(Carbowax 20M column) indicated the composition listed in Table I (entry 1).

In summary, the processes described may be employed synthetically to reductively displace several allylic functional groups[10] that are otherwise difficult to remove (OR, SR, SO_2R, SeR, OSi-*t*-$BuMe_2$) and demonstrate that these groups should also be displaceable by other nucleophiles (i.e., carbonions). This possibility is being explored.

Acknowledgment. We thank the National Science Foundation for support of our programs on hydride chemistry (CHE-7909167).

Registry No. (*E*)-$CH_3(CH_2)_6CH{=}CHCH_2OPh$, 83026-82-8; (*E*)-$CH_3(CH_2)_6CH{=}CHCH_2OCH_3$, 57648-47-2; (*E*)-$CH_3(CH_2)_6CH{=}CHCH_2SPh$, 83026-83-9; (*E*)-$CH_3(CH_2)_6CH{=}CHCH_2SO_2Ph$, 83026-84-0; (*E*)-$CH_3(CH_2)_6CH{=}CHCH_2SePh$, 83026-85-1; (*E*)-$CH_3(CH_2)_6CH{=}CHCH_2OSiMe_2$-*t*-Bu, 83026-86-2; (*Z*)-$CH_3C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCH_2OPh$, 41515-57-5; (*E*)-$CH_3C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCH_2OPh$, 35266-82-1; (*E*)-$CH_3C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCH_2Cl$, 5389-87-7; (*E*)-$C_6H_5CH{=}CHCH_2OPh$, 37464-41-8; $LiBHEt_3$, 22560-16-3; $Pd(Ph_3P)_4$, 14221-01-3; (*E*)-$CH_3(CH_2)_6CH{=}CHCH_3$, 20063-97-2; $CH_3(CH_2)_7CH{=}CH_2$, 872-05-9; (*Z*)-$CH_3(CH_2)_6CH{=}CHCH_3$, 20348-51-0; (*Z*)-$CH_3C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCH_3$, 2492-22-0; (*E*)-$CH_3C(CH_3){=}CH(CH_2)_2C(CH_3){=}CHCH_3$, 2609-23-6; (*E*)-$C_6H_5CH{=}CHCH_3$, 873-66-5.

(10) Professor E. Negishi has observed highly regio- and stereoselective reductions of allylic derivatives with propargylzinc bromide: Matsushita, H.; Negishi, E., private communication. We thank Professor Negishi for informing us of his results prior to publication.

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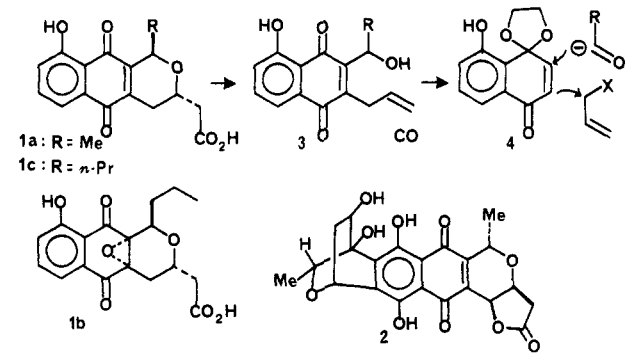
Synthesis of Naphthoquinone Antibiotics: Conjugate Addition/Electrophile Trapping with Acylnickel Carbonylate Anions

Summary: Conjugate addition of nickel acylate complexes followed by quenching with allyl iodide provide key intermediates for the synthesis of nanaomycin A and frenolicin.

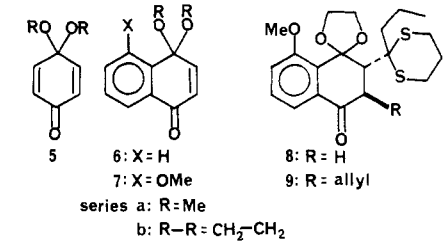
Sir: Nanaomycin A (**1a**),[3-4] frenolicin (**1b**),[5] and deoxyfrenolicin (**1c**)[4a,5b] are examples of a growing class of naphthoquinone derivatives with significant antibiotic activity. The presence of the 2,3-fused pyran ring opens the possibility that members of the class may serve as "bio-reductive alkylating agents",[6] and this feature is consistent with the significant antineoplastic activity of **1a**. As part of a general development of new approaches to naphthoquinones of this type with the goal of efficient preparation of the more complex analogue granaticin (**2**),[7,8] we have completed a short efficient synthesis of **1a** and **1c** following the strategy outlined in Scheme I.

