Table V. Crystal Data of 1b and 4a

	1b	4a
formula	$C_{32}H_{40}O_7$	$C_{35}H_{40}NO_{5.5}$
lattice type	tetragonal	monoclinic
space group	$P\bar{4}2_1c$	$C2/c$
temperature, K	100	293
cell dimensions		
a, Å	20.493 (10)	26.613 (12)
b, Å		15.862 (6)
c, Å	13.679 (5)	16.607 (6)
β, deg		115.38 (4)
V, Å^3	5745 (8)	6334 (12)
Z	8	8
D_{calcd}, g cm^{-3}	1.24	1.18
μ (Mo Kα), cm^{-1}	0.8	0.7
θ range, deg	3-25	3-25
no. of unique reflections		
measured	2796	5562
observed ($F_o^2 > 3\sigma(F_o^2)$)	2025	2604
final no. of variables	392	422
R, %	2.5	3.6
R_w, %	3.1	5.1

yellow crystals: yield 23%; mp 194-195 °C; mass spectrum, m/e 569.246 (M^+, calcd 569.241); ^1H NMR δ 7.78 (s, 2 H, Ar H), 7.7-7.1 (m, 9 H, Ar H), 3.64 (s, 8 H, OCH_2), 4.52 (AB q, J_{AB} = 12.0 Hz, 4 H, Ar CH_2), 3.43 (s, 6 H, OCH_3), 2.33 (s, 6 H, CH_3).

Anal. Calcd for $C_{34}H_{35}NO_7$: C, 71.69; H, 6.19; N, 2.46. Found: C, 71.74; H, 6.24; N, 2.11.

25,26-Dimethoxy-9,23-dimethyl-4-phenyl-13,16,19-trioxa-27-azatetracyclo[19.3.1.1^{2,6}.1^{7,11}]heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene (4a) was obtained from **12e**. Recrystallization of the product from diethyl ether afforded pure **4a** as white crystals: yield 60%; mp 104-115 °C; mass spectrum, m/e 525.257 (M^+, calcd 525.252); ^1H NMR δ 7.75-7.46 (m, 5 H, Ar H), 7.70 (s, 2 H, pyridine H), 7.21 (d, 2 H, Ar H), 7.06 (d, 2 H, Ar H), 4.58 (s, 4 H, Ar CH_2), 3.54 (s, 14 H, OCH_3 and OCH_2), 2.32 (s, 6 H, Ar CH_3).

Anal. Calcd for $C_{33}H_{35}NO_5 \cdot 0.5C_4H_{10}O$: C, 74.77; H, 7.17; N, 2.49. Found: C, 74.59; H, 7.28; N, 2.25.

25,26-Dimethoxy-9,23-dimethyl-13,16,19-trioxa-27-azatetracyclo[19.3.1.1^{2,6}.1^{7,11}]heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene (4b) was obtained from **13e**. Recrystallization of the product from diethyl ether yielded **4b** as white crystals: yield 54%; mp 134-135 °C; mass spectrum, m/e 449.218 (M^+, calcd 449.220); ^1H NMR δ 7.85 and 7.45 (A_2B, J = 7.89 Hz, 3 H, pyridine H), 7.10 (s, 2 H, Ar H), 7.05 (s, 2 H, Ar H), 4.55 (s, 4 H, Ar CH_2), 3.53 (s, 8 H, OCH_2), 3.48 (s, 6 H, OCH_3), 2.31 (s, 6 H, Ar CH_3).

Anal. Calcd for $C_{27}H_{31}NO_5$: C, 72.14; H, 6.95; N, 3.12. Found: C, 71.74; H, 6.94; N, 2.95.

25,26-Dimethoxy-3,5,9,23-tetramethyl-13,16,19-trioxa-27-azatetracyclo[19.3.1.1^{2,6}.1^{7,11}]heptacosa-1(25),2,4,6(27),7,9,11(26),21,23-nonaene (4c) was obtained from **14e**. Recrystallization of the product from acetone afforded **4c** as colorless crystals: yield 54%; mp 197-199 °C; mass spectrum, m/e 477.255 (M^+, calcd 477.252); ^1H NMR δ 7.51 (s, 1 H, pyridine H), 6.99 (s, 4 H, Ar H), 4.55 (s, 4 H, Ar CH_2), 3.47 (s, 6 H, OCH_3), 3.44 (m, 8 H, OCH_2), 2.39 (s, 6 H, pyridine CH_3), 2.27 (s, 6 H, Ar CH_3).

Anal. Calcd for $C_{29}H_{35}NO_5$: C, 72.93; H, 7.39; N, 2.93. Found: C, 73.22; H, 7.47; N, 2.82.

