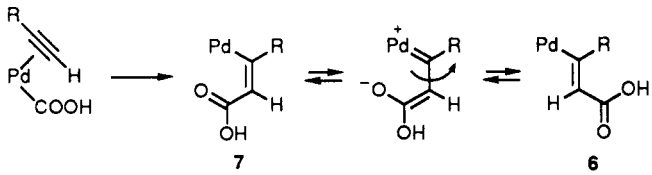
mechanism with a four-centered, bimolecular transition state that may be partially ionic or radical in character, depending on subtle stereoelectronic effects.

At this stage, we cannot favor any one of the above mentioned mechanisms for the trans insertion reaction that is believed to be the source of product **3** in our system. Our results can be explained by both the four-centred concerted mechanism put forth by Otsuka et al. and by the following cis–trans isomerization postulate:



7 **6**

The equilbrium distribution of **6** and **7** would presumably be determined by a number of factors, including the steric interactions between the R and acid groups. Thus, less of the trans insertion product **6**, and hence the fumaric derivative **3**, would be expected with bulky R groups; this is borne out by the results (Table I).

Acknowledgment. We are grateful to British Petroleum for financial support and Dr. Fausto Calderazzo for helpful discussions.

Registry No. 1 (R = Ph), 36122-35-7; 1 (R = *t*-Bu), 18261-07-9; 1 (R = CH(Me)Et), 134566-86-2; 1 (R = $(CH_2)_2Ph$), 134566-87-3; 1 (R = $(CH_2)_3Ph$), 134566-88-4; 1 (R = $(CH_2)_3Cl$), 134566-89-5; 1 (R = $(CH_2)_3CN$), 134566-90-8; 1 (R = $(CH_2)_3CH_3$), 100378-66-3; 1 (R = $(CH_2)_5CH_3$), 90926-71-9; 2 (R = *t*-Bu), 18305-61-8; 2 (R = CH(Me)Et), 134566-91-9; 2 (R = $(CH_2)_3Cl$), 134566-92-0; 2 (R = $(CH_2)_3CN$), 134566-93-1; 2 (R = $(CH_2)_3CH_3$), 69665-12-9; 2 (R = $(CH_2)_5CH_3$), 104505-48-8; 3 (R = CH(Me)Et), 6621-99-4; 3 (R = $(CH_2)_2Ph$), 5469-48-7; 3 (R = $(CH_2)_3Ph$), 134566-94-2; 3 (R = $(CH_2)_3Cl$), 134566-95-3; 3 (R = $(CH_2)_3CN$), 134566-96-4; 3 (R = $(CH_2)_3CH_3$), 5469-36-3; 3 (R = $(CH_2)_5CH_3$), 71033-48-2; HC≡CPh, 536-74-3; HC≡CC$(CH_3)_3$, 917-92-0; HC≡CCH$(CH_3)CH_2CH_3$, 922-59-8; HC≡C(CH_2)Ph, 16520-62-0; HC≡C$(CH_2)_3$Ph, 1823-14-9; HC≡C$(CH_2)_3$Cl, 14267-92-6; HC≡C$(CH_2)_3$CN, 14918-21-9; HC≡C$(CH_2)_3CH_3$, 693-02-7; HC≡C$(CH_2)_5CH_3$, 629-05-0; $PdCl_2$, 7647-10-1; $CuCl_2$, 7447-39-4; *trans*-2-octenoic acid, 1871-67-6.

Nucleophile/Electrophile Double Additions to (1-Methoxynaphthalene)tricarbonylchromium(0). Application in a Formal Synthesis of the Aklavinone AB Ring

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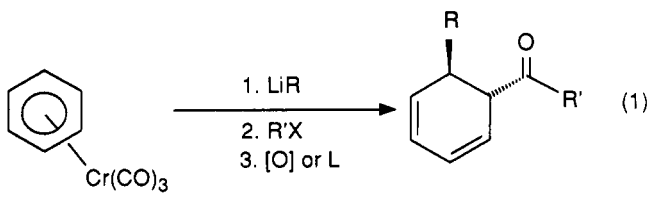
The $Cr(CO)_3$ group complexed selectively to the nonsubstituted ring of 1-methoxynaphthalene to give (1-methoxynaphthalene)$Cr(CO)_3$ (**5**). Nucleophilic addition of a series of sulfur-stabilized carbanions to **5** were studied. In general, this reaction, after oxidation, gave mixtures of all four regioisomeric disubstituted naphthalenes. 2-(Methyldithianyl)lithium (**9**) and [(phenylthio)methyl]lithium (**12**) predominantly added to the β-position of the coordinated ring of **5**. The α positions were slightly favored with the more stabilized carbanions [2-(trimethylsilyl)dithianyl]lithium (**14**) and [tris(methylthio)methyl]lithium (**16**), and, unlike nucleophiles **9**, **12**, and dithianyllithium (**6**), these carbanions rearranged on warming to −10 °C to give good selectivity for addition to C(5). In a synthetic application, **16** was added to complex **5**, followed by alkylation of the anionic benzocyclohexadienyl intermediate with methyl iodide, CO insertion and reductive elimination to give, with 6:1 regioselectivity, the *trans*-1,2-disubstituted-1,2-dihydro-5-methoxynaphthalene **19a**. This reaction introduced in a regio- and stereoselective manner an ester equivalent and an acetyl group to C(5) and C(6) of the 1-methoxynaphthalene complex. Methanolysis of the orthothioformate, double bond isomerization, reduction of the acetyl group, and introduction of the 2-OH group via epoxidation yielded the target aklavinone AB ring intermediate **2**.

Introduction

Recently, a novel trans stereoselective addition of a carbon nucleophile and an acyl group across an arene double bond was developed in these laboratories (eq 1).[1]



(1)

It involves the activation of the arene via complexation to the electrophilic $Cr(CO)_3$ group followed by a sequential addition of a carbanion and an alkyl halide to the complex. Nucleophiles add to the complexed arene from the side opposite the metal, and subsequent alkylation takes place at the metal center and is followed by CO insertion and regio- and stereoselective acyl transfer to the endo face of the cyclohexadienyl ligand.

It is well established that substituted arene complexes readily undergo carbanion addition in a highly regioselective manner.[2] The double addition, if successful with these substrates, could lead to useful alicyclic intermedi-

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(1) Kündig, E. P.; Cunningham, A. F., Jr.; Paglia, P.; Simmons, D. P.; Bernardinelli, G. *Helv. Chim. Acta* **1990**, *73*, 386 and earlier references cited.

(2) Semmelhack, M. F.; Clark, G. R.; Garcia, J. L.; Harrison, J. J.; Thebtaranonth, Y.; Wulff, W.; Yamashita, A. *Tetrahedron* **1981**, *37*, 3957 and earlier references cited.

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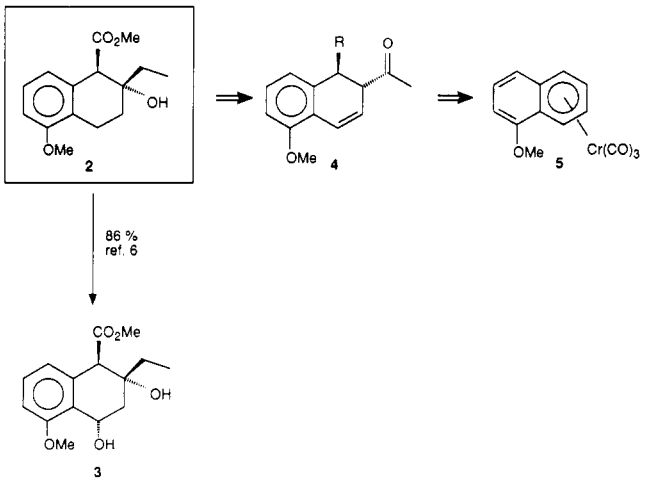
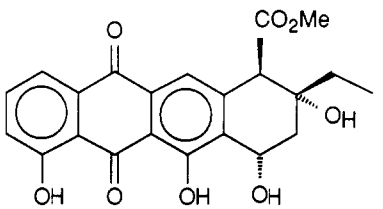
Scheme I



ates. It has to be kept in mind, however, that while a considerable range of carbanions add to give anionic cyclohexadienyl complexes, not all of these adducts can be alkylated. In the cases in which the nucleophilic addition is readily reversible, the subsequent reaction with an alkyl halide simply leads to the regeneration of the starting arene complex;[3] also, in reversible additions regioselectivity can vary with reaction time and temperature.[4] Dissociation can be largely suppressed by the addition of a polar cosolvent, such as HMPA or DMPU, and some nucleophiles add irreversibly even without cosolvent.[4] In this article we use the above observations to achieve a formal synthesis of the AB ring of aklavinone (1), the aglycone of aclacy-

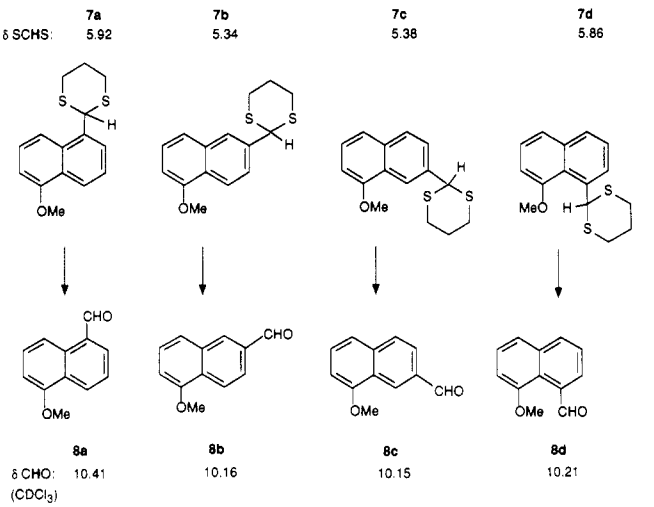


1

nomycine A. Aclacinomycine A belongs to the anthracyclinone family of antibiotics which, in recent years, have been recognized as important anticancer agents. Much attention has been focused on the synthesis of anthracyclines[5] to find compounds with better clinical efficiency and reduced cardiotoxicity. As our synthetic objective, we selected the tetrahydronaphthalene **2**, as the high-yield introduction of the benzylic hydroxy group had been described previously by Meyers and Higashiyama in their asymmetric synthesis of the AB ring (**3**) of aklavinone.[6]

We considered that **2** should be accessible from a regio- and stereoselectively functionalized dihydronaphthalene **4** (Scheme I). This, in turn, could be obtained via a nucleophile/electrophile tandem addition to (1-methoxynaphthalene)$Cr(CO)_3$ (**5**). In all previous examples of this tandem addition reaction the acyl transfer from the metal to the ring occurred to a terminal carbon of the cyclohexadienyl ring,[1] α to the center bearing the group introduced by nucleophilic addition. The pivotal question in this scheme is therefore that of regioselectivity of the addition of a suitable nucleophilic ester precursor to **5**, and this, indeed, proved the most challenging aspect of this study.

Scheme II



Results and Discussion

The orange crystalline air-stable complex **5** was obtained in 77% yield from the reaction between $Cr(CO)_6$ and 1-methoxynaphthalene. ^1H NMR shows the $Cr(CO)_3$ group to be complexed to the nonsubstituted ring. Regiosepecific incorporation of the $Cr(CO)_3$ group in the nonsubstituted ring has been observed previously with 1,4-dimethoxynaphthalene.[4,7] Complex **5** shows that a single methoxy group is already sufficient to efficiently direct complexation and thereby selectively activate the nonsubstituted ring to nucleophilic addition. As a first step toward **2**, we examined the regioselectivity of the addition of suitable nucleophiles to complex **5** by carrying out the nucleophile addition/oxidation sequence shown in eq 2, which affords disubstituted naphthalenes.