Scheme I. Strategy



Related work has demonstrated that palladium(II)-promoted intramolecular alkoxycarbonylation (e.g., conversion of **3** to **1a** and **1c**) can be an efficient, stereoselective reaction in related cases.[9] An intermediate such as **3** might be obtained by conjugate addition of a carbonyl anion equivalent to a quinone monoketal (e.g., **4**) and reaction of the resulting enolate with allyl halide. Naphthoquinone monoketals are readily available[10] and useful intermediates[11] known to undergo conjugate addition to heteroatom[12] and highly stabilized carbanion nucleophiles.[13] However, conjugate addition of reactive carbanions with quinone monoketals has not been successful; dialkylcuprates have been observed to initiate reductive cleavage of benzoquinone monoketal rather than addition.[14] In the early stages of this work, we investigated the use of HMPA to promote 1,4-addition of more reactive nucleophiles,[15] as well as the addition of cuprates.

The use of HMPA, TMEDA, or Dabco in reaction of *n*-butyllithium with quinone monoketals **5**–**7** was not



(1) Visiting Scholar from Department of Chemistry, Florida International University, Miami, FL.

(2) Recipient of a National Research Service Award from the National Cancer Institute, NIH, for 1981–1982.

(3) (a) Omura, S.; Tanaka, H.; Koyama, Y.; Oiwa, R.; Katagiri, M. *J. Antibiot.* **1974**, *27*, 363–365. (b) Tanaka, H.; Koyama, K.; Marumo, H.; Oiwa, R.; Kagatiri, M.; Nagai, T.; Omura, S. *Ibid.* **1975**, *28*, 860–867. (c) Tanaka, H.; Murumo, H.; Nagai, T.; Okada, M.; Taniguchi, T.; Omura, S. *Ibid.* **1975**, *28*, 925–930.

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(11) For a review, see: Koelsch, P. M.; Tanis, S. P. *Kodak Lab. Chem. Bull.* **1980**, *52*, 1–7.

(12) For examples with benzoquinone monoketal and leading references, see: Foster, L. H.; Payne, D. A. *J. Am. Chem. Soc.* **1978**, *100*, 2834–2344.

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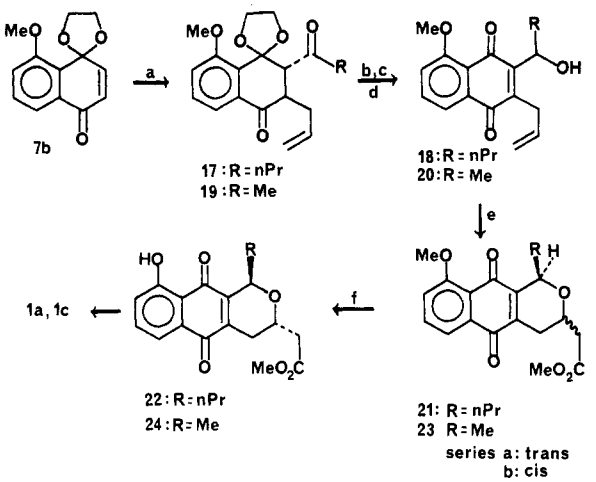
0022-3263/82/1947-4382$01.25/0

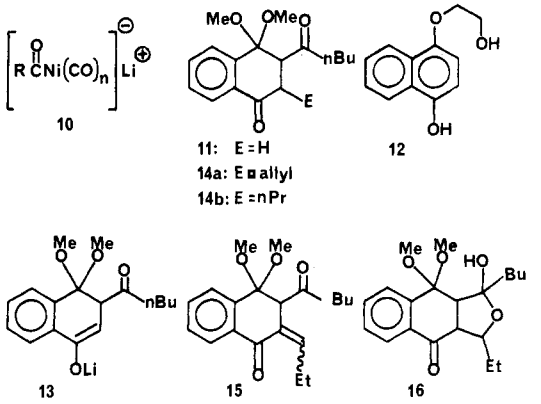
Scheme II. Synthesis[a]