28,29,30-Trimethoxy-4,9,26-trimethyl-13,16,19,22-tetraoxatetracyclo[22.3.1.1^{2,6}.1^{7,11}]triaconta-1(28),2,4,6(30),7,9,11(29),24,26-nonaene (1b) was prepared from 3,3″-bis(bromomethyl)-2,2′,2″-trimethoxy-5,5′,5″-trimethyl-1,1′:3′,1″-terphenyl[1] (2.0 g, 3.6 mmol) and triethyleneglycol (0.54 g, 3.6 mmol) as described for **3** and **4a-c**. The product was recrystallized from ethanol to give pure **1b**: yield 31%; mp 157-158 °C; mass spectrum, m/e 536.277 (M^+, calcd 536.278); ^1H NMR δ 7.13-7.08 (m, 6 H, Ar H), 4.83 (AB q, J_{AB} = 10.5 Hz, 2 H, Ar CH_2), 4.22 (AB q, J_{AB} = 10.5 Hz, 2 H, Ar CH_2), 3.74-3.20 (m, 12 H, OCH_2), 3.56 (s, 6 H, outer OCH_3), 2.88 (s, 3 H, inner OCH_3), 2.39 (s, 3 H, inner CH_3), 2.33 (s, 6 H, outer CH_3).

Anal. Calcd for $C_{32}H_{40}O_7$: C, 71.62; H, 7.51. Found: C, 71.43; H, 7.56.

X-ray Crystallography. Measurements were performed on a CAD-4 single-crystal diffractometer (Mo Kα radiation, graphite monochromator). Crystal data are shown in Table V. Intensities were measured by using the $\omega/2\theta$ scan mode (correction for Lorentz polarization and intensity variations of three control reflections; no absorption correction). The structures were solved by direct methods.[25] Refinement (on F, weight $w = 4F_o^2/\sigma^2(F_o^2)$) was performed by full-matrix least-squares. Hydrogens were located on difference Fourier maps. The methoxy hydrogens were included in the refinement; all other hydrogens were put in calculated positions (C-H distance 0.96 Å) and treated as riding on their parent C atoms. Both structures show some disorder: all aryl methyl hydrogens are rotationally disordered, and the crystal structure of **4b** contains half a solvent molecule of diethyl ether; it was found to be disordered around the twofold axis. All calculations were done by using SDP.[26] Full details will be published elsewhere.

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Supplementary Material Available: Tables of atomic positional and thermal parameters and bond distances and angles of **1b** and **4a** (12 pages). Ordering information is given on any current masthead page.

Preparation and Chemistry of the Diels-Alder Adducts of Levopimaric Acid and Activated Thiocarbonyl Dienophiles

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The reactions of levopimaric acid (1) with the activated dienophiles methyl cyanodithioformate (2) and *N*-benzoyl-*N*-phenylcyanothioformamide (3) are reported. The resulting Diels-Alder adducts were then subjected to various reaction conditions, including acid and/or base hydrolysis, permanganate oxidation, and catalytic hydrogenation, where applicable.

After reinvestigating the fundamental chemistry of the model formaldehyde-levopimaric acid adduct,[1] I became especially interested in a group of analogous heteroatomic dienophiles, the activated thiocarbonyls. First of all, these

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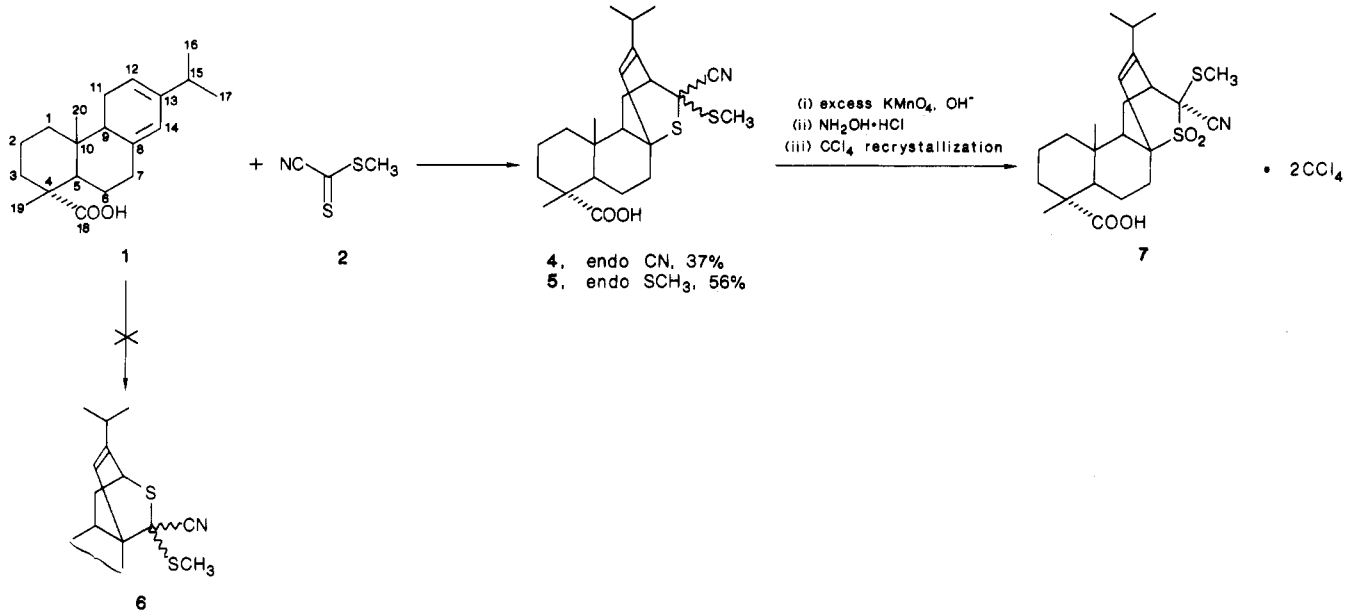
Scheme I. Cycloaddition of 2 and Levopimaric Acid (1)



