Table II. Physical and Spectral Data

product	mp, °C	IR R_f	IR cm^{-1}	MS	NMR
2	oil	0.22,[a] 0.68[b]	2865, 1700, 1414	269 (M + H)$^+$	200 MHz: δ 1.3–1.5 (m, 4 H), 1.45 (s, 9 H), 1.5–1.65 (m, 4 H), 1.8 (br d, J = 12 Hz, 2 H), 2.25–2.45 (m, 1 H), 2.5 (t, J = 6 Hz, 4 H), 2.67 (t, J = 12 Hz, 2 H), 4.16 (br d, J = 12 Hz, 2 H)
4	oil	0.13,[a] 0.58[b]	1702	303 (M + H)$^+$	200 MHz: δ 1.3–1.5 (m, 4 H), 1.5–1.65 (m, 4 H), 1.8 (br d, J = 12 Hz, 2 H), 2.3–2.5 (m, 1 H), 2.5 (t, 4 H), 2.75 (t, J = 12 Hz, 2 H), 4.25 (br d, J = 12 Hz, 2 H), 5.1 (s, 2 H), 7.25 (m, 5 H)
6	112–113	0.29[b]	1625, 1534	268 (M + H)$^+$	200 MHz: δ 1.35 (s, 9 H), 1.35–1.55 (m, 4 H), 1.55–1.7 (m, 4 H), 1.85 (d, J = 12 Hz, 2 H), 2.3–2.5 (m, 1 H), 2.54 (t, J = 6 Hz, 4 H), 2.72 (d of t, 2 H), 3.94 (d, J = 12 Hz, 2 H), 4.3 (s, 1 H)
8	175–176	0.18[b]	1618, 1547	254 (M + H)$^+$	200 MHz: δ 0.9 (t, J = 6 Hz, 3 H), 1.3–1.7 (m, 10 H), 1.85 (br d, J = 12 Hz, 2 H), 2.3–2.5 (m, 1 H), 2.52 (t, 4 H), 2.75 (d of t, 2 H), 3.2 (q, J = 6 Hz, 2 H), 3.98 (br d, J = 12 Hz, 2 H), 4.5 (br s, 1 H)
10	oil	0.13[b]	1655	211 (M + H)$^+$	200 MHz: δ 1.35–1.5 (m, 4 H), 1.5–1.65 (m, 4 H), 1.7–1.95 (m, 2 H), 2.1 (s, 3 H), 2.35–2.6 (m, 6 H), 3.03 (d of t, 1 H), 3.95 (br d, 1 H), 4.75 (br d, 1 H)
11	oil	0.56[b]	2935, 1119, 1108	226 (M + H)$^+$	200 MHz: δ 1.4–2.0 (m, 14 H), 2.3–2.5 (m, 1 H), 2.55 (t, 4 H), 3.95 (s, 4 H)
12	oil	0.34[c]	2933, 1111	209 (M + H)$^+$	200 MHz: δ 1.3–1.6 (m, 10 H), 1.75 (d of t, 2 H), 1.9–2.1 (m, 2 H), 2.1 (s, 3 H), 2.45 (t, 4 H), 2.5–2.7 (m, 1 H), 3.2 (t, 2 H)
13	oil	0.40[d]	2935, 1455	176 (M + H)$^+$	200 MHz: δ 1.3–1.5 (m, 2 H), 1.5–1.65 (m, 4 H), 2.37 (t, 4 H), 3.45 (s, 2 H), 7.3 (m, 5 H)
14	oil	0.36[a,b]	1732, 1695	341 (M + H)$^+$	300 MHz: δ 1.07 (t, 3 H), 1.15–1.3 (m, 2 H), 1.27 (s, 9 H), 1.5–1.65 (m, 4 H), 1.75 (br d, 2 H), 2.0–2.3 (m, 4 H), 2.5 (br t, 2 H), 2.7 (br d, 2 H), 3.9–4.05 (m, 4 H) (small amt iPr ester at δ 4.8)
15	76–78	0.16,[a] 0.82[b]	1695	271 (M + H)$^+$	200 MHz: δ 1.25–1.55 (m, 4 H), 1.46 (s, 9 H), 1.82 (br d, J = 12 Hz, 2 H), 2.2–2.4 (m, 1 H), 2.55 (t, J = 6 Hz, 4 H), 2.68 (t, J = 12 Hz, 2 H), 3.68 (t, J = 6 Hz, 4 H), 4.15 (br d, J = 12 Hz, 2 H)
16	oil	0.12,[a] 0.66[b]	1700	345 (M + H)$^+$	300 MHz: δ 1.2 (t, J = 6 Hz, 6 H), 1.2–1.7 (m, 7 H), 1.45 (s, 9 H), 1.95 (br d, J = 12 Hz, 2 H), 2.5–2.95 (br s, 1 H, NH), 2.65 (t, J = 6 Hz, 2 H), 2.77 (t, J = 12 Hz, 2 H), 3.4–3.75 (m, 4 H), 4.05 (br d, J = 12 Hz, 2 H), 4.50 (t, J = 6 Hz, 1 H)
17	139–141	0.45[d]	1680	249 M$^+$	300 MHz: δ 1.24–1.37 (m, 2 H), 1.47 (s, 9 H), 2.01 (d of d, 2 H), 2.91 (t, J = 12 Hz, 2 H), 3.37–3.44 (m, 1 H), 3.56 (br s, 1 H, NH), 4.03 (br d, J = 9 Hz, 2 H), 6.59 (d, 2 H), 6.68 (t, 1 H), 7.15 (d of t, 2 H)

[a] Ethyl acetate. [b] Acetone. [c] 1:1 methanol/CH_2Cl_2. [d] 4:1 hexanes/ethyl acetate.

