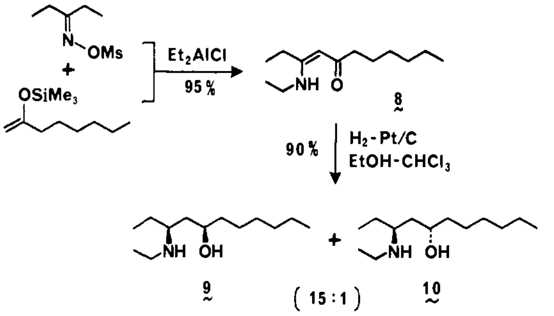
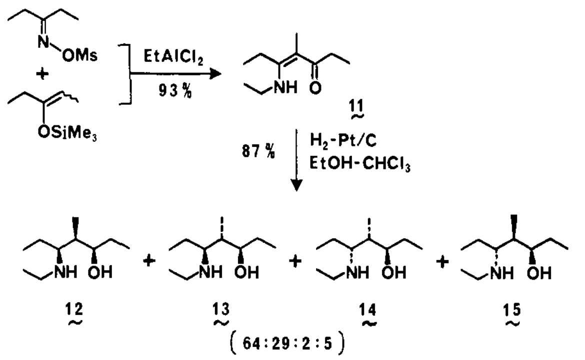
oxime mesylates, and the acetoxy moiety was left intact (entry 13). It should be added that oxime sulfonates of aromatic ketone and cyclopentanone systems are not employable; attempted condensation of various oxime substrates resulted in the formation of deteriorated reaction mixtures.

The versatility of enaminones in synthetic as well as heterocyclic chemistry serves as a stimulus for exploration of the potential applications of this methodology.[4] Accordingly, we have devised a new stereoselective approach to γ-amino alcohols by a direct hydrogenation of the enaminones.[8] Thus, the selective hydrogenation of the enaminone **8** leading to the γ-amino alcohol **9** was realized in 90% yield with reasonable stereoselectivity (~94%)[9] by using 10% platinum on charcoal as a catalyst in EtOH–$CHCl_3$ (30:1)[10] at 20 °C for 6 h and 1 atm of H_2. Under the similar conditions, the enaminone **11** was converted to the γ-amino alcohols, **12–15** (87% yield) in a ratio of 64:29:2:5.[11] Again 1,3-stereochemical control in **11** reaches to ~13:1 (64 + 29:2 + 5), which takes precedence over the 1,2 effect. These two examples clearly indicated the rigorous 1,3-stereochemical regulations exercised by an neighboring amino group in acyclic systems to the extent of 13–15:1. Such intramolecular participation of an appropriately placed heteroatom promises to be a useful strategy in the stereocontrolled synthesis of acyclic systems, since it is an effective way to reduce the conformational mobility and to increase the free energy difference of diastereomeric transition states.[12]





Acknowledgment. This work was supported by the Ministry of Education, Japanese Government (Grant-in-aid 118006).

Registry No. 2, 55314-45-9; **3**, 86921-54-2; **4**, 19980-33-7; **5**, 19980-35-9; **6**, 86921-55-3; **7**, 86921-56-4; **8**, 86921-57-5; **9**, 86921-58-6; **10**, 86953-18-6; **11**, 86921-59-7; **12**, 86921-60-0; **13**, 86992-31-6; **14**, 86992-32-7; **15**, 86992-33-8; (*E*)-$CHCH_3(CH_2)_4$—C=NOMs, 86921-61-1; –$(CH_2)_6$—C=NOMs, 80053-71-0; Me_2C=NOMs, 86921-62-2; –$(CH_2)_3$—C=NOMs, 80053-69-6; –$(CH_2)_{11}$—C=NOMs, 80053-72-1; Et_2C=NOMs, 86921-63-3; $EtAlCl_2$, 563-43-9; Et_2AlCl, 96-10-6; (1-cyclopenten-1-yloxy)trimethylsilane, 19980-43-9; (1-cyclohexen-1-yloxy)trimethylsilane, 6651-36-1; trimethyl[(1-phenylethenyl)oxy]silane, 13735-81-4; [[α-(4-acetoxyphenyl)ethenyl]oxy]silane, 86941-88-0; (1-butenyloxy)trimethylsilane, 6651-33-8; [(3,4-dihydro-2*H*-pyran-6-yl)oxy]trimethylsilane, 71309-70-1; [[(α-methoxy)hex-1-enyl]oxy]trimethylsilane, 84393-11-3; 2-(cyclopentan-1-on-2-ylidene)octahydrazocine, 86921-64-4; 2-[(α-methylamino)ethanylidene]cyclohexanone, 86921-65-5; 3-(methylamino)-1-phenyl-2-buten-1-one, 14091-93-1; 2-[(phenylcarbonyl)methylene]-7-methylhexahydro-1*H*-azepine, 86921-66-6; 2-[[(4-acetoxyphenyl)carbonyl]methylene]azacyclotridecane, 86921-67-7; 2-[(α-formyl)propylidene]hexahydro-1*H*-azepine, 86921-68-8; 3-[(α-methylamino)ethylidene]-2*H*-pyran-2-one, 86921-69-9; methyl 2-butyl-3-ethylaminopent-2-enoate, 86921-70-2.