dienophiles are several orders of magnitude more reactive than their corresponding carbonyl analogues.[2-4] Second, the diminished polarization of the thiocarbonyl group, relative to the carbonyl, often permits C=S additions to occur in either or both directions with respect to an unsymmetrical diene, such as levopimaric acid (1).[5]

Consequently, the study of these thiocarbonyl dienophiles would not only introduce new functionalities into the simple diterpene resin acid system but would also allow a simultaneous investigation into the major factors that may be responsible for the regio- and stereochemical control of the Diels–Alder addition of heteroatomic dienophiles to levopimaric acid.

Results and Discussion

Methyl Cyanodithioformate (2). A. Reaction with 1. At 0 °C methyl cyanodithioformate[6-8] **2** underwent a 1,4-cycloaddition with **1** to give a mixture of stereoisomeric products **4** and **5** in almost quantitative yield (Scheme I). The regiospecificity of the addition is evidenced by the ^{1}H NMR spectrum of the crude product mixture. A solitary resonance for the C-12 bridgehead proton, which appears as a multiplet at δ 3.43, is indicative of an α-carbon bearing cyano and methylthio groups.[6] No alternate absorption (δ 4.3–4.4)[6] was observed for the other possible regioisomer **6**.

The ^{1}H NMR spectrum also allows assignment of not only the isomer ratio of **4** and **5**—2:3, respectively—but also the stereochemistries at C-2 of the 3,6-dihydrothiopyran rings in the two adducts. Each of the two adducts displays its own characteristic absorptions for both the C-14 olefinic proton and for the methylthio group. The magnetic anisotropy of the endo cyano group of **4** causes a slight deshielding of the C-14 olefinic proton (δ 5.57) relative to that of the exo isomer **5** (δ 5.49). Similarly, the endo methylthio group of **5**, which experiences a shielding effect from the carbon–carbon double bond, appears upfield (δ 2.25) from that of **4** (δ 2.39).

The observed regiochemistry of the addition appears to be determined by electronic considerations in which the positive end of the thiocarbonyl dipole resides on carbon in analogy to the corresponding formaldehyde addition. The stereochemistry of the adducts, however, is presumably controlled by steric differences in the approach of the cyano group vs. the somewhat larger methylthio group in the transition states of the cycloaddition.

B. Chemistry of 5. 1. Hydrolysis. The fundamental chemical behavior of **5**, in general, is quite different from that of the model formaldehyde adduct of 1.[1] The dithioketal linkage of **5** is extremely stable to mildly acidic conditions (dilute HCl, 5 days). However, under more drastic conditions ($HgCl_2$, MeOH, THF, 130 °C) the adduct reverted to its precursors.

2. Oxidation with $KMnO_4$. In contrast to the formaldehyde adduct, adduct **5** and the simple adducts of **2** with cyclopentadiene and *trans*-1,3-butadiene[9,10] gave no cis hydroxylation of the olefinic bond with excess basic $KMnO_4$. Oxidation occurred only at sulfur, in all cases, and exclusively at the ring sulfur of **5** to give the corresponding monosulfone **7** (Scheme I). Support for the proposed structural assignment of **7** comes from the ^{1}H NMR, IR, and elemental analysis data. Electron-withdrawal by the sulfonyl group at C-8 causes a downfield shift of the C-14 olefinic proton (δ 5.60), the C-12 methine (δ 3.87), and the methylthio group (δ 2.53), relative to the corresponding resonances observed for the parent adduct **5**. Oxidation at both sulfur atoms is incompatible with both the observed IR spectrum of **7**, which exhibits no sulfoxide absorptions, and with the ^{1}H NMR results from the oxidation of the corresponding 1,3-butadiene adduct.[9] The methylsulfinyl group of this cyclic sulfone, reported by Vyas and Hay,[9] resonates at δ 3.43, whereas the methylsulfonyl group of the corresponding disulfone[9] resonates at δ 3.52.

