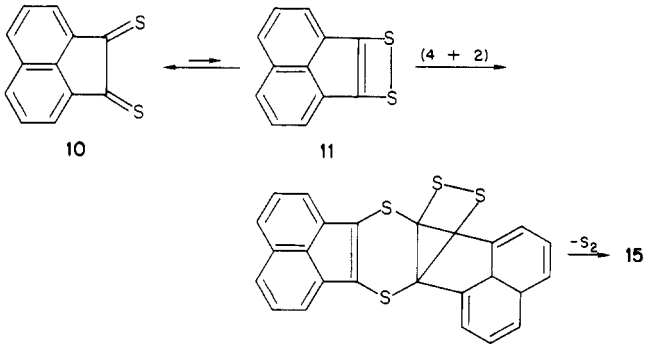
diagnostic similarities with that of the known exo adduct (18) of dimethyl dithionooxalate with norbornadiene. In adduct 18, the methylene bridge protons $H_b$ and $H_a$ ($J_{ab}$ = 9 Hz) are clearly separated at δ 2.69 and 1.65, respectively, due to the marked deshielding effect on $H_b$ of the nearby sulfurs.[11] In adduct 17, an analogous deshielding effect is observed, since $H_b$ and $H_a$ appear at δ 2.89 and 1.83, respectively ($J_{ab}$ = 9 Hz). In a similar manner, dithione 10 was efficiently trapped by norbornene to give the exo adduct 19.

In conclusion, photolysis of the dithiolone 14 generates acenaphthenedithione (10) as a highly reactive transient intermediate which could be trapped in situ by 4 + 2 additions to the strained olefins norbornadiene and norbornene. In the absence of a trapping agent, 10 is transformed fairly efficiently into the dithiine 15. We propose that this conversion proceeds by a (4 + 2) cycloaddition of dithione 10 to its strained dithiete tautomer 11, followed by loss of $S_2$ as shown below.




## Experimental Section

**General Methods.** Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. $^1H$ NMR spectra were recorded on a Bruker 250-MHz FT spectrometer using $CDCl_3$ containing $Me_4Si$ as the internal standard and are reported in δ units. Mass spectra were determined with a VG Micromass 7070H spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Organic solutions were dried over $Na_2SO_4$.

***O*-Isopropyl *S*-(2-Oxoacenaphthenyl) Dithiocarbonate (13).** A solution of potassium *O*-isopropyl xanthate[12] (3.53 g) in acetonitrile (40 mL) was added to a solution of 2-bromoacenaphthenone[8] (12, 5.00 g) in acetonitrile (60 mL). After the mixture was stirred at room temperature for 2 h, the solvent was evaporated in vacuo and water was added. The precipitate was filtered, washed with water, dried, and crystallized from benzenehexane to give needles of xanthate 13: mp 127–129 °C (5.80 g, 96%). Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.67. Found: C, 63.78; H, 4.85.

**Acenaphtho[1,2-*d*][1,3]dithiol-2-one (14).** A suspension of xanthate 13 (5.00 g) in 31% HBr/acetic acid (100 mL) was heated gently until all of the solid dissolved. Heating was continued for an additional 5 min, when the solution suddenly turned into a crystalline slurry. The precipitate was filtered and the solid was refluxed with methanol (100 mL) for 15 min. The cooled suspension was filtered, washed with methanol, and dried to give red-brown needles of dithiolone 14: mp 159–160 °C (2.88 g, 71%); NMR δ 7.54–7.62 (m, 4 H), 7.82 (dd, 2 H, $J$ = 7.5, 1.3 Hz); mass spectrum, $m/e$ 242 ($M^+$, 30%), 214 ($M^+$ - 28, 100%). Anal. Calcd for $C_{13}H_6OS_2$: C, 64.44; H, 2.50. Found: C, 64.43; H, 2.37.

**Photolysis of Dithiolone 14.** A solution of 14 (0.500 g) in a 2:1:1 mixture of acetonitrile, isopropyl alcohol, and cyclohexane (400 mL) was photolyzed ($N_2$) for 3 h with a 400-W high-pressure Hg vapor lamp covered by a Corex filter. The red solution and the solid which separated on the walls were combined, and after evaporation of the solvents, the residue was crystallized from chlorobenzene to give small red diamond-shape crystals of dithiine 15:[13] mp 262–264 °C (0.155 g, 41%); NMR δ 7.44–7.58 (m, Ar H); mass spectrum, $m/e$ 364 ($M^+$, 25%), 332 ($M^+$ - 32, 100%). Anal. Calcd for $C_{24}H_{12}S_2$: C, 79.09; H, 3.32. Found: C, 78.93; H, 3.3.