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(9) The ratio of **9/10** was determined by GLC assay (OV-101, 205 °C) as their acetyl derivatives, **16** and **17**: t_r(**16**) = 8.30 min; t_r(**17**) = 9.21 min. The authentic **16** and **17** were prepared from 1-octene by the following sequence: (a) 2-isoxazoline formation (*n*-$PrNO_2$, PhNCO, cat. NEt_3); (b) reduction ($LiAlH_4$), followed by acetylation (Ac_2O, Py); (c) separation of two diastereomers by column chromatography on silica gel; (d) reduction of each isomer ($LiAlH_4$), followed by acetylation (Ac_2O, Py) leading to **16** and **17**, respectively. The stereochemical assignments of **16** and **17** were made according to the following literature: Jäger, V.; Buss, V.; Schwarb, W. *Tetrahedron Lett.* **1978**, 3133.

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(11) Determined by GLC assay (OV-101, 190 °C) after conversion to the corresponding acetyl derivatives, **18–21**: t_r(**18**) = 5.26 min; t_r(**19**) = 5.60 min; t_r(**20**) = 6.19 min; t_r(**21**) = 6.96 min. The authentic specimen, **18** and **21**, were made from *cis*-2-pentene in an analogous fashion as described in ref 9. For preparation of the authentic **20**, the acetyl derivative **18** was transformed into a mixture of **18** and **20** by the sequence: (a) selective hydrolysis of the acetoxy moiety (K_2CO_3, MeOH); (b) oxidation of the alcohol ($(COCl)_2$, Me_2SO, NEt_3); (c) reduction of the ketone ($NaBH_4$); (d) acetylation of the resulting two isomers (Ac_2O, Py).

(12) For a review, see: Bartlett, P. A. *Tetrahedron* **1980**, *36*, 2, and references cited therein.

A Novel (η^5-Cyclohexadienyl)tricarbonylchromium Anion: The Reaction between the Dianion of (η^6-Naphthalene)tricarbonylchromium and a Proton Source

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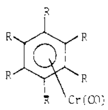
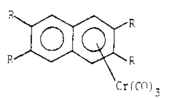
Nonaqueous electrochemical studies on the reductive behavior of various types of (arene)tricarbonylchromium complexes have been reported.[1-8] Of interest is the fact that exhaustive reduction of (benzene)tricarbonylchromium complexes (I) or (naphthalene)tricarbonylchromium complexes (II) in the presence of a proton source generates a solution with an oxidative wave at approximately –0.5 V. Oxidation at –0.4 V regenerates the original complexes.[1,7]



I



II

This behavior prompted us to investigate the product of the reaction between the dianion of (naphthalene)tricarbonylchromium and a proton source. We now wish to report our preliminary findings. Reaction of 50 mL of a 20 mM solution of (η^6-

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(2) Milligan, S. N.; Rieke, R. D. *Organometallics* **1983**, *2*, 171–173.

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(4) Gubin, S. P. *Pure Appl. Chem.* **1970**, *23*, 463–487.

(5) Ceccon, A.; Corvaja, C.; Giacometti, G.; Venzo, A. *J. Chem. Phys.* **1975**, *72*, 23–24.