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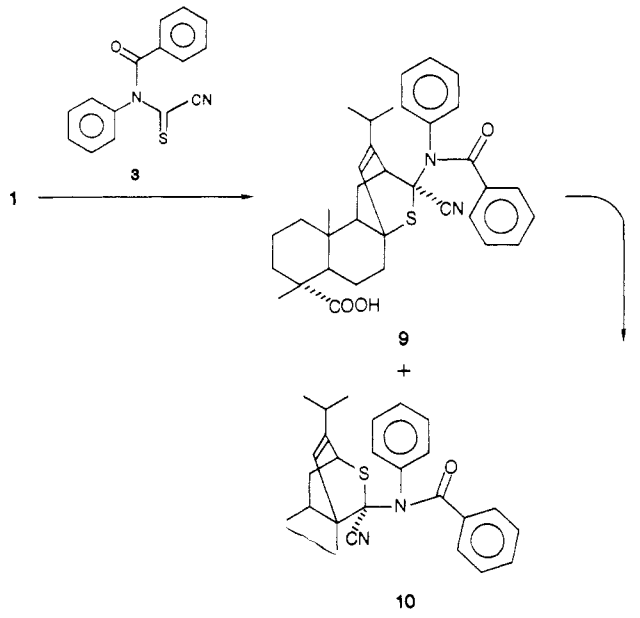
(9) Vyas, D. M.; Hay, G. W. *J. Chem. Soc., Perkin Trans 1* **1975**, 180.
(10) Vyas, D. M.; Hay, G. W. *Can. J. Chem.* **1975**, *53*, 1362.

Scheme II. Reaction of 1 with Cyanothioformamide (3)



The most nucleophilic site in adduct **5** is no longer the carbon–carbon double bond (observed for the model formaldehyde adduct) but rather the less hindered sulfur atom at C-8. Furthermore, oxidation of this atom not only deactivates the carbon–carbon double bond but also increases the steric hindrance experienced by the methylthio group.

Cyanothioformamides. The cyanothioformamides,[11] especially the N-acylated derivatives,[12,13] represent a class of reactive thiocarbonyl dienophiles capable of making large steric demands on the stereochemistry of the cycloaddition reactions of **1**. The existence of an electron-withdrawing aromatic amino or amido function on the thiocarbonyl group also increases the probability of regioselectivity during the additions.

***N*-Benzoyl-*N*-phenylcyanothioformamide (3).** N-Benzoylation of *N*-phenylcyanothioformamide (**8**) to give **3** renders this thiocarbonyl compound more dienophilic due to enhanced electron deficiency. Furthermore, **3** inherently permits a simultaneous competition between carbonyl and thiocarbonyl groups for the diene system of **1**.

Cycloaddition of 3 and 1. The N-acylated derivative **3** readily added to the resin acid **1** in 45 min at room temperature, as the color of the dienophile dissipated. If the crude product was then recrystallized from EtOH–H_2O, a single adduct **9** could be isolated in 66% yield (Scheme II).

Model and spectroscopic studies support the proposed structural assignment of **9**. The greater reactivity of the thiocarbonyl group relative to the carbonyl group of **3** is evidenced in the IR spectrum of purified **9**, which displays an amide carbonyl absorption at 1685 cm^{-1} in the absence of any absorption in the thiocarbonyl region (1200–1050 cm^{-1}). The ^1H NMR spectrum, on the other hand, allows assignment of both the regio- and stereochemistries of **9**. The broad multiplet at δ 3.40 is clearly indicative of a C-12 methine that is α only to carbon, in direct analogy to the corresponding methyl cyanodithioformate adducts **4** and **5** (δ 3.43). In addition, the marked shielding of both the C-14 olefinic proton (δ 4.49) and the isopropyl methyls at C-15 (δ 0.86 and 0.74) indicates that these groups are positioned above the plane of the phenyl and carbonyl functionalities. This endo relationship between the bulky *N*-phenylbenzamido group and the carbon–carbon double bond further reveals itself by restricting the rotation of the C-15 methyls, which appear as two distinct doublets. The characteristic chemical shift of the C-10 angular methyl group (δ 0.51) again definitively denotes the typical backside attack of **1** observed by all known dienophiles during Diels–Alder reactions.