Table III. Elemental Analysis

compd	formula	analysis
2	$C_{15}H_{28}N_2O_2$	calcd: C, 67.13; H, 10.52; N, 10.44 found: C, 67.07; H, 10.47; N, 10.30
4	$C_{18}H_{26}N_2O_2 \cdot 0.1H_2O$	calcd: C, 71.07; H, 8.69; N, 9.21 found: C, 71.04; H, 8.70; N, 9.11
6	$C_{15}H_{29}N_3O$	calcd: C, 67.37; H, 10.93; N, 15.71 found: C, 67.40; H, 10.95; N, 15.71
8	$C_{14}H_{27}N_3O \cdot 0.1H_2O$	calcd: C, 65.90; H, 10.75; N, 16.47 found: C, 65.90; H, 10.78; N, 16.62
10	$C_{12}H_{22}N_2O$	calcd: C, 66.53; H, 10.55; N, 13.32 found: C, 66.88; H, 10.49; N, 13.03
11	$C_{13}H_{23}NO_2$	calcd: C, 69.30; H, 10.29; N, 6.22 found: C, 69.22; H, 10.31; N, 6.18
12	$C_{13}H_{24}N_2$	calcd: C, 74.54; H, 11.61; N, 13.45 found: C, 74.15; H, 11.73; N, 13.38
13	$C_{12}H_{17}N$	calcd: C, 82.23; H, 9.78; N, 7.99 found: C, 81.82; H, 9.78; N, 7.99
14	$C_{18}H_{32}N_2O_4$	calcd: C, 63.51; H, 9.48; N, 8.23 found: C, 63.41; H, 9.51; N, 8.15
15	$C_{14}H_{26}N_2O_3$	calcd: C, 62.20; H, 9.70; N, 10.37 found: C, 62.17; H, 9.66; N, 10.44
16	$C_{18}H_{36}N_2O_4$	calcd: C, 62.76; H, 10.54; N, 8.14 found: C, 62.86; H, 10.60; N, 8.14
17	$C_{16}H_{24}N_2O_2$	calcd: C, 69.54; H, 8.76; N, 10.14 found: C, 69.83; H, 8.81; N, 10.14

acetate) and 17 (7:1 hexanes/ethyl acetate). All yields given are of analytically pure material, and all compounds had NMR and IR spectra and elemental analyses (±0.4%) consistent with the assigned structures.

General Procedure. A mixture of the ketone (10 mmol), amine (10 mmol), and titanium(IV) isopropoxide (3.72 mL, 12.5 mmol) was stirred at room temperature in a 100-mL round-bottom flask under a drying tube. After 1 h, the IR spectrum of the mixture showed no ketone band, and the viscous solution was diluted with absolute ethanol (10 mL). Sodium cyanoborohydride (0.42 g, 6.7 mmol) was added, and the solution was stirred for 20 h. Water (2 mL) was added with stirring, and the resulting inorganic precipitate was filtered and washed with ethanol. The filtrate was then concentrated in vacuo. The crude product was dissolved in ethyl acetate, filtered to remove the remaining inorganic solids, and concentrated in vacuo. The products were then purified by flash chromatography.

Registry No. **1**, 79099-07-3; **2**, 125541-12-0; **3**, 19099-93-5; **4**, 125541-13-1; **5**, 125541-11-9; **6**, 125541-14-2; **7**, 89805-08-3; **8**, 125541-15-3; **9**, 32161-06-1; **10**, 125541-16-4; **11**, 125541-17-5; **12**, 125541-18-6; **13**, 2905-56-8; **14**, 125541-19-7; **15**, 125541-20-0; **16**, 125541-21-1; **17**, 125541-22-2; titanium(IV) isopropoxide, 546-68-9; piperidine, 110-89-4; ethyl piperidine-4-carboxylate, 1126-09-6; 4,4-diethoxybutanamine, 6346-09-4; aniline, 62-53-3; tropinone, 532-24-1; benzaldehyde, 100-52-7; morpholine, 110-91-8; 1,2-dioxaspiro[4.5]decan-8-one, 4746-97-8.

Nickel(0)-Catalyzed Hydroacylation of Alkynes with Aldehydes to α,β-Enones

Tetsuo Tsuda,* Takao Kiyoi, and Takeo Saegusa*

Department of Synthetic Chemistry, Faculty of Engineering, Kyoto University, Yoshida, Kyoto 606, Japan

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Transition metal catalyzed reaction of alkynes with aldehydes has not been well known. By taking advantage of the nickel(0)-catalyzed cycloaddition reaction of diynes with carbon dioxide to bicyclic α-pyrones,[1] we have found

(1) Tsuda, T.; Morikawa, S.; Sumiya, R.; Saegusa, T. *J. Org. Chem.* **1988**, *53*, 3140.

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Table I. Nickel(0)-Catalyzed Reaction of 4-Octyne (1) and Aldehyde 2 (eq 1)[a]

2	ligand (L)	temp, °C	time, h	yield,[b] % α,β-enone	yield,[b] % α,β;γ,δ-dienone
2a	PEt_3	100	20	**3**, 34	**4**, 2
	$P(n\text{-}Bu)_3$	100	5	44	11
	$P(n\text{-}Bu)_3$	100	20	72	12
	$P(n\text{-}Bu)_3$	135	20	38	4
	$P(n\text{-}C_8H_{17})_3$	80	20	85 [54][c]	13 [4][c]
	$P(n\text{-}C_8H_{17})_3$	100	20	93 [65][c] (*E*:*Z* = 93:7)[d]	6
	$P(n\text{-}C_8H_{17})_3$	150	20	88 [68][c] (*E*:*Z* = 89:11)[d]	4
	$P(s\text{-}Bu)_3$	100	20	25	65
	PCy_3	100	20	44	53
	PPh_3	100	20	36	17
2b	$P(n\text{-}C_8H_{17})_3$	100	20	**5**, 13	
	$P(n\text{-}C_8H_{17})_3$	135	20	80 [59][c] (*E*:*Z* = 95:5)[d]	
2c	$P(n\text{-}Bu)_3$	135	5	**7**, 50	
	$P(n\text{-}Bu)_3$	135	20	83	
	$P(n\text{-}Bu)_3$	150	5	76 [51][c] (*E*:*Z* = 79:21)[d]	
	$P(s\text{-}Bu)_3$	135	20	44	
	PCy_3	135	20	48	

[a] **1**; 1.00 mmol; **2**:**1** = 1.5; $Ni(COD)_2$:**1** = 0.05; L:$Ni(COD)_2$ = 2; solvent; THF (8–10 mL). [b] Yield was determined by GC using an internal standard. [c] The value in brackets is the isolated yield (percent) determined by PLC. [d] The *E*:*Z* ratio was determined by 400-MHz ^1H NMR spectroscopy.

Table II. Nickel(0)-Catalyzed Reaction of Unsymmetrically Disubstituted Monoyne 9 and Benzaldehyde (2c) (eq 2)[a]

$R^1C{\equiv}CR^2$ (**9**)	L	temp, °C	yield,[b] %	α,β-enone $R^1CH{=}CR^2(COR)$ (%,[d] *E*:*Z*[e])	α,β-enone $R^2CH{=}CR^1(COR)$ (%,[d] *E*:*Z*[e])
9a	$P(n\text{-}Bu)_3$	150	**10** + **11**, 49		
9a	$P(s\text{-}Bu)_3$	150	**10** + **11**, 26		
9a	$P(t\text{-}Bu)_3$	150	**10** + **11**, 5		
9a	$P(n\text{-}C_8H_{17})_3$	115	**10** + **11**, 23		
9a	$P(n\text{-}C_8H_{17})_3$	135	**10** + **11**, [47][c]	**10** (40, 79:21)	**11** (60, 87:13)
9a	$P(n\text{-}C_8H_{17})_3$	150	**10** + **11**, 59		
9b	$P(n\text{-}C_8H_{17})_3$	150	**12** + **13**, 48	**12** (78, 90:10)	**13** (22, 47:53)
9c	$P(n\text{-}C_8H_{17})_3$	150	**14** + **15**, 28	**14** (96, 83:17)	**15** (4)
9d	$P(n\text{-}C_8H_{17})_3$	150	**16** + **17**, 71 [54][c]	**16** (29, 62:38)	**17** (71, 44:56)