Regioselectivity of Nucleophilic Addition to 5. Dithiane and 2-Methyldithiane. Complex **5** was added to a THF solution (0.15 M) of 2-lithio-1,3-dithiane[8] (**6**) at −78 °C. The temperature was raised to −30 °C over a 3-h period, and the product was decomplexed by oxidation (I_2). A mixture of all four possible regioisomers **7a–d**, identical by TLC, was obtained. The product ratio was determined by NMR integration of the dithiane methine proton signals (Scheme II).

For structural assignment the mixture was converted to the corresponding aldehydes (**8a–d**) and pure samples of the two major products were obtained by crystallization. On the basis of spectral and analytical data, the major isomer (representing 50% of the mixture) was identified as **8a**—the product of desired regiochemistry. The structures of the isomeric naphthaldehydes **8b** and **8c** were assigned on the premise that the C(1)–H NMR resonance of **8c** (8.79 ppm (br s)) should be observed at lower field

(3) Semmelhack, M. F.; Hall, H. T., Jr.; Farina, R.; Yoshifuji, M.; Clark, G.; Bargar, T.; Hirotsu, K.; Clardy, J. *J. Am. Chem. Soc.* **1979**, *101*, 3535.

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(8) (a) Corey, E. J.; Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1965**, *12*, 1075. (b) Seebach, D. *Synthesis* **1969**, 17. (c) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1975**, *40*, 231.

Table I. Reaction of Complex 5 with Sulfur-Stabilized Carbanions Followed by Oxidative Decomplexation (I_2) To Give Disubstituted Naphthalenes 7 and 8

entry	nucleophile	solvent	Lewis acid	conditions[a]	product	distribution a:b:c:d	a:isom	yield, %
1	$LiCHS(CH_2)_3S$ (6)	THF	none	−78 to −30 °C, 3 h	7	50:26:12:12	1.0:1.0	77
2	6	THF	none	−78 °C, 0.1 h; 0 °C, 14 h	7	48:26:17:9	0.9:1.0	68
3	6	THF	none	−78 °C, 1 h; 0 °C, 61 h	7	44:35:17:4	0.8:1.0	72
4	6	THF/HMPA 5:1	none	−78 °C, 1 h; −10 °C, 25 h	7	54:36:10:0	1.2:1.0	65
5	6	THF/Et_2O 1:6	none	−78 °C, 1 h; 0 °C, 18 h	7	41:29:15:15	0.7:1.0	57
6	6	THF/Tol 1:6	none	id	7	47:23:15:15	0.9:1.0	50
7	6	diglyme	none	id	7	52:29:15:4	1.1:1.0	73
8	6	THF	LiCl[b]	−78 °C, 0.1 h; 0 °C, 18 h	7	56:28:16:0	1.3:1.0	80
9	6	diglyme	LiCl[c]	−78 °C, 0.1 h; 0 °C, 12 h	7	66:22:12:0	1.9:1.0	51
10	6	diglyme	LiBr[c]	−78 °C, 0.1 h; 0 °C, 60 h	7	64:23:13:0	1.8:1.0	62
11	$LiCH_2SPh$ (12)	THF/HMPA 11:1	none	−78 to −30 °C, 3 h	8	17:50:33:0[d]	0.2:1.0	44[e]
12	$LiCH(SiMe_3)SPh$ (13)	THF	none	−78 to −10 °C, 3 h	8	58:16:10:16[f]	1.3:1.0	75[g]

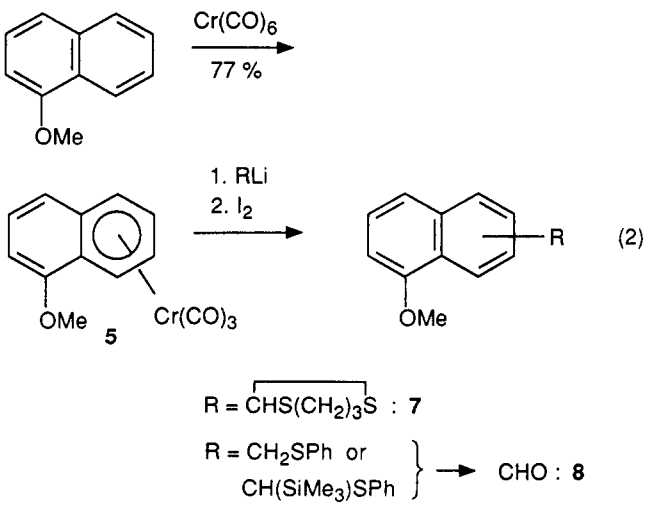
[a] In all experiments, chromium complex 5 was added as a solid to a solution of the nucleophile at −78 °C. [b] 6 equiv, dried under vacuum at 100 °C, 5 h. [c] 10 equiv. [d] Product distribution after oxidation and Pummerer rearrangement (59% yield). [e] Yield of thioanisole addition. [f] Product distribution after oxidation and sila-Pummerer rearrangement (78% yield). [g] Yield of carbanion addition.

Table II. Tandem Nucleophile/Electrophile Addition Reactions of RLi and Methyl Iodide to Complex 5

entry	nucleophile	conditions[a]	dec	product	distribution a:b:c:d	a:isom	yield, %
1	$LiCHS(CH_2)_3S$ (6)	0 °C, 12 h	PPh_3	10	42:29:17:12[b]	0.8:1.0	44
2	6	0 °C, 18 h	I_2	10	0:71:29:0		29
3	$LiC(Me)S(CH_2)_3S$ (9)	−78 to −10 °C, 3 h (+2 h)	PPh_3	11	28:46:26:0[c]	0.4:1.0	76
4	9	−78[d] to −10 °C, 2 h (+2 h)	PPh_3	11	24:52:24:0	0.3:1.0	79
5	9	0 °C, 4 h	I_2	11	6:61:33:0	0.1:1.0	55
6	$LiC(SiMe_3)S(CH_2)_3S$ (14)	−78 to −55 °C, 1 h	PPh_3	17	61:30:7:2[e]	1.6:1.0	62
7[f]	14	−78 to −10 °C, 3 h (+2 h)	PPh_3	17	84:3:1:12[e]	5.3:1.0	53
8	$LiC(SPh)_3$ (15)	−78 to −0 °C, 3 h	PPh_3	no addition[g]	no addition[g]		
9	$LiC(SMe)_3$ (16)	−78 to −50 °C, 1 h (+2 h)	PPh_3	19	49:37:9:5[h]	1.0:1.0	71
10[i]	16	−78 to −10 °C, 3 h (+2 h)	PPh_3	19	86:0:0:14	6.1:1.0	59
11[j]	16	−78 to −10 °C, 3 h (+2 h)	PPh_3	19	86:0:0:14	6.1:1.0	73[j]

[a] In all experiments, chromium complex 5 was added as a solid at −78 °C to a solution of the nucleophile in THF (unless otherwise noted). After nucleophilic addition (see conditions) MeI and HMPA were added at −78 °C and the reaction mixture was placed under an atmosphere of CO. [b] Ratio determined by integration of H–C(1) NMR resonances that appear at 4.25 (**10a**), 4.09 (**10b**), 4.55 (**10c**), and 4.24 or 4.36 (**10d**) ppm. [c] Ratio determined by integration of H–C(1) NMR resonances that appear at 4.11 (**11a**), 4.26 (**11b**), and 4.69 (**11c**) ppm. [d] HMPA was added directly after the addition of complex 5. [e] Products **17a,b** were isolated. The ratio of the products was determined by integration of the $SiMe_3$ NMR resonances at 0.25 (**17d**), 0.10 (**17a**), −0.05 (**17b**), and −0.13 (**17c**) ppm. [f] From the same reaction mixture as entry 6. [g] $MeC(SPh)_3$ (18) was isolated in 60% yield. [h] Ratio determined by integration of H–C(1) NMR resonances that appear at 4.04 (**19a**), 4.42 (**19b**), 4.79 (**19c**), and 4.61 (**19d**) ppm. [i] From the same reaction mixture as entry 9. [j] Reaction carried out in diglyme.

than that of **8b** (8.29 ppm (d, J = 2 Hz)) as a result of deshielding due to the peri-OMe group. In order to improve yields and increase the proportion of the desired isomer (**7a**), reaction conditions were varied, and the results of a selection of these experiments are reported in Table I.



While the desired isomer **7a** was always the major product, addition to carbons β to the ring junction took place to a substantial degree. **7d**[9] was a very minor product, as expected on the grounds of adverse steric interactions and electron pair repulsion between the incoming nucleophile and the peri-OMe group. Variation of solvent (entries 4–7) generally caused minimal changes of regioselectivity—except for diethyl ether (entry 5), which increased the proportions of the unwanted isomers. The observed variations with time (entries 1–3) may be ascribed to a slow rearrangement of the carbanion or, more likely in view of the results described later in this paper, reflect different rates of decay of the intermediates. The largest improvement of regioselectivity was found on addition of LiCl or LiBr (entries 8–10), but neither yields nor product distributions encouraged straightforward synthetic application.

This situation is mirrored in the results of tandem additions of dithianyllithium (**6**)/methyl iodide and of (methyldithianyl)lithium (**9**)[8]/methyl iodide to **5** (eq 3, Table II).

Nucleophilic addition of dithianyllithium was carried out as described earlier and the reaction temperature was raised from −78 to −10 °C over 3 h. Treatment with an excess of methyl iodide under a CO atmosphere in the presence of HMPA and decomplexation with PPh_3 gave

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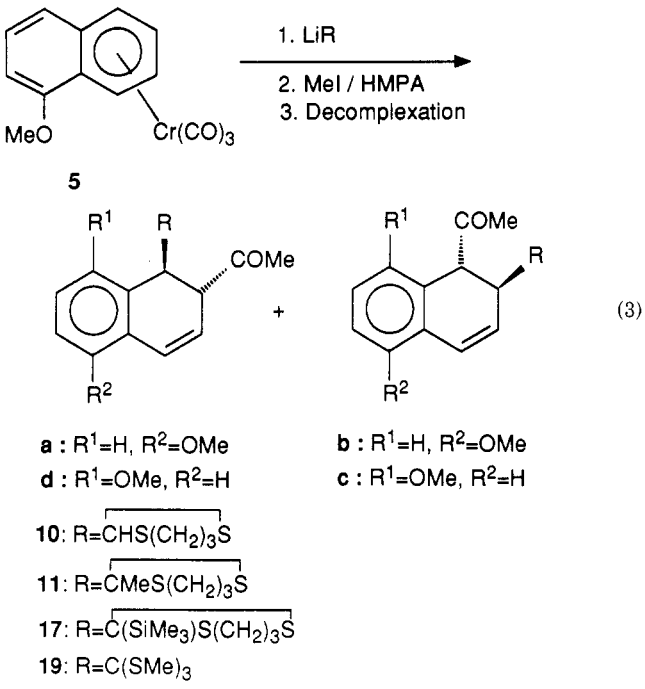
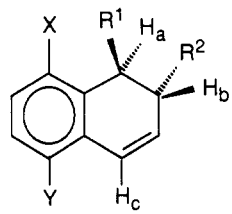