Table I. Formation of 9 and 10 vs. Time

reacn time	integeration, C-14 of **10**:C-12 of **9**	ratio of **10**:**9**
21 min	2:6	25:75
45 min	3:8	27:73
22 h	3.1:3.2	49:51

In contrast to formaldehyde and the analogous dienophile **2**, however, the thiocarbonyl functionality of **3** possesses an enhanced potential toward regioselectivity during cycloadditions with **1**. The electronegativity of the *N*-phenylbenzamido moiety of **3** may readily facilitate a partial depletion of the electron density around the thiocarbonyl sulfur atom, thus essentially reversing the C=S dipole. In fact, when the previous cycloaddition reaction of **1** and **3** was carefully monitored by NMR at room temperature, resonances representative of the alternate regioisomer **10** appeared after 20 min to the extent of no more than 25%. Increased reaction times, however, slowly led to the formation of a higher percentage of **10** at the expense of the less stable **9** (Table I).

Major differences in the individual ^1H NMR spectra of **9** and **10** unequivocally establish the regio- and stereochemical structure of the "rearranged" adduct **10**. The chemical shift of the C-12 methine of **10** (δ 4.49) signifies a downfield shift indicative of an α sulfur atom. Although neither the C-14 olefinic methine (δ 6.17) nor the isopropyl methyls (δ 1.19 and 1.05) in **10** experience any longer a shielding effect by a proximate N-phenylbenzamido group, the appearance of the isopropyl methyls as two doublets clearly necessitates their restricted rotation about C-15 and thus again requires an endo relationship between the C=C bond and the *N*-phenylbenzamido group of **10**, as in **9**.

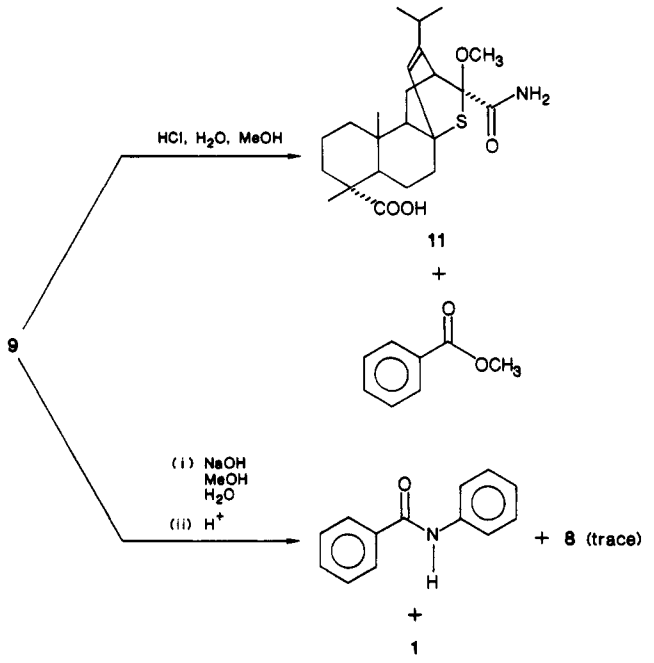
Whereas the methylthio group of **2** can successfully compete with the cyano group during the backside approach of the thiocarbonyl group to **1**, the steric bulk of the *N*-phenylbenzamido group of **3** totally prevents approach of the latter group to the diene system. Therefore, only one stereoisomer was observed during the formation of both **9** and **10**.

Chemistry of 9. A. Acidic Hydrolysis. Adduct **9** proved to be much more reactive than its closest analogue, adduct **5**, under extremely mild reaction conditions. Acidic solvolysis of **9** in MeOH at room temperature for 3 h gave **11** (Scheme III), in which the *N*-phenylbenzamido group has been replaced by an endo methoxy group and the cyano group of **9** has been hydrolyzed to the corresponding amide funtionality.

Spectroscopic analysis supports the proposed structure of **11**. The IR spectrum establishes the absence of the cyano group in **11** and the presence of the corresponding carbamoyl group, as evidenced by NH_2 stretching at 3470 cm^{-1} and the amide carbonyl at 1720 cm^{-1}. Second, the ^1H NMR spectrum clearly indicates the disappearance of both phenyl rings and the loss of their shielding effect on proximate protons. Furthermore, the isopropyl methyls, which no longer experience any significant restriction of rotational freedom, appear as a single doublet at δ 1.09.

(11) Kumelj, B.; Tisler, M. *Vestn. Slov. Kem. Drus.* **1958**, *5*, 69; *Chem. Abstr.* **1960**, *54*, 22426f.
(12) Friedrich, K.; Zamkanei, M. *Tetrahedron Lett.* **1977**, 2139.
(13) Friedrich, K.; Zamkanei, M. *Chem. Ber.* **1979**, *112*, 1867.

Scheme III. Hydrolysis of 9



A singlet at δ 3.13 has been assigned to the endo methoxy group, which is shielded by the π cloud of the carbon–carbon double bond.

