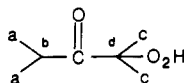


2⁸, 3⁸, and 4⁷ were prepared by low-temperature reactions of the starting ketones with O₂ and KO-*t*-C₄H₉. The high purity of 2 was shown by ¹³C NMR analysis:



C(e), 218.26; C(d), 87.95; C(b), 33.82; C(c), 21.13; C(a), 19.71. All hydroperoxide compounds used exhibited ¹H NMR resonances assignable to the OOH group: 2, 8.70; *c*-C₆H₁₁O₂H, 8.40; *n*-C₅H₁₁O₂H, 8.54; and *t*-C₄H₉O₂H, 8.98 ppm. By use of bis(trimethylsilyl)acetamide derivatization, it was possible to detect GC/MS parent and parent - CH₃ *m/e* signals for four of the hydroperoxides: 2-methylcyclohexanone hydroperoxide, 216, 201; *c*-C₆H₁₁O₂H, 188, 173; *t*-C₄H₉O₂H, 162, 147; *n*-C₅H₁₁O₂H, 176, 161.

Rates of reaction of Co²⁺ and Co³⁺ with the various alkyl hydroperoxides were followed by recording increases or decreases in absorbance at 610 nm (Co³⁺) in HOAc and at 700 nm (Co³⁺) in decalin. The starting concentrations of alkyl hydroperoxide solutions were determined by standardization with NaI/Na₂S₂O₃. Rates of reactions of the alkyl hydroperoxides with PPh₃ and *n*-(C₄H₉)₄Ni were followed by recording decreases in absorbance maxima for PPh₃ (260 nm) and increases for I₂ at 355 nm.

Numerous attempts to isolate α -ketocyclohexyl hydroperoxide (1) were unsuccessful. Preparative procedures included reaction

(13) Williams, H. R.; Mosher, H. S. *J. Am. Chem. Soc.* 1954, 76, 2984.

of 0.16 M cyclohexanone with 0.36 M KO-*t*-C₄H₉ and O₂ in glyme/*t*-C₄H₉OH at -50 °C,⁸ reaction of neat cyclohexanone with O₂ at 100 °C^{6a}, and reaction of neat cyclohexanone containing 1% *t*-C₄H₉OOCOC₄H₉ at 100 °C.^{6b} None of the product solutions contained more than trace amounts of 1, based on NaI titration.

Acknowledgment. The able technical assistance of D. F. Oldham, E. Fok, and G. F. Diffendal is grateful acknowledged. Accurate mass measurements were done by Fulton Kitson.

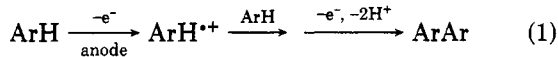
Registry No. 1, 50915-79-2; 2, 3944-52-3; 2-K, 112270-30-1; 3, 21961-02-4; 3-K, 112270-31-2; 4, 5143-76-0; 4-K, 112270-32-3; Co(OAc)₂, 71-48-7; NaBr, 7647-15-6; *c*-C₆H₁₁ON=NO-*c*-C₆H₁₁, 82522-48-3; (2-C₄H₉OC(O)O)₂, 19910-65-7; *c*-C₆H₁₁O₂H, 766-07-4; *n*-C₅H₁₁O₂H, 74-80-6; *t*-C₄H₉O₂H, 75-91-2; *n*-C₅H₁₁OSO₂CH₃, 6968-20-3; (CH₃)₂CHC(O)CH(CH₃)₂, 565-80-0; CH₃C(O)CH(CH₃)₂, 563-80-4; *c*-C₆H₁₁OOSiMe₃, 112296-48-7; *t*-C₄H₉OOSiMe₃, 3965-63-7; *n*-C₅H₁₁OOSiMe₃, 89131-58-8; PPh₃, 603-35-0; (*n*-C₄H₉)₄Ni, 311-28-4; I₂, 20461-54-5; Co²⁺, 22541-53-3; Co³⁺, 22541-63-5; Co(O₂CC₇H₁₅)₂, 1588-79-0; cyclohexanone, 108-94-1; cyclohexene, 110-83-8; cyclohexene oxide, 286-20-4; 2,4,6-tri-*tert*-butylphenol, 732-26-3; *cis*-2-octene, 7642-04-8; *trans*-2-methyl-3-pentylloxirane, 28180-70-3; *cis*-2-methyl-3-pentylloxirane, 23024-54-6; cyclohexylmagnesium chloride, 931-51-1; 2-methylcyclohexanone, 583-60-8; 1-oxo-2-methyl-2-cyclohexyl trimethylsilyl peroxide, 112270-33-4.