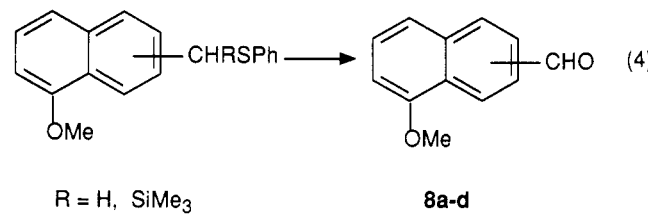
a mixture of four 1,2-disubstituted 1,2-dihydronaphthalenes (**10a–d**). ^{1}H NMR analysis of a series of dihydronaphthalenes obtained in this study showed that the vicinal coupling constant between H_a and H_b is always very small (0–2 Hz), consistent with a dihedral angle close to 90°, as subsequently shown by an X-ray crystal structure determination (of **19a**). In the same series of 5-methoxydihydronaphthalenes the chemical shift (in $CDCl_3$) of H_c falls (a) into the range δ 6.9–7.1, if H_c is peri to the OMe group, and (b) into the range δ 6.5–6.65 if it is not. This information proved to be very helpful in structural assignment of regioisomeric dihydronaphthalenes.



a) X = H, Y = OMe
b) X = OMe, Y = H

When decomplexation was carried out by oxidation (I_2), only two isomers (**10b** and **10c**) were obtained. Given the low yield and the fact that this procedure led to the elimination of the desired isomer, we did not investigate further the fate of **10a** and **10d**. With the bulkier nucleophile 2-lithio-2-methyl-1,3-dithiane (**9**), the product isomer **11d** was absent, independent of the decomplexation method, but here again the use of PPh_3 gave a better yield (entries 3 and 5) and different product distribution than oxidative decomplexation with I_2, which, as before, reduced the proportion of the desired isomer **11a**. The presence of HMPA during nucleophilic addition had no effect on isomer distribution (entry 4). When an ethanolic solution of the mixture was cooled, **11b** crystallized selectively. In a preliminary communication,[10] this product had been assigned to structure **11a**. Differential NOE data now show this to be incorrect.

Thioanisole and (Phenylthio)(trimethylsilyl)methane. Thioanisole has a higher pK_a value, and its anion (**12**)[11,12] is harder than dithianyllithium (**6**). In its addition/oxidation reaction with complex **5** (Table I, entry 11) it gave a 44% product yield, showing a single spot on TLC. This turned out again to be an inseparable mixture of four products, as shown by four CH_2SPh ^{1}H NMR singlets. This mixture was converted directly to the known naphthaldehydes **8** via oxidation with mCPBA followed by Pummerer rearrangement[13] (eq 4). This afforded **8a–c**



in the ratio 1:3:2. The more stable and softer anion **13**[14] derived from (phenylthio)(trimethylsilyl)methane (entry 12) gave a higher yield as well as a 7-fold improvement of regioselectivity, as determined after conversion of the product mixture to naphthaldehydes **8** via oxidation and mild sila-Pummerer rearrangement.[15]

Using the evidence of a sulfur/silicon-stabilized carbanion improving desired regioselectivity, we evaluated three bulky, soft carbanions in the tandem addition reaction. They are 2-lithio-2-(trimethylsilyl)-1,3-dithiane (**14**),[16] [tris(phenylthio)methyl]lithium (**15**),[17] and [tris(methylthio)methyl]lithium (**16**).[17]

2-(Trimethylsilyl)-1,3-dithiane. Surprisingly, under standard conditions (−10 °C, 2 h), only two products were isolated from the sequential addition of nucleophile **14** and methyl iodide to complex **5**. The major isomer of the 5.3:1 mixture was that of desired regiochemistry **17a**. It was isolated in 35% yield by fractional crystallization from methanol, and its structure was assigned by NMR spectroscopy including DNOE data. The minor product was assigned to **17d**, and two weak signals in the $SiMe_3$ region in the spectrum of the crude product were tentatively attributed to the isomers resulting from nucleophilic addition to C(6) and C(7) of **5**.

This result suggests the possibility that the nucleophilic addition to **5** of this more stabilized carbanion (**14**) becomes reversible on warm up and rearranges to give an equilibrium mixture in which regioisomers resulting from addition to positions α to the naphthalene ring junction are largely favored. The composition of this mixture can then be frozen by adding HMPA to allow metal alkylation by methyl iodide. The following experiment tested this hypothesis. Nucleophile **14** was reacted with **5** for 1 h at −55 °C. Half of the reaction mixture (B) was then transferred to another flask and stirred at −10 °C for 2 h before treatment with methyl iodide, HMPA, and CO. The first half of the reaction mixture (A) was treated with the same reagents but without prior warm up. As reported

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(17) (a) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 442. (b) Ellison, R. E.; Woessner, W. D.; Williams, C. C. *J. Org. Chem.* **1974**, *39*, 1430. (c) Damon, R. E.; Schlessinger, R. H. *Tetrahedron Lett.* **1976**, *17*, 1561. (d) Hengeveld, J. E.; Grief, V.; Tadanier, J.; Lee, C.-M.; Riley, D.; Lartey, P. A. *Tetrahedron Lett.* **1984**, *25*, 4075.

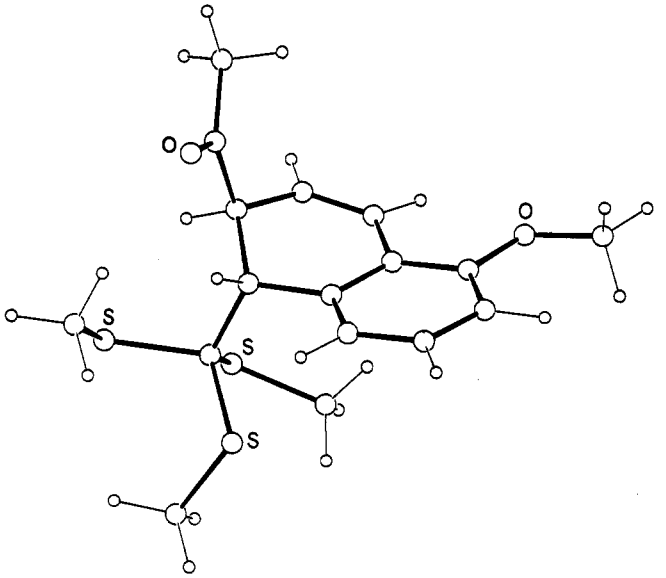


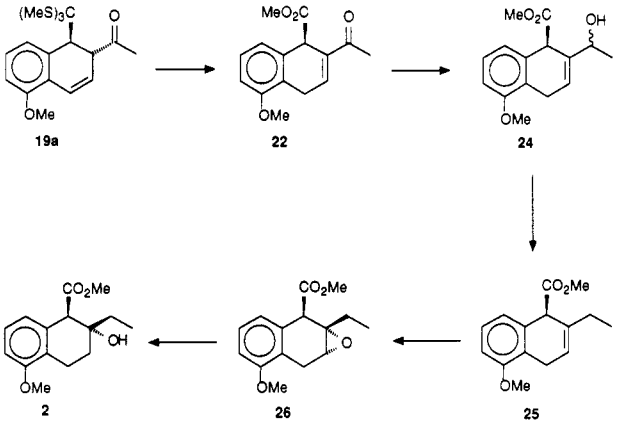
Figure 1. X-ray structure of **19a**.

in Table II, the two reactions gave different product mixtures (entries 6 and 7). Most notably, product **17b**, which was only present in trace quantities in the −10 °C reaction (entry 7) represented almost a third of the reaction mixture in the −55 °C reaction (entry 6). A sample of **17b** was isolated by preparative HPLC and characterized by ^{1}H NMR spectroscopy.

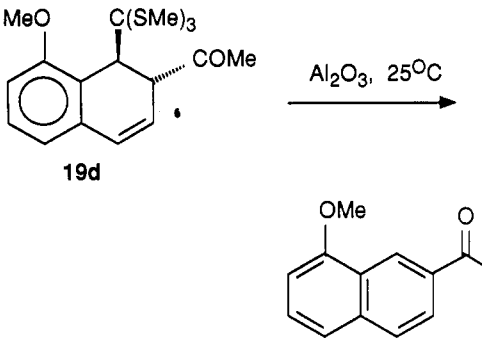
Orthothioformates. The nucleophiles **15** and **16** have both been used as ester anion equivalents in addition reactions to carbonyl compounds.[17] Their use in the nucleophile addition/acylation reaction could provide a short route to an intermediate **4** with the C(1) substituent in the correct oxidation state. Nucleophile addition/acylation reactions with the more stable phenyl compound **15** gave no addition product with **5** in the temperature range −78 to 0 °C. Subsequent addition of methyl iodide afforded $MeC(SPh)_3$ (**18**) in 60% yield (entry 8). Presumably **15** does not add due to adverse steric interactions, as has been observed previously in addition reactions to carbonyl functions.[17d]

Initial attempts to use **16** in addition/oxidation reactions with **5** failed to give substituted naphthalenes, but at this stage it was not clear whether this was due to lack of reactivity, low thermal stability of the nucleophile, and/or the incompatibility of the thioformate function with the subsequent treatment with iodine and bisulfite solution. Entry 9 shows that **16** can be used successfully in the tandem addition and it was found to behave very similarly to nucleophile **14**. Formation of the cyclohexadienyl intermediate followed by addition of methyl iodide at low temperature afforded a mixture of the four isomers (**19a–d**), but when rearrangement was induced by warming to −10 °C before alkylation, this was reduced to two products, with the desired product **19a** being the major one (6:1) (entry 10). This regioselectivity was practically invariant under a variety of reaction conditions similar to those shown for dithiane in Table I. Yield was improved, however, when diglyme was used as solvent (entry 11)—presumably because it stabilizes the carbanion better than THF in the temperature range required for equilibration. A single crystallization from methanol afforded pure **19a** (55% yield based on **5**), and this was clearly the method of choice to access a suitable intermediate **4** in the synthetic scheme. The regio- and stereochemistry of **19a** was indicated by its ^{1}H NMR spectrum and was ascertained by an X-ray structural analysis (Figure 1).[18]

Scheme III



The minor product was isolated from the mother liquor. Its ^{1}H NMR spectrum showed a doublet at 6.52 ppm, which was ascribed to H–C(4) in either **19c** or **19d**. Assignment to **19d** was confirmed by the finding that treatment of this dihydronaphthalene with activated Al_2O_3 in ether gave crystalline **20** (eq 5), the structure of which was fully assigned by NMR, IR, and MS data.



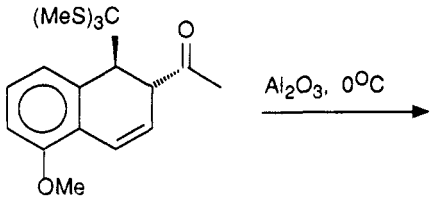
(5)

Synthesis of Tetrahydronaphthalene 2. The synthetic sequence leading from **19a** to the target molecule **2** is shown in Scheme III. The methanolysis of the orthothioester **19a** with $HgO/HgCl_2$ in aqueous MeOH[17d] gave complex mixtures, but the two step procedure using $BF_3{\cdot}OEt_2/HgO$ in aqueous THF[17c] followed by reaction with diazomethane proceeded readily to give a mixture of double-bond isomers. Slow passage of the crude material through a silica column resulted in complete conversion to **22**, which was isolated in 54% yield after crystallization. The alternative sequence **19a** → **23** → **22** (eq 6) was also attempted. Double-bond isomerization in **19a** proceeded smoothly and quantitatively with activated Al_2O_3 at 0 °C. At room temperature aromatization to 2-acetyl-5-methoxynaphthalene (**21**)[19] is competitive, and as stated earlier, this reaction was used to ascertain the structure of **19d**. Methanolysis or hydrolysis of **23**, however, gave complex mixtures, and this rendered this route impracticable.