The formation of **11** from adduct **9** appears to involve a direct stereospecific displacement of the *N*-phenylbenzamido group from the adduct itself with participation from the solvent (H_2O and MeOH). This conclusion is supported not only by similar solvolysis results reported by Larsen and Harpp[14] for the adducts of 1,1′-thiocarbonylbis(1,2,4-triazole) but also by the results from an independent methanolysis of **3**. Treatment of the dienophile **3** under similar conditions produced only **8** and methyl benzoate.

B. Basic Hydrolysis of 9. Basic hydrolysis of **9** at room temperature afforded, after neutralization, a mixture of **1**, benzanilide, and trace amounts of **8** (Scheme III). Again the possibility that the observed hydrolysis products were the result of a retrograde Diels–Alder reaction, followed by the hydrolysis of the resulting dienophile **3**, is dismissed on the grounds that only a trace of **8** was detected in the crude reaction mixture. Hydrolysis of **3** itself under the same conditions afforded instead an excellent yield of both **8** and benzanilide. The precise mechanism whereby benzanilide may be expelled from **9** is not well understood.

C. Catalytic Hydrogenation of 9. Analogous results were also obtained upon hydrogenolysis of **9** over PtO_2, in as much as abietic acid and benzanilide were identified in the reaction mixture. Again a direct mechanism is indicated since no benzanilide was detected from the corresponding hydrogenation of authentic **3**.

Conclusion. Electronic demands appear to dictate the observed regiochemistries of the levopimaric acid adducts of thiocarbonyl dienophiles **2** and **3**. On the other hand, steric hindrance seems to control not only the observed stereochemistries of the adducts but also the unusual reactivity of adduct **9**—as compared to the model formaldehyde adduct and adducts **5** and **10**. Relief of the steric strain experienced by adduct **9** is therefore readily accomplished by either rearrangement or by the displacement or elimination of the bulky endo *N*-phenylbenzamido group under a variety of mild conditions.

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Experimental Section

Melting points, which are uncorrected, were determined in an Electrothermal melting point apparatus. ^1H NMR data (90 MHz) and ^{13}C NMR data (300 MHz) are reported in δ (ppm) downfield from the internal standard Me_4Si.

Reaction of Levopimaric Acid (1) with Methyl Cyanodithioformate (2). Levopimaric acid (1) (2.00 g, 6.6 mmol) was dissolved in CH_2Cl_2 (25 mL), and the resulting solution was cooled in an ice bath. A CH_2Cl_2 solution of **2**[7,8] was added dropwise to the diene solution until the purple of the dienophile persisted. The solvent was reduced in vacuo, and petroleum ether (30–60 °C) was added to the concentrate until the turbidity point was reached. When the mixture was cooled, the crude product mixture precipitated as a white solid (2.574 g, 93%). The isomer ratio of **4** to **5** was 2:3, according to the ^1H NMR integration.

Fractional recrystallization of the crude product mixture from EtOH–H_2O preferentially afforded the major isomer **5**, whereas utilization of the solvent pair CH_2Cl_2–petroleum ether led to a mixture that was rich in the minor product **4**. However, isolation of pure **4** was prevented by its slow isomerization to **5** at room temperature. The two isomers gave the following data: mixture IR (KBr) 2640 cm^{-1} (OH), 2210 (CN), 1685 (C=O), 1640 (C=C), 1455 (CH_2), 1370 (CH_3), and 1270 (C–O); ^1H NMR of **4** in mixture (CCl_4) δ 11.73 (br s, H, OH), 5.57 (s, H, olefinic), 3.43 (br m, H, C-12 methine), 2.39 (s, 3 H, SCH_3), 1.17 (s, 3 H, C-4 methyl), 1.10 (d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6.0 Hz), and 0.64 (s, 3 H, C-10 methyl). Major product **5**: mp 151–152 °C; ^1H NMR (CCl_4) δ 11.73 (br, s, H, OH), 5.49 (s, H, olefinic), 3.48 (br m, H, C-12 methine), 2.25 (s, 3 H, SCH_3), 1.18 (s, 3 H, C-4 methyl), 1.10 (d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6.0 Hz), and 0.66 (s, 3 H, C-10 methyl); ^{13}C NMR ($CDCl_3$) δ 185.287 (C-18), 149.546 (C-13), 123.258 (C-14), and 118.525 (CN). Anal. Found: C, 65.81; H, 7.95; N, 3.37. Calcd for $C_{23}H_{33}NS_2O_2$: C, 65.83; H, 7.93; N, 3.34.

