

Figure 2. Cyclic voltammograms in CH_3CN , 0.1 M TBAP for a Pt flag electrode ($3 \text{ mm} \times 3 \text{ mm}$) coated with a film of $\text{Ru}(\text{v-bpy})_3^{2+}$ containing $5.2 \times 10^{-8} \text{ mol/cm}^2$ Ru prior to (—) and after (---) ECL: (A) anodic sweeps at 20 mV/s; (B) cathodic sweeps at 10 mV/s.

material. For comparison, ECL cells involving thin solution layers 100–1000 times thicker ($\sim 10\text{--}100 \mu\text{m}$) with the $\text{Ru}(\text{bpy})_3^{2+}/\text{CH}_3\text{CN}$ system usually last only ~ 30 min under continuous pulsing.⁸

The decay mechanism seems to involve at least in part the generation of some electroinactive products. This is evident from the cyclic voltammograms for the oxidation and reduction of the immobilized complex obtained before and after ECL. Cyclic voltammograms in CH_3CN , 0.1 M TBAP (containing no dissolved complex) for an electrode coated with the $\text{Ru}(\text{v-bpy})_3^{2+}$ polymer prior to ECL show well-defined electrochemical surface waves for both the oxidation ($E^0 = 1.13 \text{ V vs. SSCE}$) and reduction ($E^0 = -1.41$ and -1.55 V vs. SSCE) (Figure 2). After extended ECL, cyclic voltammograms for the same electrode showed waves suppressed in height and less well-defined (reduction waves) with somewhat more tailing reminiscent of diffusional processes (Figure 2).

Since no coloration of the solution was observed after ECL, extensive dissolution of the immobilized complex does not take place, and the decrease in the electrochemical response is probably due to some decomposition of the polymer film. If half of the Ru species ($\sim 5 \times 10^{-9} \text{ mol}$) had dissolved in the 5 cm^3 of solution, the micromolar amounts of material would have been readily detectable.

Experiments are currently in progress to determine the nature of the processes in this polymer and to design other polymer layers containing donor and acceptor centers that will produce ECL. These are of interest not only as probes of the behavior of polymer electrodes but also perhaps as a means of obtaining a long-lived display device based on ECL.⁹

Registry No. $(\text{Ru}(\text{v-bpy})_3)^{2+}$, 75675-24-0; $(\text{Ru}(\text{v-bpy})_3)^{2+}\text{X}$, 81206-05-5.

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(9) The support of this research by the Army Research Office and the National Science Foundation (CHE 7903729) is gratefully acknowledged.

Silicon-Directed Nazarov Cyclization

S. E. Denmark* and T. K. Jones

Roger Adams Laboratory, School of Chemical Sciences
University of Illinois, Urbana, Illinois 61801

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Recent interest in the total synthesis of cyclopentanoid and polyquinane natural products has stimulated the development of many new methods for synthesis and annelation of five-membered rings. With regard to cyclopentenone annelation the classical Nazarov¹ cyclization reaction (Scheme I) has received much attention and has been extensively modified in the preparation of the divinyl ketone precursors (or their equivalent) and in the cyclization conditions.² A major limitation common to all of these methods and, indeed, inherent in the cyclization itself is the lack of control over the position of the double bond in the cyclopentenone moiety. Normally, the double bond resides in the thermodynamically more stable position, i.e., that with the highest degree of substitution. We report a new modification of the Nazarov reaction that provides a solution to this problem and constitutes a general method for the preparation of 4,5-annelated 2-cyclopentenones.^{3,4}

The key to this modification lies in the well-documented ability of silicon to control the regio- and stereochemical outcome of certain carbonium ion processes.⁵ This property, also known as the β effect,⁶ has dominated the utilization of organosilicon