[a] (a) *n*-PrLi/Ni(CO)$_4$/Et$_2$O, -50 °C, 1.5 h; allyl iodide/HMPA, 25 °C, 15 h. (b) 2:1 dioxane/6 N HCl, 25 °C, 2 days. (c) NaBH$_4$/THF. (d) DDQ/CH$_3$OH, 0 °C, 0.5 h. (e) PdCl$_2$(CH$_3$CN)$_2$ (0.1 mol equiv)/CuCl$_2$ (3.0 mol equiv)/CH$_3$OH/CO (1.1 atm), 25 °C, 3.3 h. (f) From **21**: 10 m mol equiv of BBr$_3$/CH$_2$Cl$_2$, 0 °C, 10 min. For **23**, see ref 4a and 4b.

promising. The best results, 1:1 mixtures of products from 1,2- and 1,4-addition modes, were obtained with 2 mol equiv of HMPA in THF with **5b** and **6b**. Under the same conditions, 1,4-addition of 2-propyl-2-lithio-1,3-dithiane was more efficient. For example, with **7b** only the product of 1,4-addition was detected (**8**, 86% yield).[16] Trapping of the intermediate enolate anion was best achieved by adding a fivefold excess of allyl bromide. The product (**9**) was obtained as a single isomer (presumably trans[17]) in 60% yield.[16]

Corey and Hegedus reported that acylnickel carbonylate anions (**10**), generated from nickel tetracarbonyl and alkyllithium reagents, will react with α,β-unsaturated ketones via 1,4-addition of the acyl unit.[18] No quinone or quinone ketal examples were reported, the yields with cyclic enones were only moderate, and no attempt to trap the presumed enolate anion intermediate was reported.[18] In spite of vigorous development of other carbonyl anion equivalents capable of conjugate addition,[19] little further investigation of this reagent has appeared. We have examined the reaction of **10** with monoketals of naphthoquinones and find, with minor modifications of the published procedure, that 1,4-adducts are generally obtained in excellent yield. For example, the dimethyl ketal **6a** of napthoquinone reacts at -50 °C in THF with the acyl complex from *n*-butyllithium and Ni(CO)$_4$ to give the adduct **11** in 91% yield.[20] Yields are also good with *n*-butylmagnesium chloride (**11**, 75%). Reductive cleavage is not observed with **6a** during the addition, but structure **12** is detected (12% yield) from **6b**. The lithium enolate **13** assumed to be present in these reactions can be trapped by addition of excess allyl iodide. In this way, **14a** was obtained in 85% yield from addition of the *n*-BuLi/Ni(CO)$_4$ combination to **6a**, followed by addition of a solution of allyl iodide (5 mol equiv) in HMPA.[21] Attempted alkylation (*n*-PrI) of the enolate led to a mixture of products from O-alkylation (20%), C-alkylation (21%), and multiple alkylation (45%).[22] Similarly, reaction of the enolate **13b** with propionaldehyde was complicated by elimination (**15**, 40%) and hemiketal formation (**16**, 34%).



We have used the conjugate addition/trapping sequence in syntheses of nanaomycin A (**1a**) and deoxyfrenolicin (**1c**), in seven steps from the known[10a] juglone monoketal methyl ether, **7b** (Scheme II). Addition of *n*-propyllithium[23] to nickel carbonyl (-50 °C, 0.5 h) gave a brown solution in ether to which was added **7b** at -50 °C. After 1.5 h at -50 °C, excess allyl iodide (2 mol equiv) and HMPA were added, and the mixture was stirred at 25 °C for 15 h. The adduct **17** was isolated in 81% yield (based on **7b**) as a yellow solid, mp 113.5–114 °C.[24] Hydrolysis of the ketal, reduction of the side chain carbonyl, and oxidation converted **17** to the hydroxyquinone **18** (79% yield overall) as an orange oil.[24] A similar sequence starting from methyllithium produced **19** (54%) and then **20** (69%; mp 76–78 °C).[25]

(16) The product was obtained by preparative layer chromatography as an oil, homogeneous by analytical TLC. Consistent ^{1}H NMR, ^{13}C NMR, IR, and analytical data (combustion or high-resolution mass spectral analysis) were obtained for this compound.

(17) For related examples of alkylation of 3-substituted cyclohexanone enolate anions, see: (a) Coates, R. M.; Sandetur, L. D. *J. Org. Chem.* **1974**, *39*, 275–279. (b) Posner, G. H.; Sterling, J. J.; Whitten, C. E.; Brunelle, D. F. *J. Am. Chem. Soc.* **1975**, *38*, 4450–4455.

