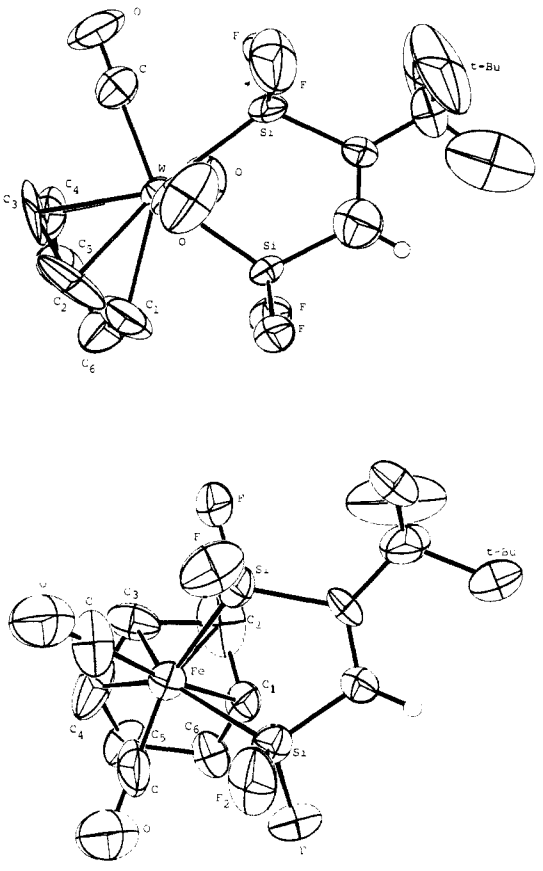
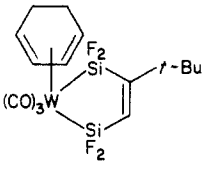


Figure 1. Molecular structure of $(C_6H_{10}Si_2F_4)Fe(C_6H_8)(CO)_2$ and $(C_6H_{10}Si_2F_4)W(C_6H_8)(CO)_3$.

$Fe(CO)_4$ complex formed initially.[4] One plausible reaction mechanism which would account for all the intermediates and products observed experimentally can be proposed in Scheme I.

It is interesting to note that when $W(CO)_6$ was used instead of $Fe(CO)_5$, only one product, **3a**, was obtained. The intermediate in the reaction of $W(CO)_6$ was also isolated and characterized as compound **7**.[6]



7

Since both compound **5** and compound **7** can be obtained as single crystals, X-ray diffraction experiments were carried out.[7] The structures are shown in Figure 1. In the case of **5**, the iron–disilacycle five-membered ring is puckered in such a way that two silicon atoms are located within 2.80–3.20 Å to carbon 1 of the cyclohexadiene ring. This steric relationship, in turn, facilitates bond formation between either of the Si atoms and the cyclohexadiene ring. On the other hand, the structure of **7** shows that the tungsten–disilacycle ring is flat and oriented nearly perpendicular to the cyclohexadiene ring so that only one silicon atom is in the vicinity (~3.0 Å) of carbon 1, whereas the other silicon atom (near the *tert*-butyl group) is located very far away (>5 Å) from any of the four diene carbons of the cyclohexadiene ring. The structural difference between intermediates **5** and **7** seems to offer an explanation for the fact that **5** led to both isomers whereas **7** lead to only one. The fact that **7** led to only **3a** on thermal decomposition is entirely in agreement with the reaction mechanism proposed above.

Acknowledgment. We thank the Chinese National Science Council for financial support to this work. C.H.L. thanks the Nuclear Energy Research Institute for a research fellowship.

Mass and NMR data for **2**, **3a,b**, **4**, **5**, and **6** (8 pages). Ordering information is given on any current masthead page.

Supplementary Material Available: Mass and NMR data for **2**, **3a,b**, **4**, **5**, and **6** (8 pages). Ordering information is given on any current masthead page.

Aldehydes, Alcohols, and Enol Acetates via Reductive Homologation of Esters

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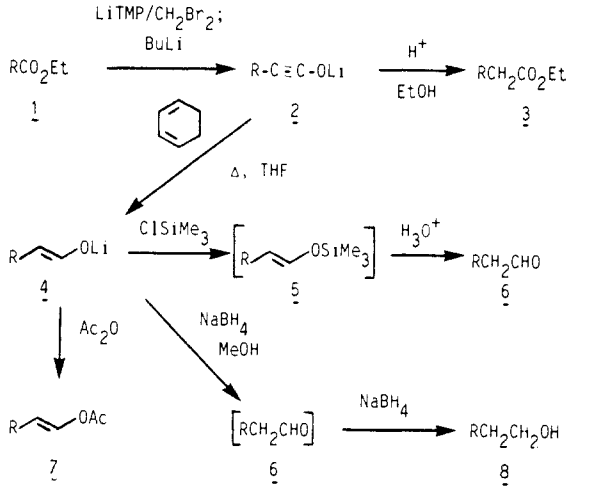
Recently we published a new method for the homologation of esters via alkynolate anion intermediates (i.e., **1** → **2** → **3**).[1] Herein we report that these electron-rich alkynolate anions, on refluxing with 1,3- and 1,4-cyclohexadienes in THF under strongly basic conditions, undergo an unprecedented reduction to afford aldehyde enolate anions **4**. These enolates (**4**) have been trapped as the corresponding enol acetates **7** after quenching with acetic