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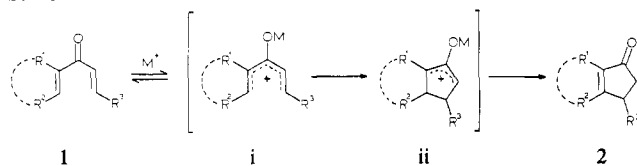
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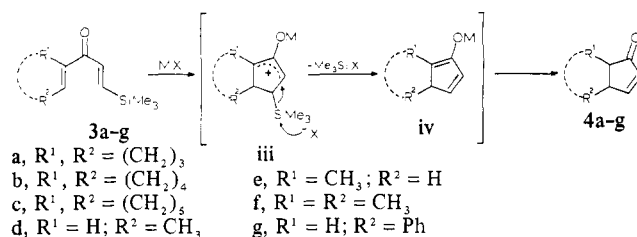
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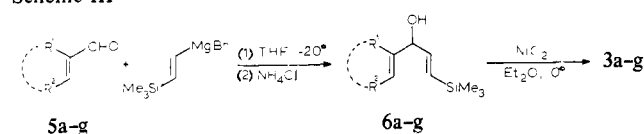
Scheme I



Scheme II

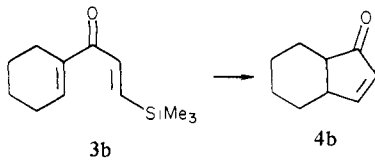


Scheme III



chemistry in synthesis.^{5a,7} We reasoned that strategic placement of a trimethylsilyl group as shown in Scheme II could direct the introduction of the new double bond in a Nazarov cyclization to the less substituted position, i.e., away from the ring fusion.⁸ The obvious advantages of such an outcome are (1) controlled introduction of potential functionality based on the double bond and (2) ready isomerization of the double bond into the more substituted position^{2b,4,9} if desired.

So that this hypothesis could be tested, a series of β -silyl divinyl ketones, **3a-g**, was prepared by the route shown in Scheme III. The Grignard reagent prepared from (*E*)-(2-bromoethenyl)trimethylsilane¹⁰ added smoothly to the α,β -unsaturated aldehydes **5a-g**¹¹ to afford the diallyl alcohols **6a-g**^{12a} in 51–92% yields.¹³ Oxidation of these alcohols with 1.8 equiv of nickel peroxide^{14,15} in ether gave the divinyl ketones **3a-g**^{12a,b} in 71–94% yields. More direct routes using α,β -unsaturated acyl derivatives have, thus far, proven unsatisfactory.¹⁶ In each case the *E* geometry of the

Table I^a


Lewis acid	temp, °C	yield, %
AlCl ₃	-30 → 25	30
SnCl ₄	-30 → 25	30
TiCl ₄	-78	0
BF ₃ ·OEt ₂	-30 → 25	23
ZnCl ₂	25	NR
CF ₃ SO ₃ SiMe ₃	-30 → 25	<i>b</i>
FeCl ₃	-30 → 25	84

^a The Lewis acid was added in one portion to a 0.08 M solution of **3b** in CH₂Cl₂ under nitrogen. ^b A trimethylsilyl dienol ether of **3b** was formed.

silyl-substituted double bond was assured by a 18.5–19.5-Hz vicinal coupling constant in the ¹H NMR spectrum.¹⁷

With the β -silyl divinyl ketones in hand we screened a variety of Lewis acids, solvents, and temperatures for the best conditions conducive to the desired cyclization. The ketone **3b** was used as test substrate for this study, and the results are shown in Table I. Of all the Lewis acids tested to date anhydrous ferric chloride¹⁸ has proven to be the most efficacious. The failure of SnCl₄ and BF₃·OEt₂ are surprising in view of their successful employment by Magnus^{2a} and Paquette^{2b} in related reactions. In general, dichloromethane²⁰ is the preferred solvent, but dichloroethane and toluene can be used as well; see Table II.

While the reasons for the striking superiority of FeCl₃ are not obvious at this time, the phenomenon appears to be general, as indicated by the results in Table II. In all of these examples only the cyclopentenone isomers **4a-g**^{12a,b} were produced, and none of their double-bond isomers **2** (R³ = H) could be detected by GLC. The yields¹³ of 4,5-annulated 2-cyclopentenones **4a-c** based on the aldehydes **5a-c** range from 39–65%. Furthermore, the successful cyclizations of **3d-g** indicate that the method is applicable to the synthesis of simple 4- and 5-substituted 2-cyclopentenones. The surprising formation of **4g**, while of little preparative value, serves to demonstrate the degree of regiocontrol possible with this method.