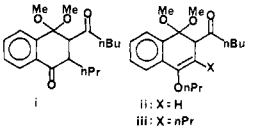
(18) Corey, E. J.; Hegedus, L. S. *J. Am. Chem. Soc.* **1969**, *91*, 4926–4927.

(19) For a review of reactions of carbonyl anion equivalents, see: Lever, O. W. *Tetrahedron* **1976**, *34*, 1943–1971.

(20) Spectral data for **11**: ^{1}H NMR (CDCl$_3$) δ 8.05 (1 H, m), 7.38–7.77 (m, 3 H), 3.83 (dd, 1 H, J = 5.48 2.9 Hz), 3.04 (dd, 1 H, J = 18.0, 5.4 Hz), 2.92 (s, 3 H), 2.80 (dd, 1 H, J = 18, 2.9 Hz), 2.44 (m, 2 H), 0.9–1.6 (m, 4 H), 0.80 (br t, 3 H); IR (neat) 1715 (s), 1700 (s) cm^{-1}; mass spectral molecular weight 290.1509, calcd for C$_{17}$H$_{22}$O$_4$ 290.1518.

(21) Spectral data for **14a**: ^{1}H NMR (CDCl$_3$) δ 7.96 (m, 1 H), 7.34–7.76 (m, 3 H), 5.8 (m, 1 H), 5.00–5.30 (m, 2 H), 3.74 (d, 1 H, J = 3.6 Hz), 3.40 (s, 3 H), 2.91 (s, 3 H), 2.6–2.96 (m, 3 H), 2.46 (t, 2 H), 1.0–1.60 (m, 4 H), 0.84 (br t, 3 H, J = 7 Hz); IR (neat) 1713 (s), 1695 (s), 1608 (s) cm^{-1}; mass spectral molecular weight 330.1817, calcd for C$_{20}$H$_{26}$O$_4$ 330.1833.

(22) The products were separated by layer chromatography and tentatively identified as i–iii by ^{1}H NMR, IR, and mass spectral analysis.



(23) The *n*-propyllithium was prepared from n-propyl bromide and lithium metal according to the procedure of H. Gilman as presented in: Jones, R. G.; Gilman, H. *Org. React.* **1951**, *6*, 352–353.

(24) Spectral data for **17**: ^{1}H NMR (CDCl$_3$) δ 7.70 (dd, 1 H, J = 7, 2 Hz), 7.13 (dd, 1 H, J = 8.0, 1.5 Hz), 7.40 (t, 1 H, J = 7.0 Hz), 6.0–5.55 (m, 1 H), 5.2–4.9 (m, 2 H), 4.5–4.0 (m, 4 H), 3.88 (s, 3 H), 3.65 (d, 1 H, J = 6.5), 3.15–2.25 (m, 5 H), 1.7–1.35 (m, 2.2 H), 0.90 (t, 3 H, J = 7.0 Hz); IR (CHCl$_3$) 3080 (w), 3000 (m), 2970 (s), 2840 (w), 1710 (s), 1690 (s), 1640 (w), 1590 (s), 1480 (s), 1270 (s) cm^{-1}. Anal. C, H. Spectral data for **18**: ^{1}H NMR (CDCl$_3$) δ 7.8–7.5 (m, 2 H), 7.25 (dd, 1 H, J = 8.0, 2.5 Hz), 6.1–5.6 (m, 1 H), 5.3–5.0 (m, 2 H), 4.9–4.6 (m, 1 H), 4.00 (s, 3 H), 3.72 (d, 1 H, J = 11 Hz), 3.38 (br d, 2 H, J = 3.5 Hz), 2.2–1.3 (m, 4 H), 0.95 (t, 3 H, J = 6.0 Hz); IR (neat) 3500 (br), 3080 (w), 2960 (s), 2880 (m), 2840 (m), 1650 (s), 1620 (s), 1590 (s), 1470 (s), 1280 (s) cm^{-1}; MS parent, m/e 300.