**Photolysis of Dithiolone 14 in the Presence of Norbornadiene.** A solution of dithiolone 14 (0.53 g) and norbornadiene (3.7 g, excess) in degassed methylene chloride (750 mL) was photolyzed ($N_2$) for 40 min with a 450-W Hanovia lamp with a Pyrex filter. The solvent was evaporated and the residue was crystallized from hexane to give adduct 17: mp 123–124 °C (0.45 g, 62%); NMR δ 7.76–7.48 (m, 6 H, Ar), 6.24 (2 H, t, $J$ = 1.7 Hz), 3.55 (2 H, d, $J$ = 2.0 Hz), 3.05 (m, 2 H), 2.89 (d of t, $J$ = 9, 1.8 Hz), 1.83 (d of t, $J$ = 1.8 Hz); mass spectrum, $m/e$ 306 ($M^+$, 18%), 240 ($M^+$ - 66, 100%), 214 ($M^+$ - 92, 8%), 208 ($M^+$ - 66 - 32, 13%), 170 ($M^+$ - 92 - 44, 20%). Anal. Calcd for $C_{19}H_{14}S_2$: C, 74.50; H, 4.61; S, 20.89. Found: C, 74.42; H, 4.67; S, 21.38.

**Photolysis of Dithiolone 14 in the Presence of Norbornene.** A solution of dithiolone 14 (0.48 g) and norbornene (3.7 g, excess) in degassed methylene chloride (450 mL) was photolyzed for 1 h with a 450-W Hanovia lamp with a Pyrex filter. The intense red solution was evaporated to dryness and the residue was crystallized several times from methanol/methylene chloride to yield adduct 19 as red plates: mp 137–138 °C (0.40 g; 59.8%); NMR δ 7.74–7.46 (m, 6 H, Ar), 3.35 (d, 2 H, $J$ = 1.5 Hz), 2.57–2.49 (m, 3 H), 1.32–1.74 (m, 5 H); mass spectrum, $m/e$ 308 ($M^+$, 90%), 214 ($M^+$ - 94, 100%), 170 ($M^+$ - 94 - 44, 50%). Anal. Calcd for $C_{19}H_{16}S_2$: C, 74.01; H, 5.23; S, 20.76. Found: C, 73.52; H, 5.23; S, 20.94.

**Acknowledgment.** This work was supported by the National Science Foundation (Grant CHE-83 03897). We also thank The Bulgarian Academy of Science, Sofia, for a leave of absence to A.O.

**Registry No.** 10, 95532-40-4; 12, 16269-27-5; 13, 95532-41-5; 14, 95532-42-6; 15, 95532-43-7; 17, 95532-44-8; 19, 95532-45-9; norbornadiene, 121-46-0; norbornene, 498-66-8; potassium *O*-isopropyl xanthate, 140-92-1.

**Supplementary Material Available:** Tables of positional and thermal parameters and their estimated standard deviations, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

---

# Reduction of β-Keto Sulfoxides: A Highly Efficient Asymmetric Synthesis of Both Enantiomers of Allylic Alcohols

Guy Solladie,* Gilles Demailly, and Christine Greck

*Ecole Nationale Superieure de Chimie, Université Louis Pasteur (ERA No. 687), 67008 Strasbourg, France*

*Received November 2, 1984*

Optically active β-keto sulfoxides are convenient intermediates for the synthesis of both enantiomers of methylcarbinols in very high enantiomeric excesses through reduction with $LiAlH_4$ or Dibal[1] (Scheme I).