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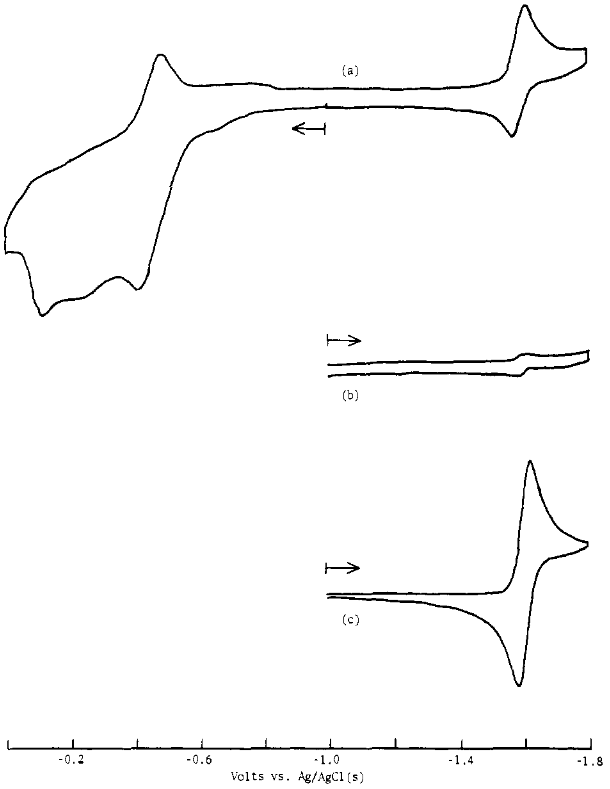
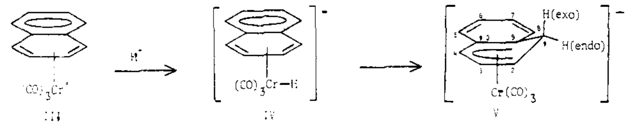


Figure 1. Cyclic voltammetric behavior of the tetraethylammonium salt of V and (η^6-naphthalene)tricarbonylchromium in propylene carbonate (0.25 M TEAP) by employing the HMDE (scan rate = 0.2 V/s): (a) CV of V scanning anodically and then cathodically from −1.0 V, (b) CV of V scanning cathodically from −1.0 V, (c) CV of (η^6-naphthalene)tricarbonylchromium scanning cathodically from −1.0 V.

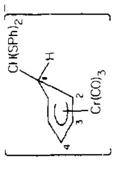
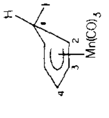
naphthalene)tricarbonylchromium in THF with 1 mL of sodium amalgam (1%) for 0.5 h yields a solution which, when treated with an equimolar amount of H_2O, has the identical infrared spectra[9] in the ν_{CO} region with the species generated electrochemically by reducing (naphthalene)tricarbonylchromium in the presence of a proton source. Methathesis with tetraethylammonium chloride followed by filtration and removal of the solvent yields a solid which shows the identical cyclic voltammetric behavior with that of the coulometrically generated species (see Figure 1).

Assignment of the solid as a (η^5-cyclohexadienyl)tricarbonylchromium anion[10] is based on spectroscopic evidence. Attempts to obtain good elemental analysis to date have met with failure due to the difficulty of recrystallizing the solid.[11] From the infrared, ^{1}H NMR, and ^{13}C NMR data, the protonated species is postulated to have the structure V.



A species of this nature would be expected to have a very low C–H stretch in the IR.[12-18] A KBr pellet infrared spectra of the

Table I. Spectroscopic Data for V,[a] *exo*-$C_6H_6[CH(SPh)_2]Cr(CO)_3^-$,[b] and $C_6H_7Mn(CO)_3$[c]

compound	ν_{CO}, cm^{-1}	^{1}H NMR shifts for cyclohexadienyl ring,[d] ppm					^{13}C NMR shifts for cyclohexadienyl ring,[e] ppm [$^1J_{CH}$, Hz]					
		H_{1exo}	H_{1endo}	H_2	H_3	H_4	C_1	C_2	C_3	C_4	C_9	C_{10}
V	1895 (s), 1800 (m), 1745 (m)	2.69		2.37	4.57	5.42	32.0 [dd, 118-128]	44.8 [d, 162]	97.8 [d, 168]		88.3 [s]	116.1 [s]
	1901, 1802, 1712		2.4	2.8	4.41	4.92						
	2020, 1942	2.3	1.6	2.35	4.16	5.20	24.2 [dd, 135]	50.1 [d, 168]	98.0 [d, 168]	79.7 [d, 177]		

[a] See ref 9 for conditions. [b] Reference 19. [c] References 14 and 27. [d] Other protons for V: $H_{5,8}$, 6.72, 6.67; $H_{6,7}$, 6.57, 6.32. [e] Other carbons for V: 134.2 [d, 157], 127.3 [d, 158], 124.8 [d, 158], 120.1 [d, 156]; C_{CO}, 243.1 [s].