[a] **9**, 1.00 mmol; **2c**:**9** = 1.5; $Ni(COD)_2$:**9** = 0.05; L:$Ni(COD)_2$ = 2; solvent, THF (8–10 mL); time, 20 h. [b] Yield was determined by GC using an internal standard. [c] The value in brackets is the isolated yield (percent) determined by PLC. [d] Regioselectivity was determined by 200- or 400-MHz ^1H NMR spectroscopy. [e] The *E*:*Z* ratio was determined by 200- or 400-MHz ^1H NMR spectroscopy.

that the nickel(0)-catalyzed reaction of diynes with aldehydes affords a variety of cycloadducts depending upon the structure of the diyne, i.e., bicyclic α-pyrans and oxoalkyl-substituted cyclopentene and pyrrole derivatives.[2] Here we have studied an unprecedented nickel(0)-catalyzed reaction of monoynes with aldehydes.

When 4-octyne (1) was reacted with isobutyraldehyde (**2a**) in tetrahydrofuran (THF) at 100 °C for 20 h in the presence of a nickel(0) catalyst (5.0 mol %) generated from $Ni(COD)_2$ and 2 equiv of $P(n\text{-}C_8H_{17})_3$, the α,β-enone **3**, i.e., a hydroacylation product of **1** with **2a**, was obtained in 93% yield along with a small amount of α,β;γ,δ-dienone **4** (eq 1). The α,β-enone formation proceeded stereose-

$$\underset{\mathbf{1}}{n\text{-PrC}{\equiv}\text{C}\text{-}n\text{-Pr}} + \text{RCHO} \xrightarrow{\text{Ni(0)-PR}_3} n\text{-PrCH}{=}\text{C}\text{-}n\text{-Pr(COR)} + n\text{-PrCH}{=}\text{C}(n\text{-Pr})\text{-C}(n\text{-Pr}){=}\text{C}\text{-}n\text{-Pr(COR)} \quad (1)$$

2a: R = *i*-Pr; **3**: R = *i*-Pr
b: R = *n*-Pr; **5**: R = *n*-Pr
c: R = Ph; **7**: R = Ph

4: R = *i*-Pr
6: R = *n*-Pr
8: R = Ph

lectively with (*E*)-**3**:(*Z*)-**3** = 93:7. The formation of **3** and **4** was highly dependent upon the structure of the tertiary phophine ligand used. The results are summarized in Table I. Tri-*n*-alkylphosphine ligands such as $P(n\text{-}Bu)_3$ and $P(n\text{-}C_8H_{17})_3$ afforded the α,β-enone predominantly. By contrast, tri-*sec*-alkylphosphines such as $P(s\text{-}Bu)_3$ and tricyclohexylphosphine (PCy_3) favored the dienone formation. For the reaction of **1** with **2a**, PMe_3, PEt_3, and PPh_3 ligands were less effective and $P(t\text{-}Bu)_3$ and $Ph_2P(CH_2)_nPPh_2$ (n = 2, 4) ligands were ineffective.

Other aldehydes could also be used for the reaction. The reaction of **1** with *n*-butyraldehyde (**2b**) at 135 °C using the $P(n\text{-}C_8H_{17})_3$ ligand gave α,β-enone **5** in 80% yield with high stereoselectivity, (*E*)-**5**:(*Z*)-**5** = 95:5. In contrast to the reaction of **1** with **2a**, the use of the tri-*sec*-alkylphosphine ligands in the reaction of **1** with **2b** did not produce the dienone **6** effectively; **5** was obtained as a major product along with a small amount (ca. 5–10%) of **6**. α,β-Enone **7** was also obtained in a high yield in the reaction of **1** with benzaldehyde (**2c**), where the dienone **8** was not detected. Stereoselectivity of the formation of **7** was (*E*)-**7**:(*Z*)-**7** = 79:21.

Regiochemistry of the nickel(0)-catalyzed hydroacylation of monoynes with aldehydes was examined using unsymmetrically substituted 1-propynes $R^1C{\equiv}CMe$ **9a–c**, **2c**, and the $P(n\text{-}C_8H_{17})_3$ ligand (eq 2). The results are summarized in Table II. Yields of α,β-enones **10–15** obtained from the methyl-substituted monoynes were not high. The regioselectivity depended upon steric bulk of the alkyl substituent R^1. A formyl hydrogen atom of the aldehyde showed a marked tendency to add regioselectively to the carbon atom bearing R^1 when R^1 is a bulky isopropyl or *tert*-butyl group, i.e., **10**:**11** = 40:60 (R^1 = *n*-Bu), **12**:**13** =

(2) Tsuda, T.; Kiyoi, T.; Miyane, T.; Saegusa, T. *J. Am. Chem. Soc.* **1988**, *110*, 8570.

$$R^1C{\equiv}CR^2 + PhCHO \xrightarrow[\textbf{2c}]{Ni(0)\text{-}PR_3}$$

9a: R^1 = *n*-Bu; R^2 = Me
b: R^1 = *i*-Pr; R^2 = Me
c: R^1 = *t*-Bu; R^2 = Me
d: R^1 = Ph; R^2 = Et

$$R^1CH{=}CR^2(COPh) + R^2CH{=}CR^1(COPh) \quad (2)$$

10: R^1 = *n*-Bu; R^2 = Me **11**: R^1 = *n*-Bu; R^2 = Me
12: R^1 = *i*-Pr; R^2 = Me **13**: R^1 = *i*-Pr; R^2 = Me
14: R^1 = *t*-Bu; R^2 = Me **15**: R^1 = *t*-Bu; R^2 = Me
16: R^1 = Ph; R^2 = Et **17**: R^1 = Ph; R^2 = Et