anhydride (see Table I). Only trans-enol acetates were obtained, except for the alkynyl case in which **22** was formed as a nearly 1:1 ratio of cis and trans isomers. The reaction was successful for esters **1** having attached R groups which were primary, secondary, aryl, and alkynyl; it failed in the tertiary (R = CMe_2CH_2Ph) and conjugated alkene (R = CH=CHPh) cases, however, which afforded no alkynolate reduction and a complex mixture of products, respectively.

† Smith Kline & French Postdoctoral Research Scientist.

(1) Kowalski, C. J.; Haque, M. S.; Fields, K. W. *J. Am. Chem. Soc.* **1985**, *107*, 1429.
(2) Yields (based on starting esters) reported in Table I are for isolated, purified product, except for the GC yield provided for aldehyde **19**. Starting esters were purchased from commercial sources except for **28b**, which was prepared in 74% yield from **28a** using the original homologation procedure.[1]
(3) Spectroscopic data (IR, NMR, and MS) and combustion analyses for new compounds are provided in the supplementary material.
(4) Occolowitz, J. L. *Aust. J. Chem.* **1967**, *20*, 2387.
(5) Hands, A. R.; Mercer, A. J. H. *J. Chem. Soc. C* **1968**, 2448.
(6) Twice the amounts of lithium tetramethylpiperidine, *n*-butyllithium, and CH_2Br_2 called for in the general procedure[1,4] were used in forming the alkynolate anion.
(7) Taguchi, T.; Takigawa, T.; Towara, Y.; Morikawa, T.; Kobayashi, Y. *Tetrahedron Lett.* **1984**, 5689.
(8) MacInnes, I.; Nonhebel, D. C.; Orszulik, S. T.; Suckling, C. J. *J. Chem. Soc., Perkin Trans. 1* **1983**, 2777.
(9) Kikukawa, K.; Naritomi, M.; He, G.; Wada, F.; Matsuda, T. *J. Org. Chem.* **1985**, *50*, 299.
(10) Merrill, R. E.; Allen, J. L. *Tetrahedron Lett.* **1977**, 1019.
(11) Fetizon, M.; Lazare, C. *J. Chem. Soc., Perkin Trans. 1* **1978**, 842.
(12) Svirskaya, P. I.; Leznoff, C. C. *J. Chem. Eng. Data* **1979**, *24*, 152.

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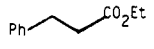
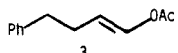
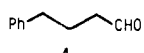
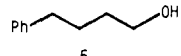
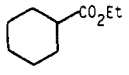
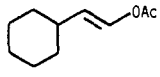
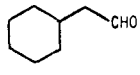
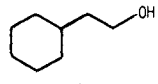
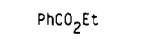
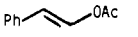
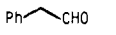
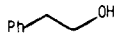
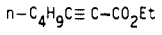
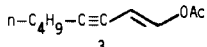
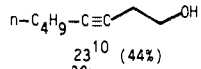
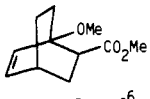
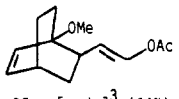
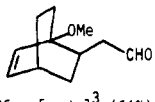
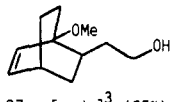
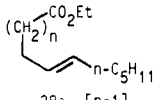
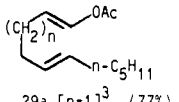
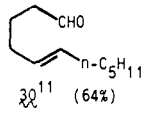
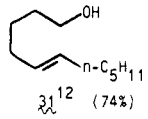
Table I. Reductive Homologation Products (Yields)[2]

starting ester	enol acetate	aldehyde	alcohol
 **9**	 **10**[3] (70%)	 **11**[4] (68%)	 **12**[5] (70%)
 **13**[6]	 **14**[7] (68%)	 **15**[8] (50%)	 **16**[8] (66%)
 **17**	 **18**[9] (65%)	 **19** (55%)[2]	 **20** (64%)
 **21**	 E&Z-**22**[3] (48%)	—	 **23**[10] (44%)
 **24a** [endo][6] **b** [exo][6]	 **25a** [endo][3] (64%) **b** [exo][3] (60%)	 **26a** [endo][3] (61%)	 **27a** [endo][3] (57%) **b** [exo][3] (55%)
 **28a** [n=1] **b** [n=2][2]	 **29a** [n=1][3] (77%) **b** [n=2][3] (65%)	 **30**[11] (64%)	 **31**[12] (74%)