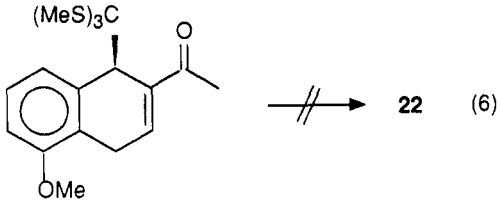
Selective reduction of the conjugated ketone in **22** ($NaBH_4/CeCl_3$/MeOH/−30 °C) afforded the allylic alcohol

(18) Crystal data for **19a** (from MeOH): $C_{17}H_{22}O_2S_3$, fw 354.5, orthorhombic, space group *Pbca*, a = 8.2636 (9) Å, b, 13.967 (2) Å, c = 30.623 (5) Å, V = 3534.4 (9) Å^3, Z = 8, ρ(calcd) = 1.33 g·cm^{-3}, m = 0.406 mm^{-1}, T = 295 K. Structure solved by direct methods, 2556 measured reflections n which 1505 are considered as observed ($|F_o| > 4\sigma(F_o)$). All coordinates of H atoms were calculated. Final residuals: R = 0.056, R_w = 0.041 ($w = 1/\sigma^2(F_o)$).

(19) (a) Diamond, J. U.S. Patent 3987116, 1976; *Chem. Abstr.* **1977**, *86*, 72285v. (b) Rama Rao, A. V.; Chanda, B. M.; Borate, H. B. *Synth. Commun.* **1984**, *14*, 257. (c) Cristau, H. J.; Bazbouz, A.; Morand, P.; Torreilles, E. *Tetrahedron Lett.* **1986**, *27*, 2965.



19a



23 // → 22 (6)

24 as an equimolar mixture of two diastereomers, which were converted via bromination (PPh_3/CBr_4) and reduction (Na-9-BBNCN/HMPA) to **25** (71%).[20,21] This transformation was carried out without isolation of the allylic bromide, which was considered to be of very limited stability. Epoxidation of **25** (mCPBA, 0 °C) yielded **26** as single diastereomer (by ^1H NMR analysis) in 78% yield. The method described by Li et al.[5c] was adopted to ring open the epoxide **26** ($NaBr/TsOH/CH_3CN$/25 °C) to give, after hydrogenolysis of the bromohydrine (H_2/Pd/C/MeOH), the target compound **2**, the spectral data of which matched those reported by Meyers and Higashiyama for the last intermediate of their synthesis of the AB ring of aklavinone.[6]

In conclusion, we have investigated the regioselectivity of nucleophilic addition of sulfur-stabilized carbon nucleophiles to (1-methoxynaphthalene)$Cr(CO)_3$ and have shown how the addition reaction can be directed and the intermediate be intercepted by a carbon electrophile to achieve over all the regio- and stereoselective addition of an ester- and a ketone function across the C(5)–C(6) naphthalene double bond. This can be used to advantage in a new and efficient approach to the aklavinone AB ring system starting from 1-methoxynaphthalene. Work now in progress focuses on the control of facial chirality in the starting complex in view of asymmetric synthesis via this tandem addition methodology.

Experimental Section

All manipulations involving organometallics were carried out under an atmosphere of purified nitrogen or argon and with an inert gas/vacuum double manifold and standard Schlenk techniques. $Cr(CO)_6$ was obtained from Pressure Chemicals or Strem Chemicals and used as received. Tetrahydrofuran and dibutyl ether were distilled from sodium–benzophenone ketyl immediately prior to use. Toluene was refluxed for 4 h over sodium before distillation. Alkanes were distilled from CaH_2. Hexamethylphosphortriamide (HMPA) (Fluka) was stirred with CaH_2 for 15 h at 60 °C before distillation under a reduced atmosphere (10 mmHg) of nitrogen. Benzene-d_6 was vacuum-transferred after stirring with CaH_2-*n*-BuLi (Fluka) was titrated before use according to the method of Gilman and Cartledge.[22] Methyl iodide (Fluka) was distilled over P_2O_5 before use. Analytical and preparative TLC were carried out by using Merck silica gel 60 F_{254} plates. Semipreparative HPLC was done on a Kontron chromatograph using a 10 × 250 mm silica column. Column chromatography, unless otherwise noted, was carried out by using the flash method described by Still.[23] ^1H and ^{13}C NMR spectra were recorded on a Bruker 400-MHz or a Varian-XL-200 spectrometer. Chemical shifts (δ) are given in ppm relative to $SiMe_4$. IR spectra were recorded on a Mattson Instruments Polaris Fourier transform spectrometer by using NaCl solution cells. Electron impact (70 eV) mass spectra were obtained on a Varian CH 4 or SM 1 spectrometer; relative intensities are given in parentheses. High-resolution mass spectra were measured on a VG analytical 7070E instrument. Melting points were determined on a Büchi 510 apparatus and are not corrected. Elemental analyses were performed by H. Eder, Service de Microchimie, Institut de Chimie Pharmaceutiquie, Université de Genève.

[(4a,5,6,7,8,8a-η)-(5-OMe)$C_{10}H_7$]$Cr(CO)_3$ (5). $Cr(CO)_6$ (7.0 g, 31.8 mmol), 1-methoxynaphthalene (9.2 mL, 63.7 mmol), dibutyl ether (160 mL), hexane (15 mL), and THF (1.5 mL) were placed in a 250-mL flask fitted with a wide-bore condenser and a magnetic stirring bar and submitted to three freeze–pump–thaw cycles. The solution was refluxed in the dark for 70 h by means of a 160 °C oil bath. The deep red solution was transferred via cannula while warm, cooled to 20 °C, diluted with hexane (60 mL), and placed on dry ice overnight. Decantation of the now pale solution left a red solid, which was taken up in hot toluene (80 mL). After filtration over Celite and concentration, hexane was added and the flask placed first at room temperature and then overnight at −40 °C to give red crystals of **5**, which were washed with cold hexane and vacuum-dried. Yield: 7.2 g (77%). ^1H NMR spectroscopy indicated the product to consist of a single regioisomer. Mp: 144–45 °C. ^1H NMR (200 MHz, C_6D_6): δ 3.28 (s, 3 H, OMe), 4.63 (dt, 1 H, J = 1.2, 7 Hz, H–C(7)), 4.72 (dt, 1 H, J = 1.2, 7 Hz, H–C(6)), 5.31 (dd, 1 H, J = 1.2, 7 Hz, H–C(5)), 5.93 (d, 1 H, J = 7.5 Hz, H–C(2)), 6.18 (dd, 1 H, J = 1.2, 7 Hz, H–C(8)), 6.60 (d, 1 H, J = 7.5 Hz, H–C(4)), 6.82 (t, 1 H, J = 7.5 Hz, H–C(3)). ^{13}C NMR (90.6 MHz, C_6D_6): δ 55.6, 85.9, 90.1, 92.7, 97.6, 107.4, 103.7, 119.1, 129.4, 156.3, 232.5. IR (hexane): 1976 (vs), 1915 (s), 1902 (s) cm^{-1}. MS: m/z 294 (15), 238 (15), 210 (16), 158 (100), 143 (38), 115 (78). Anal. Calcd for $C_{14}H_{10}CrO_4$: C, 57.15; H, 3.43. Found: C, 57.08; H, 3.40.

Addition/Oxidation Reaction of Chromium Complex 5 with 2-Lithio-1,3-dithiane (6). *n*-BuLi (1.55 M in hexane, 0.500 mL, 0.78 mmol) was added dropwise to a solution of 1,3-dithiane (100 mg, 0.83 mmol) in THF (5 mL) at − 78 °C. The reaction was stirred at −30 °C for 1.5 h. After the solution was recooled to −78 °C, chromium complex **5** (200 mg, 0.68 mmol) was added as a solid; stirring was continued for 5 min at this temperature, and then the temperature was allowed to rise to −30 °C over a 3-h period. After recooling to −78 °C, a THF solution of I_2 (0.8 g in 5 mL) was added in one portion to the dark red solution and stirred for 1 h at this temperature and then 4 h at room temperature. The reaction mixture was diluted with ether, washed with 10% aqueous sodium metabisulfite solution, saturated aqueous $NaHCO_3$, and brine, and dried with $MgSO_4$. After filtration, volatiles were evaporated in vacuo to give a brown oil, which was purified by column chromatography (SiO_2, 30 g; toluene). **7** was isolated as a pale yellow oil (145 mg, 77%) and was shown by ^1H NMR spectroscopy to consist of a mixture of the four regioisomers **7a–d** (Table I, entry 1).

Conversion of 7a–d to Naphthaldehydes 8a–d. A suspension of **7** (110 mg, 0.40 mmol) and $Cu(NO_3)_2/Al_2O_3$·$4SiO_2$ (500 mg) in CH_2Cl_2 (10 mL) was stirred for 3 h at room temperature. Filtration and solvent removal in vacuo afforded a yellow oil, which was purified by column chromatography (SiO_2, 30 g; hexane/methylenechloride 4:1). The first fraction was crystallized from hexane to give **5-methoxy-1-naphthaldehyde (8a)** (22 mg, 30%). Mp: 65–66 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 4.02 (s, 3 H, CH_3), 6.93 (b d, 1 H, J = 8.7 Hz), 7.60 (dd, 1 H, J = 8.6 Hz, 7.0 Hz), 7.61 (dd, 1 H, J = 8.6 Hz, 7.0 Hz), 8.01 (dd, 1 H, J = 7.0 Hz, 1.5 Hz), 8.60 (dt, 1 H, J = 8.7 Hz, 1.1 Hz), 8.79 (dt, 1 H, J = 8.7 Hz, 1.0 Hz), 10.40 (s, 1 H). IR ($CHCl_3$): 3020 (w), 2950 (w), 2840 (w), 2750 (w), 1695 (s), 1580 (s), 1470 (m), 1270 (m), 1160 (m) cm^{-1}. MS: m/z 186 (53), 158 (26), 143 (32), 115 (100). **8b–d** were obtained as a mixture. Crystallization from hexane furnished a sample of pure **5-methoxy-2-naphthaldehyde (8b)**. Mp: 48–50

(20) For methods of reduction of RHC(OH)R′ to RCH_2R' see: Hartwig. W. *Tetrahedron* **1983**, *39*, 2609.
(21) Hutchins, R, O.; Kandasamy, D.; Maryanoff, C. A.; Masilamani, D.; Maryanoff, B. E. *J. Org. Chem.* **1977**, *42*, 82.
(22) Gilman, H.; Cartledge, F. K. *J. Organomet. Chem.* **1964**, *2*, 447.
(23) Still, C. W.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

°C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.03 (s, 3 H, OCH_3), 6.98 (dd, 1 H, J = 8.0 Hz, 0.6 Hz, H–C(6) or (8)), 7.48 (t, 1 H, J = 8.0 Hz, H–C(7)), 7.58 (d, 1 H, J = 8.0 Hz, H–C(8) or C(6)), 7.93 (dd, 1 H, J = 9.0 Hz, 2.0 Hz, H–C(3)), 8.29 (d, 1 H, J = 2.0 Hz, H–C(1)), 8.37 (dd, 1 H, J = 9.0 Hz, 0.6 Hz, H–C(4)), 10.16 (s, 1 H, CHO). IR ($CHCl_3$): 3010 (w), 2840 (w), 1695 (s), 1580 (m), 1470 (m), 1270 (m), 1250 (m), 1100 (s) cm^{-1}. MS: m/z 186 (100), 171 (33), 143 (20), 115 (38).