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(9) All infrared data were obtained on a Perkin-Elmer 283 Infrared Spectrometer employing either KBr disks or THF solution. All NMR data were obtained on a Nicolet 360-MHz Instrument between −10 and −30 °C. ^{1}H NMR data were obtained in THF-d_8, while ^{13}C NMR data employed THF as solvent. All NMR shifts are reported downfield from Me_4Si.

(10) For a theoretical discussion of η^5-cyclohexadienyl complexes, see: Hoffman, R.; Hofmann, P. *J. Am. Chem. Soc.* **1976**, *98*, 598–604.

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solid does indeed show a low C–H stretch at 2750 cm^{-1} strongly supporting the postulated η^5-cyclohexadienyl structure.

Of more importance is a comparison of the ^1H NMR spectra[9] of the solid prepared above with the spectra of known η^5-cyclohexadienyl complexes (see Table I).[12-22] The position of the ring proton at 5.42 ppm corresponds to the proton on carbon 4, which is para to the CH_2 group, supporting the thesis that protonation must have occurred at the α-position of the complexed ring of naphthalene.

If instead of adding H_2O, D_2O is added to the dianion solution, the peak at 2.69 ppm has collapsed to a singlet from a doublet with a geminal coupling constant of 12.5 Hz. The low coupling constant between the methylene proton and the proton adjacent to it allows the assignment of the methylene proton to the exo position.[23] Hence, the mode of attack of the electrophile is endo. This is further supported by the fact that the low C–H stretch in the IR is still present for the D^+ addition reaction. It is highly likely, considering the steric bulk of the $Cr(CO)_3$ group, as well as probable charge distributions in the dianion, that the proton first attacks the chromium atom. Recently,[24] a chromium hydride, very similar to the one that would be formed, was isolated and characterized. The chromium hydride could then undergo a hydride transfer to the α-position to give the η^5-cyclohexadienyl complex.[25]

The ^{13}C NMR[9] of the anion is also supportive of the assigned structure; all but one peak behave as would be expected for structure V. Assignments were made utilizing ^{13}C–H coupling data and comparing the data with that of known η^5-cyclohexadienyl complexes.[26-30] The ^{13}C NMR data, coupled with the other spectroscopic results, is overwhelming evidence in favor of the postulated structure.

There are many novel aspects of this reaction that we hope to exploit further. This is the first η^5-cyclohexadienyl complex prepared by first reducing the parent arene complex followed by addition of an electrophile. Previous η^5-cyclohexadienyl complexes have been prepared from the reaction of the arene complex with nucleophiles such as H^- and R^-. Also novel is the mode of attack. Nucleophiles attack the ring exo to the metal center, while in the reaction of H^+ with the dianion, the mode of attack is endo. Also of interest is the fact that this is the first isolated η^5-cyclohexadienyl complex where the parent arene is not a benzene species but, instead, a polynuclear aromatic. Moreover, this work should provide a basis for the understanding of all the reductive electrochemistry of (arene)tricarbonylchromium complexes.

Acknowledgment. We thank the National Science Foundation for support of this research (Grant CHE78-06661).

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[25] A similar mechanism has been shown for the addition of CH_3I to $(\eta^5\text{-}C_9H_7)(CO)_3Cr^-$ and $(\eta^5\text{-}C_{13}H_9)(CO)_3Cr^-$: Nesmeyanov, A. N.; Ustynyuk, N. A.; Makarova, L. G.; Andrae, S.; Ustynyuk, Y. A.; Novikova, L. N.; Luzikov, Y. N. *J. Organomet. Chem.* **1978**, *154*, 45–63.

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Extraordinary Photorearrangement of Silylfurans and Subsequent Thermal Rearrangements