Quenching solutions of enolate anions **4** from these reductions with aqueous acid afforded aldehydes **6** directly, but the yields were very poor (e.g., 22% for **9** → **11**). Since these conditions seemed too vigorous for the sensitive aldehyde functionality, the reactions were first quenched with $ClSiMe_3$ to generate silyl enol ethers **5**. Although these silyl ethers could be isolated (e.g., in 71% yield starting from ester **9**), they could also be hydrolyzed in situ. By stirring with aqueous acid, or shaking with *n*-Bu_4NF, they afforded aldehydes **6** in moderate yields (see Table I). Only the extremely sensitive aldehyde,[13] expected from alkynyl ester **21**, could not be obtained. Alternatively, when the enolate solutions were quenched into methanolic $NaBH_4$, the aldehydes **6** were rapidly reduced to the primary alcohols (i.e., **4** → **6** → **8**). The yields of alcohols **8** were generally similar to those of the corresponding enol acetates **7** (see Table I).

Studies are under way to elucidate the mechanism of these alkynolate anion reductions, and will subsequently be reported. It is worth noting, however, that 1,3-cyclohexadiene could be successfully replaced by the 1,4-isomer, or by inexpensive α- or γ-terpinene, but cyclohexene did not effect reduction. It is also noteworthy that if oxygen entered the reaction vessel upon addition of the diene, the reduction sometimes proceeded slowly or not at all. Addition of more base (*n*-butyllithium) always led to reaction in such cases; in fact, some of the more sluggish reductions (i.e., **13** and **24**) were clearly accelerated (e.g., from 20 to 1 h) by using extra (dibromomethyl)lithium and *n*-butyllithium in the alkynolate formation procedure.[6]

This novel reduction procedure[14] greatly extends the scope of our original homologation chemistry. Esters can now be homologated directly, not just to esters **1** → **3** but also to the corresponding aldehydes **6** and alcohols **8**. In addition, this chemistry provides a method of generating aldehyde enolate anions **4**,[15] enol

(13) This aldehyde has been reported to be extremely sensitive by: Barbot, F.; Miginiac, P. *Synthesis* **1983**, 651.

(14) **General Procedure.** Under a N_2 atmosphere, 4.4 mmol of *n*-butyllithium in hexane was added dropwise to a stirred, 0 °C solution of 4.8 mmol of 2,2,6,6-tetramethylpiperidine in 6 mL of THF. This mixture was added dropwise to a stirred solution of 4.4 mmol of dibromomethane in 6 mL of THF, cooled, with a −90 °C bath (dry ice/diethyl ether). After 5 min, a solution of 2.0 mmol of the starting ester **1** in 4 mL of THF was added dropwise, and 5 min later a solution of 10 mmol of *n*-butyllithium in hexane was added dropwise. The mixture was warmed by using a room temperature bath and stirred for 30 min; 20 mmol of 1,3-cyclohexadiene was added with careful exclusion of oxygen, and the mixture was refluxed for 30–60 min. The resulting enolate anion (**4**) was then quenched as follows to afford: **Enol Acetates 7.** The solution was cooled to 0 °C and 3 mL of acetic anhydride was added. After warming to room temperature for 5 min, the mixture was diluted with 200 mL of ether and washed with cold 2% H_2SO_4, 5% $NaHCO_3$, and brine. The product was purified by preparative TLC or flash chromatography on silica gel. **Alcohols 8.** The solution was cooled to 0 °C and added via cannula to a stirred, freshly prepared, 0 °C solution of 10 mmol of $NaBH_4$ in 10 mL of methanol. After 30 min, the mixture was diluted with 200 mL of ether, washed with water, and then further washed and purified as described above. **Aldehydes 6.** The solution was cooled to −90 °C and 3 mL of chlorotrimethylsilane (stored over CaH_2) was added. For aldehydes **11** and **30**, 10 mL of ether was added and the mixture was warmed to 0 °C, after which 15 mL of 10% HCl was added. After stirring for 10 min, the mixture was diluted with 200 mL of ether and worked up as above. For all other aldehydes, the quenched enolate solution was warmed to room temperature, diluted with 250 mL of petroleum ether, and washed with water and then 10% H_2SO_4. The solution was then shaken vigorously for 10 min with 8 mL of 1 M *n*-Bu_4NF in THF, washed with three 30-mL portions of water, and then further washed and purified as described above.