Communications

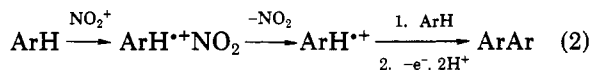
On the Formation of Biaryls in Aromatic Nitration. The Role of the Nitrosonium Ion^{1,2}

Summary: NOBF₄ and NO₂ in CH₂Cl₂/CF₃COOH mixtures were found to be efficient catalysts for the synthesis of certain biaryls via an oxygen-promoted oxidative dimerization step. The need for better control of the presence, role, and action of NO⁺ in aromatic nitration reactions was pointed out.

Sir: Many of the common side reactions in electrophilic aromatic nitration (EAN) are of the oxidative substitution type³ and can in some cases be suspected to proceed via an initial electron transfer (ET) step.⁴ As an example, the formation of biaryls upon anodic oxidation of aromatics (eq 1) is mediated by radical cations⁵ and hence the for-



mation of biaryls can be taken as evidence *in favor* of an initial ET step in EAN (eq 2).



(1) Aromatic Nitration via Electron Transfer. 7. Part 6, see ref 4.

(2) Presented at the EUCHEM Conference on "Electron Transfer Reactions in Organic Chemistry", Visby, Sweden, June 1987.

(3) Suzuki, H. *Synthesis* 1977, 217. Examples include quinone formation, nitroxylation, biaryl coupling, and side-chain substitution reactions. 4,4'-Dimethoxy-1,1'-binaphthyl was reported as the sole product in a NO₂⁺-based nitration of 1-methoxynaphthalene. Alcorn, P. G. E.; Wells, P. R. *Aust. J. Chem.* 1965, 18, 1391.

(4) Ebersson, L.; Radner, F. *Acc. Chem. Res.* 1987, 20, 53.

(5) Ebersson, L.; Nyberg, K. *Acc. Chem. Res.* 1973, 6, 106.

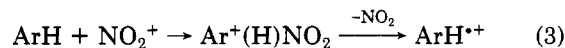
Table I. Reactions of Substituted Naphthalenes with NOBF₄ in CF₃COOH/CH₂Cl₂ Mixtures ([ArH] = [NOBF₄] = 0.04 M^a)

1-X-C ₁₀ H ₇ X =	consumed ArH, % (yield of ArAr, %)			
	20%		80%	
	CF ₃ COOH/CH ₂ Cl ₂		CF ₃ COOH/CH ₂ Cl ₂	
	1 h	20 h	1 h	20 h
CN	0 (0)	0 (0)	0 (0)	0 (≈0)
Br	10 (1)	28 (8) ^b	32 (6)	77 (43)
H	40 (0)	59 (0)	78 (0)	100 (0)
CH ₃	82 (54)	100 (41)	100 (56)	
OCH ₃	100 (41)			

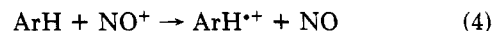
^a Reaction of 1.00 mmol of ArH in 20 (5) mL of CH₂Cl₂ with 1.00 mmol of NOBF₄ suspended in 5 (20) mL of CF₃COOH in tightly stoppered, magnetically stirred 25-mL Erlenmeyer flasks at 20 °C. ^b After 120 h: 46 (27).

However, the evidence *against* the action of NO₂⁺ as a powerful outer-sphere ET oxidant^{4,6} nowadays must be regarded as fairly substantial, and we have therefore suggested either or both of two other routes to be responsible for the formation of radical cations under EAN conditions^{4,6b} (eq 3 and 4).

inner-sphere ET:



oxidation by NO⁺:



(6) Ebersson, L.; Radner, F. (a) *Acta Chem. Scand.* 1984, 38, 861; (b) 1985, 39, 357; (c) 1985, 39, 343.