Tandem Addition Reaction of Carbanion 6 and Methyl Iodide to Complex 5. To a solution of 1,3-dithiane (198 mg, 1.65 mmol) in THF (10 mL) was added dropwise *n*-BuLi (1.59 M in hexane, 0.98 mL, 1.56 mmol) at −78 °C, and the mixture was stirred for 2 h at −30 °C. After recooling to −78 °C, chromium complex **5** (400 mg, 1.36 mmol) was added in one portion via a solid addition tube. The temperature was allowed to rise to −10 °C over a period of 3 h, and stirring was continued at this temperature for an additional 2 h. MeI (0.500 mL) and HMPA (2 mL) were added at −78 °C, the gas phase over the reaction was changed to CO (1 atm) and the mixture was stirred for 12 h at 0 °C. To this solution was added PPh_3 (4.0 g) in THF (10 mL). After 6 h at room temperature, the suspension was diluted with ether/hexane (1:1, 80 mL) and stirred for 1 h. After filtration, the solution was washed with H_2O (3×) and brine (1×) and then dried ($MgSO_4$). Filtration, solvent removal, and chromatography (SiO_2, 30 g; hexane/ether 10:1) yielded a mixture of **10a–d** (42:29:17:12) as a colorless oil (191 mg, 43.8%). Partial separation was achieved by column chromatography, and ^{1}H NMR spectral comparison of enriched samples allowed structural assignment.

***trans*-1-(1,3-Dithian-2-yl)-2-acetyl-5-methoxy-1,2-dihydronaphthalene (10a).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.77–1.89 (m, 1 H, H–C(5′)), 2.01–2.10 (m, 1 H, H-C(5′)), 2.15 (s, 3 H, $COCH_3$), 2.65–2.92 (m, 4 H, $2SCH_2$), 3.76 (d, 1 H, J = 7.6 Hz, SCHS), 3.76 (d, 1 H, J = 7.2 Hz, H–C(2)), 3.80 (s, 3 H, OCH_3), 4.25 (d, 1 H, J = 7.6 Hz, H–C(1)), 6.07 (dd, 1 H, J = 10.0 Hz, 7.2 Hz, H–C(3)), 6.75 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.90 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.00 (d, 1 H, J = 10.0 Hz, H–C(4)), 7.15 (t, 1 H, J = 8.0 Hz, H–C(7)).

***trans*-1-Acetyl-2-(1,3-dithian-2-yl)-5-methoxy-1,2-dihydronaphthalene (10b).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88–2.08 (m, 2 H, 2 H–C(5′)), 2.02 (s, 3 H, $COCH_3$, 2.65–2.76 (m, 2 H, 2 SCH), 2.86–2.97 (m, 2 H, 2 SCH), 3.37 (ddd, 1 H, J = 9.6 Hz, 6.0 Hz, and 2.0 Hz, H–C(2)), 3.77 (d, 1 H, J = 9.6 Hz, SCHs), 3.84 (s, 3 H, $ArOCH_3$), 4.09 (d, 1 H, J = 2.0 Hz, H–C(1)), 6.10 (dd, 1 H, J = 10.0 Hz, 6.0 Hz, H–C(3)), 6.90 (d, 1 H, J = 10.0 Hz, H–C(4)), 6.82 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.85 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.02 (t, 1 H, J = 8.0 Hz, H–C(7)).

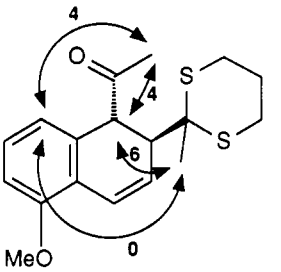
***trans*-1-Acetyl-2-(1,3-dithian-2-yl)-8-methoxy-1,2-dihydronaphthalene (10c).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88–2.08 (m, 2 H, 2H–C(5′)), 2.00 (s, 3 H, $COCH_3$), 2.65–2.76 (m, 2 H, 2 SCH), 2.86–2.97 (m, 2 H, 2 SCH), 3.43 (dd, 1 H, J = 9.0 Hz, 8.0 Hz, H–C(2)), 3.75 (d, 1 H, J = 9.0 Hz, SCHS), 3.89 (s, 3 H, $ArOCH_3$), 4.55 (s, 1 H, H–C(1)), 6.12 (dd, 1 H, J = 10.0 Hz, 8.0 Hz, H–C(3)), 6.50 (d, 1 H, J = 10.0 Hz, H–C(4)), 6.77 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 6.86 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 7.24 (t, 1 H, J = 8.0 Hz, H–C(6)).

***trans*-1-(1,3-Dithian-2-yl)-2-acetyl-8-methoxy-1,2-dihydronaphthalene (10d):** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.77–1.88 (m, 1 H, H–C(5′)), 2.01–2.09 (m, 1 H, H–C(5′)), 2.16 (s, 3 H, $COCH_3$), 3.83 (dd, 1 H, J = 6.6 Hz, 1.0 Hz, 1.0 Hz, H–C(2)), 3.89 (s, 3 H, $ArOCH_3$), 4.24 (d, 1 H, J = 5.4 Hz, SCHS or H–C(1)), 4.36 (d, 1 H, J = 5.4 Hz, SCHS or H–C(1)), 6.08 (dd, 1 H, J = 10.0 Hz, 6.6 Hz, H–C(3)), 6.57 (dd, 1 H, J = 10.0 Hz, 1.0 Hz, H–C(4)), 6.70 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7), 6.81 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 7.17 (t, 1 H, J = 8.0 Hz, H–C(6)).

Tandem Addition Reaction of (2-Methyl-1,3-dithianyl)lithium (9) and Methyl Iodide to Complex 5. The reaction was carried out exactly as that described for 1,3-dithiane except for the scale, which was 200 mg (0.68 mmol) of **5** to afford 174 mg (76.5%) of an oil shown by ^{1}H NMR spectroscopy (H–C(1) resonance) to consist of a mixture of **11a–c** in the ratio 28:46:26. Column chromatography (SiO_2, 40 g; hexane/ether 10:1) eluted first a mixture of compounds **11b** and **11c** (125 mg) and then **11a** (49 mg) containing traces of the other two isomers. Pure **11b** was obtained by fractional crystallization from the mixture in ethanol.

***trans*-1-(2-Methyl-1,3-dithian-2-yl)-2-acetyl-5-methoxy-1,2-dihydronaphthalene (11a).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.34 (s, 3 H, Me–C(2′)) 1.85–1.95 (m, 1 H, H–C(5′)), 2.04–2.12 (m, 1 H, H–C(5′)), 2.16 (s, 3 H, $COCH_3$), 2.65–2.72 (m, 1 H, SCH), 2.80–2.87 (m, 1 H, SCH), 2.93–3.01 (m, 1 H, SCH), 3.15–3.22 (m, 1 H, SCH), 3.81 (s, 3 H, $ArOCH_3$), 4.11 (s, 1 H, H–C(1)), 4.19 (d, 1 H, J = 6.4 Hz, H–C(2)), 6.16 (dd, 1 H, J = 10.0 Hz, 6.4 Hz, H–C(3)), 6.76 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.98 (d, 1 H, J = 10.0 Hz, H–C(4)), 7.02 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.13 (t, 1 H, J = 8.0 Hz, H–C(7)). IR ($CHCl_3$): 3000 (m), 1710 (s), 1575 (m), 1470 (s), 1265 (s) cm^{-1}. MS: m/z 334 (trace), 227 (0.4), 133 (100), 59 (50).

***trans*-1-Acetyl-2-(2-methyl-1,3-dithian-2-yl)-5-methoxy-1,2-dihydronaphthalene (11b).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.00 (s, 3 H, Me–C(2′)), 1.82–1.94 (m, 1 H, H–C(5′)), 1.98 (s, 3 H, $COCH_3$), 2.08–2.17 (m, 1 H, H–C(5′)), 2.62–2.72 (m, 2 H, 2 SCH), 3.11–3.18 (m, 2 H, 2 SCH), 3.72 (d, 1 H, J = 6.0 Hz, H–C(2)), 3.84 (s, 3 H, OCH_3), 4.26 (s, 1 H, H–C(1)), 6.12 (dd, 1 H, J = 10.0 Hz, 6.0 Hz, H–C(3)), 6.79 (d, 1 H, J = 8.0 Hz, H–C(6) or H-C(8)), 6.85 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.03 (d, 1 H, J = 10.0 Hz, H–C(4)), 7.19 (t, 1 H, J = 8.0 Hz, H–C(7)).



DNOE of **11b** (%)

***trans*-1-Acetyl-2-(2-methyl-1,3-dithian-2-yl)-8-methoxy-1,2-dihydronaphthalene (11c).** ^{1}H NMR ($CDCl_3$, 400 MHz): δ 0.95 (s, 3 H, Me–C(2′)), 1.82–1.94 (m, 1 H, H–C(5′)), 1.96 (s, 3 H, $COCH_3$), 2.08–2.17 (m, 1 H, H–C(5′)), 2.62–2.72 (m, 2 H, 2 SCH), 3.19–3.30 (m, 2 H, 2 SCH), 3.80 (d, 1 H, J = 6.0 Hz, H–C(2)), 3.89 (s, 3 H, $ArOCH_3$), 4.68 (s, 1 H, H–C(1)), 6.15 (dd, 1 H, J = 10.0 Hz, 6.0 Hz, H–C(3)), 6.61 (d, 1 H, J = 10.0 Hz, H–C(4)), 6.77 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 6.84 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 7.22 (t, 1 H, J = 8.0 Hz, H–C(6)).

