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.

References and Notes

(1) J. Valentine, *Chem. Rev.*, **73,** 235 (1973); V. J. Choy and C. J. O'Conner, *Coord. Chem. Rev.*, **9,** 145 (1972); G. Henrici-Olive and S. Olive, *Angew. Chem., Int. Ed. Engl.*, **13,** 29 (1974); L. Vaska, *Acc. Chem. Res.*, **9,** 175 (1976).

(2) H. Suzuki, K. Mizutani, Y. Moro-oka, and T. Ikawa, *J. Am. Chem. Soc.*, **101,** 748 (1979).

(3) P. J. Chung, H. Suzuki, Y. Moro-oka, and T. Ikawa, *Chem. Lett.*, 63 (1980); *J. Chem. Soc., Chem. Commun.*, submitted for publication.

(4) 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.

(5) J. A. McGinnety, N. C. Payne, and J. A. Ibers, *J. Am. Chem. Soc.*, **91,** 6301 (1969); A. Nakamura, Y. Tatsuno, M. Yamamoto, and S. Otsuka, *ibid.*, **93,** 6052 (1971); R. W. Mitchell, J. D. Ruddick, and G. Wilkinson, *J. Chem. Soc. A*, 3224 (1971); A. L. Balch and J. Miller, *J. Organomet. Chem.*, **32,** 263 (1971); L. M. Haines and E. Singleton, *ibid.*, **30,** C81 (1971); L. M. Haines, *Inorg. Chem.*, **10,** 1685 (1971).

(6) M. C. Baird, D. N. Lawson, J. T. Mague, J. A. Osborn, and G. Wilkinson, *Chem. Commun.*, 129 (1966); G. L. Geoffroy and M. E. Keeney, *Inorg. Chem.*, **16,** 205 (1977).

(7) M. J. Bennett and P. B. Donaldson, *J. Am. Chem. Soc.*, **93,** 3307 (1971).

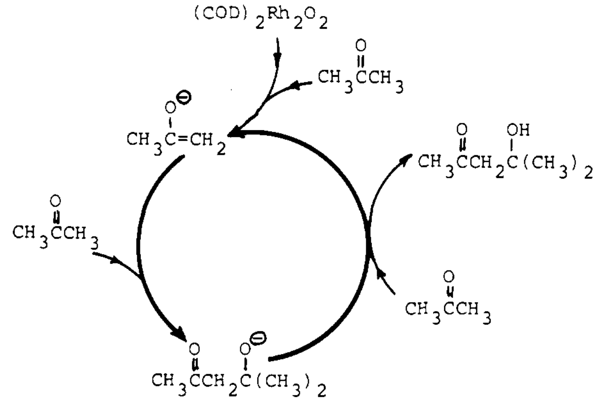
(8) **2b:** NMR ($CDCl_3$) δ 3.17 (4 H, m), 3.60 (4 H, m), 4.23 (4 H, m), 5.37 (4 H, m); IR (KBr) $\nu_{C=C}$ 1455 cm^{-1}. Anal. Calcd for $C_{20}H_{24}O_2Rh_2$: C, 47.83; H, 4.82. Found: C, 47.44; H, 5.28. **2c:** NMR ($CDCl_3$) δ 1.13 (8 H, v br), 3.73 (8 H, v br); IR (KBr) $\nu_{C=C}$ 1480 cm^{-1}. Anal. Calcd for $C_{14}H_{16}O_2Rh_2$: C, 39.84; H, 3.82. Found: C, 39.22; H, 4.30.

(9) **5:** yellow prisms; mp 129–138 °C dec; NMR ($CDCl_3$) 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, $\nu_{C\cdots C\ \pi\text{-allyl}}$ 1479 cm^{-1}. Anal. Calcd for $C_{12}H_{22}O_2Rh_2$: C, 35.66; H, 5.49. Found: C, 35.31; H, 5.40.

(10) **6a:** pale yellow prisms; mp >140 °C dec; NMR ($CDCl_3$) 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 $C_{16}H_{26}O_2Rh_2$: C, 42.13; H, 5.75. Found: C, 41.97; H, 5.73. **6c:** yellow prisms; mp >125 °C dec; NMR ($CDCl_3$) δ 1.10 (6 H, t), 1.65 (8 H, m), 2.50 (12 H, m), 3.53 (8 H, br s); IR (KBr) ν_{C-O} 1099, ν_{Rh-O} 540 cm^{-1}. Anal. Calcd for $C_{20}H_{34}O_2Rh_2$: 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).

(11) **8b:** yellow prisms; mp 104–112 °C; NMR ($CDCl_3$) 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, $\nu_{C\cdots C}$ 1505, ν_{C-O} 1270 cm^{-1}. Anal. Calcd for $C_{13}H_{19}O_3Rh$: C, 47.87; H, 5.87. Found: C, 47.86; H, 6.02. **8c:** yellow prisms; mp 134–138 °C; NMR ($CDCl_3$) 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, $\nu_{C\cdots C}$ 13, ν_{C-O} 1143 cm^{-1}. Anal. Calcd for $C_{13}H_{19}O_4Rh$: 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.