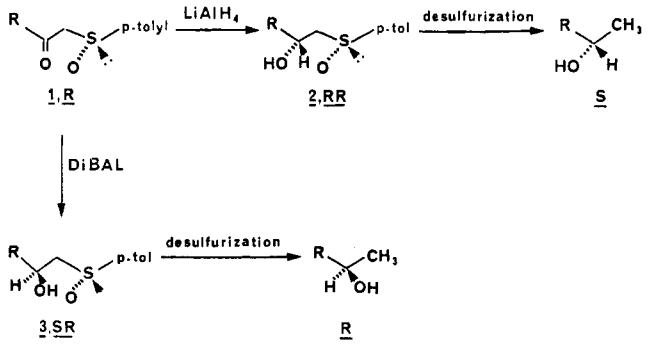
The application of this process to α,β-unsaturated β-keto sulfoxides in order to obtain optically active allylic alcohols was not straightforward because of the difficulty first in synthesizing high yields of α,β-unsaturated β-keto sulfoxides and then in desulfurizing the resulting β-hydroxy sulfoxide without reduction of the double bond.

Optically active β-keto sulfoxides are generally obtained from carboxylic esters and (+)-(*R*)-methyl *p*-tolyl sulfoxide at −78 °C.[1-3] In the case of α,β-unsaturated esters a

(1) Solladié, G.; Greck, C.; Demailly, G.; *Tetrahedron Lett.* **1982**, *23*, 5047.
(2) (a) Kunieda, N.; Nokami, J.; Kinoshita, M. *Chem. Lett.* **1974**, 369. (b) Nokami, J.; Kunieda, N.; Kinoshita, M. *Chem. Lett.* **1977**, 249.
(3) Solladié, G. *Synthesis* **1981**, 185.

0022-3263/85/1950-1552$01.50/0 

**Scheme I**




**Scheme II**

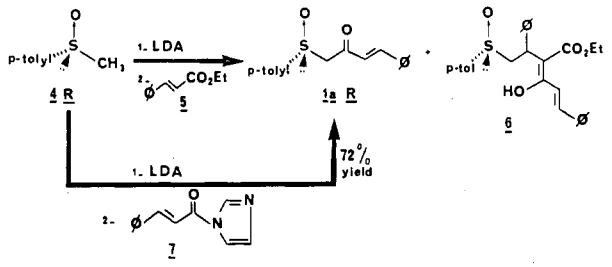



**Table I. Condensation of Sulfoxide 4,*R* with Ester 5**

| reactn temp, °C | yield, % 6[a] | 1a |
|---|---|---|
| −78 | 45 | 37 |
| −40 | 30 | 54 |
| 0 | 10 | 70 |

[a] 6 is the result of 1,4 addition followed by a 1,2 addition of the adduct.

**Table II. Optically Active α,β-Unsaturated Sulfoxides 1,*R***

| | R | yield, % | $[\alpha]_D$ (*c* 1, $CHCl_3$) |
|---|---|---|---|
| 1a | $C_6H_5$ | 72[a] | +278° |
| 1b | $CH_3$ | 65[b] | +245° |
| 1c | $CH_3$, $CH_3$ | 52[a] | +174° |
| 1d | $n$-$C_7H_{15}$ | 55[b] | +200° |

[a] From the imidazole. [b] From the ester.

competitive 1,4 addition was observed at −78 °C. However, when the reaction was conducted at 0 °C, less than 10% of 1,4 addition was detected (Scheme II, Table I). Finally, in using, instead of the ester, the corresponding imidazole, pure 1,2 addition was obtained at −78 °C.

Several α,β-unsaturated β-keto sulfoxides were prepared either from the corresponding esters at 0 °C or from the imidazole at −78 °C (Table II).

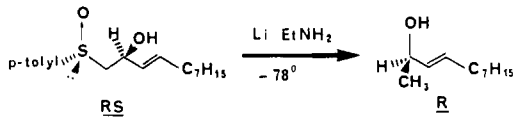
In each case a pure *E* isomer was obtained whatever the stereochemistry of the starting ester (as shown by $^1H$ NMR).