Table II. Effect of Reaction Conditions on the Biaryl Coupling of 1-Methoxynaphthalene^a

source of NO _x ^b	ratio ArH/NO _x	atmosphere ^c	mmol ArAr formed	mmol ArH recovered	yield based on NO _x ¹⁹ (%)	material balance (%)
NOBF ₄	20	argon	0.02	0.96	40	100
NOBF ₄	20	air	0.48	0.00	960	96
NOBF ₄	20	oxygen	0.24	0.00	480	48
NOBF ₄	100	air	0.27	0.46	2700	100
NO ₂	20	argon	0.01	1.00	20	102
NO ₂	20	air	0.35	0.28	700	98

^a Reaction of 1.00 mmol of 1-methoxynaphthalene for 20 min with 0.01–0.05 mmol of NOBF₄ (NO₂) in 8 mL of CH₂Cl₂/2 mL of CF₃COOH in different atmospheres at 20 °C. Reactions were performed in 25-mL Erlenmeyer flasks and with magnetical stirring. ^b NOBF₄ initially dissolved in CF₃COOH; NO₂ initially dissolved in CH₂Cl₂. ^c A gentle stream of Ar, a balloon filled with O₂, and an ordinary drying tube to furnish the ambient air, respectively.

The presence of NO⁺ and/or lower oxides of nitrogen⁷ in any sample of nitric acid that has not been carefully purified as well as in most, if not all, commercial samples of nitronium salts⁸ calls for some attention to what roles NO⁺ can exert in EAN. This paper demonstrates that eq 4 provides a reasonable explanation for the formation of biaryls (and polymerization products) in EAN and describes how NO⁺ or NO₂ can be used as catalysts in a highly efficient biaryl synthesis, in which oxygen is used as the stoichiometric oxidant.

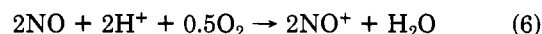
The action of NOBF₄ on readily oxidizable aromatics,⁹ e.g. pyrene, has generally resulted in the formation of the corresponding radical cation salt,^{6,10} whereas with less readily oxidizable aromatics, e.g. mesitylene, charge-transfer complexes were formed.^{11,12} Treatment of naphthalene with NOBF₄ in CH₂Cl₂/sulfolane caused no reaction,^{6a} whereas in CF₃COOH polymer formation was observed.¹⁵ It therefore appeared appropriate to investigate the action of NOBF₄ on some substituted naphthalenes (1-X-C₁₀H₇; X = OCH₃, CH₃, H, Br, CN) in media of varying acidity.¹⁶

Table I summarizes the reactions of equimolar amounts of NOBF₄ and the naphthalenes in mixtures of CH₂Cl₂ and CF₃COOH. The rate of consumption parallels the ease of oxidation of the ArH and increases as the acidity of the system increases.¹⁷ The use of stoichiometric amounts of NOBF₄ has a detrimental effect on the reaction as demonstrated by the low ratios of consumed ArH to formed ArAr.¹⁸ Increasing the ArH:NO⁺ ratio to 2:1 has only a limited improving effect on the yields and mass balances. With X = CH₃ and OCH₃ strange color phenomena and lower yields were observed when the reaction mixtures were exposed to air. The reactions were therefore sus-

pected of being promoted by oxygen, as confirmed by the results presented in Table II.

When mixtures of X = OCH₃ and 1–5 mol % of NOBF₄ in 20% CF₃COOH/CH₂Cl₂ were exposed to air via a drying tube, the biaryl was formed in quantitative yields. Yields based on NO⁺ were 1000–4000%,¹⁹ to be compared with <50% when the reactions were performed under argon. The use of neat oxygen was not advantageous; yields were actually lowered due to further oxidations.²⁰ With X = CH₃ similar results were observed; in air a 520% yield based on NO⁺ was found. Other suitable substrates for this coupling reaction are the polyalkoxybenzenes; e.g., starting with 1,2,4-trimethoxybenzene, 2,2',4,4',5,5'-hexamethoxybiphenyl could be isolated in 92% substance yield.

When the source of NO_x was changed to NO₂/N₂O₄ the same general reaction pattern persisted, demonstrating the rapid interconversion between the lower oxidation states of nitrogen in this system.²¹ The catalytic reaction can at present best be represented as follows (eq 5–7):



Note that by replacing NO + 1/2 O₂ with NO₂ in eq 6, one possible explanation for the catalytic action of NO₂ emerges.

Biaryl coupling is only one of the possible side reactions in aromatic nitration that can be initiated by NO⁺. Another example is nitrous acid catalyzed nitration and since nitroaromatics can be formed via this route, great care must be taken when analyzing data from the EAN of aromatics easier to oxidize than mesitylene. We therefore

(7) Ross, D. S.; Moran, K. D.; Malhotra, R. *J. Org. Chem.* 1983, 48, 2120.