Addition/Oxidation Reaction of Chromium Complex 5 with (Thioanisole)lithium (12) and [(Phenylthio)(trimethylsilyl)methyl]lithium (13). To a solution of thioanisole (103 mg, 0.83 mmol) in THF (4.5 mL) and HMPA (0.4 mL) was added a solution of *t*-BuLi (1.60 M in pentane, 0.500 mL, 0.80 mmol) at −78 °C, and the resulting mixture was stirred for 2 h at the same temperature. Chromium complex **5** (200 mg, 0.68 mmol) was added as a solid, and the temperature was gradually raised to −30 °C over a period of 3 h. After recooling to −78 °C, a solution of I_2 (800 mg) in THF (5 mL) was added in one portion. The mixture was stirred for 1 h at −78 °C and then 4 h at room temperature, then poured into 10% aqueous sodium bisulfite solution (30 mL), and extracted with two 30-mL portions of ether. The combined ether solution was washed with saturated sodium bicarbonate solution (1×) and brine (1×) and dried ($MgSO_4$). $MgSO_4$ was removed by filtration, and ether was evaporated in vacuo to give a brown oil, which was purified by column chromatography (SiO_2, 40 g; hexane/toluene 10:1) to give 84 mg (44%) of product. ^{1}H NMR showed 4 CH_2SPh singlets at 4.28, 4.25, 4.55, and 4.80 in the ratio 18:52:26:3. The mixture was taken up in CH_2Cl_2 (4 mL), treated with a solution of mCPBA (50%, 90 mg, 0.26 mmol) in CH_2Cl_2 (4 mL) at −15 °C, and stirred for 2 h at this temperature. After solvent removal under reduced pressure, the residue was purified by column chromatography (SiO_2, 15 g; CH_2Cl_2/acetone 30:1) to give a colorless oil (51 mg). This was taken up in THF/pyridine (4:1, 5 mL), trifluoroacetic anhydride (0.3 mL) was added dropwise at 0 °C, and the mixture was stirred for 3 h at room temperature, then diluted with ether, and washed successively with water, aqueous HCl (1 N), water, and saturated aqueous $NaHCO_3$. After drying over $MgSO_4$, filtration, and

solvent removal, the product was purified by chromatography (SiO_2, 15 g; hexane/CH_2Cl_2 3:1) to give **8** (23.5 mg, 59%) as a 1:3:2 mixture of **8a**, **8b**, and **8c**.

To a solution of (phenylthio)(trimethylsilyl)methane (163 mg, 0.83 mmol) in THF (5 mL) was added *n*-BuLi (1.59 M in hexane, 0.520 mL, 0.83 mmol) at −78 °C, and the solution was stirred for 30 min at 0 °C. After the solution was recooled, to −78 °C, chromium complex **5** (200 mg, 0.68 mmol) was added as a solid and, over a period of 3 h, the temperature was raised to −10 °C. After 3 h at this temperature, the dark red solution was cooled again to −78 °C and a solution of I_2 (800 mg) in THF (5 mL) was added in one portion. Treatment as in the preceeding preparation followed by column chromatography (SiO_2, 20 g; hexane/toluene 5:1) yielded a brown oil (180.8 mg, 75.4%). This was taken up in CH_2Cl_2 (10 mL), and the mixture was cooled to −15 °C, treated with a solution of mCPBA (55%, 180 mg, 0.57 mmol) in CH_2Cl_2 (10 mL), and stirred for 1 h at the same temperature and then for 1 h at room temperature. The resulting yellow solution was washed with saturated aqueous sodium bicarbonate solution (1×), H_2O (1×), and brine (1×) and dried ($MgSO_4$). $MgSO_4$ was filtered off, and the solvent was removed in vacuo to give a yellow oil, which was dissolved in THF (10 mL), left at room temperature for 12 h, and then refluxed for 5 min. After the solution was cooled to room temperature, H_2O (2.5 mL) was added and the solution was stirred for 2 h at room temperature. THF was evaporated to give a yellow suspension, which was diluted with 10% aqueous Na_2CO_3 solution and extracted with ether (2×) and the ether layer was dried over $MgSO_4$. $MgSO_4$ was filtered off and ether was evaporated to give a brown oil, which was purified by column chromatography (SiO_2, 20 g; CH_2Cl_2/hexane 6:1). A pale brown oil (74 mg, 77.9%) was obtained. ^1H NMR analysis showed this to be a mixture of the four regioisomers **8a–d**. Their ratio was determined by integration of the aldehyde resonance at 10.41, 10.16, 10.15, and 10.21.

Tandem Addition Reaction of Carbanion 14 and Methyl Iodide to Complex 5. To a solution of 2-(trimethylsilyl)-1,3-dithiane[16] (0.170 mL, 0.884 mmol) in THF (5 mL) was added *n*-BuLi (1.59 M in hexane, 0.560 mL, 0.884 mmol) dropwise at −78 °C, and the mixture was stirred for 1.5 h at −40 °C. After the solution was recooled to −78 °C, chromium complex **5** (200 mg, 0.680 mmol) was added as a solid in one portion and, over a period of 3 h, the temperature was allowed to rise to −10 °C. The solution was stirred for 3 h at −10 °C and then cooled to −78 °C. MeI (0.300 mL) and HMPA (1 mL) were added at −78 °C, and the reaction was stirred for 12 h at 0 °C before treatment of the brown solution with PPh_3 (2.0 g) in THF (5 mL). After 6 h at room temperature, precipitates were filtered off and the mother liquor was diluted with ether/hexane (1:1, 40 mL), washed with two 20-mL portions of H_2O and with brine, and dried ($MgSO_4$). $MgSO_4$ was filtered off, and the volatiles were removed in vacuo to give a brown oil, which was purified by column chromatography (SiO_2, 50 g; hexane/ether 10:1). A colorless oil (138 mg, 51.7%) was obtained as a mixture of two regioisomers. The ratio of the regioisomers, assigned to **17a** and, tentatively, **17d**, was determined by comparison of the ^1H NMR integral values of the $SiMe_3$ group, which appeared at δ 0.10 and 0.25, respectively, in the ratio 7.9:1. This oil was crystallized from MeOH to give compound **17a** (93 mg, 34.8%) as needles.

***trans*-1-[2-(Trimethylsilyl)-1,3-dithian-2-yl]-2-acetyl-5-methoxy-1,2-dihydronaphthalene (17a).** Mp: 124–125 °C. ^1H NMR ($CDCl_3$, 400 MHz): 0.10 (s, 9 H, $SiMe_3$), 1.76–2.00 (m, 2 H, 2 H–C(5′)), 2.18 (s, 3 H, $COCH_3$), 2.38–2.44 (m, 2 H, 2 SCH), 3.01–3.12 (m, 2 H, 2 SCH), 3.82 (s, 3 H, OCH_3), 4.04 (d, 1 H, J = 6.4 Hz, H–C(2)), 4.28 (s, 1 H, H–C(1)), 6.20 (dd, 1 H, J = 9.80 Hz, 6.4 Hz, H–C(3)), 6.74 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.03 (d, 1 H, J = 9.8 Hz, H–C(4)), 7.11 (t, 1 H, J = 8.0 Hz, H–C(7)), 7.16 (d, 1 H, J = 8.0 Hz, H–C(8) or H–C(6)). IR ($CHCl_3$): 3010 (m), 1710 (s), 1475 (s), 1265 (s), 850 (s) cm^{-1}. MS: m/z 314 (10), 294 (12), 277 (15), 262 (22), 191 (100). Anal. Calcd for $C_{20}H_{28}S_2SiO_2$ (392): C, 61.18; H, 7.19. Found: C, 60.97; H, 7.32.

In a separate experiment, a solution of the anion **14** (1.77 mmol in 10 mL of THF) was prepared as described above. (1-Methoxynaphthalene)chromium tricarbonyl (**5**) (400 mg, 1.36 mmol) was added as a solid in one portion, and the temperature was allowed to rise to −55 °C over a period of 1 h. The solution was cooled to −78 °C, and half of the reaction mixture was transferred via a precooled Teflon transfer tube to another Schlenk flask (solution B). The first half of the reaction mixture (solution A) was treated with MeI (0.300 mL, 4.82 mmol) and HMPA (1 mL), and then the temperature was allowed to rise from −78 to 0 °C over a period of 12 h. A solution of PPh_3 (2.0 g) in THF (5 mL) was added to the dark red solution, and the mixture was stirred for 1 h at 0 °C and then 4 h at room temperature. The green suspension obtained was diluted with ether/hexane (1:1, 30 mL), stirred for 1 h at room temperature, and filtered, and the mother liquor was washed with H_2O (2×) and brine (1×) and then dried over $MgSO_4$. $MgSO_4$ was filtered off, and the solvent was evaporated to give a yellow oil, which was purified by silica gel column chromatography (hexane/ether 6:1) to give 165 mg, 61.8%, of a mixture of **17a–d** in the ratio shown in Table II, entry 6. Precipitation from MeOH gave a mixture of **17a,b**. A sample of this mixture was separated by preparative HPLC on a 10 × 250 mm silica column, eluent CH_2Cl_2/hexane 3:1, 7 mL/min. The retention time for **17a** was 9 min and for **17b** was 11 min.

***trans*-1-Acetyl-2-[2-(trimethylsilyl)-1,3-dithian-2-yl]-5-methoxy-1,2-dihydronaphthalene (17b).** ^1H NMR ($CDCl_3$, 400 MHz): −0.05 (s, 9 H, $SiMe_3$), 1.84–2.12 (m, 2 H, 2 H–C(5′)), 2.04 (s, 3 H, $COCH_3$), 2.30–2.50 (m, 2 H, 2 SCH), 3.08–3.18 (m, 2 H, 2 SCH), 3.86 (s, 3 H, OCH_3), 3.94 (dt, 1 H, J = 5.5 Hz, 1.5 Hz, H–C(2)), 4.35 (br s, 1 H, H–C(1)), 6.37 (dd, 1 H, J = 10 Hz, 5.5 Hz, H–C(3)), 6.81 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.86 (d, 1 H, J = 8 Hz, H–C(8) or H–C(6)), 6.93 (dd, 1 H, J = 10.0 Hz, 1.5 Hz, H–C(4)), 7.18 (t, 1 H, J = 8.0 Hz, H–C(7)).

The transferred solution (B) was treated exactly the same way, except that before addition of MeI and HMPA (at −78 °C) the reaction was stirred for 2 h at −10 °C. Workup and purification as above afforded 140 mg (52.4%) of a mixture of **17a–d** in the ratio shown in Table II, entry 7.

Tandem Addition Reaction of Carbanion 16 and Methyl Iodide to Complex 5 (Table II, Entry 11). To a solution of tris(methylthio)methane (0.280 mL, 2.04 mmol) in diglyme (10 mL) was added *n*-butyllithium (1.59 M, in hexane, 1.28 mL, 2.0 mmol) dropwise at −78 °C. After stirring for 0.5 h, (1-methoxynaphthalene)$Cr(CO)_3$ (**5**) (400 mg, 1.36 mmol) was added in one portion as a solid at −78 °C and the temperature was allowed to rise to −10 °C slowly over a period of 3 h. The red solution was stirred another 2 h at −10 °C and then recooled to −78 °C. To this dark red solution was added MeI (0.600 mL) and HMPA (2 mL), and then the atmosphere was changed to 1 atm of CO. After the solution was stirred for 14 h at 0 °C, PPh_3 (4.0 g) in THF (10 mL) was added and the mixture stirred for 6 h at room temperature. Ether/hexane (1:1, 80 mL) was added, and after 1 h at room temperature, the precipitates formed were filtered off. The mother liquor obtained was washed with H_2O (50 mL × 3), brine (20 mL × 1), dried ($MgSO_4$), and concentrated to give a yellow oil, which was purified by column chromatography (silica gel, 30 g; hexane/ether 10:1) to give **19** (352 mg, 73%) as a colorless oil. ^1H NMR spectroscopy showed the presence of two regioisomers in the ratio 6:1 (**19a** and **19d**) (integration of H–C(1) appearing at 4.04 and 4.61 ppm). Recrystallization from MeOH yielded pure **19a** (267 mg, 55.4%) as colorless prisms.