The reduction of these β-keto sulfoxides was conducted at −78 °C either with $LiAlH_4$ or Dibal, giving, as shown in Table III opposite diastereosomers in very high diastereoisomeric excesses as determined by NMR from the nonequivalent ABX parts corresponding to the $CH_2$ α to the sulfoxide group.[1] The absolute configurations *RR* of the hydroxy sulfoxides **2a** and **2d**, were determined by chemical correlation with the known 4-phenyl-2-butanol[4] and undecanol-2[5] by reduction of the double bond and desulfurization with Raney nickel. Those of compounds **2b** and **2c** were deduced from NMR characteristics in

**Table III. Reduction of α,β-Unsaturated Sulfoxide 1,*R***

| α,β-unsaturated sulfoxide | $LiAlH_4$ 2,*RR*/3,*SR* | $LiAlH_4$ yield, % | Dibal 2,*RR*/3,*SR* | Dibal yield, % |
|---|---|---|---|---|
| 1a | 80/20 | 90 | 5/95 | 95 |
| 1b | 81/19 | 90 | 10/90 | 91 |
| 1c | 89/11 | 92 | 5/95 | 95 |
| 1d | 95/5 | 95 | 5/95 | 97 |

**Scheme III**




$CDCl_3$: a smaller nonequivalence for the $CH_2$ α to the sulfoxide group was always observed in the diastereoisomer *RR*[1,6] as well as a more deshielded signal for the proton α to the hydroxyle.

In the desulfurization of unsaturated β-hydroxy sulfoxides with Raney nickel proceeding with simultaneous reduction of the double bond, we found that lithium in ethylamine at −78 °C desulfurized readily the molecule without concomitant reduction of the double bond, thus allowing the obtention of optically active allylic alcohols (Scheme III).

## Experimental Section

**α,β-Unsaturated β-Keto Sulfoxides. General Procedure. A. From α,β-Unsaturated Esters.** To a solution of LDA (16 mmol) in 40 mL of THF at −30 °C was dropwise added (+)-(*R*)-methyl *p*-tolyl sulfoxide[3] (8 mmol) in 40 mL of THF. Temperature is then allowed to reach 0 °C and a solution of 12 mmol of α,β-unsaturated ester in 20 mL of THF was dropwise added. After 3 h at 0 °C, the reaction mixture wad decomposed with a saturated ammonium chloride solution. The organic layer was separated and the aqueous solution acidified with 10% HCl till pH 3–4 and extracted with $CH_2Cl_2$. After evaporation of the solvent, the residue is purified by chromatography on silica gel (eluent ether/hexane, 60/40).

**B. From α,β-Unsaturated Imidazolides.** To a solution of 12 mmol (1.62 g) of imidazole in 10 mL of THF at 0 °C, was dropwise added 6 mmol of the corresponding acid chloride. After 0.5 h at room temperature, the amine hydrochloride was filtered; the solid washed with 10 mL of THF. The imidazolide in THF solution was used without any further purification.

To a solution of LDA (16 mmol) in 40 mL of THF, at −30 °C, was dropwise added a solution of 8 mmol of (+)-(*R*)-methyl *p*-tolyl sulfoxide[3] in 40 mL of THF. The reaction mixture is first allowed to reach 0 °C and then cooled at −78 °C. The preceding solution of imidazolide in THF was then dropwise added. After 3 h at −78 °C the reaction mixture was allowed to reach 0 °C and then decomposed with a saturated ammonium chloride solution. The same workup as in part A was used.

**Reduction of β-Keto Sulfoxides. General Procedure. A. With Lithium Aluminum Hydride.** To a suspension of 1 mmol of $LiAlH_4$ in 10 mL of $Et_2O$ at −78 °C was added a solution of 1 mmol of β-keto sulfoxide in 10 mL of THF. After 3 h at −78 °C, the reaction mixture was decomposed with a saturated ammonium chloride solution and extracted with ether. The diastereoisomeric excesses were determined on the crude product by NMR after the solvent evaporation. The product can be easily purified by chromatography (eluent ether/hexane).

**B. With Diisobutyl Aluminium Hydride.** To 1.1 mL (1.1 mmol) of a 1 M solution of Dibal in hexane diluted by 9 mL of THF at −78 °C was added 1 mmol of β-keto sulfoxide in 10 mL of THF. After 1 h at −78 °C, the reaction mixture was decomposed by adding 10 mL of MeOH at −78 °C. The solvent was then evaporated and the residue diluted with water and extracted with

(4) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, 1115.
(5) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1914**, 1923.
(6) Demailly, G.; Greck, C.; Solladié, G. *Tetrahedron Lett.* **1984**, *25*, 4113.

$CH_2Cl_2$. The organic layer was washed with a 5% HONa solution, dried, and evaporated. The diastereoisomeric excesses were determined on the crude product by NMR. Finally the product was purified by chromatography as in part A.

