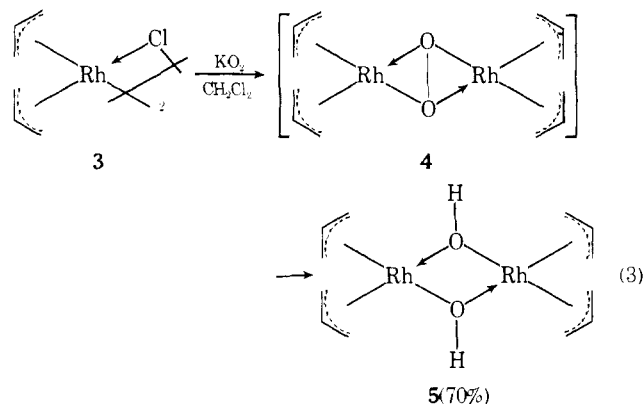


proceeded in dry CH_2Cl_2 solvent in the presence of an excess of potassium superoxide at room temperature. A solution of the rhodium complex **1a** (2.1 g, 4.28 mmol, 30 mL) was added dropwise to finely powdered KO_2 (49 mmol, 5.7 equiv) suspended in CH_2Cl_2 (15 mL) under dry nitrogen pressure. Rapid evolution of oxygen was observed and the color of the solution changed from reddish yellow to dark green within 3 min. Evolution of oxygen terminated after 20 min and the mixed solution changed reddish brown. The mixture was stirred for 4 h more after which KCl and excess KO_2 were removed by filtration. The reddish filtrate was concentrated under reduced pressure, and addition of petroleum ether and cooling to 0°C afforded a crude product (1.3 g, 2.87 mmol, 67% yield). Recrystallization from DME gave yellowish brown crystals: mp 132°C dec; $^1\text{H NMR}$ (CDCl_3) δ 1.63 (8 H, m), 2.42 (8 H, m), 3.60 (8 H, br s); IR (KBr) $\nu_{\text{C}=\text{C}}$ 1465 cm^{-1} ; mol wt (cryoscopy in benzene) calcd 454.2, found 447. Anal. Calcd for $\text{C}_{16}\text{H}_{24}\text{Rh}_2\text{O}_2$: C, 42.31; H, 5.33; Cl, 0.00. Found: C, 42.08; H, 5.65; Cl, 0.00. Dioxygen complexes **2b** and **2c** were prepared similarly from the corresponding rhodium complexes.⁸ Incorporation of dioxygen in the complexes **2** was confirmed by the reaction of **2** with triphenylphosphine. When **2a** was heated in the sealed tube with PPh_3 (1.1 equiv) under nitrogen pressure, the coordinated oxygen in **2a** was recovered quantitatively as triphenylphosphine oxide (eq 2).



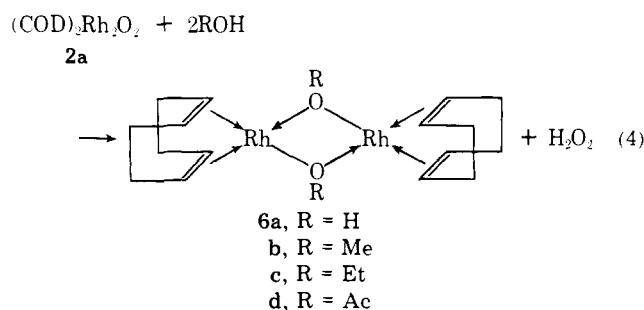
Preparation of dioxygen complex of trivalent rhodium was also examined by the reaction of KO_2 with a stable rhodium complex $[(\text{C}_3\text{H}_5)_2\text{RhCl}]_2$ (**3**). Although the reaction proceeded rapidly at room temperature, the recovered material was only

the hydroxy bridged binuclear complex $[(\text{C}_3\text{H}_5)_2\text{Rh}(\text{OH})]_2$ (**5**) (eq 3).⁹ We think that the dioxygen complex