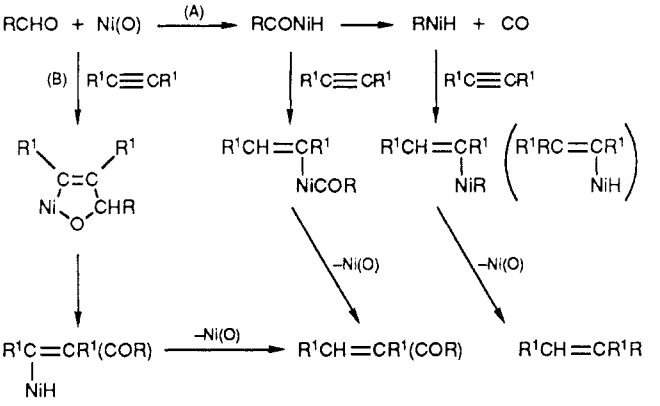
78:22 (R^1 = *i*-Pr), and **14**:**15** = 96:4 (R^1 = *t*-Bu). Isomer ratio of (*E*)-**10** to (*Z*)-**11** determined by GC analysis indicates that the reaction temperature between 115 °C and 150 °C did not affect the regio- and stereoselectivity of the **10** + **11** formation; (*E*)-**10**:(*E*)-**11** ratios were 33:67 (115 °C), 38:62 (135 °C), and 35:65 (150 °C). A phenyl-substituted monoyne **9d** also gave α,β-enones **16** and **17** in its reaction with **2c**. The reaction of 1-(trimethylsilyl)-1-hexyne and **2a** produced (*E*)-2-methyl-4-(trimethylsilyl)-5-nonen-3-one (**18**) as a major product in ca. 10% yield, which is an isomerization product of the corresponding α,β-enone. The reaction of **2c** with 1-hexyne, i.e., a terminal monoyne, however, did not produce the corresponding α,β-enone. Thus the present novel nickel(0)-catalyzed hydroacylation reaction of disubstituted monoynes with aldehydes provides a convenient synthetic method of α,β-disubstituted α,β-enones.

There are two possible routes for the formation of α,β-enones;[3] route A involving an RCONiH complex and route B via a Ni(II)-metallacycle (Scheme I[4]). At the present time, no decisive mechanistic conclusion can be drawn. Available experimental results, however, favor route A.[5] In the reaction of **9b** and **2c** in Table II, it was observed that CO gas is evolved in the gas phase and a nickel–carbonyl complex, assignable to $Ni(CO)_2[P(n\text{-}C_8H_{17})_3]_2$ on the basis of IR absorptions[6] at 1987 and 1922 cm^{-1} of the liquid phase, is formed.[7] In the reaction of **9a** with **2c** at 135 °C using the $P(n\text{-}C_8H_{17})_3$ ligand, olefinic side products (*E*)-2-phenyl-2-heptene (**19**) and (*E*)-3-phenyl-2-heptene (**20**) were detected in 12% and 4% yields, respectively. These two findings indicate intermediacy of the RCONiH complex.[8] Its decarbonylation evolves CO gas with concomitant formation of an RNiH complex which reacts with the monoyne to produce the olefin (Scheme I[4]).

Experimental Section

IR spectra were determined on a Hitachi 260-50 grating spectrophotometer. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were taken on a JEOL JNM-JX-400 instrument. ^1H NMR (200 MHz) spectra were taken on a Varian GEMINI-200 instrument. The NMR measurement was carried out in $CDCl_3$ unless otherwise indicated. All chemical shifts are reported in δ downfield from internal tetramethylsilane except the ^1H NMR measurement of the product **18** where its chemical shifts are reported in δ determined by internal C_6H_6. Coupling constants (*J*) are reported in hertz. Mass spectra were obtained on a JEOL DX-300 instrument. Gas chromatographic analyses (GC) were made on a Shimadzu 4CPT instrument. GC quantitative analyses of reaction products were made with internal standards with calibration based upon authentic samples employing a 20% silicone DC 550 on Celite 545 column. GC analysis of CO gas was carried out using an activated charcoal column. Preparative layer chromatography (PLC) was carried out by using 20 × 20 × 0.2 cm plates prepared with Merck silica gel 60PF-254. Preparative medium-pressure liquid chromatography (MPLC) was carried out by using a prepacked silica gel column (CPS-223L-1) supplied by Kusano Kagaku Co.

Scheme I



Tetrahydrofuran (THF) was distilled from $LiAlH_4$ under nitrogen. Monoynes **1**, **9a–d**, and 1-hexyne and aldehydes **2a–c** were commercial reagents, which were distilled under nitrogen after drying over anhydrous $MgSO_4$. 1-(Trimethylsilyl)-1-hexyne was prepared according to the reported method.[9] Bis(1,5-cyclooctadiene)nickel(0) ($Ni(COD)_2$) was purchased from Kanto Kagaku, Inc. Phosphorus ligands were commercial reagents and were used without further purification.

Nickel(0)-Catalyzed Reaction of 4-Octyne (1) with Isobutyraldehyde (2a). The reaction was carried out under nitrogen. In a 50-mL stainless steel autoclave were placed THF (8.50 mL), a THF solution (1.20 mL) of $Ni(COD)_2$ (0.050 mmol), and $P(n\text{-}C_8H_{17})_3$ (0.046 mL, 0.10 mmol). After the mixture was stirred for several minutes, **1** (0.147 mL, 1.00 mmol) and **2a** (0.136 mL, 1.50 mmol) were added. The reaction mixture was magnetically stirred for 20 h at 80 °C. Addition of heneicosane (0.0297 g, 0.100 mmol) as a GC internal standard and subsequent GC analysis showed the formation of **3** in 85% yield along with the formation of **4** in 13% yield. The solution was concentrated to give a residue which was purified by PLC (hexane:ether = 15:1 v/v) to give the mixture of **3** and **4** (0.124 g). Further purification of the mixture by MPLC (hexane:EtOAc = 30:1 v/v) gave **3** (0.0985 g, 54%) and **4** (0.0051 g, 4%). **3**: IR (neat, cm^{-1}) 1665, 1635; MS *m*/*e* (relative intensity) 182 (M^+, 8), 139 (100), 69 (98), 55 (37), 43 (30); HRMS (*m*/*e*) 182.1693, calcd for $C_{12}H_{22}O$ 182.1670. Anal. Calcd for $C_{12}H_{22}O$: C, 79.06; H, 12.16. Found: C, 78.99; H, 12.29. Separation of (*E*)-**3** and (*Z*)-**3** by PLC was unsuccessful. ^1H NMR analysis of **3** revealed the following data. (*E*)-**3**: ^1H NMR 0.89 (t, *J* = 7.3, 3 H), 0.97 (t, *J* = 7.4, 3 H), 1.07 (d, *J* = 6.8, 6 H), 1.31 (sext, *J* = 7.5, 2 H), 1.50 (sext, *J* = 7.4, 2 H), 2.24 (q, *J* = 7.4, 2 H), 2.27 (t, *J* = 7.8, 2 H), 3.30 (sept, *J* = 6.8, 1 H), 6.55 (t, *J* = 7.2, 1 H). (*Z*)-**3**: ^1H NMR 2.08 (br q, *J* = 7.6, 2 H), 2.2 (tq, *J* = 7, 1, 2 H), 2.75 (sept, *J* = 6.9, 1 H), 5.50 (tt, *J* = 7.6, 1.2, 1 H). (*E*)-**3**:(*Z*)-**3** ratio of **3** obtained by the reaction at 100 °C was determined by ^1H NMR; (*E*)-**3**:(*Z*)-**3** = 93:7. The stereochemistry of (*E*)-**3** was determined by ^1H NMR NOE measurement. **4**: IR (neat, cm^{-1}) 1695, 1615, 800; ^1H NMR 0.83 (t, *J* = 7.3, 3 H), 0.84 (t, *J* = 7.3, 3 H), 0.91 (t, *J* = 7.2, 3 H), 0.93 (t, *J* = 7.3, 3 H), 1.10 (d, *J* = 7.0, 6 H), 1.24 (sext, *J* = 7.7, 2 H),