(15) Ladjama, D.; Riehl, J. J. *Synthesis* **1979**, 504.

acetates **7**,[16] and silyl enol ethers **5**. Since alkynolate anion formation occurs with complete retention of starting ester stereochemistry,[1] the derived reduction products are also formed with retained stereochemistry; thus, the endo ester **24a** affords only endo products **25a**, **26a**, and **27a**, while exo ester **24b** affords only exo products. The extended scope of products afforded by the remarkable reduction reaction reported herein, coupled with the stereochemical integrity of the original homologation chemistry, combine to provide a broad new methodology which should be useful in organic synthesis.

Supplementary Material Available: Spectroscopic and analytical data for **10–12**, **14**, **18**, (*E*)- and (*Z*)-**22**, **23**, **25a,b**, **26a**, **27a,b**, **28b**, **29a,b**, **30**, and **31** (3 pages). Ordering information is given on any masthead page.

(16) For references to the general preparation of enol esters, see: Mitsudo, T.; Yoshihisa, Y. H.; Watanabe, Y. *J. Org. Chem.* **1985**, *50*, 1566.

Synthesis of Eight-Membered Carbocycles via Intramolecular [6π + 2π] Photocycloaddition of Alkenyltropones

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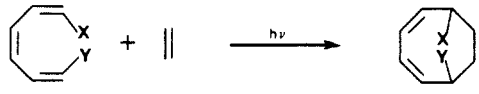
The synthesis of carbocyclic natural products containing a bicyclo[6.3.0]undecane skeleton has been of considerable interest recently.[1] Approaches to the preparation of the cyclooctane portion of these structures have utilized acyclic closure,[1k] fragmentation,[1f,g] and ring expansion[1c-e] strategies. Herein, we report the direct construction of the bicyclo[6.3.0]undecane nucleus via a novel [6π + 2π] intramolecular photochemical cycloaddition reaction.[2f]

A straightforward symmetry "allowed" photochemical cycloaddition of a linearly conjugated 6π-electron system with a 2π-electron moiety (eq 1) would certainly fall victim to alternative



(1)

1a X = Y = H **2a**
1b X,Y = CO **2b**

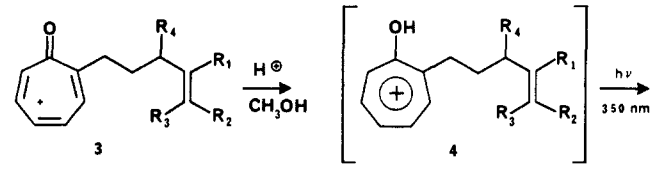
modes of reaction, such as electrocyclization of the triene or [2π + 2π] cycloaddition.[2] One 6π-electron system in which these undesired reaction pathways are minimized is tropone (**1b**).[3,4] Tropone and its derivatives have a rich photochemical history, although [6π + 2π] cycloaddition with a simple alkene has not been reported.[3-5]

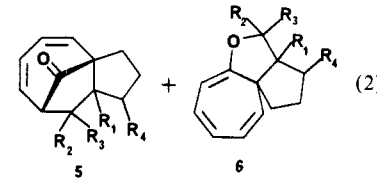
Table I

alkenyltropone 3[3a]	Cycloadducts[3b,c]
3a: R_1 = CH,	**7** 18(5); **8** 48(20)
3b: R_2 = CH,	**9** 10(5); **10** 37(18); **11** 5; **14**[3b] 31(15)
3c: R_3 = CH,	**10** 43(22); **11** 8(5); **14**[3b] 31(14)
3d: R_4 = CH,	**12** 28(19); **13** 13(4); **15**[3b] 29(14)

We recognized that a successful [6π + 2π] cycloaddition reaction would depend critically on the alkene intercepting an excited state of tropone in the desired regiochemical orientation prior to the intervention of other unwanted photochemical processes.[3,4] An intramolecular variant of this tropone/alkene cycloaddition strategy seemed a reasonable way to provide sufficient kinetic and regiochemical advantages to allow this reaction to occur.

In fact, when we irradiated alkenyltropone **3** in various aprotic solvents complex reaction mixtures resulted from which only minor amounts of cycloadducts were isolated. However, upon irradiation in *acidic* methanol, the desired intramolecular [6π + 2π] cycloaddition reaction proceeded smoothly to produce adduct **5** along with lesser amounts of the isomeric [8 + 2] adduct **6**[5] (eq 2). The





(2)

requirement for acid implicates the *hydroxytropylium ion* **4** as the 6π-electron component in this cycloaddition and represents one of the novel features of this process.

In a typical experiment, a 20 mM solution of alkenyltropone **3**[6] in 4:1 methanol/1 M H_2SO_4 was irradiated at room temper-

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