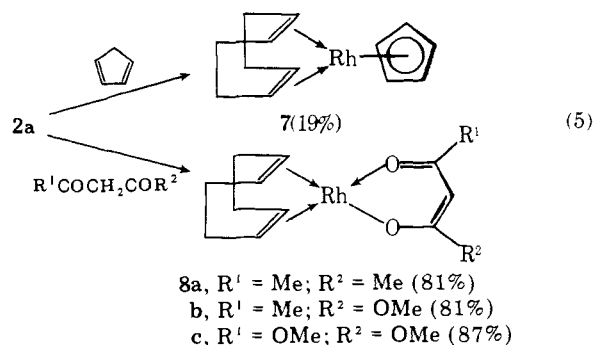


$[(\text{C}_3\text{H}_5)_2\text{Rh}]_2\text{O}_2$ (**4**) is the intermediate and hydrogen abstraction of **4** from solvent gives **5** as the final product.

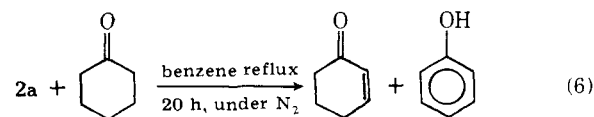
The dioxygen bridge in the complex **2** is labile and readily reacts with water, MeOH, EtOH, and acetic acid. The reaction gave RO^- ($\text{R} = \text{H}, \text{Me}, \text{Et}, \text{and Ac}$) bridged complexes¹⁰ and hydrogen peroxide (eq 4) which suggests that dioxygen is



coordinated as O_2^{2-} in the complexes. The basic nature of the coordinated dioxygen was further demonstrated by the reaction of **2a** with active methylene compounds. Treatment of **2a** in DME with cyclopentadiene ($\text{pK}_a = 15$), acetylacetonate ($\text{pK}_a = 9$), methyl acetoacetate ($\text{pK}_a = 11$), and dimethyl malonate ($\text{pK}_a = 13$) resulted in the abstraction of proton by the coordinated dioxygen giving the corresponding rhodium complexes **7** and **8** (eq 5) and hydrogen peroxide.¹¹ Dimerization of ace-



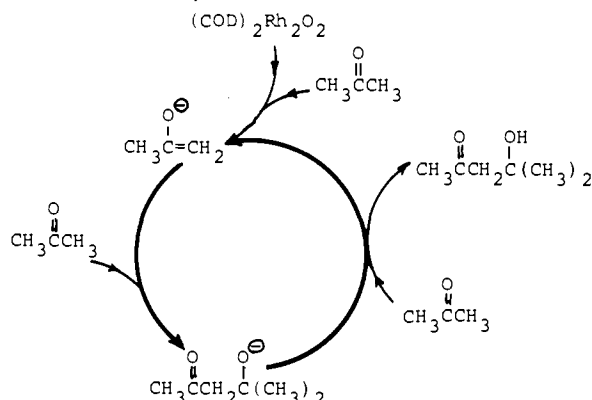
tone was observed in the presence of **2a**. The reaction proceeded catalytically and stirring of an acetone solution of **2a** (0.11 mmol, 9 mL) for 2 days under nitrogen pressure gave 2.28 mmol of diacetone alcohol.¹² Interestingly, no Baeyer-Villiger reaction products were obtained in the treatment of **2a** with cyclohexanone. The reaction afforded only the dehydrogenated products, phenol and cyclohexenone (eq 6), instead of ϵ -ca-



prolactone.¹³ Attempts to force interaction between the olefinic ligands and the coordinated dioxygen were unsuccessful. Warming of **2a** in the refluxing benzene gave minor amounts of cis-ligand coupling products and the elimination of COD prevailed, accompanying the decomposition of the complex.