(12) We suggest the following reaction scheme where dioxygen complex **2** initiates the base-catalyzed aldol condensation of acetone.



(13) **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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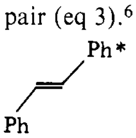
On the Selectivity of Tertiary Amine Oxidations

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 radical[5] followed by deprotonation to yield an α-amino radical (eq 1). The α-amino radical may be further oxidized chemically 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]

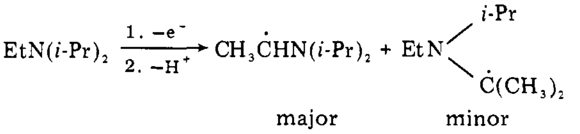
$$R_2\ddot{N}CH_2R \xrightarrow{-e^-} R_2\overset{+\cdot}{N}CH_2R \xrightarrow{-H^+} R_2\ddot{N}\dot{C}HR \qquad (1)$$

$$R_2\ddot{N}\dot{C}HR \xrightarrow{-e^-} R_2\overset{+}{N}{=}CHR \xrightarrow{H_2O} R_2NH + RCHO \qquad (2)$$



$$+ Et_3N \xrightarrow[2.\ -H^+]{1.\ -e^-} PhCH_2\dot{C}HPh + Et_2\ddot{N}\dot{C}HMe \longrightarrow PhCH_2CHPhCHMeNEt_2 + PhCH_2CH_2Ph + Et_2NCH{=}CH_2 \qquad (3)$$

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.



$$EtN(i\text{-}Pr)_2 \xrightarrow[2.\ -H^+]{1.\ -e^-} \underset{\text{major}}{CH_3\dot{C}HN(i\text{-}Pr)_2} + \underset{\text{minor}}{EtN\langle^{i\text{-}Pr}_{\dot{C}(CH_3)_2}} \qquad (4)$$

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

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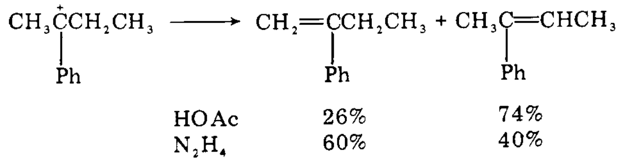
Table I. Selectivity and Reactivity of Tertiary Amines with Singlet *trans*-Stilbene

no.	amine	% a[a]	% b[a]	a/b,[b] cor	k_{rel}[b]
1	$CH_3\overset{a}{C}H_2N[\overset{b}{C}H(CH_3)_2]_2$	92	8	12 ± 1	1.0
2	$\overset{a}{C}H_3N[\overset{b}{C}H(CH_3)_2]_2$	>95	<5	>20 ± 2	0.92
3	$\overset{a}{C}H_3N(\overset{b}{C}H_2CH_3)_2$	63	37	2.3 ± 0.2	0.54
4	$(\overset{a}{C}H_3)_2N\overset{b}{C}H_2CH_3$	84	16	1.8 ± 0.2	
5	$(\overset{a}{C}H_3)_2N\overset{b}{C}H(CH_3)_2$	83	17	0.8 ± 0.1	0.97
6	$\overset{a}{C}H_3N(\overset{b}{C}D_3)$-*t*-Bu	69	31	2.2 ± 0.2	0.63

[a] Percent amine product determined by GC analysis for **1, 3, 4,** and **5** and by both NMR and MS isotope ratios for **6**. [b] See text.

amines. Reactivity increases with decreasing amine oxidation potential, in accord with an electron-transfer mechanism for singlet quenching.[3,6] Triisopropylamine and Dabco are more reactive quenchers of stilbene fluorescence than amine **1**, in accord with their lower oxidation potentials.[5] Thus the failure of these amines to form adducts must result from inefficient deprotonation of the aminium radical rather than inefficient aminium radical formation.

The results obtained for amines **3–5** are indicative of relatively nonselective deprotonation of the aminium radical by the stilbene radical anion. The small isotope effect for amine **6** is consistent with the small extent of bond breaking expected in a nonselective process. Deprotonation of aminium radicals is unlike the deprotonation of carbonium ions, the more substituted alkene generally predominating in E_1 reactions.[9] Cram and Sahyun observed that the yield of less-substituted alkene increases with increasing base strength. The low selectivity of amine **3–5** oxidation by stilbene may reflect the high basicity of the stilbene anion radical. Another example of nonselective



$$CH_3\underset{Ph}{\overset{+}{C}}CH_2CH_3 \longrightarrow CH_2{=}\underset{Ph}{C}CH_2CH_3 + CH_3\underset{Ph}{C}{=}CHCH_3$$

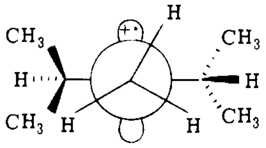
HOAc	26%	74%
N_2H_4	60%	40%

(5)

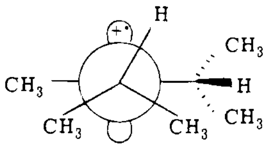
proton transfer from a radical cation (*p*-cymene) to a radical anion (trifluoroacetophenone) has recently been reported by Wagner and Puchalski.[8]