***trans*-1-[Tris(methylthio)methyl]-2-acetyl-5-methoxy-1,2-dihydronaphthalene (19a).** MP: 100–101 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 1.98 (s, 9 H, $S(CH_3)_3$), 2.19 (s, 3 H, $COCH_3$), 3.81 (s, 3 H, $ArOCH_3$), 4.04 (s, 1 H, H–C(1)), 4.21 (d, 1 H, J = 6.7 Hz, H–C(2)), 6.27 (dd, 1 H, J = 9.8 Hz, 6.7 Hz, H–C(3)), 6.77 (dd, 1 H, J = 5.0 Hz, 4.0 Hz, H–C(7)), 6.98 (d, 1 H, J = 9.8 Hz, H–C(4)), 7.12 (d, 1 H, J = 5.0 Hz, H–C(6) or H–C(8)), 7.13 (d, 1 H, J = 4.0 Hz, H–C(6) or H–C(8)). IR ($CHCl_3$): 3000 (m), 2900 (m), 1720 (s), 1475 (s), 1270 (s) cm^{-1}. MS: m/z 307 (7), 217 (11), 153 (100), 91 (48). Anal. Calcd for $C_{17}H_{22}O_2S_3$: C, 57.54; H, 6.25. Found: C, 57.35; H, 6.19.

Chromatography (hexane/ether 15:1) of the viscous oil obtained from the mother liquor gave **19d** as a colorless oil.

***trans*-1-[Tris(methylthio)methyl]-2-acetyl-8-methoxy-1,2-dihydronaphthalene (19d).** ^1H NMR ($CDCl_3$, 400 MHz): δ 2.00 (s, 9 H, $S(CH_3)_3$), 2.16 (s, 3 H, $COCH_3$), 3.86 (s, 3 H, $ArOCH_3$), 4.18 (d, 1 H, J = 6.4 Hz, H–C(2)), 4.61 (s, 1 H, H–C(1)), 6.25 (dd, 1 H, J = 9.6 Hz, 6.4 Hz, H–C(3)), 6.52 (d, 1 H, J = 9.6 Hz, H–C(4)), 6.63 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 6.75 (d, 1 H, J = 8.0 Hz, H–C(5) or H–C(7)), 7.16 (t, 1 H, J = 8.0 Hz, H–C(6)). IR ($CHCl_3$): 3000 (m), 2920 (m), 1715 (s), 1575 (m),

1470 (m), 1270 (s), 1100 (m), 1080 (m) cm^{-1}. MS: *m/z* 336 (1.0), 307 (8.5), 263 (70), 226 (37), 200 (58), 185 (100). Evidence for reversibility of the addition of **16** was obtained by carrying out the reaction in THF (scale: 1.36 mmol of **5**) and separating the reaction mixture into two portions under reaction conditions identical with those described for nucleophile **14**. Solution A yielded, after workup, **19** (172 mg, 71%) (Table II, entry 9). ^1H NMR analysis and integration of the resonances associated with H–C(1) showed this to be a mixture of four isomers **19a–d** in the ratio 49:37:9:5. Spectral data for **19b** and **19c** were obtained from the mixture. Solution B (2 h at −10 °C before addition of methyl iodide) yielded, after workup and purification as above, **19** (142 mg, 58.9%) as a 6:1 mixture of **19a** and **19d** (Table II, entry 10).

***trans*-1-Acetyl-2-[tris(methylthio)methyl]-5-methoxy-1,2-dihydronaphthalene (19b).** ^1H NMR ($CDCl_3$, 400 MHz): δ 2.01 (s, 3 H, $COCH_3$), 2.08 (s, 9 H, $S(CH_3)_3$), 3.47 (d, 1 H, *J* = 6.0 Hz, H–C(2)), 3.83 (s, 3 H, $ArOCH_3$), 4.42 (s, 1 H, H–C(1)), 6.03 (dd, 1 H, *J* = 6.0 Hz, 10.0 Hz, H–C(3)), 6.79 (d, 1 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 6.93 (d, 1 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 6.96 (d, 1 H, *J* = 10.0 Hz, H–C(4)), 7.21 (t, 1 H, *J* = 8.0 Hz, H–C(7)).

***trans*-1-Acetyl-2-[tris(methylthio)methyl]-8-methoxy-1,2-dihydronaphthalene (19c).** ^1H NMR ($CDCl_3$, 400 MHz): δ 3.56 (dt, 1 H, *J* = 6.0 Hz, 1.0 Hz, H–C(2)), 3.92 (s, 3 H, $ArOCH_3$), 4.79 (b s, 1 H, H–C(1)), 6.50 (dd, 1 H, *J* = 10.0 Hz, 1.0 Hz, H–C(4)), 6.89 (d, 1 H, *J* = 8.0 Hz, H–C(5) or H–C(7)). Other signals were not assigned because of overlap with signals of other regioisomers.

Reactions with Al_2O_3: Aromatization and Isomerization. A suspension of activated Al_2O_3 (dried at 170 °C under vacuum for 5 h, 100 mg) and compound **19a** (30 mg, 0.085 mmol) in ether (5 mL) was stirred for 12 h at room temperature under nitrogen. Al_2O_3 was filtered off, and ether was evaporated to give a colorless oil, which was purified by column chromatography (SiO_2, 18 g; hexane/ether 10:1). The first product eluted was **23** (oil, 20 mg, 66.7%) followed by **21** (leaflets, 5 mg, 29.4%). When the reaction was repeated at 0 °C, **23** was the only product (quantitative yield).

1-[Tris(methylthio)methyl]-2-acetyl-5-methoxy-1,4-dihydronaphthalene (23). ^1H NMR ($CDCl_3$, 200 MHz): δ 1.95 (s, 9 H, $S(CH_3)_3$), 2.50 (s, 3 H, $COCH_3$), 3.63 (dd, 1 H, *J* = 23.0 Hz, 5.7 Hz, H–C(4)), 3.79 (dt, 1 H, *J* = 23.0 Hz, 1.5 Hz, H–C(4)), 3.84 (s, 3 H, $ArOCH_3$), 4.74 (b s, 1 H, H C(1)), 6.80 (dd, 1 H, *J* = 7.5 Hz, 1.5 Hz, H–C(6) or H–C(8)), 7.06–7.22 (m, 3 H, H–C(3), H–C(7), and H–C(6) or H–C(8)). IR ($CHCl_3$): 3010 (m), 2925 (m), 1670 (s), 1580 (m), 1475 (m), 1270 (m), 1255 (m), 1100 (m) cm^{-1}. MS: *m/z* 307 (2), 153 (100), 91 (41).

2-Acetyl-5-methoxynaphthalene (21).[19] ^1H NMR ($CDCl_3$, 400 MHz): δ 2.73 (s, 3 H, $COCH_3$), 4.02 (s, 3 H, $ArOCH_3$), 6.94 (d, 1 H, *J* = 7.0 Hz, H–C(2) or H–C(4)), 7.46 (t, 1 H, *J* = 7.0 Hz, H–C(3)), 7.54 (d, 1 H, *J* = 7.0 Hz, H–C(2) or H–C(4)), 8.00 (dd, 1 H, *J* = 8.2 Hz, 1.5 Hz, H–C(7)), 8.32 (d, 1 H, *J* = 8.2 Hz, H–C(8)), 8.42 (d, 1 H, *J* = 1.5 Hz, H–C(5)). IR ($CHCl_3$): 3000 (w), 1675 (s), 1465 (m), 1370 (m), 1275 (s), 1110 (m) cm^{-1}. MS: *m/z* 200 (91), 185 (100), 157 (25), 127 (41).

2-Acetyl-8-methoxynaphthalene (20). Regioisomer **19d** (150 mg, 0.423 mmol) was stirred with activated Al_2O_3 (500 mg) in ether (15 mL) at room temperature for 12 h. Al_2O_3 was filtered off, ether was removed in vacuo, and the liquid product was purified by column chromatography (SiO_2, 20 g; hexane/ether 10:1) followed by crystallization from hexane to afford colorless leaflets of **20** (55 mg, 65%). Mp: 54–55 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.75 (s, 3 H, $COCH_3$), 4.06 (s, 3 H, $ArOCH_3$), 6.89 (d, 1 H, *J* = 7.6 Hz, H–C(2) or H–C(4)), 7.45 (d, 1 H, *J* = 7.6 Hz, H–C(2) or H–C(4)), 7.52 (t, 1 H, *J* = 7.6 Hz, H–C(3)), 7.84 (d, 1 H, *J* = 8.6 Hz, H–C(5)), 8.07 (dd, 1 H, *J* = 8.6 Hz, 2.0 hz, H–C(6)), 8.91 (d, 1 H, *J* = 2.0 Hz, H–C(8)). IR ($CHCl_3$): 1680 (s), 1465 (m), 1275 (s) cm^{-1}. MS: *m/z* 200 (70), 185 (100), 127 (42).

1-(Carbomethoxy)-2-acetyl-5-methoxy-1,4-dihydronaphthalene (22). To a suspension of **19a** (1.45 g, 4.09 mmol) in 80% aqueous THF (16.4 mL) was added HgO (4.42 g, 20.4 mmol) and $BF_3{\cdot}Et_2O$ (7.71 mL, 61.4 mmol) at 0 °C, and the solution was stirred for 3.5 h at this temperature. The reaction mixture was diluted with CH_2Cl_2, washed with saturated aqueous NH_4Cl solution (1×) and brine (1×), and then dried ($MgSO_4$). After $MgSO_4$ was removed by filtration, the resulting clear solution was treated with a solution of CH_2N_2 in ether until the reaction mixture turned yellow. The solvent was evaporated in vacuo to afford a yellow oil, which was purified by slow column chromatography (SiO_2, 60 g; hexane/ether 5:1), followed by recrystallization from ether/hexane to give **22** (571 mg, 53.7%) as colorless prisms. Mp: 101–103 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 2.43 (s, 3 H, $COCH_3$), 3.54 (dt, 1 H, *J* = 24 Hz, 3.0 Hz, H–C(4)), 3.65 (s, 3 H, CO_2CH_3), 3.73 (ddd, 1 H, *J* = 24 Hz, 5.2 Hz, 3.0 Hz, H–C(4)), 3.85 (s, 3 H, $ArOCH_3$), 4.86 (t, 1 H, *J* = 3.0 Hz, H–C(1)), 6.79 (d, 1 H, *J* = 8.0 Hz, H–C(6) or H–C(9)), 7.12 (d, 1 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 7.22 (t, 1 H, *J* = 8.0 Hz, H–C(7)), 7.33 (dd, 1 H, *J* = 5.2 Hz, 3.0 Hz, H–C(3)). IR ($CHCl_3$): 3010 (m), 1740 (s), 1670 (s), 1590 (s), 1475 (m), 1270 (s) cm^{-1}. MS: *m/z* 261 (28), 260 (12), 229 (31), 201 (100), 200 (38), 185 (36), 115 (86). Anal. Calcd for $C_{15}H_{16}O_4{\cdot}^1/_2H_2O$: C, 66.90; H, 6.36. Found: C, 66.85; H, 6.09.