(3) The mechanistic discussion on the formation of α,β-enones may be applicable to that of α,β;γ,δ-dienones.
(4) For simplification, the phosphine ligand coordinated toward the nickel atom is omitted in Scheme I.
(5) The hydridoacylmetal complex is generally accepted as a key intermediate in the transition metal complex catalyzed hydroacylation of alkenes with aldehydes; see, for example: (a) Vora, K. P.; Locow, C. F.; Miller, R. G. *J. Organomet. Chem.* **1980**, *192*, 257. (b) Kondo, T.; Tsuji, Y.; Watanabe, Y. *Tetrahedron Lett.* **1987**, *28*, 6229 and the cited references.
(6) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2956.
(7) Pressurizing the reactions of **1–2a** and **9a–2c** with CO gas (25 kg/cm²) inhibited the formation of the corresponding α,β-enones.
(8) The intermediacy of the RCONiH complex may also be possible in the previously reported Ni(0)-catalyzed reaction of diynes and aldehydes.[2] In this reaction mechanism, bicyclic α-pyrans may be formed by electrocyclic ring closure of α,β;γ,δ-dienone intermediates.
(9) Brandsma, L.; Verkruijsse, H. D. *Synthesis of Acetylenes, Allenes, and Cumulenes*; Elsevier: New York, 1981; p 57.

1.32 (sext, J = 7.5, 2 H), 1.33 (sext, J = 7.6, 2 H), 1.41 (sext, J = 7.3, 2 H), 1.92 (t, J = 7.8, 2 H), 2.07 (t, J = 8.0, 2 H), 2.08 (q, J = 7.3, 2 H), 2.28 (t, J = 8.1, 2 H), 2.81 (sept, J = 7.0, 1 H), 5.11 (t, J = 7.5, 1 H); ^{13}C NMR (C_6D_6) 14.2, 14.4, 14.6, 18.3, 21.8, 22.4, 23.1, 23.4, 30.1, 31.8, 33.5, 34.7, 38.4, 39.0, 39.8, 44.8, 45.3, 211.4; MS m/e (relative intensity) 292 (M^+, 2.7), 250 (21), 249 (100), 221 (5), 207 (2), 71 (2); HRMS (m/e) 292.2780, calcd for $C_{20}H_{36}O$ 292.2766.

The α,β-enones **5**, **7**, **10**–**17** and the $\alpha,\beta;\gamma,\delta$-dienone **6** along with the products **18**–**20** were similarly obtained as described above. Complete separation of regio- and/or stereoisomers by PLC and MPLC was unsuccessful. A separable isomer was identified by its IR, ^{1}H NMR, MS, HRMS, and ^{13}C NMR data and/or combustion analysis. A structure of an unseparable isomer was determined by ^{1}H NMR analysis of its isomer mixture. E- and/or Z-stereochemistry of products was determined by ^{1}H NMR NOE measurement. The product purity was judged to be ≥95% for the products **4**, **5**, **10**, **11**, **12**, **13**, **19** and **20** and ≥90% for the products **6**, **14**, **15**, **16**, **17**, and **18** by ^{1}H NMR spectral determinations.