In contrast to the nonselective deprotonation of amines **3–5**, deprotonation of **1** and **2** is highly selective for formation of the less stable α-amino radical. Assuming that deprotonation requires at least partial overlap of the half vacant nitrogen p orbital with the developing carbon radical p orbital, the conformations of aminium radical **2** required for loss of type a and b protons are as shown. Steric interactions are clearly greater in b than in a. It is, in fact, impossible for a space-filling model

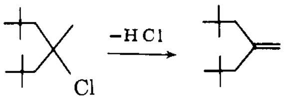
a



b



to attain conformation b. The situation is even worse for triisopropylamine, thus accounting for its lack of reactivity. The bicyclic structure of Dabco also prevents overlap of the nitrogen and α-carbon p orbitals.[11] We conclude that the selective oxidation of the tertiary amines **1** and **2** and the innertness of triisopropylamine are due to a stereoelectronic effect which is most evident when two or three of the alkyl groups are highly branched. We are aware of one apparently analogous E_1 reaction (eq 6) in which the less-substituted alkene is the sole product.[12]



(6)

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References and Notes

(1) (a) Smith, P. A. S.; Loeppky, R. N. *J. Am. Chem. Soc.* **1967,** *89,* 1147. (b) Deno, N. C.; Fruit, R. E. *Ibid.* **1968,** *90,* 3502. (c) Audeh, C. A.; Lindsay Smith, J. R. *J. Chem. Soc. B* **1970,** 1280. (d) Audeh, C. A.; Lindsay Smith, J. R. *Ibid.* **1971,** 1741. (e) Lindsay Smith, J. R.; Mead, L. A. V. *J. Chem. Soc., Perkin Trans. 2* **1973,** 206.
(2) (a) Smith, P. J.; Mann, C. K. *J. Org. Chem.* **1969,** *34,* 1821. (b) Portis, L. C.; Bhat, V. V.; Mann, C. K. *Ibid.* **1970,** *35,* 2175. (c) Masui, M.; Sayo, H. *J. Chem. Soc. B* **1971,** 1593. (d) Lindsay Smith, J. R.; Masheder, D. *J. Chem. Soc., Perkin Trans. 2* **1976,** 47.
(3) Cohen, S. G.; Parola, A.; Parsons, G. H. *Chem. Rev.* **1973,** *73,* 141.
(4) Kapeller-Adler, R. "Amine Oxidases and Methods for Their Study"; Wiley-Interscience: New York, 1970.
(5) Chow, Y. L.; Danen, W. C.; Nelsen, S. F.; Rosenblatt, D. H. *Chem. Rev.* **1978,** *78,* 243.
(6) (a) Lewis, F. D.; Ho, T.-I. *J. Am. Chem. Soc.* **1977,** *99,* 7991. (b) Lewis, F. D. *Acc. Chem. Res.* **1979,** *12,* 152.
(7) Quantum yields for combination and disproportionation product formation have been measured and will be reported in a full paper.
(8) Wagner, P. J.; Puchalski, A. E. *J. Am. Chem. Soc.* **1978,** *100,* 5948.
(9) Saunders, W. H.; Cockerill, A. F. "Mechanisms of Elimination Reactions"; Wiley: New York, 1973; p 212.
(10) Cram, D. J.; Sahyun, M. R. V. *J. Am. Chem. Soc.* **1963,** *85,* 1257.
(11) Ojanpera, S.; Parola, A.; Cohen, S. G. *J. Am. Chem. Soc.* **1974,** *96,* 7379.
(12) Brown, H. C.; Moritani, I. *J. Am. Chem. Soc.* **1955,** *77,* 3607.

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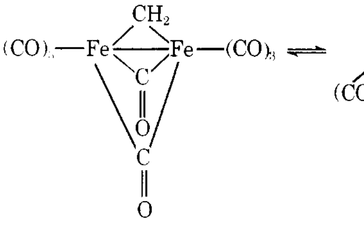
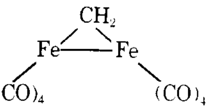
Synthesis, Crystal Structure, and Chemical Reactivity of Octacarbonyl-μ-methylene-diiron

Sir:

Complexes which possess a CH_2 group bridging two bonded transition metal atoms are of interest, inter alia, because of their relationship to methylene groups on metal surfaces in heterogeneous reactions. The electronic structure of such complexes has been studied theoretically.[1] We report the preparation, X-ray structural analysis, and chemical properties of the novel organometallic complex, $Fe_2(CO)_8CH_2$ (**1**), in which a CH_2 group bridges two iron atoms simultaneously linked by a metal-metal bond. Other complexes which possess a CH_2 group bridging two bonded transition metal atoms have recently been reported; e.g., Os-Os,[2] Ru-Ru,[3] Rh-Rh,[4] and Mn-Mn[5] containing species.



1a



1b

Compound **1** is formed in 60% yield following reaction of the $[Fe_2(CO)_8]^{2-}$ ion with CH_2I_2 in acetone at 0 °C. The material crystallizes from ethyl acetate as air stable, golden

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