**Desulfurization with Lithium/Ethylamine. General Procedure.** β-Hydroxy sulfoxide (1 mmol) is dissolved in 10 mL of ethylamine under Argon and cooled at −78 °C. Then 30 mmol (0.21 g) of lithium were slowly added, and the reaction mixture was allowed to react till a persistant blue color was obtained. Ammonium chloride (0.8 g) was then added and the excess lithium was removed. After evaporation of the ethylamine, the residue was diluted with water and extracted with ether. After the usual workup, the product was purified by chromatography (eluent ether/hexane, 30/70).

**Registry No.** **1a**, 95482-76-1; **1b**, 95482-77-2; **1c**, 95482-78-3; **1d**, 95482-79-4; **2a**, 95482-80-7; **2b**, 95482-82-9; **2c**, 73773-39-4; **2d**, 95482-84-1; **3a**, 95482-81-8; **3b**, 95482-83-0; **3c**, 73766-48-0; **3d**, 95482-85-2; **4**, 1519-39-7; **5**, 4192-77-2; **6**, 95512-42-8; (*E*)-$C_6H_5CH$=CHCOCl, 17082-09-6; $(CH_3)_2C$=HCOCl, 3350-78-5; (*E*)-$CH_3CH$=$CHCO_2Et$, 623-70-1; (*E*)-$CH_3(CH_2)_6CH$=$CHCO_2Et$, 7367-88-6; (*S*)-(*E*)-$C_6H_5CH$=CHCH(OH)$CH_3$, 81176-43-4; (*R*)-(*E*)-$C_6H_5CH$=CHCH(OH)$CH_3$, 62413-47-2; (*S*)-(*E*)-$CH_3CH$=CHCH(OH)$CH_3$, 926-58-9; (*R*)-(*E*)-$CH_3CH$=CHCH(OH)$CH_3$, 35666-69-4; (*S*)-$(CH_3)_2C$=CHCH(OH)$CH_3$, 50373-46-1; (*R*)-$(CH_3)_2C$=CHCH(OH)$CH_3$, 74112-34-8; (*S*)-(*E*)-$CH_3(CH_2)_6CH$=CHCH(OH)$CH_3$, 95586-07-5; (*R*)-(*E*)-$CH_3(CH_2)_6CH$=CHCH(OH)$CH_3$, 95586-08-6; imidazole, 288-32-4.

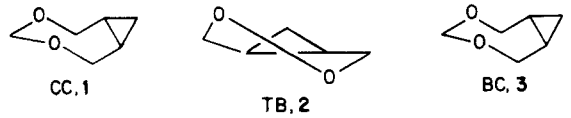
## Conformational Analysis of 1,3-Dioxacycloheptanes. 5. Conformations of 4-Isopropyl-3,5-dioxabicyclo[5.*n*.0]alkanes

Michael H. Gianni,* Bruce Prezzavento, and Keith Shea

*Saint Michael's College, Winooski, Vermont 05404*

*Received October 2, 1984*

Interest in twist conformations of the 1,3-dioxacycloheptanes[1,2] has led to an investigation of the effect that three-membered rings have on the conformations of these compounds. Previous studies have shown that low barriers in the pseudorotation process make conformational analysis of these compounds difficult and that construction of a three-membered ring[3] or a double bond[4] at $C_5$–$C_6$ is sufficient to stop the pseudorotation process. The 3,5-dioxabicyclo[5.1.0]octanes[3] have well-defined boat–chair (BC), chair–chair (CC), and twist-boat (TB) conformations.




NMR data indicate that *exo*- and *endo*-4-isopropyl-3,5-dioxabicyclo[5.1.0]octanes prefer the CC **4** and BC **5** conformations, respectively. In contrast, *endo*- and *exo*-4-isopropyl-3,5,8-trioxabicyclo[5.1.0]octanes prefer the TB conformations **6** and **7**, respectively.[3,5]

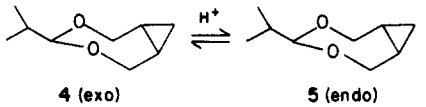
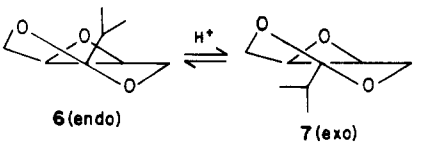