(8) Elsenbaumer, R. L. *J. Org. Chem.*, in press.

(9) E° for the NO⁺/NO couple is 1.51 V vs NHE in CH₃NO₂ (Cauquis, G.; Serve, D. *C.R. Séances Acad. Sci., Ser. C* 1968, 267, 460). In CH₂Cl₂/sulfolane rapid ET from pyrene (E° = 1.60 V) was observed whereas in the case of mesitylene (E° = 2.43 V) no ET occurred.^{6a}

(10) Bandlish, B. K.; Shine, H. J. *J. Org. Chem.* 1977, 42, 561.

(11) (a) Hunziker, E.; Penton, J. R.; Zollinger, H. *Helv. Chim. Acta* 1971, 54, 2043. (b) Milligan, B. J. *J. Org. Chem.* 1983, 48, 1495.

(12) These CT complexes do not undergo¹³ light-induced internal ET with subsequent radical coupling in the way the corresponding ArH-C(NO₂)₂ CT complex does.¹⁴

(13) Radner, F., unpublished results.

(14) Sankararaman, S.; Kochi, J. K. *Recl. Trav. Chim. Phys-Bas* 1986, 105, 278.

(15) Morkovnik, A. S.; Okhlobystin, O. Y. *J. Gen. Chem. USSR (Engl. Transl.)* 1985, 55, 616.

(16) The effect of acidity on the oxidizing power of NO⁺ has been under discussion for some time, see ref 4.

(17) With naphthalene the following results were obtained after 1 h (% CF₃COOH, % consumed ArH): 0, 0; 20, 40; 80, 78; 100, 100. The yields and material balances were determined by GC (2.5 m, 5% OV 1701 on Chrom WHP; C₁₈H₃₈ internal standard) unless otherwise noted.

(18) 2ArH + 2NO⁺ → ArAr + 2NO; ArAr + NO⁺ → oligomeric products; ArAr = 4,4'-di-X-1,1'-dinaphthyl. With X = H, i.e., naphthalene, solely polymeric products were formed.

(19) Yield based on NO⁺ defined as (mmol ArAr formed)/(mmol NO⁺ added) × 100.

(20) The detrimental effect of neat oxygen was decreased when the reaction was performed on a larger scale. Treatment of 10 mmol ArH, X = OCH₃, with 0.1 mmol of NOBF₄ in 80 mL of CH₂Cl₂/20 mL of CF₃COOH in a flask equipped with an oxygen-filled balloon for 24 h resulted in complete conversion and gave, after workup, ArAr in 70% yield (3500% based on NO⁺). Also note that some ArH may be lost via other routes as well; e.g., reaction of ArH⁺ with O₂. We are presently investigating this possibility.

(21) NO₂/N₂O₄ dissociates ionically to NO⁺/NO₃⁻ in dilute solutions of strong acids (Addison, C. C. *Chem. Rev.* 1980, 80, 21). [NO₂] is probably very low in experiments 5 and 6, Table II, since no nitromethoxynaphthalenes were detected. (For the formation of ArNO₂ from ArH + NO₂ or ArH⁺ to NO₂, see ref 4, 6b,c, and 14.)

(22) Other reagents for oxidative biaryl coupling include (apart from electrochemical methods^{22a}) FeCl₃,^{22b} Ti(OCOCF₃)₃,^{22c} and Ru(OCOCF₃)₄.^{22d} These reagents generally have a greater oxidizing power and are hence applicable to a larger number of substrates. The present method appears advantageous for the more readily oxidizable substrates.