Reaction of 18 under alkoxycarbonylation conditions[9,26] involved a mixture of $PdCl_2(CH_3CN)_2$ (0.1 mol equiv) and $CuCl_2$ (3.0 mol equiv) in methyl alcohol under a positive pressure of CO (1.1 atm). After 3.3 h at 25 °C, the crude product was obtained and chromatographed to provide a mixture of **21a** and **21b** (70% yield). Analytical HPLC indicated a ratio of **21a/21b** = 3:1. The major component (**21a**, trans) was obtained by crystallization as orange needles, mp 134–136 °C. The minor product (**21b**, cis) was also obtained by crystallization from the mother liquor, mp 144–148.5 °C and the isomers were identified by NMR spectral analysis.[27] Treatment of the phenol ethers with BBr_3 causes demethylation to the phenol for both **21a** and **21b** and complete isomerization of the cis arrangement in **21b** into the natural trans series, **22** (84% yield of **22**). The ester **22** has been converted to (±)-deoxyfrenolicin (**1c**) and correlated with a sample of (+)-frenolicin derived from nature.[9a]

Reaction of **20** under the same alkoxycarbonylation conditions (25 °C/6 h) produced pyrano ester isomers **23a** and **23b** in 89% yield and a ratio of trans/cis = 3:2. The major isomer (**23a**) was isolated by crystallization from hexane–ethyl acetate, mp 132.5–135 °C. The minor isomer (**23b**) was crystallized from the mother liquor, mp 144.5–145 °C; it can be equilibrated with **23a** in sulfuric acid.[4] The phenol methyl ether is cleaved with $AlCl_3$ and the methyl ester is hydrolyzed with dilute aqueous base to give nanaomycin A (**1a**).[4a,b] A formal synthesis of **1a** is completed.

Acknowledgment. We acknowledge support for this work from the National Institutes of Health, through Research Grant AI-15916 and a postdoctoral fellowship to E. Spiess.

(25) Characterization data for **19**: mp 126–127 °C; ^1H NMR ($CDCl_3$) δ 7.65 (d, 1 H, J = 9.0 Hz), 7.38 (t, 1 H, J = 9.0 Hz), 7.08 (d, 1 H, J = 9.0 Hz), 6.0–5.4 (m, 1 H), 5.0–4.85 (m, 2 H), 4.4–4.0 (m, 4 H), 3.88 (s, 3 H), 3.55 (d, J = 9.0 Hz), overlapping with 3.4–2.25 (m, 4.3 H together), 2.25 (s, 3 H); IR ($CHCl_3$) 3080 (w), 3000 (m), 2900 (m), 2840 (w), 1710 (s), 1690 (s), 1640 (w), 1585 (s), 1470 (s), 1440 (m), 1290 (s) cm^{-1}. Anal. C, H. Characterization of **20**: mp 76–78 °C; ^1H NMR ($CDCl_3$) δ 7.63–7.4 (m, 2 H), 7.13 (dd, 1 H, J = 8.5, 2.5 Hz), 6.0–5.58 (m, 1 H), 5.2–4.65 (m, 3 H), including apparent dq at δ 4.78 (1 H, J = 11, 7 Hz). Irradiation at δ 1.50 gives δ 4.8 (d, 1 H, J = 1 Hz), 3.92 (s, 3 H), 3.63 (d, 1 H, J = 11 Hz; collapses to s with irradiation at δ 4.7), 3.36 (dt, 2 H, J = 6, 1.5 Hz), 1.51 (d, 3 H, J = 7.0 Hz); IR ($CHCl_3$) 3500 (br), 3080 (w), 3000 (m), 2930 (s),2840 (w), 1650 (s), 1630 (s), 1570 (s) cm^{-1}. Anal. C, H.

(26) For discussion of this general reaction, see: (a) Stille, J. K.; Hines, L. F.; Fries, R. W.; Wong, P. K.; James, D. E.; Lau, K. *Adv. Chem. Ser.* **1974**, *No. 132*, 90. (b) Collman, J. P.; Hegedus, L. S. "Principles and Applications of Organotransition Metal Chemistry"; University Science Books: Mill Valley, CA, 1980, pp 585, 604. (c) James, D. E.; Stille, J. K. *J. Am. Chem. Soc.* **1976**, *98*, 1810. The problems assocatied with Pd-promoted addition of nucleophiles to alkenes followed by carbonylation have been discussed recently; the same paper described examples of intramolecular addition of amine nucleophiles with CO trapping which are efficient in a limited number of examples: Hegedus, L. S.; Allen, G.; Olsen, D. J. *J. Am. Chem. Soc.* **1980**, *102*, 3583.