Several comments are in order. In all cyclizations, 1.05 equiv of FeCl₃ were necessary for complete reaction. In the bicyclic series **a-c** the rate of cyclization follows roughly the ease of deformation of the endocyclic double bond. The stereochemistry of the ring fusion in these cases was established by hydrogenation (Pd/C, 1 atm, EtOAc, 25 °C) to the saturated ketones **7b** and **7c** and comparison to known derivatives.²² While an unambiguous

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(8) A similar effect might be operating in the AgBF₄-induced annelation with (1-phenylthioethenyl)trimethylsilane reported by Magnus.^{2a}

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(12) (a) Satisfactory ¹H NMR (90 or 220 MHz), IR, and mass spectra were obtained for this compound. (b) Satisfactory microanalytical data were obtained for this compound.

(13) Yields refer to isolated, chromatographically homogeneous materials.

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(16) Calas and co-workers have prepared β -silyl divinyl ketones **3d** and **3g** (among others) by the Friedel-Crafts acylation of (*E*)-1,2-bis(trimethylsilyl)ethene with α,β -unsaturated acid chlorides. They make no mention of observing Nazarov cyclization under their conditions (AlCl₃, CH₂Cl₂, 0 °C), which is consistent with our results. Pillot, J. P.; Dunogues, J.; Calas, R. *Bull. Soc. Chim. Fr.* **1975**, 2143.

(17) GLC analysis (11% QF-1 on Chromosorb G 60–80, 6 ft × 1/8 in.) of **3a**, **3b**, and **3f** showed the presence of 6.9 and 5% of the *Z* isomers, respectively. **3f** was >99% *E* about the trisubstituted double bond.

(18) Purchased from Aldrich, 98%. We have found that purification of FeCl₃ by sublimation or dehydration of the hexahydrate¹⁹ did not improve the yield of the cyclization.

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Table II. Ferric Chloride Induced Cyclizations^a

substrate	solvent	temp, °C	time, h	product	yield, %
3a	(CH ₂ Cl) ₂ ^b	20	2.5	4a, ^c 100% cis ^d	55
3b	CH ₂ Cl ₂	0	4	4b, ^{3a} 100% cis ^d	84
3c	CH ₂ Cl ₂	0	1	4c, 85/15 cis-trans ^d	74
3d	CH ₂ Cl ₂	20	12	4d ^e	54
3e	CH ₂ Cl ₂	-20 ^f	6	4e ^g	42
3f	CH ₂ Cl ₂	-10 ^f	0.5	4f, ^j 59/41 cis-trans ^h	95
3g	PhCH ₃ ⁱ	20	8	4g	27

^a All reactions were done with 1.05 equiv of FeCl₃ and 0.08 M in divinyl ketone. The reactions mixtures (usually brown) were quenched with water and extracted with Et₂O, and the products were chromatographed on SiO₂ and distilled. ^b CH₂Cl₂ gave poorer yields. ^c DNP, mp 193–194 °C (lit. 188, 21a 192–194^{21b}). ^d Capillary GC analysis 10 m OV-101; 70 °C; for assignment see text. ^e DNP, mp 168.5–169.5 °C (lit.⁹ 170–172 °C). ^f At 0 °C the reaction was over instantaneously. ^g The ratio of diastereomers could not be accurately determined. ^h GLC analysis 11% QF-1 on Chromosorb G 60-80; for assignment see text. ⁱ In CH₂Cl₂ the cyclization required 18 h at 20 °C. ^j Reference 21c.