(23) (a) Nyberg, K. In *Organic Electrochemistry*; Baizer, M., Ed.; Marcel Dekker: New York, 1972; Chapter 20. Anderson, J. T.; Stocker, J. H. In *Organic Electrochemistry*; Baizer, M., Lund, H., Eds.; Marcel Dekker: New York, 1983; Chapter 21. (b) Nyberg, K. *Chem. Scr.* 1974, 5, 115, 120. Jempty, T. C.; Gogings, K. A. Z.; Mazur, Y.; Miller, L. L. *J. Org. Chem.* 1981, 46, 4545. (c) McKillop, A.; Turell, A. G.; Young, D. W.; Taylor, E. C. *J. Am. Chem. Soc.* 1980, 102, 6504, 6513. (d) Landlais, Y.; Lebrun, A.; Robin, J. P. *Tetrahedron Lett.* 1986, 27, 5377.

suggest that in all reports on nitration of reactive aromatics, a description of the method of removal of lower NO_x species should be included. For nitronium salt nitrations the method of Elsenbaumer⁸ is recommended whereas with the HNO_3 -based reagents NaN_3 may be the scavenger of choice.²⁴ Note that urea normally is not powerful enough as NO_x scavenger under these circumstances.

Finally, it may be noted that the present catalytic system in principle can be used for other applications, e.g. according to the scheme



We are presently investigating the scope and utility of these reactions.

Acknowledgment. I thank Professor Lennart Ebersson for stimulating discussions, Dr. Roland L. Elsenbaumer for kindly providing a preprint, and the Swedish Natural Science Research Council for financial support.

Registry No. 1- $\text{BrC}_{10}\text{H}_7$, 90-11-9; 1- HC_{10}H_7 , 91-20-3; 1- $\text{CH}_3\text{C}_{10}\text{H}_7$, 90-12-0; 1- $\text{OCH}_3\text{C}_{10}\text{H}_7$, 2216-69-5; NOBF_4 , 14635-75-7; NO_2 , 10102-44-0; N_2O_4 , 10544-72-6; 4,4'-dibromo-1,1'-binaphthyl, 49610-35-7; 4,4'-dimethyl-1,1'-binaphthyl, 19224-41-0; 4,4'-dimethoxy-1,1'-binaphthyl, 19817-09-5; 1,2,4-trimethoxybenzene, 135-77-3; 2,2',4,4',5,5'-hexamethoxybiphenyl, 14262-07-8.

(24) See, e.g.: Clemens, A. H.; Ridd, J. H.; Sandall, J. B. P. *J. Chem. Soc., Perkin Trans. 2* 1985, 1227. Fitzpatrick, J.; Meyer, T. A.; O'Neill, M. E.; Williams, D. L. H. *Ibid.* 1984, 927.

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Received August 7, 1987

Optically Enriched Alkyltrimethylsilanes by Haller-Bauer Cleavage of Optically Active, Nonenolizable α -Silyl Phenyl Ketones

Summary: Conversion of *l*-menthyl ester 5 to phenyl ketones 7 and Haller-Bauer cleavage (MNH_2 , C_6H_6 , Δ) delivers the tertiary silanes 8 with 88–92% retention of configuration. The intermediate α -silyl carbanions are therefore generated in chiral condition and protonated almost exclusively on that surface from which benzamide is departing. The cyclic phenyl ketone (–)-12 also undergoes C–C bond cleavage with excellent (96–98%) levels of configurational retention.

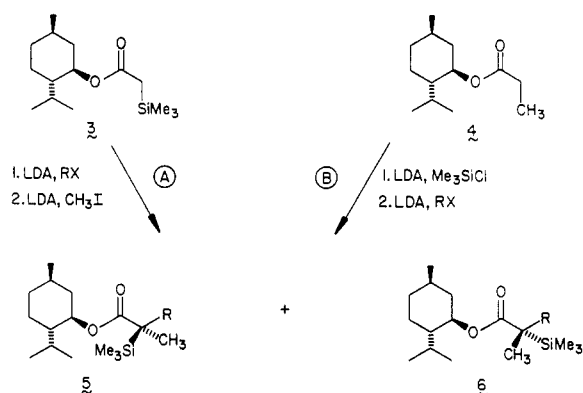
Sir: Optically active C-centered organosilanes¹ are rapidly gaining interest in their own right² and as important mechanistic probes.³ However, progress in this area has

(1) Hathaway, S. J.; Paquette, L. A. *J. Org. Chem.* 1983, 48, 3351.

(2) (a) Hayashi, T.; Konishi, M.; Ito, H.; Kumada, M. *J. Am. Chem. Soc.* 1982, 104, 4962. (b) Hayashi, T.; Kabeta, K.; Yamamoto, T.; Tameo, K.; Kumada, M. *Tetrahedron Lett.* 1983, 24, 5661. (c) Hayashi, T.; Konishi, M.; Okamoto, Y.; Kabeta, K.; Kumada, M. *J. Org. Chem.* 1986, 51, 3772. (d) Hayashi, T.; Yamamoto, A.; Iwata, T.; Ito, Y. *J. Chem. Soc., Chem. Commun.* 1987, 398. (e) Coppi, L.; Ricci, A.; Taddei, M. *Tetrahedron Lett.* 1987, 28, 965.