5 (PLC, hexane:ether = 15:1 v/v): IR (neat, cm^{-1}) 1665, 1630; MS m/e (relative intensity) 182 (M^+, 19), 139 (77), 69 (52), 57 (100), 56 (48), 43 (64); HRMS (m/e) 182.1685, calcd for $C_{22}H_{22}O$ 182.1670. (*E*)-**5**: ^{1}H NMR 0.89 (t, J = 7.4, 3 H), 0.93 (t, J = 7.5, 3 H), 0.97 (t, J = 7.5, 3 H), 1.32 (sext, J = 7.5, 2 H), 1.50 (sext, J = 7.4, 2 H), 1.63 (sext, J = 7.4, 2 H), 2.23 (q, J = 7.5, 2 H), 2.26 (t, J = 7.8, 2 H), 2.61 (t, J = 7.4, 2 H), 6.58 (t, J = 7.3, 1 H); ^{13}C NMR 13.9, 13.9, 14.2, 18.5, 22.3, 22.6, 27.7, 30.9, 39.4, 142.1, 142.3, 202.1. (*Z*)-**5**: ^{1}H NMR 2.12 (qt, J = 7.4, 1.0, 2 H), 2.20 (tq, J = 7.4, 1.1, 2 H), 2.49 (t, J = 7.3, 2 H), 5.50 (tt, J = 7.5, 1.2, 1 H). **6**: IR (neat, cm^{-1}) 1685, 1615; ^{1}H NMR 0.95 (t, J = 7.5, 3 H), 0.99 (t, J = 7.3, 3 H), 1.005 (t, J = 7.4, 3 H), 1.008 (t, J = 7.4, 3 H), 1.03 (t, J = 7.5, 3 H), 1.40–1.60 (m, 6 H), 1.61 (sext, J = 7.5, 2 H), 1.82 (sext, J = 7.30, 2 H), 2.13 (q, J = 7.2, 2 H), 2.17 (t, J = 7.7, 2 H), 2.20 (t, J = 8.3, 2 H), 2.24 (t, J = 8.1, 2 H), 2.48 (t, J = 7.2, 2 H), 5.33 (t, J = 7.3, 1 H); MS m/e (relative intensity) 292 (M^+, 4), 250 (21), 249 (100), 221 (8), 207 (3), 71 (8); HRMS (m/e) 292.2786, calcd for $C_{20}H_{36}O$ 292.2766. **7** (PLC, hexane:ether = 15:1 v/v): IR (neat, cm^{-1}) 1640, 1595; MS m/e (relative intensity) 216 (M^+, 74), 187 (31), 173 (69), 145 (45), 105 (100); HRMS (m/e) 216.1525, calcd for $C_{15}H_{20}O$ 216.1514. Anal. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32. Found: C, 83.49; H, 9.51. (*E*)-**7**: ^{1}H NMR 0.94 (t, J = 7.4, 3 H), 0.96 (t, J = 7.3, 3 H), 1.46 (sext, J = 7.4, 2 H), 1.47 (sext, J = 7.4, 2 H), 2.27 (q, J = 7.4, 2 H), 2.47 (t, J = 7.6, 2 H), 6.20 (t, J = 7.4, 1 H), 7.40 (t, J = 7.4, 2 H), 7.49 (t, J = 7.4, 1 H), 7.65 (d, J = 7.9, 2 H); ^{13}C NMR 14.0, 14.2, 22.2, 22.3, 28.7, 30.9, 128.0, 129.4, 131.4, 139.2, 141.3, 145.6, 199.0. (*Z*)-**7**: ^{1}H NMR 0.80 (t, J = 7.4, 3 H), 0.91 (t, J = 7.3, 3 H), 1.34 (sext, J = 7.3, 2 H), 1.45 (sext, J = 7.0, 2 H), 1.83 (qt, J = 7.4, 1.0, 2 H), 2.29 (td, J = 7.8, 1.2, 2 H), 5.67 (tt, J = 7.6, 1.3, 1 H), 7.48 (t, J = 7.5, 2 H), 7.56 (t, J = 7.3, 1 H), 7.92 (d, J = 7.0, 2 H). (*E*)-**10** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane:ether = 10:1 v/v): IR (neat, cm^{-1}) 1640, 1595, 1450, 700; ^{1}H NMR 0.91 (t, J = 7.2, 3 H), 1.25–1.45 (m, 4 H), 1.97 (d, J = 1.3, 3 H), 2.28 (q, J = 7.3, 2 H), 6.30 (tq, J = 7.4, 1.4, 1 H), 7.41 (t, J = 7.4, 2 H), 7.50 (t, J = 7.3, 1 H), 7.62 (d, J = 7.0, 2 H); MS m/e (relative intensity) 202 (M^+, 31), 159 (39), 145 (45), 105 (100); HRMS (m/e) 202.1365, calcd for $C_{14}H_{18}O$ 202.1357. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.96; H, 9.14. *E*-Stereochemistry of (*E*)-**10** was determined by ^{1}H NMR NOE measurement. (*E*)-**11** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane:ether = 10:1 v/v): ^{1}H NMR 0.93 (t, J = 7.1, 3 H), 1.30–1.45 (m, 4 H), 1.88 (d, J = 7.0, 3 H), 2.49 (t, J = 7.3, 2 H), 6.30 (q, J = 7.0, 1 H), 7.40 (t, J = 7.4, 2 H), 7.49 (t, J = 7.4, 1 H), 7.63 (d, J = 7.0, 2 H). *E*-Stereochemistry of (*E*)-**11** was determined by ^{1}H NMR NOE measurement. (*Z*)-**10** (PLC, hexane:ether = 15:1 v/v): ^{1}H NMR 0.78 (t, J = 7.2, 3 H), 1.86 (q, J = 7.0, 2 H), 1.97 (d, J = 1.4, 3 H), 5.70 (tq, J = 8.0, 1.6, 1 H). (*Z*)-**11** (PLC, hexane:ether = 15:1 v/v): ^{1}H NMR 0.86 (t, J = 7.1, 3 H), 1.51 (d, J = 7.1, 3 H), 2.31 (t, J = 7.7, 2 H), 5.77 (qt, J = 7.1, 1.3, 1 H). The methylene and phenyl protons of (*Z*)-**10** and (*Z*)-**11** were not identified. (*E*)-**12** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane:ether = 15:1 v/v): IR (neat, cm^{-1}) 1696, 1635; ^{1}H NMR 1.04 (d, J = 6.7, 6 H), 1.98 (d, J = 1, 3, 3 H), 2.78 (d of sept, J = 9.5, 6.7, 1 H), 6.10 (dq, J = 9.5, 1.4, 1 H), 7.41 (t, J = 7.4, 2 H), 7.50 (t, J = 7.4, 1 H), 7.63 (d, J = 7.9, 2 H); MS m/e (relative intensity) 188 (M^+, 36), 173 (30), 145 (22), 105 (100), 83 (9), 77 (12), 55 (12); HRMS (m/e) 188.1187, calcd for $C_{13}H_{16}O$ 188.1201. *E*-Stereochemistry of (*E*)-**12** was determined by ^{1}H NMR NOE measurement. (*Z*)-**12** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane:ether = 15:1 v/v): ^{1}H NMR 0.89 (d, J = 6.6, 6 H), 1.94 (d, J = 1.5, 3 H), 2.18 (d of sept, J = 10.3, 6.5, 1 H), 5.47 (dq, J = 10.4, 1.6, 1 H), 7.30–7.60 (m, 3 H), 7.71 (d, J = 7.0, 2 H). (*E*)-**13** (PLC, MPLC; hexane:ether = 15:1 v/v): ^{1}H NMR 1.25 (d, J = 7.0, 6 H), 1.87 (d, J = 7.0, 3 H), 3.02 (sept, J = 7.1, 1 H), 6.00 (q, J = 7.1, 1 H), 7.30–7.60 (m, 3 H), 7.93 (d, J = 7.1, 2 H). *E*-Stereochemistry of (*E*)-**13** was determined by ^{1}H NMR NOE measurement. (*Z*)-**13** (PLC, MPLC; hexane:ether = 15:1 v/v): ^{1}H NMR 1.08 (d, J = 6.8, 6 H), 1.49 (dd, J = 7.1, 1.2, 3 H), 2.66 (sept of quint, J = 6.9, 1.3, 1 H), 5.73 (qd, J = 7.1, 1.5, 1 H), 7.30–7.60 (m, 3 H), 8.08 (d, J = 7.2, 2 H). (*E*)-**14** (PLC, MPLC; hexane:ether = 15:1 v/v): IR (neat, cm^{-1}) 1648, 1272, 718; ^{1}H NMR 1.20 (s, 9 H), 2.08 (d, J = 1.4, 3 H), 6.25 (q, J = 1.3, 1 H), 7.41 (t, J = 7.5, 2 H), 7.50 (t, J = 7.4, 1 H), 7.64 (d, J = 7.0, 2 H); MS m/e (relative intensity) 202 (M^+, 39), 188 (15), 187 (100), 172 (13), 159 (12), 145 (11), 129 (10), 122 (12), 105 (66), 97 (11), 77 (12); HRMS (m/e) 202.1360, calcd for $C_{14}H_{18}O$ 202.1358. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.89; H, 8.87. *E*-Stereochemistry of (*E*)-**14** was determined by ^{1}H NMR NOE measurement. (*Z*)-**14** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane:ether = 10:1 v/v): ^{1}H NMR 0.97 (s, 9 H), 1.92 (d, J = 1.5, 3 H), 5.53 (q, J = 1.6, 1 H), 7.48 (t, J = 7.9, 2 H), 7.57 (t, J = 7.3, 1 H), 7.97 (d, J = 7.1, 2 H). *Z*-Stereochemistry of (*Z*)-**14** was determined by ^{1}H NMR NOE measurement. **15** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane:ether = 10:1 v/v): ^{1}H NMR 1.13 (s, 9 H), 1.46 (d, J = 7.1, 3 H), 5.78 (q, J = 7.0, 1 H), 7.46 (t, J = 7.3, 2 H), 7.56 (t, J = 7.4, 1 H), 7.95 (d, J = 6.8, 2 H). Stereochemistry of **15** could not clearly determined by ^{1}H NMR NOE measurement. (*E*)-**17** (PLC and MPLC, hexane:ether = 15:1 v/v): IR (neat, cm^{-1}) 1655, 1600, 760, 700; ^{1}H NMR 1.05 (t, J = 7.4, 3 H), 2.27 (quint, J = 7.5, 2 H), 6.45 (t, J = 7.6, 1 H), 7.20–7.55 (m, 8 H), 7.78 (d, J = 7.0, 2 H); MS m/e (relative intensity) 236 (M^+, 60), 221 (18), 131 (21), 105 (100), 91 (14); HRMS (m/e) 236.1193, calcd for $C_{17}H_{16}O$ 236.1201. ^{1}H NMR analysis of the product mixture (PLC, hexane:ether = 15:1 v/v) revealed the following data. Phenyl protons except *o*-phenyl protons of benzoyl groups could not be assigned. (*E*)-**16**: ^{1}H NMR 1.19 (t, J = 7.6, 3 H), 2.77 (q, J = 7.4, 2 H), 7.05 (s, 1 H), 7.87 (d, J = 7.1, 2 H). (*Z*)-**16**: ^{1}H NMR 1.17 (t, J = 7.5, 3 H), 2.53 (q, J = 7.5, 2 H), 6.71 (s, 1 H), 8.67 (d, J = 7.1, 2 H). (*Z*)-**17**: ^{1}H NMR 1.03 (t, J = 7.5, 3 H), 2.10 (quint, J = 7.6, 2 H), 6.25 (t, J = 6.8, 1 H), 7.98 (d, J = 7.1, 2 H). Stereochemistries of (*Z*)-**16**, (*E*)-**17**, and (*Z*)-**17** were determined by ^{1}H NMR NOE measurement. **18** (PLC, hexane; MPLC, hexane:ether = 20:3 v/v): IR (neat, cm^{-1}) 1645, 950; ^{1}H NMR (C_6D_6) 0.28 (s, 9 H), 0.99 (t, J = 7.4, 3 H), 1.18 (d, J = 6.7, 6 H), 1.49 (sext, J = 7.3, 2 H), 2.17 (qd, J = 7.3, 1.4, 2 H), 3.00 (sept, J = 6.8, 1 H), 5.59 (d, J = 11.2, 1 H), 5.59 (dt, J = 14.9, 7.1, 1 H), 6.39 (ddt, J = 15.3, 10.5, 1.4, 1 H); MS m/e (relative intensity) 260 (M^+, 42), 245 (100), 231 (27), 218 (37), 217 (48), 73 (69); HRMS (m/e) 260.1580, calcd for $C_{16}H_{24}OSi$ 260.1596. GC analysis of the reaction mixture obtained by the reaction of **9a** with **2c** at 135 °C using P(n-C_8H_{17})$_3$ revealed the formation of **19** and **20** in 12 and 4% yields, respectively. Separation of **19** and **20** by PLC and MPLC was unsuccessful. The mixture of **19** and **20** (PLC, hexane:ether = 15:1 v/v; MPLC, hexane): IR (neat, cm^{-1}) 1580, 1440, 835, 745; MS m/e (relative intensity) 174 (M^+, 20), 131 (100), 118 (42), 117 (28), 91 (64); HRMS (m/e) 174.1394, calcd for $C_{13}H_{18}$ 174.1408. **19**: ^{1}H NMR 0.93 (t, J = 7.1, 3 H), 1.25–1.50 (m, 4 H), 2.03 (d, J = 1.3, 3 H), 2.20 (q, J = 7.0, 2 H), 5.79 (td, J = 7.2, 1.3, 1 H), 7.15–7.45 (m, 5 H). **20**: ^{1}H NMR 0.88 (t, J = 7.4, 3 H), 1.30–1.40 (m, 4 H), 1.79 (d, J = 6.9, 3 H), 2.50 (t, J = 6.4, 2 H), 5.74 (q, J = 6.9, 1 H), 7.15–7.40 (m, 5 H). *E*-Stereochemistries of **19** and **20** were determined by ^{1}H NMR NOE measurement.