assignment for the major isomer in **4c** was not feasible, support for the assignment was obtained by equilibration of a 76/24 mixture of perhydroazulen-1-ones (NaOCH₃, CH₃OH, 25 °C) to a 24/76 mixture in which the trans compound should predominate.²⁶ The results in the acyclic series **d–g** stand in striking contrast to the failure of related Lewis acid catalyzed Nazarov cyclizations to produce simple cyclopentenones.^{2a,b,c} The formation

of dimer **4e** can be explained by the enhanced reactivity of **3e** towards Michael addition. We could not suppress its formation by dilution. The stereochemical assignment for the isomers of **4f** was secured by equilibration (basic Al₂O₃, activity I, CH₂Cl₂, 25 °C, 14 h) to a 90/10 mixture (GLC) in which the trans compound predominates.^{21c} It appears that the stereochemistry at C-5 is determined by the kinetic protonation of an enolate (**iv**, Scheme II) since neither **4b**, **4c**, nor **4f** is formed with isomer ratios near those at equilibrium.²⁷ Finally, the remarkable differences in reactivity for the acyclic cases are fully consistent with the mechanism shown in Scheme I, with the rate-determining step being the conrotatory closure²⁹ of the pentadienyl cation **i** to the oxyallyl cation **ii**.^{1h,i,30}

We are currently investigating other methods of inducing cyclization, mechanistic aspects, and applications to the synthesis of cyclopentanoid natural products.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was supported in part by the University of Illinois NSF Regional Instrumentation Facility (NSF CHE 79-16100) and the University of Illinois Mass

(22) The melting points for oxime and DNP are given below.

oxime, ^{12b} mp 92.5–94.5 °C
 oxime, lit.²³ mp (cis) 88–89 °C
 oxime, lit.²⁴ mp (trans) 145–146 °C

DNP, ^{12b} mp 170–171 °C
 DNP, lit.²⁵ mp (cis) 189–190 °C
 DNP, lit.²⁴ mp (trans) 229 °C

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(27) This requires the assumption that the equilibrium ratios of ring-fusion isomers for **4b** and **4c** are similar to those in the perhydro series. Equilibrium cis/trans ratios: **7b**,²⁸ 3/1; **7c**, 24/76 (this work).

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Registry No. 3a, 81255-86-9; 3b, 81255-87-0; 3c, 81255-88-1; 3d, 59376-60-2; 3e, 81255-89-2; 3f, 81255-90-5; 3g, 59376-62-4; 4a, 23668-30-6; 4a DNP, 1160-37-8; 4b, 81255-91-6; *cis*-4c, 81255-92-7; *trans*-4c, 81255-93-8; 4d, 23033-96-7; 4d DNP, 23034-00-6; 4e, isomer 1, 81255-94-9; 4e, isomer 2, 81255-95-0; *cis*-4f, 33765-38-7; *trans*-4f, 32556-65-3; 4g, 81255-96-1; 5a, 6140-65-4; 5b, 1192-88-7; 5c, 6140-67-6; 5d, 123-73-9; 5e, 78-85-3; 5f, 497-03-0; 5g, 14371-10-9; 6a, 81255-97-2; 6b, 81255-98-3; 6c, 81255-99-4; 6d, 81256-00-0; 6e, 81256-01-1; 6f, 81256-02-2; 6g, 81256-03-3; 7b oxime, 81256-04-4; *cis*-7c DNP, 81256-05-5; *trans*-7c DNP, 81256-06-6; (*E*)-(2-bromoethenyl)trimethylsilane, 13682-94-5.

An ESR Study of Olefin Iron Carbonyl Radical Anions

Paul J. Krusic*

Contribution No. 2925
Central Research and Development Department
E. I. du Pont de Nemours and Company
Wilmington, Delaware 19898

Joseph San Filippo, Jr.