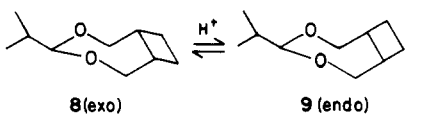

**Table I. Equilibrium Data for *endo*/*exo*-4-Isopropyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane**

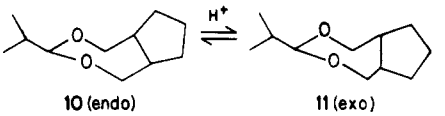
endo ⇌ exo

| *T*, K | *K* | −Δ *G*°, kcal/mol | −Δ*H*°, kcal/mol | −Δ*S*°, gibbs |
|---|---|---|---|---|
| 298 | 3.36 ± 0.15 | 0.72 | 1.62 | 3.0 |
| 323 | 2.60 ± 0.14 | 0.61 | | |
| 348 | 2.27 ± 0.12 | 0.57 | | |

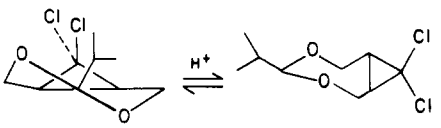



We have extended these studies to include four- and five-membered rings and now report that *exo*- and *endo*-4-isopropyl-3,5-dioxabicyclo[5.2.0]nonanes prefer the CC **8** and BC **9** conformations, respectively. The five-membered ring homologues *exo*- and *endo*-4-isopropyl-3,5-dioxabicyclo[5.3.0] decanes prefer CC **11** and BC **10** conformations, respectively. The NMR spectra indicate that each of these conformations is well-defined, and we conclude that even the five-membered ring raises the torsional energy about the $C_1$–$C_7$ bond sufficiently high to stop the pseudorotational process in the CC and BC conformations.




A recent report that 8,8-dichloro-3,5-dioxabicyclo-[5.1.0]octane exists preferentially in the CC conformation is of special interest.[6] Models indicate that the endo (BC) of 4-isopropyl-8,8-dichloro-3,5-dioxabicyclo[5.1.0]octane has a chlorine atom proximate to the oxygen atoms in the ring. This would create a dipole–dipole interaction which the molecule can avoid by assuming a TB conformation. The alternative is to ring flip but that would put the isopropyl group in an axial position which is conformationally intolerable. To test the effect of such a dipole–dipole interaction the *endo*- **12** and *exo*-**13** isomers were synthesized by the addition of dichlorocarbene to 2-isopropyl-1,3-dioxacyclohept-5-ene. The NMR spectrum of the endo isomer is consistent with a TB conformation while the NMR spectrum of the exo isomer indicates that a CC conformation is preferred. It is interesting to note that the endo and exo epoxides **6** and **7** each prefer a TB conformation in solution. However, X-ray[8] data indicate that




(1) Gianni, M. H.; Saavedra, J.; Savoy, J.; Kuivila, H. G. *J. Org. Chem.* **1974**, *39*, 804. (b) Gianni, M. H.; Saavedra, J.; Savoy, J. *J. Org. Chem.* **1973**, *38* 3871.
(2) Bocain, D. F.; Straus, H. L. *J. Am. Chem. Soc.* **1977**, *99*, 2876.
(3) Gianni, M. H.; Cody, R.; Asthana, M. R.; Wursthorn, K.; Patanode, P.; Kuivila, H. G. *J. Org. Chem.* **1977**, 42, 365.
(4) Gianni, M. H.; Adams, M.; Kuivila, H. G.; Wursthorn, K. *J. Org. Chem.* **1975**, 40, 450.
(5) Favini, G.; Pitea, D.; Sottocornola, M.; Todeschini, R. *J. Mol. Struct. Theochem.* **1982**, 53.
(6) Taylor, K. G.; Chaney, J. *J. Am. Chem. Soc.* **1976**, *98*, 4158. (b) Taylor, K. G.; Chaney, J.; Dick, J. C. *J. Am. Chem. Soc.* **1976**, *98*, 4163.
(7) Weinhold, F.; Brunk, T. K. *J. Am. Chem. Soc.* **1979**, *101*, 265.

0022-3263/85/1950-1554$01.50/0 