1-(Carbomethoxy)-2-(1-hydroxyethyl)-5-methoxy-1,4-dihydronaphthalene (24). To a solution of **22** (400 mg, 1.54 mmol) in MeOH (20 mL) was added $CeCl_3{\cdot}7H_2O$ (570 mg, 1.53 mmol) at 0 °C, and the suspension was stirred until all $CeCl_3{\cdot}7H_2O$ had dissolved. The resulting solution was cooled to −40 °C, and $NaBH_4$ (58.0 mg, 1.53 mmol) was added in one portion; then the solution was stirred for 2 h at the same temperature. An aqueous solution of citric acid (10% solution, 20 mL) was added to the reaction mixture at −40 °C, and the resulting mixture was stirred for 10 min at 0 °C. The reaction mixture was diluted with H_2O (50 mL) and extracted with ether (2×), and the combined ether layer was washed with H_2O (3×) and brine (1×) and dried ($MgSO_4$). $MgSO_4$ was filtered off, and ether was evaporated to give **24** as a colorless oil (395 mg, 97.8%), which was used in the next step without further purification. Data for **24**: ^1H NMR ($CDCl_3$, 400 MHz) δ 1.34 (d, 3 H, *J* = 6.0 Hz, CH_3), 1.36 (d, 3 H, *J* = 5.0 Hz, CH_3), 1.68 (b d, 1 H, *J* = 4.0 Hz, OH), 1.83 (b d, 1 H, *J* = 4.0 Hz, OH), 3.22–3.58 (m, 4 H, $H_2C(4) \times 2$), 3.63 (s, 3 H, CO_2CH_3), 3.64 (s, 3 H, CO_2CH_3), 3.83 (s, 6 H, $ArOCH_3 \times 2$), 4.35–4.41 (m, 1 H), 4.48–4.55 (m, 1 H), 4.49 (t, 1 H, *J* = 3.0 hz, H–C(1)), 4.59 (t, 1 H, *J* = 3.0 Hz, H–C(1)), 6.14 (dd, 1 H, *J* = 5.0 Hz, 2.4 Hz, H–C(3)), 6.21–6.23 (m, 1 H, H–C(3)), 6.77 (d, 2 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 6.97 (d, 2 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 7.00 (d, 2 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 7.18 (t, 1 H, *J* = 8.0 Hz, H–C(7)), 7.19 (t, 1 H, *J* = 8.0 Hz, H–C(7)). IR ($CHCl_3$): 3600 (w), 3450 (w), 3000 (w), 2950 (w), 1725 (s), 1590 (m), 1475 (m), 1260 (s), 725 (s) cm^{-1}. MS: *m/z* 244 (10), 228 (10), 185 (39), 84 (67), 59 (100).

1-(Carbomethoxy)-2-ethyl-5-methoxy-1,4-dihydronaphthalene (25). A mixture of **24** (323 mg, 1.23 mmol), CBr_4 (816 mg, 2.46 mmol), and PPh_3 (485 mg, 1.85 mmol) in CH_2Cl_2 (10 mL) was stirred for 6 h at 0 °C and then for 2 h at room temperature in the dark. After CH_2Cl_2 was evaporated in vacuo, the colorless residue obtained was purified by column chromatography (SiO_2, 30 g/ hexane/ether 10:1) to afford a colorless oil. This oil was dissolved in HMPA (5 mL), Na-9-BBNCN (1 M solution in HMPA, 4 mL) was added, and the reaction mixture was stirred for 3 h at 70 °C and then for 12 h at room temperature. The resulting solution was diluted with ether, washed with H_2O (4×) amd brine (1×), and dried ($MgSO_4$). $MgSO_4$ was filtered off, and ether was evaporated to give a colorless oil, which was purified by column chromatography (SiO_2, 20 g; hexane/ether 10:1). **25** (215 mg, 71.0%) was obtained as a colorless oil. ^1H NMR ($CDCl_3$, 200 MHz): δ 1.09 (t, 3 H, *J* = 7.5 Hz, CH_3), 1.99–2.27 (m, 2 H, CH_2Me), 3.16–3.54 (m, 2 H, $ArCH_2$), 3.63 (s, 3 H, CO_2CH_3), 3.84 (s, 3 H, $ArOCH_3$), 4.43 (t, 1 H, *J* = 3.5 Hz, H–C(1)), 5.84–5.90 (m, 1 H, H–C(4)), 6.76 (d, 1 H, *J* = 8.0 Hz, H–C(6), or H–C(8)), 6.89 (d, 1 H, *J* = 8.0 Hz, H–C(6) or H–C(8)), 7.16 (t, 1 H, *J* = 8.0 Hz, H–C(7). IR ($CHCl_3$): 2940 (s), 1730 (s), 1600 (m), 1475 (m), 1265 (s) cm^{-1}. MS: *m/z* 246 (11), 244 (29), 187 (100), 159 (30), 115 (60), 59 (30).

1-(Carbomethoxy)-2,3-epoxy-2-ethyl-5-methoxy-1,2,3,4-tetrahydronaphthalene (26). To a solution of **25** (150 mg, 0.609 mmol) in CH_2Cl_2 (8 mL) was added mCPBA (0.2 M solution in CH_2Cl_2, 4.5 mL, 0.9 mmol) at 0 °C, and the resulting mixture was stirred for 18 h at the same temperature. The resulting pale yellow solution was washed with saturated $NaHCO_3$ aqueous solution (2×), H_2O (1×), and brine (1×) and dried ($MgSO_4$). $MgSO_4$ was filtered off, and CH_2Cl_2 was evaporated to give a pale brown oil, which was purified by column chromatography (SiO_2, 20 g; hexane/ether 10:1%). A colorless oil of **26** (127 mg, 78.2%) was obtained. Crystallization from hexane afforded colorless prisms

(97 mg, 60.7%). Mp: 71–73 °C. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.04 (t, 3 H, J = 7.6 Hz, CH_3), 1.59 (dq, 1 H, J = 15.2 Hz, 7.6 Hz, CH_2CH_3), 1.97 (dq, 1 H, J = 15.2 Hz, 7.6 Hz, CH_2CH_3), 3.00 (d, 1 H, J = 18.0 Hz, H–C(4)), 3.45 (d, 1 H, J = 2.6 Hz, H–C(3)), 3.58 (dd, 1 H, J = 18.0 Hz, 2.6 Hz, H–C(4)), 3.65 (s, 3 H, CO_2CH_3), 3.81 (s, 3 H, $ArOCH_3$), 4.24 (s, 1 H, H–C(1)), 6.75 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.79 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.13 (t, 1 H, J = 8.0 Hz, H–C(7)). IR ($CHCl_3$): 3020 (w), 1735 (s), 1600 (m), 1475 (m), 1260 (m) cm^{-1}. MS: m/z 262 (8), 174 (17), 115 (27), 57 (100). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.43; H, 6.87.

1-(Carbomethoxy)-2-ethyl-2-hydroxy-5-methoxy-1,2,3,4-tetrahydronaphthalene (2).[6] To a suspension of **26** (10 mg, 0.0381 mmol) and NaBr (47 mg, 0.457 mml) in CH_3CN (3 mL) was added a solution of $TsOH·H_2O$ (7.25 mg, 0.0381 mmol) in CH_3CN (1 mL) at room temperature over a period of 2 h, and then the solution was stirred for 3 h. The resulting suspension was diluted with ether, washed with H_2O (3×) and brine (1×), and dried ($MgSO_4$). $MgSO_4$ was filtered off, and ether was evaporated in vacuo to give a colorless oil, which was dissolved in MeOH (2 mL). To this solution was added AcOH (0.02 mL). NH_4OAc (8.0 mg), and Pd–C (10%, 20 mg), and the mixture was stirred for 4 h under a hydrogen atmosphere. Pd–C was filtered off, and MeOH was evaporated in vacuo to afford a pale yellow oil, which was dissolved in ether, washed with H_2O (2×) and saturated $NaHCO_3$ aqueous solution (1×), and dried ($MgSO_4$). $MgSO_4$ was filtered off, and ether was evaporated in vacuo to give a colorless oil, which was purified by column chromatography (SiO_2, 5 g; hexane/ether 4:1). Compound **2** was obtained as a colorless oil (7.2 mg, 71.5%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.05 (t, 3 H, J = 7.4 Hz, CH_3), 1.58 (dq, 1 H, J = 14.8 Hz, 7.4 Hz, CH_2CH_3), 1.65 (s, 1 H, OH), 1.66 (dq, 1 H, J = 14.8 Hz, 7.4 Hz, CH_2CH_3), 1.81–1.87 (m, 1 H, H–C(3)), 2.29 (ddd, 1 H, J = 13.8 Hz, 10.6 Hz, 7.2 Hz, H–C(3)), 2.68 (ddd, 1 H, J = 18.4 Hz, 10.6 Hz, 7.2 Hz, H–C(4)), 2.91 (ddd, 1 H, J = 18.4 Hz, 7.2 Hz, 2.6 Hz, H–C(4)), 3.68 (s, 3 H, CO_2CH_3), 3.83 (s, 3 H, $ArOCH_3$), 3.85 (s, 1 H, H–C(1)), 6.74 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 6.78 (d, 1 H, J = 8.0 Hz, H–C(6) or H–C(8)), 7.13 (t, 1 H, J = 8.0 Hz, H–C(7)). IR ($CHCl_3$): 3600 (w), 3020 (m), 2950 (m), 1730 (s), 1590 (m), 1470 (s), 1260 (s), 910 (s) cm^{-1}. MS: m/z 264 (8), 246 (5), 232 (31), 187 (60), 175 (87), 57 (100). High-resolution MS for $C_{15}H_{20}O_4$: calcd 264.1362, obsd 264.1360.

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Supplementary Material Available: Tables of crystal data, all atomic coordinates, displacement parameters, and bond distances and angles and an X-ray structure of **19a** with atom numbering (7 pages); a table of structure factors for **19a** (13 pages). Ordering information is given on any current masthead page.

Isomerization of a Vinylcyclobutene to a Cyclohexadiene: A Nickel(I)-Promoted Rearrangement

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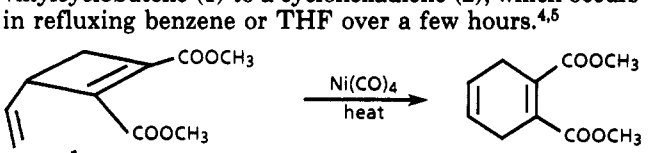
The nickel-promoted isomerization of a 3-vinylcyclobutene to the corresponding 1,4-cyclohexadiene was studied by using $(PPh_3)_2Ni(C_2H_4)$ as the nickel source. Through the use of chemical and electrochemical experiments, it was determined that nickel(I) and not nickel(0) promotes this isomerization reaction at room temperature. The corresponding platinum–vinylcyclobutene complex **4** has been characterized by a single-crystal X-ray diffraction study: $C_{46}H_{42}O_4P_2Pt$, monoclinic, $P2_1/n$, with a = 10.774 (1) Å, b = 20.281 (4) Å, c = 18.297 (2) Å, β = 97.37 (1)°, Z = 4, $R(F)$ = 0.0378, and $R_w(F)$ = 0.0371.

The ability of transition metals to promote the rearrangement (isomerization) of organic molecules is well-known.[2] However, in spite of all these reactions, there are very few examples of a net 1,3-migration of an sp^2-hybridized carbon.[3] Recently, we have been studying such a reaction in the $Ni(CO)_4$-promoted ring expansion of a vinylcyclobutene (**1**) to a cyclohexadiene (**2**), which occurs in refluxing benzene or THF over a few hours.[4,5]



1 2

In an attempt to find a solid (nonvolatile) nickel(0) source that would promote the isomerization of **1** to **2**, we began investigating the use of $(PPh_3)_2Ni(C_2H_4)$.[6] In this

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(2) For some leading references see: (a) Bishop, K. C. *Chem. Rev.* **1976**, *76*, 461. (b) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley-Interscience Publication: New York, 1986. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.

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