Wright-Rieman Chemical Laboratories
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

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Recently we reported an electron spin resonance study of a series of iron carbonyl radical anions $\text{Fe}_n(\text{CO})_m^-$ ($n = 2-4$), which are formed in the reduction of $\text{Fe}(\text{CO})_5$ by alkali metals as well as in the chemical one-electron oxidation of iron carbonylate dianions in THF.¹ Despite considerable effort, we failed to observe the ESR spectrum of the simplest member of this family, the 17-electron $\text{Fe}(\text{CO})_4^-$ radical anion,² although many observations strongly implicated its involvement as a short-lived reaction intermediate.³ We now find that the closely related (π -olefin)- $\text{Fe}(\text{CO})_3^-$ radical anions are sufficiently stable, for certain olefins, to be studied by ESR. These radical anions exist in equilibrium with their diamagnetic dimers and are substitutionally labile as recently observed for other 17-electron species.⁴

Depending on the reaction temperature, time, and stoichiometry, three paramagnetic species can be obtained by reaction of saturated THF solutions of disodium tetracarbonylferrate,⁵ $\text{Na}_2\text{Fe}(\text{CO})_4$, with dilute THF solutions of methylmaleic anhydride (~ 0.02 M). With excess $\text{Fe}(\text{CO})_4^{2-}$ at -80°C , the spectrum of the thermally labile radical anion of this activated olefin is observed consisting of a quartet of doublets ($\Delta H \sim 0.2$ G) for the three

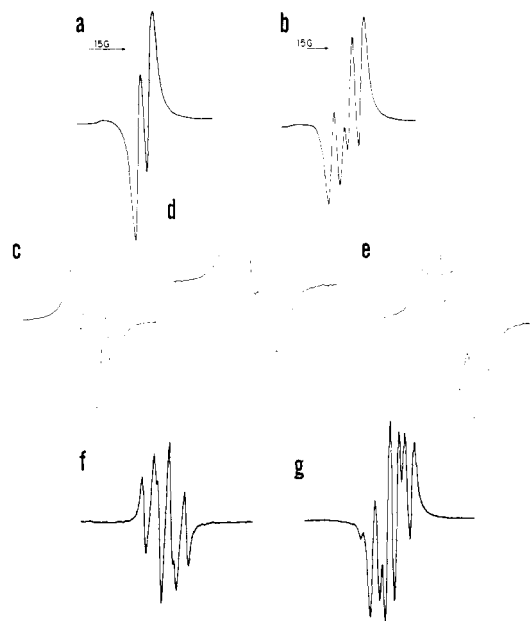
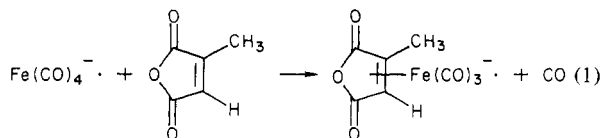


Figure 1. ESR spectra of (a) (methylmaleic anhydride) $\text{Fe}(\text{CO})_3^-$ in THF at -80°C ; (b) (methylmaleic anhydride) $^{57}\text{Fe}(\text{CO})_3^-$ in THF at -80°C ; (c) (maleic anhydride) $\text{Fe}(\text{CO})_3^-$ in THF/HMPA (9:1 v/v) at -80°C ; (d) (maleic- d_2 anhydride) $\text{Fe}(\text{CO})_3^-$ at -80°C (same solvent); (e) (methylmaleic anhydride) $\text{Fe}(\text{CO})_3^-$ at -80°C (same solvent); (f) (acrylonitrile) $\text{Fe}(\text{CO})_3^-$ at -90°C (same solvent); (g) (butadiene) $\text{Fe}(\text{CO})_3^-$ at -100°C in THF/HMPA (2:1 v/v).

methyl protons (7.06 G) and the single vinylic proton (5.77 G). The radical anion $\text{Fe}_2(\text{CO})_8^-$ is also formed ($g = 2.0385$).¹ If the reaction is carried out at room temperature with excess olefin, $\text{Fe}_2(\text{CO})_8^-$ and a third species are produced as evidenced by the observation of a doublet partially overlapped by the $\text{Fe}_2(\text{CO})_8^-$ line. Longer reaction times at room temperature lead to spectra in which this doublet ($a^H = 3.6$ G, $\Delta H = 2.3$ G, $g = 2.0407$, -80°C)⁶ is unencumbered by other resonances. In view of the collective evidence presented below, this doublet spectrum is assigned to (methylmaleic anhydride) $\text{Fe}(\text{CO})_3^-$ (I) in which the unpaired electron resides mostly on iron and interacts weakly with only the vinylic proton of the olefin.⁷ This is in sharp contrast to the uncomplexed organic radical anion in which the hyperfine interaction with the methyl protons (7.06 G) is the major one. The observation of the free organic radical anion implies the initial formation of $\text{Fe}(\text{CO})_4^-$, which either undergoes ligand substitution to give I⁸ (reaction 1) or dimerizes to $\text{Fe}_2(\text{CO})_8^{2-}$.