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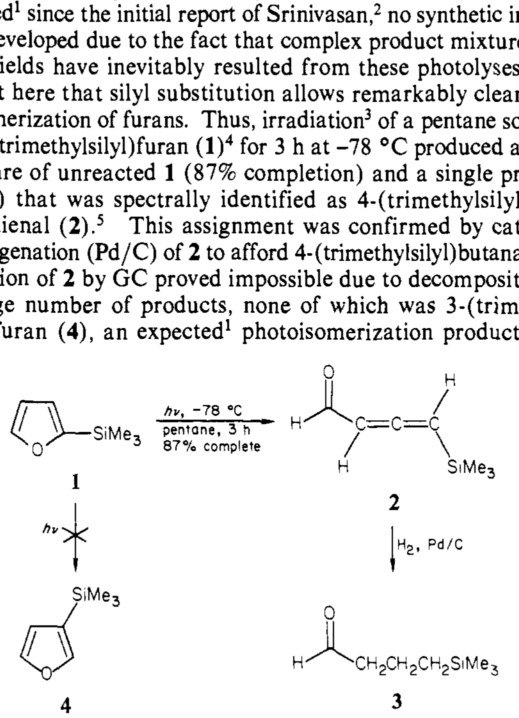
Although the photochemistry of furans has been extensively studied[1] since the initial report of Srinivasan,[2] no synthetic interest has developed due to the fact that complex product mixtures and low yields have inevitably resulted from these photolyses. We report here that silyl substitution allows remarkably clean photoisomerization of furans. Thus, irradiation[3] of a pentane solution of 2-(trimethylsilyl)furan (**1**)[4] for 3 h at −78 °C produced a clean mixture of unreacted **1** (87% completion) and a single product (68%) that was spectrally identified as 4-(trimethylsilyl)-2,3-butadienal (**2**).[5] This assignment was confirmed by catalytic hydrogenation (Pd/C) of **2** to afford 4-(trimethylsilyl)butanal (**3**).[6] Isolation of **2** by GC proved impossible due to decomposition to a large number of products, none of which was 3-(trimethylsilyl)furan (**4**), an expected[1] photoisomerization product of **1**.



Among the unprecedented features of the photolysis of **1** are the extreme cleanness, the high yield of an allene,[7] and the absence of a rearranged furan (i.e., **4**).

In order to determine whether the silicon substitution was the controlling factor in changing the course of furan photochemistry, we chose next a close analogue of the previously studied 2,5-di-*tert*-butylfuran (**13**).[8] Irradiation of a pentane solution of 2,5-bis(trimethylsilyl)furan (**5**) at −78 °C for 2 h resulted in 65% disappearance of **5** and clean formation of two products: allenyl ketone **6** (84%)[9] and allenyl aldehyde **7** (10%).[9] Ketone **6** (an oil at room temperature) was isolated pure by repeated low-temperature crystallization from pentane, but aldehyde **7** was identified from its ^1H NMR spectrum alone. Quite surprisingly attempts to hydrogenate **6** led to quantitative conversion by palladium catalysis to 2,4-bis(trimethylsilyl)furan (**10**).[10] This

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[1] Padwa, A. "Rearrangements in Ground and Excited States"; DeMayo, P., Ed.; Academic Press: New York, 1980; Vol. 3.

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[5] **2**: ^1H NMR (C_6C_6) δ 0.21 (s, 9 H), 5.13 (d, $J = 7$ Hz, 1 H), 5.45 (t, $J = 7$ Hz, 1 H), 9.52 ($HC{=}O$, d, $J = 7$ Hz); IR 1935 ($C{=}C{=}C$), 1692 cm^{-1} ($O{=}CC{=}C$).

[6] **3**: ^1H NMR (CCl_4) δ 0.15 (s, 9 H), 0.48 (m, 2 H), 1.72 (m, 2 H), 2.51 (m, 2 H), 9.72 (t, 1 H); IR $\nu_{C=O}$ 1730 cm^{-1}; calcd for $C_6H_{13}OSi$ ($M^+ - CH_3$) *m/e* 129.0736, measured *m/e* 129.0731.

[7] The highest previously reported yield of an allene from furan photolysis is 9%.[8]

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[9] **6**: ^1H NMR (CCl_4) δ 0.21 (s, 9 H), 0.22 (s, 9 H), 5.32 (d, $J = 7$ Hz, 1 H), 5.59 (d, $J = 7$ Hz, 1 H); CMR ($DCCl_3$) δ −1.5, −1.0, 87.6, 96.9, 216.8, 235.4; IR $\nu_{C=O}$ 1595, $\nu_{C=C=C}$ 1942 cm^{-1}; calcd for $C_{10}H_{20}OSi_2$ (M^+) *m/e* 212.1053, measured *m/e* 212.1059. **7**: ^1H NMR (CCl_4) δ 5.15 (d, $J = 8$ Hz, 1 H), 9.42; IR $\nu_{C=O}$ 1680, $\nu_{C=C=C}$ 1915 cm^{-1}.

0002-7863/83/1505-6316$01.50/0