(27) The stereochemistry of each isomer (**21a, 21b**) was determined by analogy with the eleutherin–isoleutherin system: Cameron, D. W.; Kingston, D. G. I.; Sheppard, N.; Lord Todd *J. Chem. Soc.* **1964**, 98. The pseudochair arrangement with the C-11 alkyl group equatorial is preferred. In the ^1H NMR spectra, the homoallylic (homobenzylic) coupling between H at C-12 and H at C-9 is greater when the C-9 H is pseudo-axial (eleutherin, C-9 shows J = 3.5 and 2.9 Hz for coupling to the $H_{a'}$ and $H_{e'}$ at C-12). The CH_2 unit at C-12 in **21b** gave rise to two ddd patterns at δ 2.84 (pseudoequatorial H with J = 18, 2.6, 2.6 Hz) and δ 2.21 (pseudo-axial H with J = 18, 10.4, and 3.9 Hs). The homoallylic coupling constants are therefore 3.9 Hz (C-9 axial/C-12 axial) and 2.6 Hz (C-9 ax/C-12 eq), consistent with a cis-pyran configuration.

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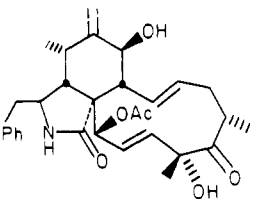
Model Study for Synthesis of the Cytochalasin D Cycloundecanone Ring System

Summary: Thiocarbonyl Diels–Alder additions are used to assemble **6** and **12**, precursors of sulfur-bridged cycloundecenones **3a,b**, via ylide rearrangement. Either **6** or **12** is converted into allylic iodides upon reaction with Me_3SiI, and internal S-alkylation followed by a 2,3-shift gives the desired **3**. A novel method for α-sulfur bond cleavage in ketone **3b** or **3i** with $PhMe_2SiLi$ described. Complete desulfurization of **3** with Raney Ni affords 5-acetoxycycloundecanone (**17**).

Sir: Cytochalasin D is an important tool for probing aspects of cell membrane function.[1] The molecule contains an 11-membered carbocycle in addition to an isoindolone unit, derivatives of which we have recently synthesized.[2] Cycloundecanes are found in other natural products, but the cytochalasin carbocycle is unique in its complexity and poses a major challenge.[3] Our plans for cycloundecanone construction include ring expansion methods, one of which is described here.

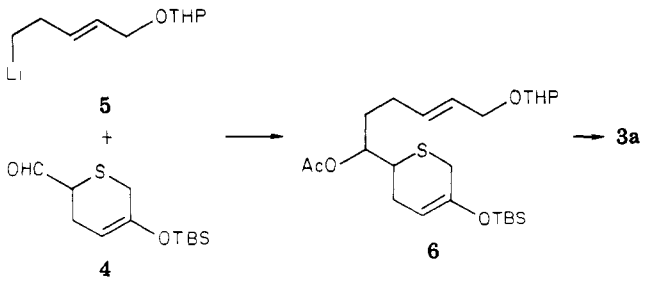


cytochalasin D

Earlier work in our laboratory has shown that sulfur-bridged lactones of 10 or 11 members can be made via the [2,3] sigmatropic rearrangement of bicyclic sulfonium ylides.[4] Application of this concept to carbocycle synthesis requires the preparation of a functionalized thian-3-one such as **1**. Ring expansion via internal S-alkylation and ylide generation would be expected to form the sulfur-bridged cycloundecanone **3**.

Two different routes to the desired ylide precursor **1** have been developed, both of which rely upon thiocarbonyl Diels–Alder additions. In the shorter route (a series, Scheme I) the adduct of the transient thioaldehyde NCCSH[5] with 2-(*tert*-butyldimethylsiloxy)-1,3-butadiene is converted into **4** by DIBAL reduction (84%). Condensation of **4** with the organolithium reagent **5** followed by

Scheme I. Route a



(1) Tanenbaum, S. W., Ed. "Frontiers of Biology"; North-Holland Publishing Co.: New York, 1980; Vol. 46.

(2) Vedejs, E.; Campbell, J. B., Jr.; Gadwood, R. C.; Rodgers, J. D.; Spear, K. L.; Watanabe, Y. *J. Org. Chem.* **1982**, *47*, 1534.

(3) For a previous study directed at the cyochalasin cycloundecane ring by a fragmentation approach, see: Clark, D. A.; Fuchs, P. L. *J. Am. Chem. Soc.* **1979**, *101*, 3567.

(4) Vedejs, E.; Gapinski, D. M.; Hagen, J. P. *J. Org. Chem.* **1981**, *46*, 5451.

(5) Vedejs, E.; Eberlein, T. H.; Varie, D. L. *J. Am. Chem. Soc.* **1982**, *104*, 1445.

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