Similar results were obtained with maleic and dimethylmaleic anhydrides. The maleic anhydride iron tricarbonyl radical anion (II) gives a triplet appropriate for two equivalent vinylic protons ($a^H = 3.5$ G, $g = 2.0412$, $\Delta H = 1.8$ G, -80°C), while the dimethylmaleic anhydride analogue produces only a single line ($g = 2.0389$, $\Delta H = 3.0$ G, -70°C). The lack of hyperfine structure in the latter case is in sharp contrast to the septet for the six methyl

(1) Krusic, P. J.; San Filippo, J., Jr.; Hutchinson, B.; Hance, R. L.; Daniels, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2129-2131.

(2) $\text{Fe}(\text{CO})_4^-$ has been studied by matrix-isolation IR [Burdett, J. K. *Coord. Chem. Rev.* **1978**, *27*, 1-58. Burdett, J. K. *J. Chem. Soc., Chem. Commun.* **1973**, 763-764] and in the gas phase by mass spectrometry and ion cyclotron resonance [Dunbar, C. R.; Ennever, J. F.; Fackler, J. P., Jr. *Inorg. Chem.* **1973**, *12*, 2734-2736. Richardson, J. H.; Stephenson, L. M.; Brauman, J. I. *J. Am. Chem. Soc.* **1974**, *96*, 3671-3673. Dunbar, R. C.; Hutchinson, B. B. *Ibid.* **1974**, *96*, 3816-3820. Compton, R. N.; Stockdale, J. A. D. *Int. J. Mass Spectrom. Ion Phys.* **1976**, *22*, 47-55. Engelking, P. C.; Lineberger, W. C. *J. Am. Chem. Soc.* **1979**, *101*, 5569-5573].

(3) For example, $\text{Fe}(\text{CO})_4^-$ must be formed in the reaction of $\text{Fe}(\text{CO})_4^{2-}$ with alkyl iodides (but not bromides or chlorides) since we detected the ESR spectra of the corresponding alkyl radicals (*n*-butyl, isopropyl, and *tert*-butyl) by mixing in the ESR cavity 0.1 M $\text{Na}_2\text{Fe}(\text{CO})_4$ in 9:1 v/v THF/HMPA with 0.2 M alkyl iodide in THF at flow rates of about 9 mL/min. Cf.: Krusic, P. J.; Fagan, P. J.; San Filippo, J. Jr. *J. Am. Chem. Soc.* **1977**, *99*, 250-252.

(4) See, for example: Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1978**, *100*, 4095-4103.

(5) Commercial disodium tetracarbonylferrate dioxanate, $\text{Na}_2\text{Fe}(\text{CO})_4 \cdot 1.5\text{C}_4\text{H}_8\text{O}_2$ was used. All operations and reactions were carried out in a nitrogen glovebox. Solvents were rigorously dry and deoxygenated.

(6) The line widths of all iron carbonyl radical anions of this work are strongly temperature dependent and are narrowest at about -80°C .

(7) Paramagnetic olefin-transition-metal complexes are rare. See: Kasai, P. H.; McLeod, D., Jr.; Watanabe, T. *J. Am. Chem. Soc.* **1980**, *102*, 179-190 and references cited therein.

(8) The displacement of CO from $\text{Fe}(\text{CO})_4^-$ by maleic anhydride and its methyl-substituted derivatives has been recently observed in the gas phase by negative ion mass spectrometry. Weddle, G. H.; Ridge, D. P., private communication.