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- Although the dioxygen bridged structure of the complex **2** seems to be reasonable, it is tentative. We are now trying to prepare single crystals of **2** suitable for the X-ray analysis of the crystal structure.
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- 2b**: NMR (CDCl₃) δ 3.17 (4 H, m), 3.60 (4 H, m), 4.23 (4 H, m), 5.37 (4 H, m); IR (KBr) $\nu_{C=C}$ 1455 cm⁻¹. Anal. Calcd for C₂₀H₂₄O₂Rh₂: C, 47.83; H, 4.82. Found: C, 47.44; H, 5.28. **2c**: NMR (CDCl₃) δ 1.13 (8 H, v br), 3.73 (8 H, v br); IR (KBr) $\nu_{C=C}$ 1480 cm⁻¹. Anal. Calcd for C₁₄H₁₆O₂Rh₂: C, 39.84; H, 3.82. Found: C, 39.22; H, 4.30.
- 5**: yellow prisms; mp 129–138 °C dec; NMR (CDCl₃) δ 1.10 (4 H, m), 2.18 (4 H, m), 3.02 (4 H, m), 4.38 (4 H, m), 4.67 (4 H, m), -2.40 (2 H, br s); IR (KBr) ν_{OH} 3580 and 3549, $\nu_{C=C}$ π -allyl 1479 cm⁻¹. Anal. Calcd for C₁₂H₂₂O₂Rh₂: C, 35.66; H, 5.49. Found: C, 35.31; H, 5.40.
- 6a**: pale yellow prisms; mp > 140 °C dec; NMR (CDCl₃) δ 1.72 (8 H, m), 2.32 (10 H, m), 3.88 (8 H, br s); IR (KBr) ν_{OH} 3600, $\nu_{C=C}$ 1467 cm⁻¹. Anal. Calcd for C₁₆H₂₆O₂Rh₂: C, 42.13; H, 5.75. Found: C, 41.97; H, 5.73. **6c**: yellow prisms; mp > 125 °C dec; NMR (CDCl₃) δ 1.10 (6 H, t), 1.65 (8 H, m), 2.50 (12 H, m), 3.53 (8 H, br s); IR (KBr) $\nu_{C=O}$ 1099, ν_{Rh-O} 540 cm⁻¹. Anal. Calcd for C₂₀H₃₄O₂Rh₂: C, 46.89; H, 6.69. Found: C, 46.60; H, 6.73. The spectral and physical data of **6b** and **6d** were in agreement with those reported by S. D. Robinson and B. L. Shaw, *J. Chem. Soc.*, 4997 (1965).
- 8b**: yellow prisms; mp 104–112 °C; NMR (CDCl₃) δ 1.75 (4 H, m), 1.83 (3 H, s), 2.45 (4 H, m), 3.48 (3 H, s), 4.00 (4 H, br s), 4.70 (1 H, s); IR (KBr) $\nu_{C=O}$ 1600, $\nu_{C=C}$ 1505, ν_{C-O} 1270 cm⁻¹. Anal. Calcd for C₁₃H₁₉O₃Rh: C, 47.87; H, 5.87. Found: C, 47.86; H, 6.02. **8c**: yellow prisms; mp 134–138 °C; NMR (CDCl₃) δ 1.80 (4 H, m), 2.47 (4 H, m), 3.47 (6 H, s), 4.03 (4 H, br s), 4.17 (1 H, s); IR (KBr) $\nu_{C=O}$ 1605, $\nu_{C=C}$ 13, ν_{C-O} 1143 cm⁻¹. Anal. Calcd for C₁₃H₁₉O₄Rh: C, 45.63; H, 5.60. Found: C, 45.34; H, 5.59. The spectral and physical data of **7** and **8a** were in agreement with those reported by R. B. King, *Inorg. Chem.*, **2**, 528 (1963), and by F. Bonati and G. Wilkinson, *J. Chem. Soc.*, 3156 (1964), respectively.
- We suggest the following reaction scheme where dioxygen complex **2** initiates the base-catalyzed aldol condensation of acetone.