Permanganate Oxidation of 5. Adduct **5** (0.200 g, 0.48 mmol) was dissolved in a solution of *t*-BuOH (100 mL) and H_2O (50 mL). NaOH (0.2 g, 5 mmol) was added with stirring. When the NaOH had dissolved, $KMnO_4$ (0.385 g, 2.4 mmol) was added as the solid. After 52.5 h, NH_2OH·HCl was added to the brown mixture. The resulting mixture was acidified with concentrated HCl and was then diluted with H_2O until precipitation was complete. The white precipitate (0.135 g, 63%) was filtered and washed with H_2O. Recrystallization of the crude product from CCl_4 gave **7** as colorless crystals (0.089 g, 25 %): mp ~110 °C dec; IR (KBr) 3400 and 2660 cm^{-1} (OH), 2200 (CN), 1680 (C=O), 1640 (C=C), 1385 and 1370 (CH_3), 1325 and 1128 (SO_2), and 770 and 755 (CCl_4); ^1H NMR ($CDCl_3$) δ 5.60 (s, H, olefinic), 3.87 (br m, H, C-12 methine), 2.53 (s, 3 H, SCH_3), 1.20 (s, 3 H, C-4 methyl), 1.17 and 1.07 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 3 Hz), and 0.67 (s, 3 H, C-10 methyl). Anal. Found: C, 39.72; H, 4.43; N, 1.81. Calcd for $C_{23}H_{33}NS_2O_4 \cdot 2CCl_4$: C, 39.54; H, 4.38; N, 1.84. Attempts to remove the CCl_4 from the sample by heating in vacuo resulted in decomposition.

Preparation of *N*-Phenylcyanothioformamide (8). Compound **8** (83%) was prepared from phenyl isothiocyanate (12.8 mL, 107 mmol) and NaCN (7.686 g, 157 mmol), according to the literature procedure,[11] with the exception that dry DMF (30 mL) was utilized instead of an aqueous medium.

Preparation of *N*-Benzoyl-*N*-phenylcyanothioformamide (3). Compound **3** was obtained as dark red crystals (87%) from the reaction of **8** (6.387 g, 39 mmol) with benzoyl chloride (20.4 mL, 180 mmol) in the presence of pyridine (10.4 mL). Dry benzene (100 mL) was substituted for the aqueous medium described in the literature.[12] The crude reaction mixture was successively washed with dilute HOAc, 6 N HCl, dilute NaOH, H_2O, and petroleum ether. **3** was then recrystallized from CCl_4 with seeding.

Short-Term Reaction of 1 and 3. To a CH_2Cl_2 solution (100 mL) of **1** (3.00 g, 9.93 mmol) was added portionwise dienophile **3** (2.92 g, 11.0 mmol). The mixture, which became red-orange with time, was allowed to stir at room tempature for 45 min. The solvent was removed in vacuo to give a red-orange gum that was crystallized from EtOH–H_2O to give **9** as white needles (3.710 g, 66 %): mp 154–156.5 °C; IR (KBr) 3260 cm^{-1} (OH), 2210 (CN),

1720 and 1685 (C=O), 1670 (C=C), 1450 (CH_2), and 750 and 700 (monosubsituted Ar); ^1H NMR (CCl_4) δ 8.26 (br s, H, OH), 7.80–7.70 and 7.35–6.86 (m, 10 H, Ar), 4.49 (s, H, olefinic), 3.40 (br m, H, C-12 methine), 1.13 (s, 3 H, C-4 methyl), 0.86 and 0.74 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 7.5 Hz), and 0.51 (s, 3 H, C-10 methyl). Anal. Found: C, 73.84; H, 7.09; N, 4.92. Calcd for $C_{35}H_{40}N_2SO_3$: C, 73.91; H, 7.09; N, 4.93.

Rearrangement of 9 to 10. Adduct **9** (1.012 g, 1.78 mmol) was stirred in CH_2Cl_2 at room temperature. The mixture quickly and progressively transformed from colorless to pink, to orange, and finally to orange-brown. After continuous stirring for 3 days, the mixture was concentrated by rotary evaporation. The residue was recrystallized from benzene as colorless prisms of adduct **10** (0.331 g, 33%): mp 188.6–189.1 °C; IR (KBr) 2225 cm^{-1} (CN), 1750 and 1690 (C=O), 1625 (C=C), 1455 (CH_2), 1380 (CH_3), and 740 and 695 (monosubstituted Ar); ^1H NMR (acetone-d_6) δ 7.13 and 6.93 (m, 10 H, Ar), 6.17 (s, H, olefinic), 4.66 (m, H, C-12 methine), 1.19 and 1.05 (2 d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 7.5 Hz), 1.10 (s, 3 H, C-4 methyl), 0.60 (s, 3 H, C-10 methyl). Anal. Found: C, 73.97; H, 7.13; N, 4.85. Calcd for $C_{35}H_{40}N_2SO_3$: C, 73.91; H, 7.09; N, 4.93.