Acknowledgment. We thank Yosuke Horii for performing some of the experiments described.

Registry No. **1**, 1942-45-6; **2a**, 78-84-2; **2b**, 123-72-8; **2c**, 100-52-7; **3**, 125540-54-7; (*Z*)-**3**, 125540-64-9; (*E*)-**3**, 125540-66-1; **4**, 125540-55-8; **5**, 125540-56-9; (*Z*)-**5**, 125540-65-0; (*E*)-**5**, 125540-68-3; **6**, 125567-47-7; **7**, 125540-57-0; (*Z*)-**7**, 125540-67-2; (*E*)-**7**, 125540-69-4; **9a**, 1119-65-9; **9b**, 21020-27-9; **9c**, 999-78-0; **9d**, 622-76-4; **10**, 125540-58-1; (*E*)-**10**, 125540-70-7; (*Z*)-**10**,

125540-71-8; **11**, 125540-59-2; (*E*)-**11**, 125540-72-9; (*Z*)-**11**, 125540-73-0; (*E*)-**12**, 67615-58-1; (*Z*)-**12**, 67615-57-0; (*E*)-**13**, 125540-60-5; (*Z*)-**13**, 125540-74-1; (*E*)-**14**, 64235-56-9; (*Z*)-**14**, 125540-75-2; **15**, 125540-61-6; (*E*)-**16**, 57558-82-4; (*Z*)-**16**, 57558-65-3; (*E*)-**17**, 125540-62-7; (*Z*)-**17**, 125540-76-3; **18**, 125540-63-8; **19**, 83021-58-3; **20**, 125540-77-4; $Ni(COD)_2$, 1295-35-8; $TMSC{\equiv}C(CH_2)_3CH_3$, 3844-94-8.

Supplementary Material Available: ^1H NMR spectra showing the purity of the products **4**–**6** and **10**–**20** (12 pages). Ordering information is given on any current masthead page.