- 2a** (1.26 mmol) was treated by cyclohexanone (2.16 mmol) in the refluxing benzene (10 mL) for 20 h. Phenol (0.18 mmol) and cyclohexenone (0.06 mmol) were obtained and unreacted **2a** (0.98 mmol) was recovered as **6b** after the column chromatography (silica gel–MeOH).

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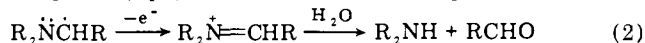
On the Selectivity of Tertiary Amine Oxidations

Sir:

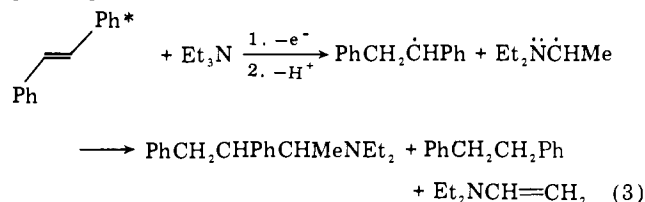
Tertiary amines can be oxidized by chemical one-electron oxidants,¹ electrochemically,² photochemically,³ and enzymatically.⁴ The mechanisms of all but the latter are thought to involve one-electron oxidation to yield a planar aminium radical⁵ followed by deprotonation to yield an α -amino radical (eq 1). The α -amino radical may be further oxidized chemi-



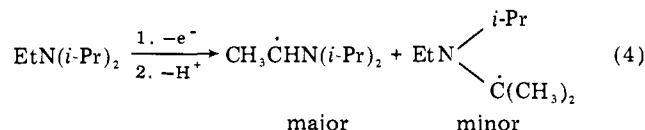
cally or electrochemically to the immonium salt, which is readily hydrolyzed to yield a secondary amine and a carbonyl compound (eq 2). The second oxidation step does not occur in



some photochemical reactions owing to the absence of a suitable oxidant.^{3,6} For example, singlet *trans*-stilbene and triethylamine yield mainly the products expected for free-radical cross termination of an α -amino and 1,2-diphenylethyl radical pair (eq 3).⁶



Oxidation of nonsymmetrical amines, e.g., R_2NR' , can yield two different α -amino radicals, resulting in competitive dealkylation (eq 2) or radical combination (eq 3) processes. Smith and Mann^{2a} first observed that electrochemical oxidation of ethyldiisopropylamine resulted in selective formation of the less stable secondary α -amino radical (eq 4). Selective



formation of the less stable α -amino radical has been observed for several highly branched tertiary amines.^{1–3} Selectivity has been attributed to both steric^{2a,3} and kinetic acidity^{2c,d} effects on the deprotonation step. In contrast, the oxidation of less substituted amines such as dimethyl-*n*-alkyl- and dimethylbenzylamines is, in most cases, reported to be nonselective,^{1,2} a result in accord with neither a simple steric nor a kinetic acidity effect. We report our investigation of the photochemical reactions of *trans*-stilbene with several tertiary amines, the results of which serve to elucidate the origin of amine oxidation selectivity.

Irradiation of degassed acetonitrile solutions of *trans*-stilbene (0.01 M) and the tertiary amines (1.0 M) listed in Table I leads to the formation of addition products (eq 3). The products are labeled as a or b depending on the orientation of aminium radical deprotonation. The product ratios a/b have been statistically corrected for the number of abstractable protons of type a vs b. The observed a/b ratios for amines **1–5** may be slightly larger than the selectivity of deprotonation owing to the competition between radical-pair disproportionation vs. combination (eq 3), which increases with α -amino radical substitution.⁷ The a/b ratio for amine **6** provides a value of the isotope effect for aminium radical deprotonation. No amine adduct or stilbene reduction was observed upon irradiation of stilbene with triisopropylamine or with Dabco (1,4-diazabicyclo[2.2.2]octane).

The relative reactivities of tertiary amines with singlet stilbene given in Table I are obtained from the slopes of linear Stern–Volmer plots for quenching of stilbene fluorescence by