Acid Hydrolysis of 9. Adduct **9** (0.200 g, 0.35 mmol) was dissolved in MeOH (20 mL). HCl (6 N, 5 drops) was added, and the mixture was stirred at room temperature for 3 h. The reaction mixture was diluted with H_2O until precipitation was complete. After the mixture was stirred overnight, the precipitate was filtered and washed with water to give **11** as an almost-white solid (0.132 g, 93%), which was recrystallized from aqueous EtOH. The bright yellow solid that formed initially during the recrystallization was removed by filtration and was discarded. The solvolysis product **11** was then allowed to recrystallize from the filtrate, upon standing, as colorless needles: mp 147–148.2 °C; IR (KBr) 3470 cm^{-1} (NH_2), 3370 (OH), 1720 and 1687 (C=O), 1645 (C=C), 1271 and 1100 (C–O); ^1H NMR ($CDCl_3$ and D_2O) δ 5.40 (s, H, C-14 methine), 3.58 (m, H, C-12 methine), 3.13 (s, 3 H, OCH_3), 1.15 (s, 3 H, C-4 methyl), 1.09 (d, 6 H, C-15 methyls, $J_{15,16(17)}$ = 6 Hz), 0.61 (s, 3 H, C-10 methyl). Anal. Found: C, 65.50; H, 8.40; N, 3.31. Calcd for $C_{23}H_{35}NSO_4$: C, 65.52; H, 8.37; N, 3.32.

Acid Hydrolysis of 3. Dienophile **3** (0.2 g, 0.75 mmol) was stirred in a solution of MeOH (25 mL) and HCl (6 N, 5 drops) at room temperature for 23 h. The orange reaction mixture was then diluted with $CHCl_3$ and H_2O. The layers were separated, and the aqueous layer was extracted with $CHCl_3$. The combined organic extracts were dried over anhydrous $CaCl_2$ and evaporated to give an orange oil. Analysis of the crude product mixture by TLC ($CHCl_3$ or C_6H_6/SiO_2) and ^1H NMR revealed a mixture of **8** and methyl benzoate.

Base Hydrolysis of 9. Compound **9** (0.070 g, 0.12 mmol) was slurried in an aqueous solution of NaOH (0.5%, 40 mL). When MeOH (20 mL) was added portionwise to the resulting suspension, the sample dissolved and a gas evolved. After being stirred at room temperature for 3 h, the reaction mixture became turbid and benzanilide precipitated as a white solid. The precipitate (0.011 g) was filtered and washed with H_2O: mp 164–166 °C, mixed mp 164.3–165 °C.

The filtrate was concentrated under vacuum, diluted with H_2O, and acidified to pH 2 with dilute HCl. The turbid mixture was twice extracted with ether. The extracts were dried over $CaCl_2$ and evaporated to give a foul-smelling, yellow gum (0.05 g). The combined gravimetric and ^1H NMR spectral results indicated a quantitative yield of **1** and benzanilide. TLC ($CHCl_3/SiO_2$) revealed only a trace of **8**.

Base Hydrolysis of 3. **3** (0.036 g, 0.14 mmol) was added to a solution of NaOH (0.1 g, 2.5 mmol) in MeOH (30 mL) and H_2O (20 mL) at room temperature. After the red crystals of the dienophile dissolved, a bright yellow solution immediately developed, a gas evolved, and a small amount of white solid precipitated.

After 1.6 h, the bright yellow mixture was filtered, and the filtrate was neutralized with dilute HCl. The solution was extracted first with $CHCl_3$ and then with ether (2 × 25 mL). The combined extracts were washed with H_2O, dried over $CaCl_2$, and evaporated to afford an orange solid. TLC analysis ($CHCl_3/SiO_2$) revealed a mixture of **8** and benzanilide as the major products of the reaction.

Hydrogenation of 9. Adduct **9** (0.100 g, 0.18 mmol) and Adam's catalyst (0.050 g, 0.22 mmol) were added to EtOH (52 mL). After the adduct had dissolved, the mixture was hydrogenated at 40 psi for 6 h at room temperature. The catalyst was removed by filtration, and the solvent was removed under reduced pressure to give a brown gum. Analysis of the crude product mixture by TLC ($CHCl_3/SiO_2$) and ^1H NMR indicated the presence of abietic acid and benzanilide.

Hydrogenation of 3. Dienophile **3** (0.05 g, 0.19 mmol) and Adam's catalyst (0.051 g, 0.22 mmol) were slurried in EtOH (58 mL). Upon dissolution of the dienophile, the mixture was treated with hydrogen at 40 psi for 3.75 h at room temperature. The catalyst was removed by filtration and the resulting light yellow, foul-smelling solution was analyzed by TLC ($CHCl_3/SiO_2$), which excluded the presence of both **8** and benzanilide.