(3) (a) Hayashi, T.; Ito, H.; Kumada, M. *Tetrahedron Lett.* 1982, 23, 4605. (b) Hayashi, T.; Konishi, M.; Kumada, M. *J. Am. Chem. Soc.* 1982, 104, 4963. (c) Wetter, H.; Scherer, P. *Helv. Chim. Acta* 1983, 66, 118. (d) Hayashi, T.; Okamoto, Y.; Kabeta, K.; Hagihara, T.; Kumada, M. *J. Org. Chem.* 1984, 49, 4224. (e) Coppi, L.; Mordini, A.; Taddei, M. *Tetrahedron Lett.* 1987, 28, 969. (f) Hayashi, T.; Matsumoto, Y.; Ito, Y. *Organometallics* 1987, 6, 884. (g) Russell, A. T.; Procter, G. *Tetrahedron Lett.* 1987, 28, 2041, 2045.

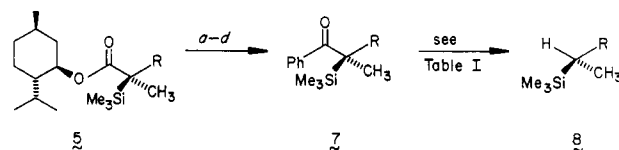
Scheme I^a



R	route A		route B	
	initial	purified ^c 5	initial	purified ^c 6
a, CH_2Ph	55 ^a 45	>99% de	31 69	20:80
b, $\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$	55 45	82% de	38 62	10:90
c, $\text{CH}_2\text{CH}_2\text{Ph}$	55 ^b 45	>99% de	25 75	8:92
d, $(\text{CH}_2)_4\text{CH}_3$	50 50	89% de	38 62	10:90

^a Obtained as colorless crystals, mp 68 °C, $[\alpha]_D^{25}$ –56.6° (c 1.4, CHCl_3). ^b Obtained as colorless crystals, mp 60.5 °C, $[\alpha]_D^{25}$ +3.1° (c 2.2, CHCl_3). ^c These figures apply to 40–50% mass return of the starting mixture after one chromatographic separation.

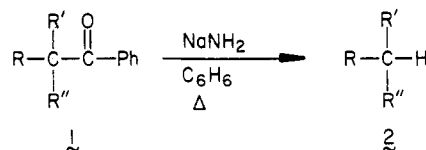
Scheme II^a



^a (a) Dibal, CH_2Cl_2 , 0 °C; (b) Ag_2CO_3 , Celite; (c) PhLi ; (d) $\text{CrO}_3\cdot\text{py}_2$.

been hampered by the unavailability of a general synthetic method capable of reliably delivering silanes of known absolute configuration. Herein, we outline a relatively simple protocol capable of realizing this objective.

The cleavage of nonenolizable ketones by amide ion (e.g., 1 → 2, the Haller-Bauer reaction)⁴ is recognized to fail if



at least one of the R groups cannot assist in stabilization of the intermediate carbanion. Thus, while the reaction works well when R = phenyl⁵ or cyclopropyl,⁶ alkyl substitution alone curtails debenzoylation.^{4a} Since Me_3Si substituents stabilize carbanions quite effectively,⁷ we have proceeded to examine the fate of optically active α -silyl ketones under Haller-Bauer conditions. Relevantly, bond scission in these systems proceeds invariably with high levels of configurational retention. These observations, when coupled with a new asymmetric synthesis of func-

(4) (a) Hamlin, K. E.; Weston, A. W. *Org. React. (N.Y.)* 1957, 9, 1. (b) Kaiser, E.; Warner, C. D. *Synthesis* 1975, 395.

(5) Paquette, L. A.; Gilday, J. P.; Ra, C. S. *J. Am. Chem. Soc.* 1987, 109, 6858 and references cited therein.

(6) Paquette, L. A.; Uchida, T.; Gallucci, J. C. *J. Am. Chem. Soc.* 1984, 106, 335 and relevant references cited therein.

(7) Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* 1984, 106, 6467 and references cited therein.