Sulfinic Acids and Related Compounds. 24. Monothioquinone *S,S*-Dioxides and Their Relation to Convergent Syntheses Involving Hydroxyarenesulfonyl Chlorides[1,2]

Lamar Field* and Chew Lee

Department of Chemistry and Center in Molecular Toxicology, Vanderbilt University, Nashville, Tennessee 37235

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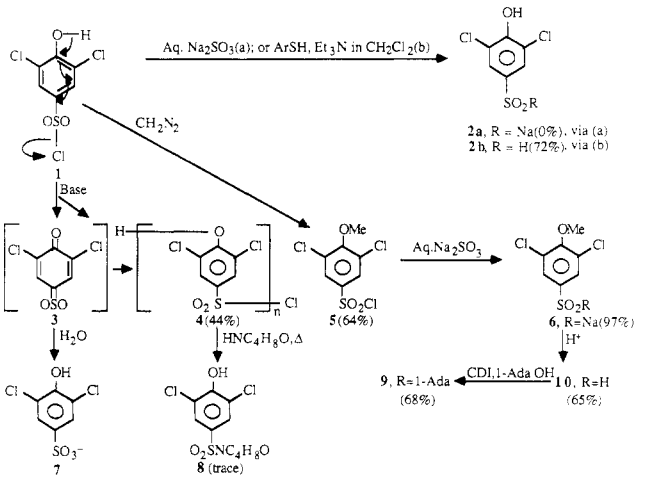
Molecules containing di- or trisulfide linkages together with sulfinate [S(O)OR] functions are promising antiradiation agents.[3] More flexible approaches to such agents might be afforded by convergent syntheses in which di- or trisulfides in one molecule could be connected to sulfinates in another, for example by reaction of CO_2H in one molecule with OH in the other. Convergent syntheses with aliphatic compounds were reported earlier.[4] For a convergent approach to aromatic systems, attractive hydroxyarenesulfinic acid components were **2a** (Scheme I) and **13a** (Scheme II), since the precursor sulfonyl chlorides **1** and **11** were known.[5] Although convergent syntheses ultimately were developed (vide infra), an emphasis of this paper is the unexpected intervention of the monothioquinone *S,S*-dioxides **3** (Scheme I) and **14** (Scheme II) in initial efforts.[6]

When **1** was reduced conventionally with aqueous Na_2SO_3 (pH ca. 9), the sole product was the *sulfonate* salt **7**, and no *sulfinate* salt (**2a**) could be isolated (Scheme I); as Scheme I indicates, however, we were able to reduce **1** to the sulfinic acid (**2b**) by a new approach with an arenethiol and amine,[1a] thus showing that **2a** was in fact an achievable target (the structure of **2b** was confirmed as a thiuronium salt and by dimethylation). At first, we attributed the exclusive formation of **7** with sodium sulfite simply to facile hydrolysis of **1** and, when modifications still led only to **7**, we turned to **11** (Scheme II). Again, the chief product was the sulfonate (**12**), although the sulfinate (**13a**) could be obtained;[8] the new route,[1a] as in the para series, with a thiol and amine gave the sulfinic acid (**13b**) without problems (Scheme II). Ultimately it occured to us that the dominating formation of the sulfonates **7** and **12** is best explained via the aromatic counterparts of sulfenes shown as **3** (Scheme I) and **14** (Scheme II).

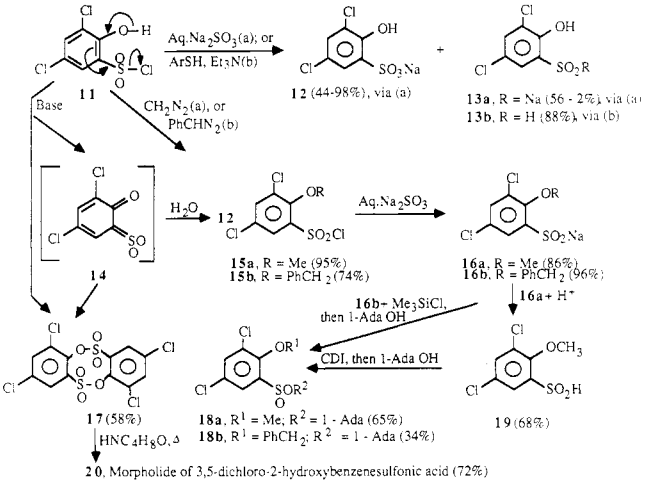
The likelihood of sulfene-like intermediates was strengthened for **1** by blocking the para hydroxyl group to give **5**, which then no longer could give **3** and which could be reduced smoothly with sodium sulfite to the sulfinate **6** (Scheme I); the identity of **6** was confirmed by conversion through **10** to the 1-adamantyl ester **9**. Similarly (Scheme II), blocking the ortho hydroxyl group of **11** with a methyl (**15a**) or benzyl (**15b**) group permitted smooth reduction to the sulfinate salts (**16a**, **16b**), which were characterized as esters (**18a**, **18b**).[9]

Scheme I[a]



[a] 1-Ada = 1-adamantyl; Ar = p-$CH_3C_6H_4$; CDI = carbonyldiimidazole; Me = CH_3; Ph = C_6H_5.

Scheme II[a]



[a] 1-Ada = 1-adamantanol; CDI = carbonyldiimidazole; Me = methyl; Ar = p-$CH_3C_6H_4$; Ph = phenyl.

(1) (a) Paper 23: Lee, C.; Field, L. *Synthesis*, in press. (b) This investigation was supported by the U.S. Army Medical Research and Development Command, Department of the Army, under Research Contract No. DAMD 17-85-C-5181; this paper has been designated as Contribution No. 1860 to the U.S. Army Drug Development Program. We thank Dr. John H. Hillhouse for calling our attention to the work of Cremlyn and Cronje (ref 5).

(2) This paper is abstracted from the Ph.D. Dissertation of C. Lee, which may be consulted for further details (Vanderbilt University, May 1989).

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(5) Cremlyn, R. J.; Cronje, T. *Phosphorus Sulfur* **1979**, *6*, 413.

(6) The term monothioquinone *S,S*-dioxide is used in preference to alternatives mentioned in references below; cf. ref 1a in the present ref 7.

(7) Thea, S.; Cevasco, G.; Guanti, G.; Hopkins, A.; Kashefi-Naini, N.; Williams, A. *J. Org. Chem.* **1985**, *50*, 2158.

(8) For example, ratios of the sulfonate (**12**) to the sulfinate (**13a**) were as follows: for 1:4 Me_2CO/H_2O, 3 h at ca. 25 °C, 86:14; for H_2O, 3 h at ca 25 °C, 49:51; for H_2O, 3 h at 0 °C, 44:56.

(9) The uses shown in Scheme II of CDI and Me_3SiCl for preparing sulfinic esters have been reported recently.[10]

0022-3263/90/1955-2558$02.50/0